CHEMICAL REVIEWS

Review

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Polyhydrides of Platinum Group Metals: Nonclassical Interactions and σ-Bond Activation Reactions

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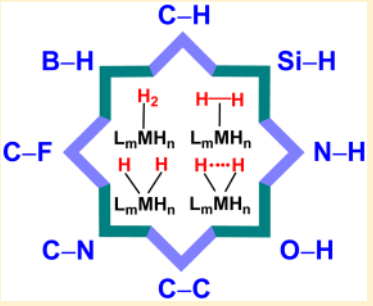
ABSTRACT: The preparation, structure, dynamic behavior in solution, and reactivity of polyhydride complexes of platinum group metals, described during the last three decades, are contextualized from both organometallic and coordination chemistry points of view. These compounds, which contain dihydrogen, elongated dihydrogen, compressed dihydride, and classical dihydride ligands promote the activation of B−H, C−H, Si−H, N−H, O−H, C−C, C−N, and C−F, among other σ-bonds. In this review, it is shown that, unlike other more mature areas, the chemistry of polyhydrides offers new exciting conceptual challenges and at the same time the possibility of interacting with other fields including the conversion and storage of regenerative energy, organic synthetic chemistry, drug design, and material science. This wide range of possible interactions foresees promising advances in the near future.



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1. INTRODUCTION

Hydride is the ligand with the smallest number of valence electrons. It can only make single bonds to transition metal centers, which are among the strongest metal−ligand bonds.[1] Despite the strength of the M−H bonds, this ligand shows a great mobility and hydride site exchange is often observed.[2] On the other hand, hydride has almost no steric influence. With its uniquely small steric requirement, this ligand is ideal for achieving high coordination numbers.

A major milestone for the understanding of the chemistry of transition metal hydride complexes was the discovery that the hydrogen molecule can coordinate to a transition metal retaining almost intact the H−H bond.[3−6] In contrast to the M−H bond, the metal−dihydrogen interaction is weak. Metal-dihydrogen and metal-dihydride forms are both parts of the same redox equilibrium. Reducing metal centers favor the oxidized dihydride form. However, oxidizing metal centers stabilize the reduced dihydrogen. The coordination enhances the acidity of the hydrogen molecule,[7,8] which can undergo heterolytic cleavage[9] and position exchange, through proton transfer, when a hydride coligand is also present in the complex. In addition, the hydrogen atoms rapidly rotate around the metal−dihydrogen axis.

Other factors that have significantly contributed to the development of the field are the improvement of the quality of the characterization techniques, including X-ray and neutron diffractions,[10] and NMR spectroscopy,[11−13] and the availability of more sophisticated programs and more potent computers for DFT calculations,[14−18] which are making possible the study of real molecules. Thus, today, it is possible to have a quite exact knowledge of the coordination polyhedra of the majority of the hydride complexes and the separation between the hydrogen atoms bound to the metal center, in the solid state and in solution, and their mobility in solution.

What do we understand by polyhydride complexes? We define polyhydride complexes as compounds having enough hydrogen atoms bound to the metal center of a L_nM fragment to form at least two different types of ligands. These ligands can be classified in four types depending upon the separation between the coordinated hydrogens: (i) classical hydrides (>1.6 Å), (ii) dihydrogen (0.8−1.0 Å), (iii) elongated dihydrogen (1.0−1.3 Å), and (iv) compressed dihydrides (1.3−1.6 Å). The distinction between elongated dihydrogen and compressed dihydrides is formal, since for these species, the energy cost to move the two hydrogens atoms between 1.00 and 1.60 Å is lower than 4 kcal mol^{-1} (i.e., the energy of the complex is practically independent of the separation between the hydrogen atoms).[19] The main difference between them is the activation barrier for the combined rotation of both hydrogen atoms around the $M-H_2$ axis, less than 8 kcal mol^{-1} for the elongated dihydrogen, and between 8 and 12 kcal mol^{-1} for the compressed dihydrides.[20] Nonclassical interactions are called those that occur around the metal coordination sphere, between hydrogen atoms separated by less than 1.6 Å.

A noticeable feature of polyhydride complexes is the combined movements of the hydrogen atoms bound to the metal center, in agreement with the mobility of hydride and dihydrogen ligands. These position exchanges are thermally activated and take place with activation barriers which are much lower than those involved in the movements of the rest of the ligands. Mass, geometry, rigidity, and size of the heavy coligands are factors that determine the geometry of the polyhydride skeleton and prevent position exchanges of these groups. In addition to the thermally activated site exchanges, some polyhydrides undergo quantum exchange coupling,[21] which manifests in the high field region of the ^1H NMR spectra through large values of the observed H−H coupling constants (J_{obs}), which increase as the temperature increases. The phenomenon involves the exchange of the hydrogen nuclei. It occurs by tunneling through a barrier between the two sides of the double-well potential,[22] which is even lower than those calculated for the hydrogen movements. For each temperature and a given hydrogen−hydrogen separation (a), J_{obs} is determined by eq 1, according to a two-dimensional harmonic oscillator model.[23] Constant J_{mag} is the portion of J_{obs} due to the Fermi contact interaction, parameter λ is the hard sphere radius of the hydrides, and ν describes the H−M−H vibrational wag mode that allows the movement along the H−H vector. They are characteristic for each compound and considered temperature invariant.

$$J_{obs} = J_{mag} + 2\left[\left(\frac{\nu a}{\pi\lambda \coth[h\nu/2kT]}\right) \exp\left\{\frac{-2\pi^2 m\nu(a^2+\lambda^2)}{h \coth[h\nu/2kT]}\right\}\right] \quad (1)$$

Saturated polyhydrides have the ability of losing molecular hydrogen to afford unsaturated species, which coordinate and subsequently activate σ-bonds, including B−H, C−H, Si−H, N−H, and O−H bonds, among others. In this respect, platinum group metals occupy a prominent place between the metal elements.[24−29] The activation of B−H bonds[30,31] is a reaction of great interest concerning the borylation of organic molecules[32−36] and the dehydrocoupling of ammonia-borane.[37−39] The C−H bond activation is a classical issue in organometallics because of its connection with the functionalization of nonactivated organic substrates.[40−47] The metal-mediated rupture of Si−H bonds is notable due to the relevance of the $M-SiR_3$ species in the hydrosilylation of unsaturated organic substrates, the direct synthesis of chlorosilanes, and SiH/OH coupling.[48] The N−H bond activation promoted by platinum group metals is a key step in reactions of hydroamination of unsaturated organic molecules[49] and for the use of ammonia in homogeneous catalysis.[50] The cleavage of O−H bonds is of potential relevance to metal-mediated solar-energy conversion routes.[51] It is expected that water splitting driven by sunlight will constitute a growing area of particular interest in the near future.[52]

The coordination of a σ-E−E′ bond to a transition metal involves σ-donation from the σ-orbital of the coordinated bond to empty orbitals of the metal and back bonding from the metal to the σ^*(EE′) orbital. The activation toward homolysis or heterolysis of the coordinated bond depends on the electronic nature of the metal center. Nucleophilic metal centers enhance the back-donation, resulting in the homolytic addition of E−E′ to the metal. On the other hand, electrophilic metal centers increase the σ-donation to the metal, promoting the heterolytic cleavage of the E−E′ bond. The cation acceptor can be an external Lewis base, including the solvent of the reaction, a hydride ligand or a group in the coordination sphere of the metal with free electron pairs (Scheme 1).

A third form of cleavage is the σ-bond metathesis, which involves the transfer of E or E′ from E′ or E to another ligand R

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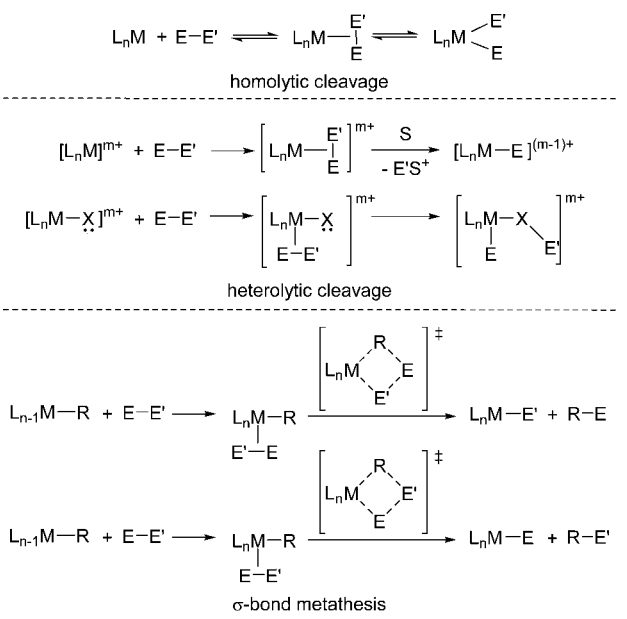
Scheme 1. Types of σ-Bond Activation Reactions



in a concerted fashion through a four-center, four-electron transition state (two of the M−R bond and two of the E−E′ bond) that avoids the formal 2-electrons oxidation of the metal.[53]

The discovery of the dihydrogen complexes, the improvement of the quality of the characterization techniques, the dynamic and quantum mechanical behavior of the hydride ligands in solution, and the σ-bond activation reactions have converted the polyhydride complexes of platinum group metals in one of the most fascinating and relevant families of transition-metal compounds in the last three decades. This review contextualizes about 1000 compounds reported between 1985 and 2015, after the publication of the review of Hlatky and Crabtree dedicated to the memory of E. L. Mutterties.[54] We describe their preparation, structure, some relevant behavior of the hydrogen atoms bound to the metal in solution, and their participation in σ-bond activation reactions. We have not considered those parts previously reviewed, such as the reactivity of the dihydride-bis(dihydrogen) derivative $RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2$ reported before 1998,[55] ruthenium-promoted Si−H bond activation reactions carried out prior to 2006,[25] and dehydrogenation and related reactions catalyzed by iridium pincer polyhydrides previous to 2011.[56]

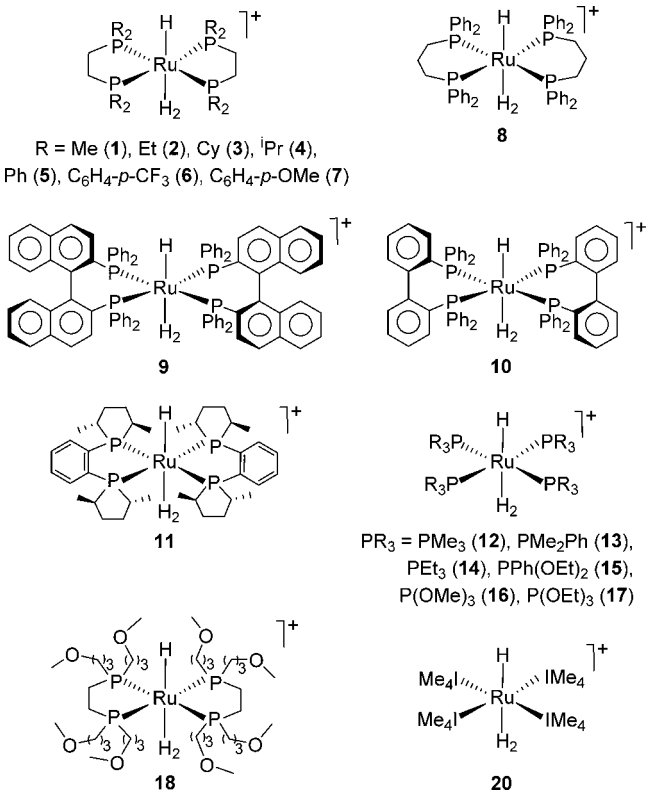
2. RUTHENIUM

2.1. Phosphine Complexes

Phosphine-ruthenium-polyhydride compounds are generally d^6-species. In spite of this, complexes with three, four, five, and six hydrogen atoms directly bound to the metal center have been reported.

The RuH_3-compounds include the cationic *trans*-hydride-dihydrogen derivatives $[RuH(\eta^2\text{-}H_2)(\text{diphosphine})_2]^+$ (diphosphine = $R_2P(CH_2)_2PR_2$, R = Me (**1**), Et (**2**), Cy (**3**), ^{i}Pr (**4**), Ph (**5**), C_6H_4-*p*-CF_3 (**6**), C_6H_4-*p*-OMe (**7**); $Ph_2P(CH_2)_3PPh_2$ (**8**); 2,2′-bis(diphenylphosphino)-1,1-binaphthyl (**9**); 2,2′-bis(diphenylphosphino)-1,1-biphenyl (**10**); 1,2-bis((2*S*,5*R*)-2,5-dimethylphospholano)benzene (**11**)) and $[RuH(\eta^2\text{-}H_2)(PR_3)_4]^+$ (PR_3 = PMe_3 (**12**), PMe_2Ph (**13**), PEt_3 (**14**), $PPh(OEt)_2$ (**15**), $P(OMe)_3$ (**16**), $P(OEt_3)_3$ (**17**)), which have been prepared by protonation of the corresponding *trans*-dihydrides or by coordination of H_2 to the metal center of the respective unsaturated cations $[RuH(\text{diphosphine})_2]^+$[57−72] and $[RuH(PR_3)_4]^+$.[73−77] By using 1,2-[bis(dimethoxypropyl)-phosphino]ethane (DMeOPrPE), the water-soluble complex $[RuH(\eta^2\text{-}H_2)(DMeOPrPE)_2]^+$ (**18**) has been obtained.[78] A tetrakis-NHC complex has also been reported. The unsaturated compound $[RuH(IMe_4)_4][BAr^F{}_4]$ (**19**) coordinates H_2 to afford $[RuH(\eta^2\text{-}H_2)(IMe_4)_4][BAr^F{}_4]$ (**20**; IMe_4 = 1,3,4,5-tetramethylimidazol-2-ylidene; Ar^F = 3,5-$C_6H_3(CF_3)_2$).[79] The *trans* hydride-dihydrogen stereochemistry shown in Chart 1 for these compounds has been confirmed in the solid state by means of single crystal neutron diffraction of the $[BPh_4]^-$-salt of **5**, at 12 K.[80] The dihydrogen ligand eclipses a *trans* P−Ru−P axis that is bent away from the hydrogens with a P−Ru−P angle of 167.9(4)°. The H−H distance is 0.82(3) Å, increasing to about 0.94 Å when corrected for the shortening caused by the torsional libration of the dihydrogen ligand. The long Ru−(H_2) distance of 1.81(2) Å, compared to the terminal hydride to ruthenium distance of 1.64(2) Å, is consistent with the lability of the dihydrogen ligand, which is partially lost from the crystal under exposure to vacuum. In solution, the hydride and dihydrogen ligands slowly exchange their positions. The activation energy of the process depends upon the phosphines.

Chart 1. *trans*-Hydride-Dihydrogen Cations $[L_nRuH(\eta^2\text{-}H_2)]^+$



Ab initio calculations suggest that when the bite angle of the diphosphine is increased, the most favored geometry changes from octahedral, with the hydride trans to the hydrogen molecule, to a very distorted cis complex.[81] This seems to be the case of compounds with 1,4-bis(diphenylphosphino)-butane[61] and some xantphos-type diphosphines.[82] For intermediate bite angles, equilibria with classical trihydride

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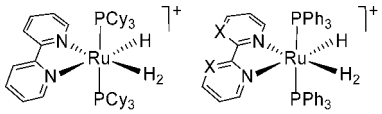
species appear to take place.[62,63] The cis hydride-dihydrogen disposition has been stabilized by using bulky phosphines and rigid quelating N−N ligands (Chart 2).[83,84] These compounds,

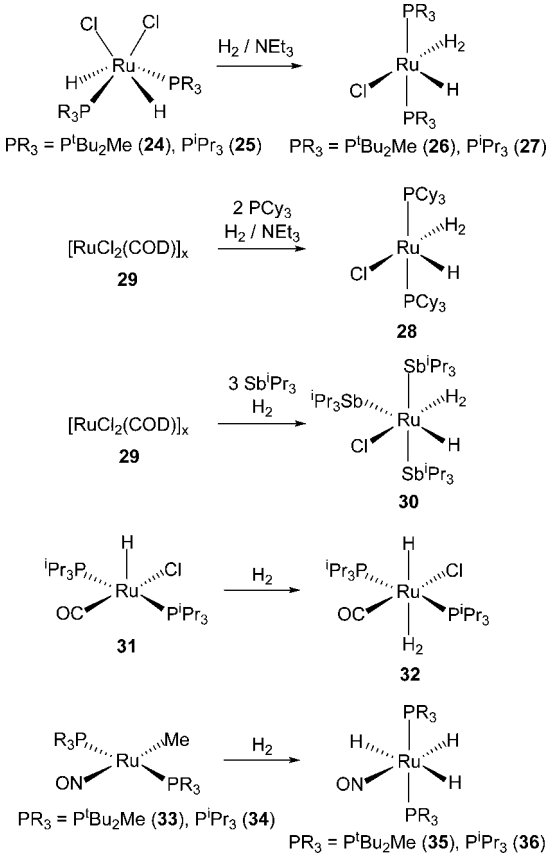
Chart 2. *cis*-Hydride-Dihydrogen Cations $[L_nRuH(\eta^2\text{-}H_2)]^+$



$[RuH(\eta^2\text{-}H_2)(N{-}N)(PR_3)_2]^+$ (N−N = 2,2′-bipyridine, PR_3 = PCy_3 (**21**), PPh_3 (**22**); N−N = bipyrimidine, PR_3 = PPh_3 (**23**)), which have been prepared by protonation of the corresponding dihydrides, exhibit very fast hydride-dihydrogen exchange ($\Delta G^{\ddagger}$ = 2−3 kcal mol^{-1}), which precludes decoalescence of the high field resonance in the ^1H NMR spectra even at low temperatures.

Neutral five- and six-coordinate $RuH(\eta^2\text{-}H_2)$-complexes are also known (Scheme 2). Although the low stability of the five-

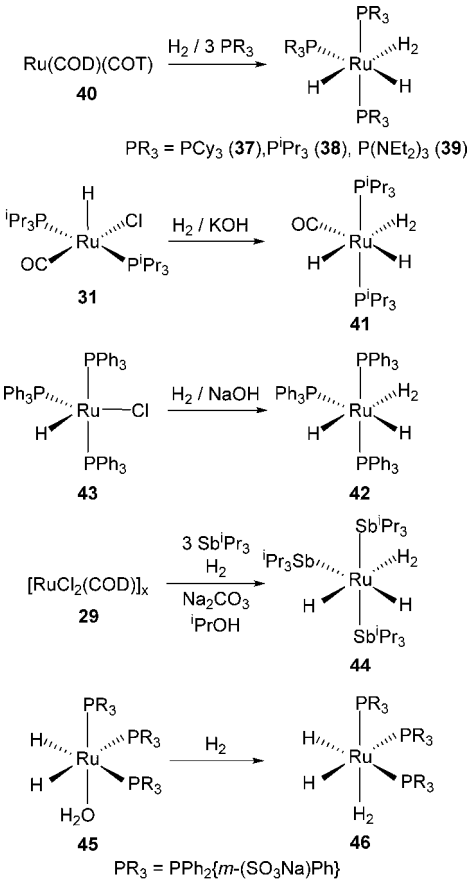
Scheme 2. Preparation of L_nRuH_3 Complexes



coordinate species prevents isolation, they have proved to be useful synthetic intermediates to prepare interesting five-coordinate hydride-vinylidene derivatives[85,86] and Grubbs-type carbene catalysts.[87] These intermediates have been generated through two different methods. Treatment of toluene solutions of $RuH_2Cl_2(PR_3)_2$ (PR_3 = P^tBu_2Me (**24**), P^iPr_3 (**25**)) with NEt_3 under 1.5 atm of H_2, at room temperature, affords $RuHCl(\eta^2\text{-}H_2)(PR_3)_2$ (PR_3 = P^tBu_2Me (**26**), P^iPr_3 (**27**)).[88] The tricyclohexylphosphine counterpart $RuHCl(\eta^2\text{-}H_2)(PCy_3)_2$ (**28**) however has been prepared by reacting $[RuCl_2(\eta^4\text{-}COD)]_x$ (**29**, COD = 1,5-cyclooctadiene), PCy_3, and NEt_3 in *sec*-butyl alcohol, at 80 °C, under 1.5 atm of H_2.[87] By using triisopropylstibane instead of tricyclohexylphosphine, the same procedure yields the six-coordinate stibane derivative $RuHCl(\eta^2\text{-}H_2)(Sb^iPr_3)_3$ (**30**).[89] Reaction of H_2 with the coordinatively unsaturated complex $RuHCl(CO)(P^iPr_3)_2$ (**31**) leads to $RuHCl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ (**32**).[90] In contrast, the hydrogenolysis of the square-planar compounds $RuMe(NO)(PR_3)_2$ (PR_3 = P^tBu_2Me (**33**), P^iPr_3 (**34**)) gives the classical trihydrides $RuH_3(NO)(PR_3)_2$ (PR_3 = P^tBu_2Me (**35**), P^iPr_3 (**36**)).[91]

The RuH_4-complexes are dihydride-dihydrogen species,[92−94] which show a marked tendency to lose the dihydrogen ligand and to form dimers in the absence of coordinating molecules.[95,96] These compounds can be obtained according to Scheme 3. Complexes $RuH_2(\eta^2\text{-}H_2)(PR_3)_3$ (PR_3 = PCy_3 (**37**), P^iPr_3 (**38**), $P(NEt_2)_3$ (**39**)) have been prepared by hydrogenation of $Ru(\eta^4\text{-}COD)(\eta^6\text{-}COT)$ (**40**, COT = cyclooctatetraene) in the presence of 3 equiv of phosphine.[97] Compounds $RuH_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ (**41**)[90] and $RuH_2(\eta^2\text{-}H_2)(PPh_3)_3$ (**42**)[98] are usually generated by hydrogenolysis of the corresponding chloride-hydride precursors, **31** and $RuHCl(PPh_3)_3$ (**43**), in the presence of a base. The stibane derivative $RuH_2(\eta^2\text{-}H_2)(Sb^iPr_3)_3$ (**44**) has been synthesized through a procedure intermediate between both methods, involving the hydrogenation of the diolefin and the hydrogenolysis of the Ru−Cl bonds of the polymeric material **29** in the presence of 3 equiv of Sb^iPr_3, Na_2CO_3, and 2-propanol as solvent.[89] The

Scheme 3. Preparation of $L_nRuH_2(\eta^2\text{-}H_2)$ Complexes



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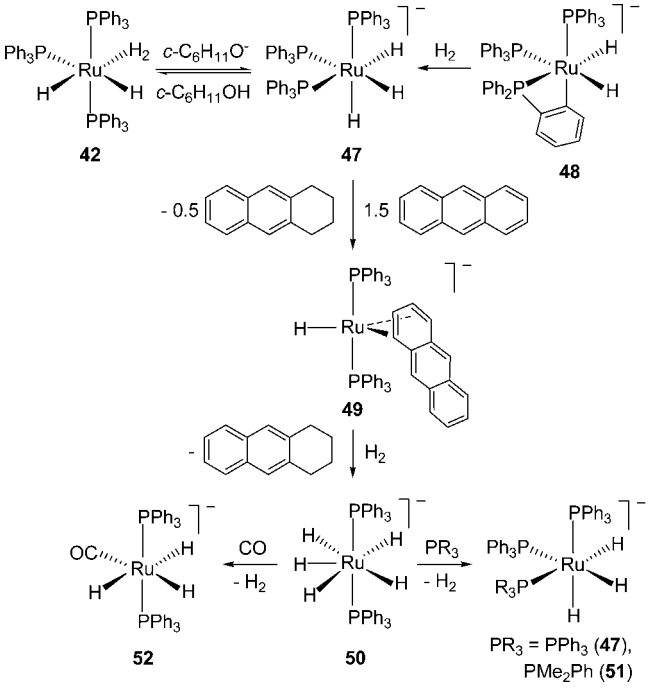
replacement of the water molecule of $RuH_2(H_2O)(mtppms)_3$ (**45**, mtppms = sodium 3-diphenylphosphinobenzenesulfonate) by molecular hydrogen has afforded the water-soluble dihydride-dihydrogen $RuH_2(\eta^2\text{-}H_2)(mtppms)_3$ (**46**).[99]

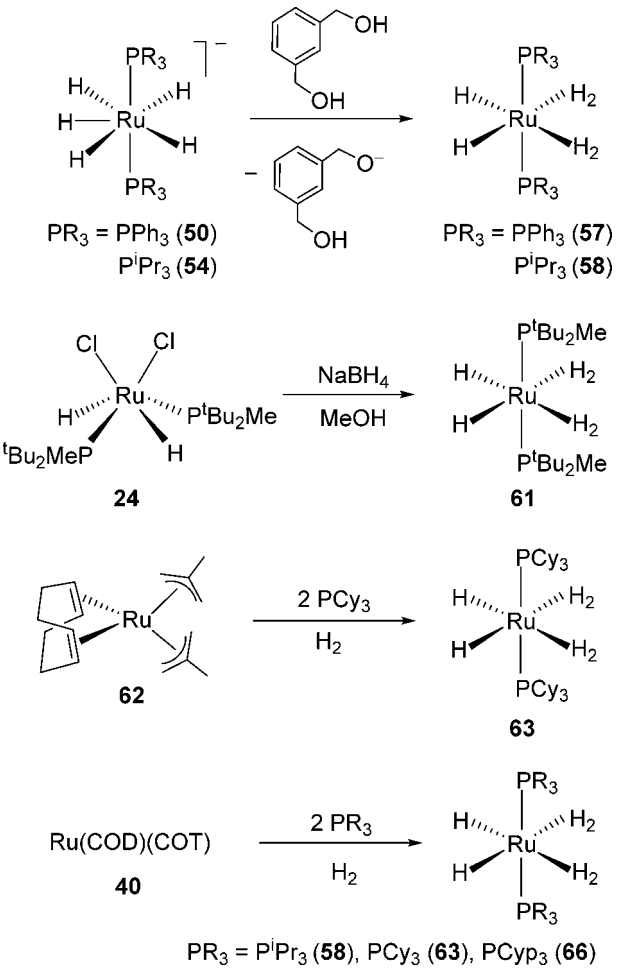
The dihydride-dihydrogen **42** is deprotonated by *c*-$C_6H_{11}O^-$ to reach an equilibrium with the anionic trihydride $[RuH_3(PPh_3)_3]^-$ (**47**) and cyclohexanol ($K_{eq} \approx 0.13$ at ambient temperature in THF).[100] This anion is conveniently prepared by means of reaction of $[RuH_2(PPh_3)_2\{\kappa^2\text{-}P,C\text{-}PPh_2(C_6H_4)\}]^-$ (**48**) with H_2 (1 atm).[101,102] After adding a slight excess of 18-crown-6-ether to its THF solutions, single crystals of the $[K(C_{12}H_{24}O_6)]^+$-salt of **47** suitable for X-ray diffraction analysis were obtained. The structure revealed a *fac*-disposition of both hydride and phosphine ligands in an octahedral environment.[103] Complex **47** reacts with 1.5 equiv of anthracene in THF to form 0.5 equiv of 1,2,3,4-tetrahydroanthracene and $[RuH(PPh_3)_2(anthracene)]^-$ (**49**), which has been isolated as the K^+-salt. In THF, at 25 °C, anion **49** rapidly reacts with molecular hydrogen to yield the pentahydride $[RuH_5(PPh_3)_2]^-$ (**50**), which has been also isolated as the K^+-salt, and 1 equiv of 1,2,3,4-tetrahydroanthracene. In agreement with this sequence of reactions, complexes **47**–**50** have been found to serve as catalyst precursors for the hydrogenation of anthracene with rates which ultimately level off to approximately the same value, suggesting that they give rise to a common catalytic mechanism. On the basis of NMR data, a pentagonal bipyramidal structure has been proposed for **50**. This compound is the entry to anionic trihydride derivatives. Its reactions with phosphines and CO rapidly afford $[RuH_3(PR_3)(PPh_3)_2]^-$ ($PR_3 = PPh_3$ (**47**), PMe_2Ph (**51**)) and $[RuH_3(CO)(PPh_3)_2]^-$ (**52**), according to Scheme 4. The triisopropylphosphine counterpart $[RuH_3(CO)(P^iPr_3)_2]^-$ (**53**) has been generated under hydrogen, by reaction of the chloride-hydride **31** with KH in the presence of crown ethers, and isolated as the $[KQ]^+$-salts (Q = 2.2.2-crypt, 18-crown-6, 1-aza-18-crown-6).[104] On the other hand, the related salts $[KQ][RuH_5(P^iPr_3)_2]$ (**54**) have been formed in a one-pot synthesis procedure starting from $RuCl_3 \cdot xH_2O$.[105] Treatment of $[RuCl_2(dcypb)(CO)]_2$ (**55**, dcypb =1,4-bis(dicyclohexylphosphino)butane) with 8 equiv of K-$[HB^sBu_3]$ affords $[RuH_3(CO)(dcypb)]^-$ (**56**), stabilized by interactions with a K^+ countercation and an intact $K[HB^sBu_3]$ moiety in the third coordination sphere. Complex **56** effects reduction of benzophenone under mild conditions. It is also active for ortho functionalization of this ketone under 20 atm of ethylene.[106]

Pentahydrides **50** and **54** undergo protonation with 1,3-benzenedimethanol to give the dihydride-bis(dihydrogen) derivatives $RuH_2(\eta^2\text{-}H_2)_2(PR_3)_2$ ($PR_3 = PPh_3$ (**57**), P^iPr_3 (**58**)).[107] These compounds are very unstable with respect to loss of H_2 and form the trihydride-bridged polyhydride dimers $(PR_3)_2HRu(\mu\text{-}H)_3RuH_2(PR_3)_2$ ($PR_3 = PPh_3$ (**59**), P^iPr_3 (**60**)). The classical or nonclassical nature of the terminal RuH_2 unit of these species is not clear and appears to depend upon the phosphine.[107−109] In addition to the protonation of anionic pentahydrides, RuH_6-complexes can be obtained by a variety of procedures (Scheme 5). Complex $RuH_2(\eta^2\text{-}H_2)_2(P^tBu_2Me)_2$ (**61**) has been prepared by reaction of the dichloride-dihydride **24** with $NaBH_4$ in the presence of methanol.[86] Leitner and co-workers have observed that a mixture of $Ru(\eta^3\text{-}C_4H_7)_2(\eta^4\text{-}COD)$ (**62**) and PCy_3 reacts with hydrogen to give $RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2$ (**63**) in high yield, whereas $Ru(\eta^3\text{-}C_4H_7)_2\{Cy_2P\text{-}(CH_2)_3PCy_2\}$ (**64**) leads to $\{Cy_2P(CH_2)_3PCy_2\}HRu(\mu\text{-}$

Scheme 4. Hydrogenation of Anthracene Promoted by Ruthenium Complexes and Related Reactions



Scheme 5. Preparation of $RuH_2(\eta^2\text{-}H_2)_2(PR_3)_2$ Complexes



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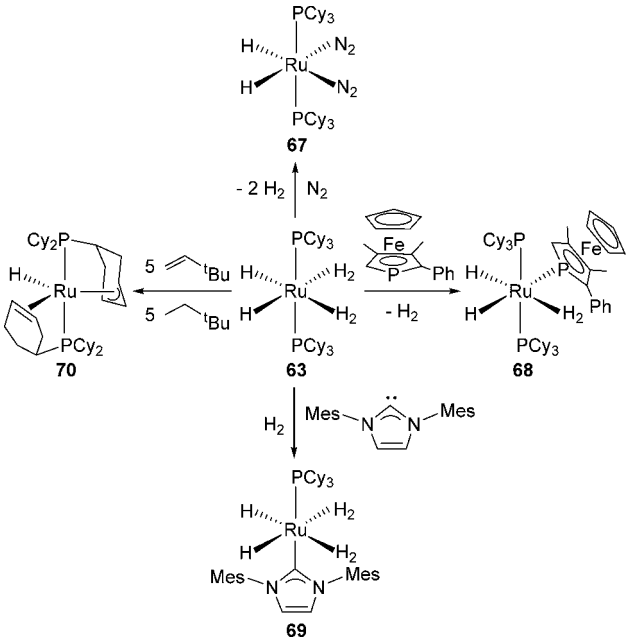
$H)_3RuH_2\{Cy_2P(CH_2)_3PCy_2\}$ (**65**) under identical conditions.[110] Grubbs has shown that complex **63** can be also obtained by hydrogenation (2 atm) of the polymeric material **29** in the presence of 2 equiv of PCy_3 and NaOH (excess) in *sec*-butyl alcohol;[111] modifications to this method have been described in several patents.[112,113] The most general procedure to prepare this type of compounds appears to be the hydrogenation of **40** in the presence of 2 equiv of phosphine.[97] In this way, complex $RuH_2(\eta^2\text{-}H_2)_2(PCyp_3)_2$ (**66**, $PCyp_3$ = tricyclopentylphosphine) has been obtained, in addition to **58** and **63**. The nonclassical nature of these compounds has been corroborated through the neutron diffraction structure of **66**.[114] The H−H distances in the coordinated hydrogen molecules are equal [0.825(8) and 0.835(8) Å], in excellent agreement with the results from DFT calculations at the B3LYP level (0.853 Å). The Ru−(H_2) distances lie between 1.730(5) and 1.764(5) Å, whereas the Ru−H bond lengths of 1.628(4) and 1.625(4) Å are in the expected range for classical hydrides. The separation between each hydride and its *cis* dihydrogen ligand of about 2.1 Å rules out the presence of any *cis* interaction. In solution, the hydride and dihydrogen ligands of these compounds rapidly exchange their positions. Furthermore, the dihydrogen ligands exchange with uncoordinated H_2 molecules. In agreement with both processes, the exposure of **63** and **66** to 3 bar of D_2 over a day has afforded the respective $RuD_2(\eta^2\text{-}D_2)_2(PR_3)_2$ (PR_3 = PCy_3,[115,116] $PCyp_3$[117]).

The tricyclohexylphosphine derivative **63** is the best-studied complex of this family. Its reactivity, which was reviewed by Sabo-Etienne and Chaudret in 1998,[55] is dominated by substitution and hydrogen transfer reactions. Substitutions (Scheme 6) can give rise to unusual complexes as the

Scheme 6. Some Reactions of 63

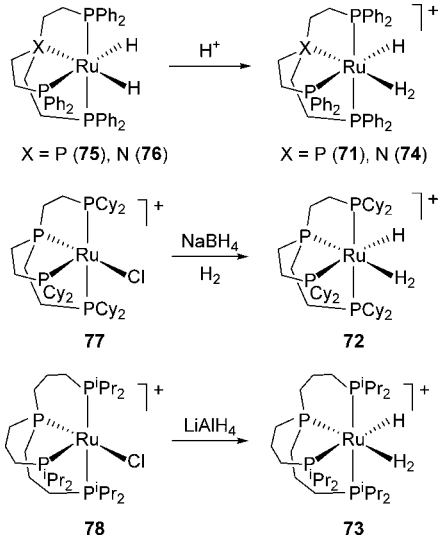


bis(dinitrogen) derivative $RuH_2(\eta^2\text{-}N_2)_2(PCy_3)_2$ (**67**) or the mixed phosphine-phosphine′ dihydride-dihydrogen compound $RuH_2(\eta^2\text{-}H_2)(PR_3)(PCy_3)_2$ (**68**, PR_3 = 2-phenyl-3,4-dimethylphosphaferrocene).[118] In contrast to this ferrocenephosphine, the treatment of **63** with 1,3-dimesitylimidazol-2-ylidene (IMes), under hydrogen, in hydrocarbon solvents leads to the mixed phosphine-NHC dihydride-bis(dihydrogen) $RuH_2(\eta^2\text{-}H_2)_2(IMes)(PCy_3)$ (**69**).[119] Rapid hydrogen transfer of up to five hydrogen molecules from **63** to unsaturated organic substrates can be achieved at room temperature to form $RuH\{(\eta^3\text{-}C_6H_8)PCy_2\}\{(\eta^2\text{-}C_6H_9)PCy_2\}$ (**70**). The regeneration of **63** upon bubbling hydrogen into solutions of **70** confers to this compound hydrogen store character. This property makes **63** a good catalyst precursor for hydrogenation reactions, including those of arenes.[120,121] It is also a catalyst precursor for the dehydrogenative silylation of alkenes and the ortho alkylation of aromatic ketones.[55]

2.2. Complexes with Tetrapodal and Tripodal Phosphine Ligands

Tetrapodal tetra- and triphosphines stabilize the cationic *cis*-hydride-dihydrogen derivatives $[RuH(\eta^2\text{-}H_2)(PP_3)]^+$ (PP_3 = $P(CH_2CH_2PPh_2)_3$ (**71**), $P(CH_2CH_2PCy_2)_3$ (**72**), $P(CH_2CH_2CH_2P^iPr_2)_3$ (**73**)) and $[RuH(\eta^2\text{-}H_2)(NP_3)]^+$ (**74**, NP_3 = $N(CH_2CH_2PPh_2)_3$) related to **21**−**23**. Complexes **71**[122,123] and **74**[124] have been prepared by protonation of the corresponding dihydrides $RuH_2\{P(CH_2CH_2PPh_2)_3\}$ (**75**) and $RuH_2\{N(CH_2CH_2PPh_2)_3\}$ (**76**), whereas the treatment of tetrahydrofuran solutions of the cationic five-coordinate chloride-precursors $[RuCl(PP_3)]^+$ (PP_3 = $P(CH_2CH_2PCy_2)_3$ (**77**), $P(CH_2CH_2CH_2P^iPr_2)_3$ (**78**)) with $NaBH_4$ or $LiAlH_4$, and subsequently with ethanol, affords **72**[125] and **73**[126] (Scheme 7).

Scheme 7. Preparation of Cationic *cis*-Hydride-Dihydrogen-Ruthenium(II) Complexes Containing Tetrapodal Phosphine Ligands



The *trans*-disposition of the dihydrogen ligand to the bridging atom of the phosphine has been confirmed by means of the X-ray diffraction structures of **73**[126] and **74**.[124] For complex **71**, a barrier to the rotation of the dihydrogen ligand (d_{H2} = 0.87 Å) of 1.36 kcal mol^{-1} has been determined by inelastic neutron scattering.[127] This compound has shown to be an efficient catalyst precursor for the dimerization of terminal alkynes to *Z*-1,4-disubstituted enynes,[128] the hydrogenation of phenylacetylene to styrene,[129] and the chemoselective reduction of *α*,*β*-unsaturated ketones to allylic alcohols via hydrogen transfer.[130,131]

The ligand *meso*-tetraphos-1 *S*,*R*-$Ph_2PCH_2CH_2P(Ph)$-$CH_2CH_2P(Ph)CH_2CH_2PPh_2$ stabilizes a *trans*-hydride-dihy-

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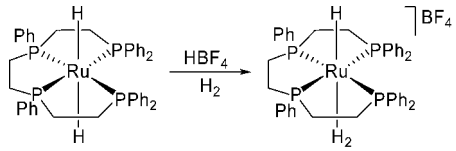
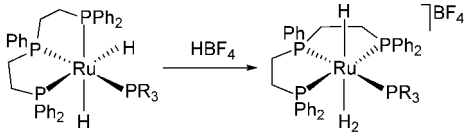
drogen counterpart,[132] in contrast to the phosphines shown in Scheme 7. Thus, the addition of $HBF_4{\cdot}OEt_2$ to diethyl ether solutions of the dihydride RuH_2(*meso*-tetraphos-1) (**79**), under hydrogen (1 atm), leads to [RuH(η^2-H_2)(*meso*-tetraphos-1)]BF_4 (**80**), which displays a dihydrogen H−H distance of 0.89 Å according to T_1(min) and J_{H-D} values (Scheme 8). In contrast to **71**−**74**, the position exchange between the hydride and dihydrogen ligands of **80** is slow.

Scheme 8. Protonation of 79



The protonation of the *cis*-dihydrides $RuH_2(P_3)(PR_3)$ (P_3 = $PPh(CH_2CH_2PPh_2)_2$; PR_3 = $P(OCH_2)_3CEt$ (**81**), PMe_2Ph (**82**)), containing tridentate and monodentate phosphines, with $HBF_4{\cdot}OEt_2$ gives the *trans*-hydride-dihydrogen derivatives [RuH(η^2-H_2)(P_3)(PR_3)]BF_4 (PR_3 = $P(OCH_2)_3CEt$ (**83**), PMe_2Ph (**84**)).[133] In the reaction, the binding mode of the triphos ligand changes from facial to meridional, which makes possible to place the η^2-dihydrogen molecule *trans* to the high *trans*-influence terminal hydride ligand (Scheme 9).

Scheme 9. Protonation of 81 and 82



PR_3 = $P(OCH_2)_3CEt$ (**81**) PR_3 = $P(OCH_2)_3CEt$ (**83**)
PMe_2Ph (**82**) PMe_2Ph (**84**)

2.3. Half Sandwich Compounds

Most complexes of this type are cyclopentadienyl (Cp) and pentamethylcyclopentadienyl (Cp*) trihydride derivatives. A noticeable characteristic of these species is the exceptionally large value of the H−H coupling constants of the hydride ligands, in the ^{1}H NMR spectra, which has been attributed to a quantum-mechanical exchange process,[134,135] although it has not been quantified on the basis of the two-dimensional harmonic oscillator model described in eq 1.

A facile general access to Cp-complexes has been reported by Nikonov and co-workers (Scheme 10). Treatment of the cationic precursors [Ru(η^5-C_5H_5)(CH_3CN)$_2$(PR_3)]PF_6 (PR_3 = PPh_3 (**85**), P^iPrPh_2 (**86**), P^iPr_2Ph (**87**), P^iPr_3 (**88**)) and the related NHC-supported derivative [Ru(η^5-C_5H_5)(py)$_2$(IPr)]-PF_6 (**89**; py = pyridine, IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene) with $LiAlH_4$ in tetrahydrofuran, followed by quenching the reaction mixture with degassed water, leads to the trihydride derivatives $RuH_3(\eta^5$-$C_5H_5)(PR_3)$ (PR_3 = PPh_3 (**90**), P^iPrPh_2 (**91**), P^iPr_2Ph (**92**), P^iPr_3 (**93**))[136] and $RuH_3(\eta^5$-$C_5H_5)$(IPr) (**94**),[137] respectively, in good yields.

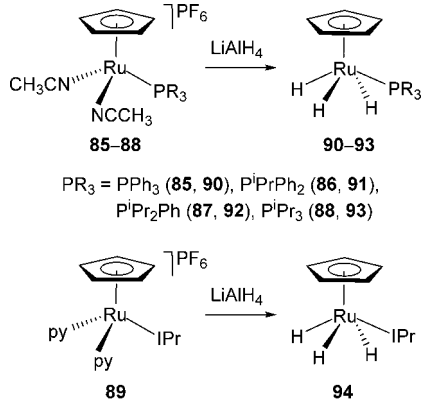
The related Cp*-complexes have been mainly prepared by three different methods, using $Li[HBEt_3]$, $NaBH_4$, and H_2 as hydride sources.

Treatment of the ruthenium(III) precursors $RuCl_2(\eta^5$-$C_5Me_5)(PR_3)$ (PR_3 = PMe_3 (**95**), PPh_3 (**96**), PCy_3 (**97**), P^iPr_3 (**98**)) with 2 equiv of $Li[HBEt_3]$ in tetrahydrofuran directly leads to the trihydrides $RuH_3(\eta^5$-$C_5Me_5)(PR_3)$ (PR_3 = PMe_3 (**99**), PPh_3 (**100**), PCy_3 (**101**), P^iPr_3 (**102**)),[138] according to Scheme 11. Similarly, the addition of 2 equiv of $Li[HBEt_3]$ to the ruthenium(II) NHC-precursors $RuCl(\eta^5$-$C_5Me_5)$(IMes) (**103**) and $RuCl(\eta^5$-$C_5Me_4Et)$(IMes) (**104**) affords $RuH_3(\eta^5$-$C_5Me_5)$(IMes) (**105**) and $RuH_3(\eta^5$-$C_5Me_4Et)$(IMes) (**106**), respectively.[139]

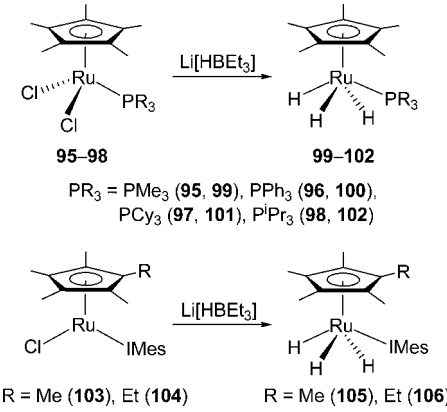
Sometimes $NaBH_4$ has been used instead of $Li[HBEt_3]$ (Scheme 12). Thus, reactions of $NaBH_4$ with $RuCl_2(\eta^5$-$C_5Me_5)$-(PR_3) (PR_3 = PMe_3 (**95**), PPh_3 (**96**), PCy_3 (**97**), P^iPr_3 (**98**), PEt_3 (**107**), PPh_2Me (**108**), P(pyrrolyl)$_3$ (**109**)) and $RuCl_2(\eta^5$-$C_5Me_5)(EPh_3)$ (EPh_3 = $SbPh_3$ (**110**), $AsPh_3$ (**111**)) in ethanol result in the formation of the trihydrides $RuH_3(\eta^5$-$C_5Me_5)$-(PR_3) (PR_3 = PEt_3 (**112**), PPh_2Me (**113**),[140] P(pyrrolyl)$_3$ (**114**)[141]) and $RuH_3(\eta^5$-$C_5Me_5)$ (EPh_3) (EPh_3 = $SbPh_3$ (**115**), $AsPh_3$ (**116**)),[142] in addition to **99**−**102**. In this case, the reactions take place via the tetrahydrideborate intermediates $Ru(\kappa^2$-$H_2BH_2)(\eta^5$-$C_5Me_5)(PR_3)$, which decompose in the alcohol. Starting from $RuCl(\eta^5$-$C_5Me_5)(\kappa^2$-*P*,*N*-^{i}Pr$_2$PCH$_2$X) (X = pyridyl (**117**), quinolyl (**118**)), the same procedure gives $RuH_3(\eta^5$-$C_5Me_5)(\kappa^1$-*P*-^{i}Pr$_2$PCH$_2$X) (X = pyridyl (**119**), quinolyl (**120**)).[143]

Reactions of Ru(A)(η^5-C_5Me_5)(P^iPr_2Ph) (A = $OSiPh_3$ (**121**), NHPh (**122**), OCH_2CF_3 (**123**)) with hydrogen give, at −60 °C, Ru(A)(H)$_2$(η^5-C_5Me_5)(P^iPr_2Ph) (A = $OSiPh_3$ (**124**), NHPh (**125**), OCH_2CF_3 (**126**)), where the two hydride

Scheme 10. Preparation of $RuH_3(\eta^5$-$C_5H_5)$L Complexes Using $LiAlH_4$



Scheme 11. Preparation of $RuH_3(\eta^5$-$C_5Me_4R)$L Complexes by Using $Li[HBEt_3]$



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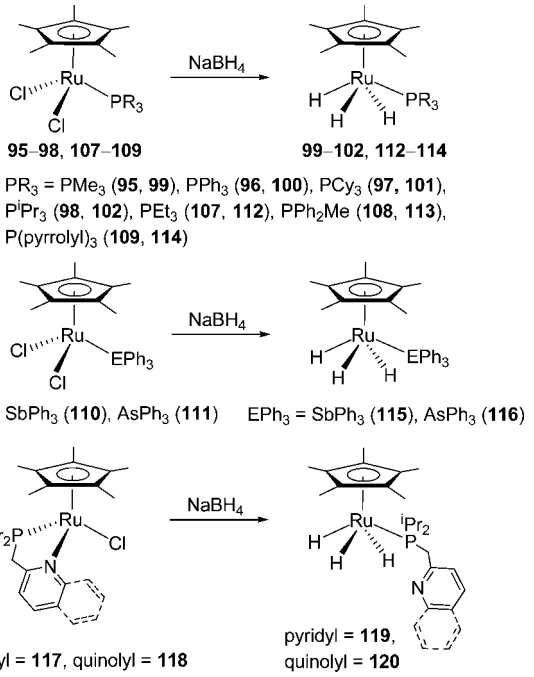
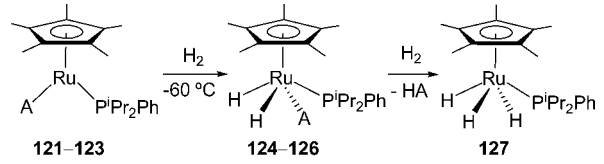
Scheme 12. Preparation of $RuH_3(\eta^5\text{-}C_5Me_5)L$ Complexes by Using $NaBH_4$



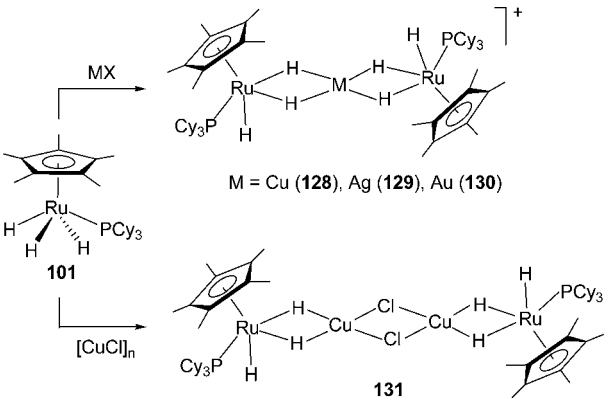
ligands are *cisoid* disposed. These molecules react with additional hydrogen to yield $RuH_3(\eta^5\text{-}C_5Me_5)(P^iPr_2Ph)$ (**127**) and liberate HA (Scheme 13).[144]

Scheme 13. Sequential Hydrogenolysis of 121−123



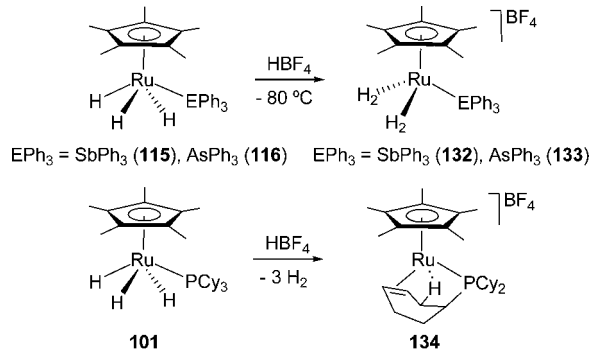
These trihydride derivatives are good Lewis bases that have been used to prepare acid−base adducts with metallic Lewis acids (Scheme 14). Addition of $[Cu(CH_3CN)_4]PF_6$, $AgBF_4$, and $[Au(THT)_2]PF_6$ (THT = tetrahydrothiophene) to tetrahydrofuran solutions of **101** leads to the heterometallic derivatives $[\{RuH(\eta^5\text{-}C_5Me_5)(PCy_3)(\mu\text{-}H)_2\}_2M]A$ (M = Cu (**128**), Ag (**129**), Au (**130**); A = BF_4 or PF_6),[145] whereas the reaction of **101** with $[CuCl]_n$ affords $[\{RuH(\eta^5\text{-}C_5Me_5)(PCy_3)(\mu\text{-}H)_2\}Cu(\mu\text{-}Cl)]_2$ (**131**),[146] which has been characterized by X-ray diffraction analysis. The d^{10} cation of these adducts has a significant effect on the quantum-mechanical exchange coupling of the hydride ligands, increasing the H−H coupling constant, with regard to the starting trihydride, with increasing electronegativity of the coinage metal.[145]

Scheme 14. Reactions of 101 with Metallic Lewis Acids



These trihydride complexes are also Brønsted bases (Scheme 15). Thus, for instance, complexes **115** and **116** are protonated

Scheme 15. Protonation of $RuH_3(\eta^5\text{-}C_5Me_5)L$ Complexes



by $HBF_4{\cdot}OEt_2$ in dichloromethane at −80 °C, furnishing the cationic bis(dihydrogen) derivatives $[Ru(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}H_2)_2(EPh_3)]BF_4$ (EPh_3 = $SbPh_3$ (**132**), $AsPh_3$ (**133**)). These species are unstable and decompose at temperatures higher than 0 °C.[142] On the other hand, the protonation of **101** with $HBF_4{\cdot}OEt_2$ produces the evolution of 3 mol of H_2 and the formation of $[Ru(\eta^5\text{-}C_5Me_5)(C_6H_9PCy_2)]BF_4$ (**134**), containing a cyclohexenyl group coordinated through the C−C double bond and a strong agostic interaction.[146]

The reactions of **119** and **120** with weak Brønsted acids such as $PhCO_2H$, indole, and salicylic acid in benzene or toluene result in the formation of hydrogen-bonded adducts between the proton donor and the pendant pyridyl of quinolyl group. In dichloromethane, there is spectroscopic evidence for the proton transfer to a hydride to yield a dihydride-dihydrogen species. In agreement with this, the protonation with CF_3SO_3H (HOTf) initially gives $[RuH_3(\eta^5\text{-}C_5Me_5)(\kappa^1\text{-}P\text{-}^iPr_2PCH_2XH)]^+$ (X = pyridyl (**135**), quinolyl (**136**)). Then, the NH-proton is transferred to one of the hydrides. The protonation of the resulting dihydride-dihydrogen species $[RuH_2(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}H_2)(\kappa^1\text{-}P\text{-}^iPr_2PCH_2X)]^+$ (X = pyridyl (**137**), quinolyl (**138**)) affords the bis(dihydrogen) derivatives $[Ru(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}H_2)_2(\kappa^1\text{-}P\text{-}^iPr_2PCH_2XH)]^{2+}$ (X = pyridyl (**139**), quinolyl (**140**)), in equilibrium with the corresponding dicationic dihydride-dihydrogen tautomers $[RuH_2(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}H_2)(\kappa^1\text{-}P\text{-}^iPr_2PCH_2XH)]^{2+}$ (X = pyridyl (**140**), quinolyl (**142**); Scheme 16).[143]

2.4. Complexes with Tris(pyrazoyl)borate and Related Ligands

The tris(pyrazolyl)borate (Tp) group avoids four-legged piano stool structures, typical for Cp and Cp* ligands, and enforces dispositions allowing N−M−N angles close to 90°. These structures favor the nonclassical interactions between the hydrogen atoms bound to the metal center. Thus, in contrast to Cp and Cp*, the TpRu-polyhydride species always contain at least a dihydrogen ligand.

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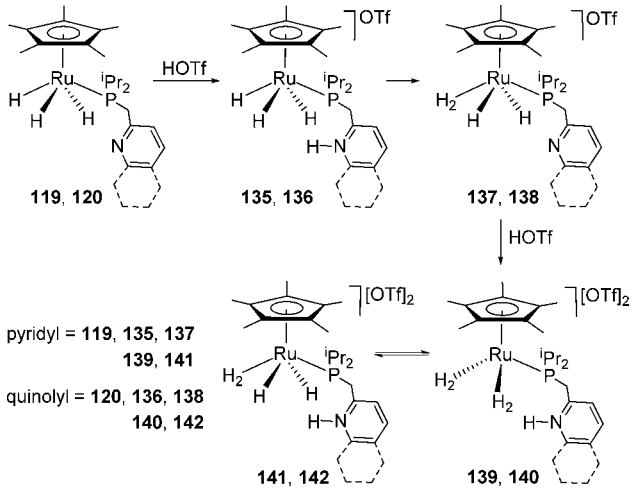
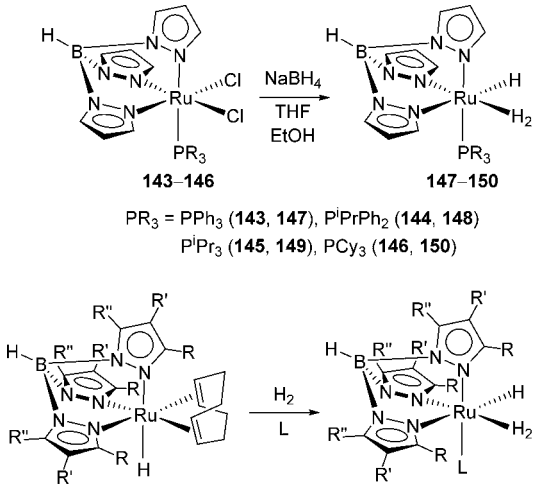
Scheme 16. Double Protonation of 119 and 120



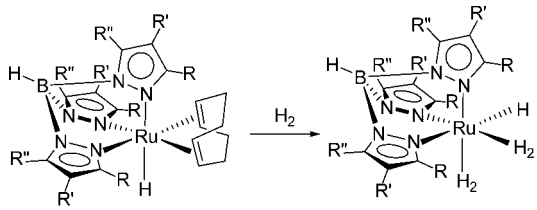
Several hydride-dihydrogen complexes have been isolated and characterized with Tp-type ligands. They have been mainly prepared through two procedures. Reduction of the ruthenium(III) precursors $RuCl_2Tp(PR_3)$ (PR_3 = PPh_3 (**143**), P^iPrPh_2 (**144**), P^iPr_3 (**145**), PCy_3 (**146**)) with $NaBH_4$ in a mixture of tetrahydrofuran-ethanol affords $RuHTp(\eta^2\text{-}H_2)(PR_3)$ (PR_3 = PPh_3 (**147**), P^iPrPh_2 (**148**), P^iPr_3 (**149**), PCy_3 (**150**)),[147] whereas the hydrogenation of $RuHTp^R(\eta^4\text{-COD})$ (Tp^R = hydridetris(3,5-dimethylpyrazolyl)borate (Tp^{Me2}; **151**), hydridetris(3-isopropyl-4-bromopyrazolyl)borate (Tp′; **152**)) in the presence of a monodentate ligand leads to $RuHTp^R(\eta^2\text{-}H_2)L$ (Tp^R = Tp^{Me2}, L = PCy_3 (**153**), py (**154**), THT (**155**); Tp^R = Tp′, L = PCy_3 (**156**), py (**157**), THT (**158**), $NHEt_2$ (**159**)).[148,149] The octahedral geometry of these compounds (Scheme 17) has been confirmed by the X-ray structure of **149**.[150] The H−H distance of about 1.0 Å is consistent with the T_1(min) values found for these species.[147−153]

Scheme 17. Hydride-Dihydrogen−Ruthenium(II) Complexes with Tp-Type Ligands



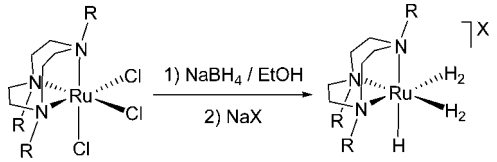
Hydrogenation of **151** and **152** in the absence of a monodentate ligand yields the hydride-bis(dihydrogen) complexes $RuHTp^R(\eta^2\text{-}H_2)_2$ (Tp^R = Tp^{Me2} (**160**), Tp′ (**161**)), according to Scheme 18. These compounds have been characterized by classical analytical and spectroscopic methods, including T_1 measurements and J_{H-D} coupling constants.[148,149]

Scheme 18. Hydride-bis(Dihydrogen)-Ruthenium(II) Complexes with Tp-Type Ligands



1,4,7-Triazacyclononane (TACN) and 1,4,7-trimethyl-1,4,7-triazacyclononane (TACN*) are neutral Tp counterparts, which also enforce dispositions allowing N−Ru−N angles close to 90° and therefore favor nonclassical interactions. Thus, the treatment of $RuCl_3$(TACN) (**162**) and $RuCl_3$(TACN*) (**163**) with $NaBH_4$ in ethanol leads to the respective cationic hydride-bis(dihydrogen) derivatives $[RuH(\eta^2\text{-}H_2)_2(TACN)]^+$ (**164**) and $[RuH(\eta^2\text{-}H_2)_2(TACN^*)]^+$ (**165**), after the addition of $Na[BPh_4]$, $NaBF_4$, or $[NH_4]PF_6$ (X^- in Scheme 19). At

Scheme 19. Hydride-bis(Dihydrogen)-Ruthenium(II) Complexes with TACN-Type Ligands



room temperature, these cations lose molecular hydrogen. Complex **164** is converted into the tetranuclear octahydride cluster compound $[\{(TACN)Ru\}_4(\mu\text{-}H)_6(\mu_3\text{−}H)_2]^{4+}$ (**166**), whereas the dehydrogenation of **165** affords the diruthenium-trihydride derivative $[\{(TACN^*)Ru\}_2(\mu\text{-}H)_3]^{2+}$ (**167**). Reactions of **165** with 5d-polyhydrides give rise to heterobimetallic dinuclear species.[154,155]

2.5. Complexes with Pincer Ligands

Molecular hydrogen displaces the water molecule of the POP-cations $[RuH(H_2O)(POP)(PPh_3)]^+$ (POP = 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (xantphos; **168**), bis(2-diphenylphosphinophenyl)ether (DPEphos; **169**), $(Ph_2PCH_2CH_2)_2O$ (**170**)) to give the respective *trans*-hydride-dihydrogen derivatives $[RuH(\eta^2\text{-}H_2)(POP)(PPh_3)]^+$ (POP = xantphos (**171**), DPEphos (**172**), $(Ph_2PCH_2CH_2)_2O$ (**173**)). The *trans*-disposition of the hydride and dihydrogen ligands (Chart 3), which agrees well with the low thermal stability of these compounds, is strongly supported by the presence of two high field resonances in the ^1H NMR spectra of the complexes. The values of T_1(min) of the dihydrogen signal and J_{H-D} coupling constants are consistent with dihydrogen H−H distances of about 0.9 Å.[156]

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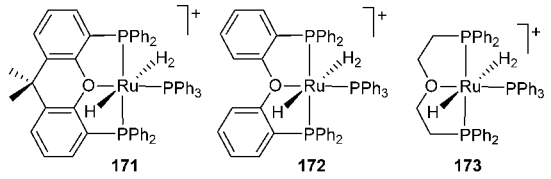
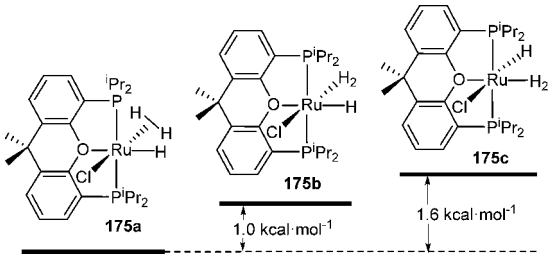
Chart 3. *trans*-Hydride-Dihydrogen Derivatives [RuH(η^2-H_2)(POP)(PPh_3)]$^+$



Molecular hydrogen also displaces the dimethyl sulfoxide ligand of the neutral complex RuHCl{xant(P^iPr_2)$_2$}(κ^1-*S*-DMSO) (**174**, xant(P^iPr_2)$_2$ = 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene) to afford RuHCl(η^2-H_2)-{xant(P^iPr_2)$_2$} (**175**). DFT calculations have revealed that there are three isomers with the chloride ligands *cis*-disposed to the oxygen atom of the diphosphine and the hydrogen atoms bonded to the metal center lying in the perpendicular plane to the P−Ru−P direction, which differ by 1.6 kcal mol^{-1} (ΔG at 1 atm and 298.15 K): the *trans*-Cl−Ru−H_2 derivatives **175a** and **175b** and the *trans*-O−Ru−H_2 species **175c** (Chart 4). The

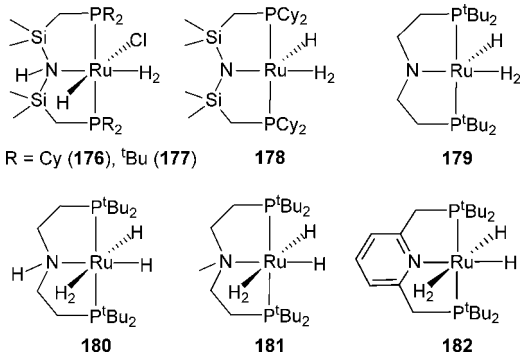
Chart 4. Relative Energies of RuHCl(η^2-H_2){xant(P^iPr_2)$_2$} Isomers



main difference between **175a** and **175b** is the separation between the atoms of the dihydrogen: 1.248 Å for the first of them and 0.907 Å for the second one. The separation in **175c** of 0.933 Å is similar to that of **175b**. The average of these distances, 1.03 Å, is consistent with the J_{H-D} value found, suggesting a fast equilibrium between the three isomers in solution. The *trans*-disposition of the π-donor oxygen and chlorine atoms causes the destabilization of **175**. Thus, there are also three *trans*-hydride-dihydrogen structures (d_{H2} = 0.812−0.820 Å), which lie between 8.6 and 11.0 kcal mol^{-1} above **175a**.[157]

The PNP-complexes RuHCl(η^2-H_2){($R_2PCH_2SiMe_2$)$_2$NH} (R = Cy (**176**), ^{t}Bu (**177**)) are also *cis*-hydride-dihydrogen species. The X-ray structure of **177** has revealed that the dihydrogen ligand occupies the position *trans* to the NH group, in the solid state. Lithium 2,2,6,6-tetramethylpiperidine and Me_3SiCH_2Li remove HCl from **176** to afford the five-coordinate amido derivative RuH(η^2-H_2)-{($Cy_2PCH_2SiMe_2$)$_2$N} (**178**). DFT calculations suggest an square pyramidal geometry for this compound with the hydride in the apex and the dihydrogen, *trans* to the N atom, in the base (Chart 5).[158] The related compound RuH(η^2-H_2)-{(^{t}Bu$_2$PCH$_2$CH$_2$)$_2$N} (**179**), containing CH_2 instead of $SiMe_2$, has been generated by hydrogenation of **62** in the presence of (^{t}Bu$_2$PCH$_2$CH$_2$)$_2$NH. Under hydrogen atmosphere, complex **179** is in equilibrium with the dihydride-dihydrogen RuH$_2$(η^2-H_2){(^{t}Bu$_2$PCH$_2$CH$_2$)$_2$NH} (**180**), resulting from the addition of H_2 along the Ru−N bond of **179**. By using (^{t}Bu$_2$PCH$_2$CH$_2$)$_2$NMe instead of (^{t}Bu$_2$PCH$_2$CH$_2$)$_2$NH,

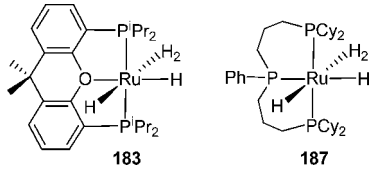
Chart 5. PNP Ruthenium Polyhydrides



the hydrogenation yields the dihydride-dihydrogen RuH$_2$(η^2-H_2){(^{t}Bu$_2$PCH$_2$CH$_2$)$_2$NMe} (**181**). Because the methyl group blocks the nitrogen position, cooperative properties acting as a proton donor or acceptor are avoided for this atom. Thus, the formation of **179** is not possible due to the absence of a neighboring proton source.[159] Complexes **179** and **180** catalyze the hydrogenation of aromatic and aliphatic nitriles into amines and imines.[160] Complex RuH$_2$(η^2-H_2)(dtbpmp) (**182**, dtbpmp =2,6-bis(di-*tert*-butylphosphino)methylpyridine), which also catalyzes the hydrogenation of nitriles to amines,[161] can be generated in a similar way as **181** by means of the hydrogenation of **62** in the presence of the diphosphine.[162]

The same method has not been successful to prepare RuH$_2$(η^2-H_2){xant(P^iPr_2)$_2$} (**183**), which is an efficient catalyst precursor for the hydrogen transfer from 2-propanol to ketones, the alkylations of nitriles and ketones with alcohols, and the regio- and stereoselective head-to-head (*Z*)-dimerization of terminal alkynes. In contrast to **62**, the hydrogenation of **40** in the presence of xant(P^iPr_2)$_2$ leads to **183** in about a 40% yield. Nevertheless, the most efficient procedure to generate this compound is the decomposition of the tetrahydrideborate RuH(κ^2-H_2BH_2){xant(P^iPr_2)$_2$} (**184**), which can be obtained starting from RuCl$_2$){xant(P^iPr_2)$_2$}(κ^1-*S*-DMSO) (**185**), via the allenylidene intermediate RuCl$_2$(=C=C=CPh_2){xant-(P^iPr_2)$_2$} (**186**). DFT calculations suggest that the *trans*-disposition of the coordinated hydrogen molecule to one of the hydride ligands is favored with regard to the π-donor atom.[157] A related PPP-complex, RuH$_2$(η^2-H_2)(Cyttp) (**187**, Cyttp = PhP($CH_2CH_2CH_2PCy_2$)$_2$), has been prepared by metathesis reaction of RuCl$_2$(Cyttp) (**188**) with NaH in tetrahydrofuran under atmospheric hydrogen pressure[163] (Chart 6).

Chart 6. Dihydride-Dihydrogen Complexes with POP- and PPP-Pincer Ligands



The direct hydrogenation route even allows preparing RuH$_5$-species. Thus, complex **62** cleanly reacts with H_2 (7 bar) at 50 °C in the presence of 1,3-bis(di-*tert*-butylphosphino)-methylbenzene to give the hydride-bis(dihydrogen) derivative RuH{2,6-($CH_2P^tBu_2$)C_6H_3}(η^2-H_2)$_2$ (**189**).[164] DFT calculations show that the arrangement of the two dihydrogen ligands in a *cis* position is clearly favored over the alternative *trans*

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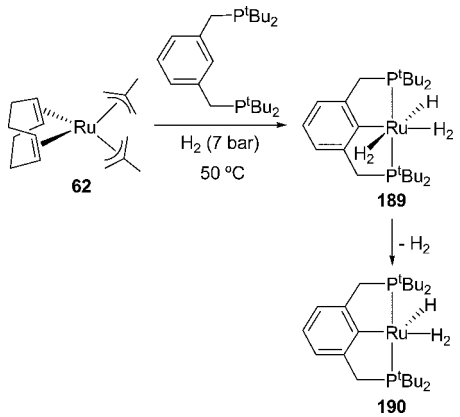
disposition.[165] Complex **189** loses molecular hydrogen to afford the five-coordinate hydride-dihydrogen RuH{2,6-($CH_2P^tBu_2$)C_6H_3}(η^2-H_2) (**190**) with the same geometry as **179** (Scheme 20).[164,165]

Scheme 20. Ruthenium(II)-Polyhydrides with PCP-Pincer Ligands

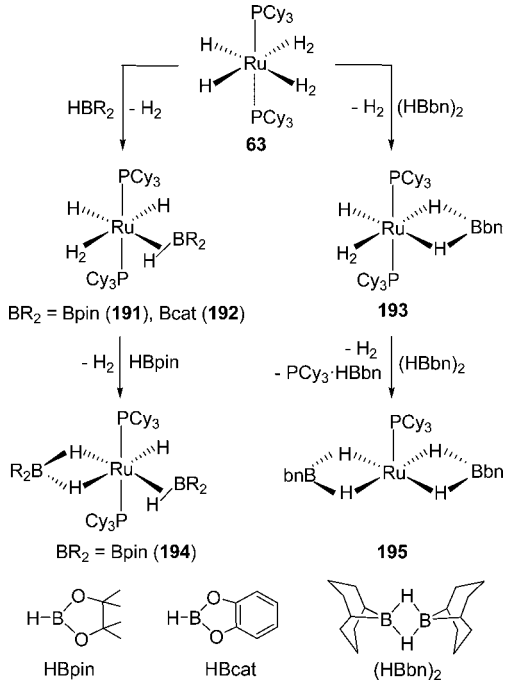


2.6. Ruthenium-Polyhydride Complexes Involved in σ-Bond Activation Reactions

2.6.1. B−H Bond Activation Reactions and Related Processes. Boranes displace the coordinated hydrogen molecules of the dihydride-bis(dihydrogen) complex **63**. The reactions with 1 equiv of either pinacolborane (HBpin) or catecholborane (HBcat) lead to the dihydride-σ-borane-dihydrogen derivatives RuH$_2$(η^2-HBR$_2$)(η^2-H$_2$)(PCy$_3$)$_2$ (BR$_2$ = Bpin (**191**), Bcat (**192**)). In contrast to the boronate esters, the reaction with the diborane 9-borabicyclo[3.5.1]nonane ((HBbn)$_2$), containing a more acidic boron than HBpin and HBcat, affords the hydride-dihydrideborate-dihydrogen derivative RuH(κ^2-H$_2$Bbn)(η^2-H$_2$)(PCy$_3$)$_2$ (**193**), as a result of the substitution of a dihydrogen ligand and the hydride stabilization of the resulting σ-borane intermediate.[166] In the presence of an excess of borane, the second coordinated hydrogen molecule is displaced. Thus, the hydride-dihydrideborate-σ-borane complex RuH(κ^2-H$_2$Bpin)(η^2-HBpin)(PCy$_3$)$_2$ (**194**)[167] and the bis-(dihydrideborate) derivative Ru(κ^2-H$_2$Bbn)$_2$(PCy$_3$)(**195**)[168] are formed with HBpin and (HBbn)$_2$, respectively, under these conditions (Scheme 21). Complexes **63** and **194** catalyze HBpin-borylation of linear and cyclic alkenes with the same efficiency and selectivity. Hydroboration into the corresponding linear pinacolboronates is achieved for 1-hexene, 1-octene, styrene, and allylbenzene. However, hydroboration and dehydrogenative borylation are competitive for cyclic substrates, having the ring size a marked influence on the selectivity. Hydroboration of a C$_6$-ring is selectively achieved, whereas allylboronate, a mixture of allylboronate and vinylboronate, and only vinylboronate are formed with C$_7$-, C$_8$-, and C$_{10}$-rings, respectively.[169]

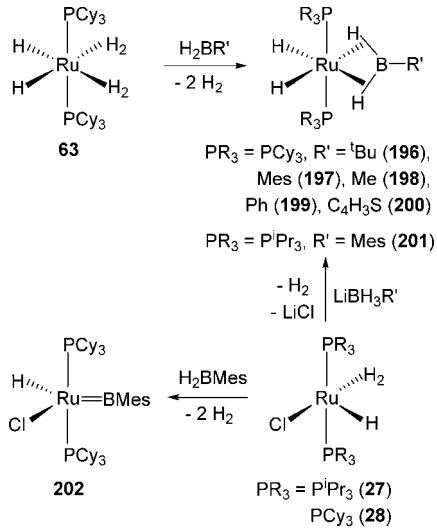
Primary alkyl- and arylboranes displace both coordinated hydrogen molecules of **63**. The reactions of the latter with *tert*-butylborane (H_2B^tBu) and mesitylborane (H_2BMes) lead to the bis(σ-borane) derivatives RuH$_2$(η^2,η^2-H$_2$BR′)(PCy$_3$)$_2$ (R′ = ^{t}Bu (**196**),[170] Mes (**197**)[171]). An alternative synthesis of these compounds involves the reaction of the chloride-hydride-dihydrogen complexes **27** and **28** with the corresponding lithium trihydrideborate. In addition to **196** and **197**,

Scheme 21. Reactions of 63 with Boranes



complexes RuH$_2$(η^2,η^2-H$_2$BR′)(PR$_3$)$_2$ (PR$_3$ = PCy$_3$, R′ = Me (**198**), Ph (**199**), C$_4$H$_3$S (**200**); PR$_3$ = P^{i}Pr$_3$, R′ = Mes (**201**)) have been prepared by this procedure.[172] The reaction of **28** with mesitylborane gives the borylene RuHCl(=BMes)(PCy$_3$)$_2$ (**202**) and H$_2$, as a result of the activation of both B−H bonds of the borane (Scheme 22).[173]

Scheme 22. Bis(σ-Borane) and Borylene Derivatives



Amine-boranes (H_3B−NH_nR_{3-n}, n = 1−3) undergo stoichiometric dehydrogenation in the presence of **63**.[174,175] The resulting aminoboranes coordinate to the metal center[27,176,177] to form the bis(σ-B−H) aminoborane derivatives RuH$_2$(η^2,η^2-H$_2$BNRR′)(PCy$_3$)$_2$ (NRR′ = NH$_2$ (**203**), NMe$_2$ (**204**), NHMe (**205**))[174,175] related to **196**−**201**. Peripheral tertiary amine and methoxy functions in the borane are tolerated; as a consequence, complexes RuH$_2${η^2,η^2-H$_2$BN(Me)CH$_2$CH$_2$X}(PCy$_3$)$_2$ (X = NMe$_2$, (**206**),

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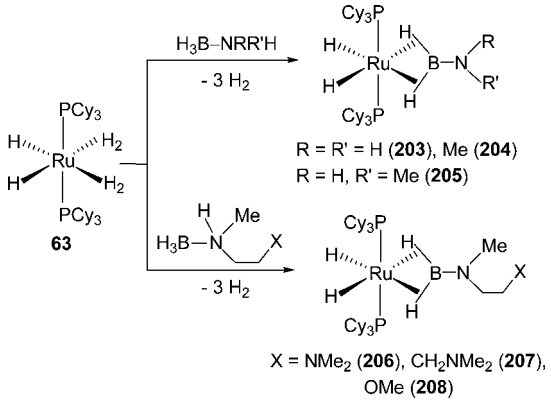
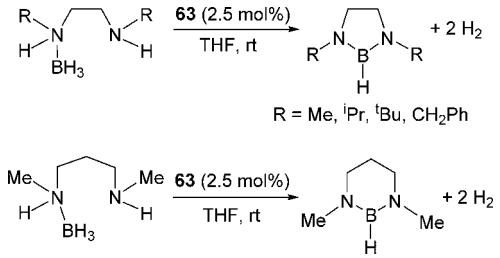
CH_2NMe_2 (**207**), OMe (**208**)) have also been isolated and characterized (Scheme 23). However, if the peripheral function is a secondary amine, a catalytic dehydrogenative cyclization takes place to yield 1,3,2-diazaborolidines (Scheme 24).[178,179]

Scheme 23. Reactions of 63 with Amineboranes

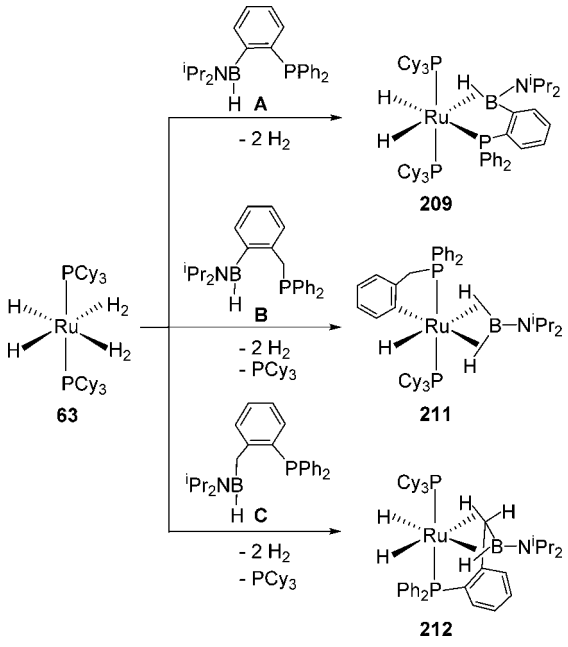


Scheme 24. Catalytic Formation of 1,3,2-Diazaborolidines Promoted by 63



The reactions of **63** with the phosphine-aminoboranes $Ph_2P(CH_2)_nC_6H_4$-*o*-$(CH_2)_{n'}BHN^iPr_2$ ($n = n' = 0$ (**A**); $n = 1$, $n' = 0$ (**B**); $n = 0$, $n' = 1$ (**C**)) are of particular interest (Scheme 25). Complex **63** initially reacts with **A** to give

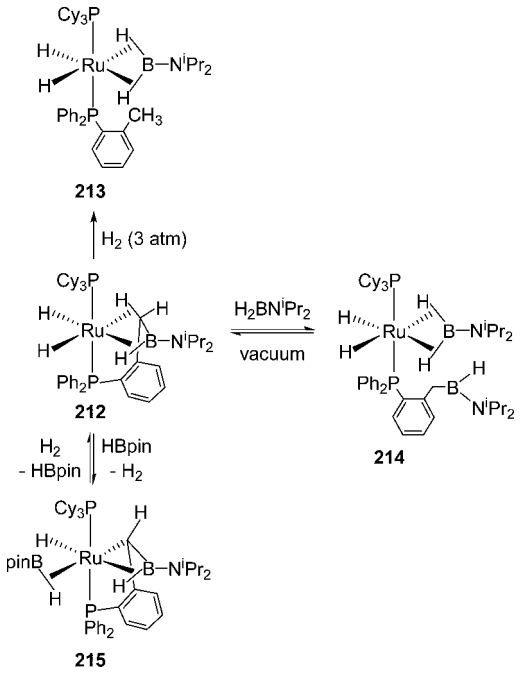
Scheme 25. Reactions of 63 with Phosphine-Aminoboranes



$RuH_2(PPh_2C_6H_4$-*o*-$BHN^iPr_2)(PCy_3)_2$ (**209**), as a result of the displacement of both dihydrogen molecules by the phosphine-aminoborane. In solution, **209** dissociates a PCy_3 ligand to form the unsaturated species $RuH_2(PPh_2C_6H_4$-*o*-$BHN^iPr_2)(PCy_3)$ (**210**), with a hydride ligand trans to a vacant. In both cases, the phosphine-aminoborane acts as a bifunctional chelate ligand through the phosphine moiety and a Ru–H–B agostic interaction.[180] The behavior of **B**, containing a methylene linker between the phosphorus atom and the aryl bridge, is different. No agostic σ-B–H complex is formed; the reaction leads to a new bis(σ-borane)-ruthenium complex, $RuH(C_6H_4$-*o*-$CH_2PPh_2)(\eta^2,\eta^2$-$H_2BN^iPr_2)(PCy_3)$ (**211**), via B–C bond cleavage and Ru–C bond formation.[181] In contrast to **B**, the phosphine-aminoborane **C**, with a methylene linker between the boron atom and the aryl bridge, saturates a **C**-counterpart of **210**, $RuH_2(PPh_2C_6H_4$-*o*-$CH_2BHN^iPr_2)(PCy_3)$ (**212**) by means of an additional δ-agostic interaction.[182]

The coordination mode of **C** in **212** shows the stabilization of a 14-valence electrons fragment RuH_2P_2 through connected σ-bonds of different polarity and allows selective B–H, C–H, and B–C bond activations as illustrated by reactions with H_2 and boranes (Scheme 26). Pressurization of a benzene-d_6

Scheme 26. B–H, C–H, and B–C Bond Activation Reactions on 212



solution of **212** under 3 atm of H_2 leads to B–C bond cleavage of the ligand and quantitative and irreversible formation of $RuH_2(\eta^2,\eta^2$-$H_2BN^iPr_2)(PPh_2C_6H_4$-*o*-$CH_3)(PCy_3)$ (**213**). Addition of diisopropylaminoborane to **212** gives rise to an equilibrium mixture between the latter and $RuH_2(\eta^2,\eta^2$-$H_2BN^iPr_2)\{PPh_2(C_6H_4$-*o*-$CH_2BHN^iPr_2)\}(PCy_3)$ (**214**). Reaction of **212** with HBpin leads to the five-membered metallacycle complex $RuH\{PPh_2(C_6H_4$-*o*-$CHBHN^iPr_2)\}(\eta^2$-HBpin)(PCy_3) (**215**) featuring a Ru–C single bond as a result of a further activation of the agostic C–H bond and loss of H_2. The reaction is reversible as shown by exposure of **215** to H_2, with the bis(agostic) complex **212** and free HBpin being restored.

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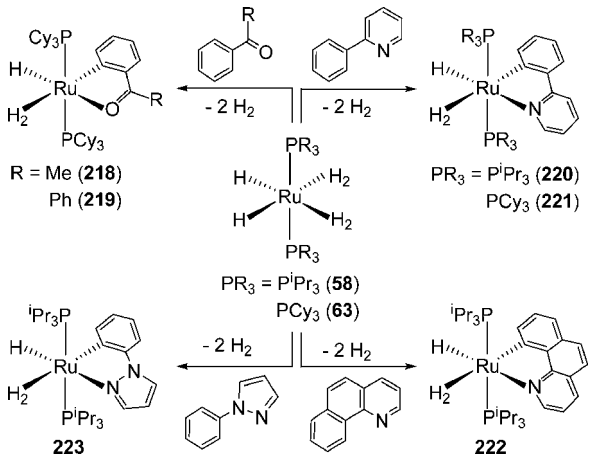
Complex **63** is undoubtedly the best studied from the B−H bond activation point of view. There are however a few other compounds that also promote relevant processes involving B−H cleavage, which should be mentioned. The dihydride-bis(dihydrogen) **66** catalyzes the reduction of CO_2 with HBpin to give formaldehyde which, under mild conditions, leads to imines by condensation with primary amines.[183−185] The cationic hydride-dihydrogen **74**, containing a NP_3-tetrapodal polyphosphine, catalyzes the kinetically controlled dehydrogenation of ammonia-borane, with release of 2 equiv of H_2 per equiv of $H_3B{-}NH_3$ and concomitant polyborazylene and cyclic polyaminoborane formation.[124] The dihydride-dihydrogen PNP-pincer complex **182** catalyzes the anti-Markovnikov-type addition of HBpin to terminal alkynes yielding *Z*-vinylboronates under mild conditions. The hydride-dihydrideborate complex RuH(κ^2-H_2Bpin)(dtbpmp) (**216**), which was identified at the end of the reaction, is proposed as the direct precursor for the catalytic cycle involving rearrangement of coordinated alkyne to vinylidene as the key step for the apparent trans-hydroboration.[186]

2.6.2. C−H Bond Activation. The dihydride-bis(dihydrogen) **63** catalyzes the hydrogenation of benzonitrile to benzylamine, at room temperature and under mild pressure. The catalytic resting state, RuH{κ^2-*N*,*C*-(NH=CHC_6H_4)}(η^2-H_2)(PCy_3)$_2$ (**217**), results from the trapping of the intermediate imine by means of a chelate-assisted *ortho*-CH bond activation of the phenyl group.[187]

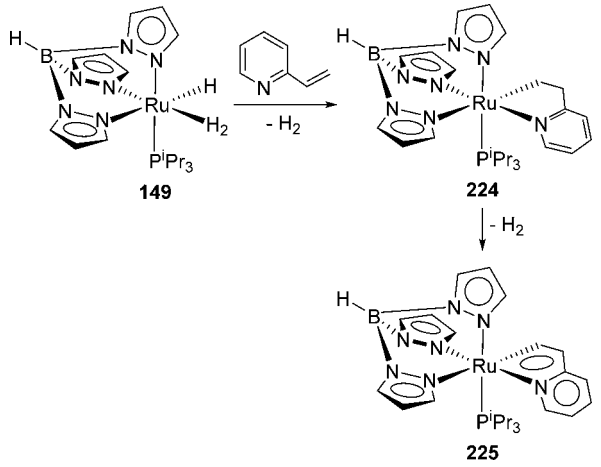
The chelate-assistance strategy is considered to be one of the most efficient ways to achieve selectivity in C−H bond activation. Complexes **58** and **63** promote the chelate assisted C−H bond activation of acetophenone, benzophenone, 2-phenylpyridine (Ph-py), benzoquinoline (Hbq), and phenylpyrazole (Ph-pz) to afford the corresponding orthometalated hydride-dihydrogen derivatives RuH{κ^2-*O*,*C*-[OC(R)C_6H_4]}(η^2-H_2)(PCy_3)$_2$ (R = Me (**218**), Ph (**219**)), RuH{κ^2-*N*,*C*-(py-C_6H_4)}(η^2-H_2)(PR_3)$_2$ (PR_3 = P^iPr_3 (**220**), PCy_3 (**221**)), RuH{κ^2-*N*,*C*-(bq)}(η^2-H_2)(P^iPr_3)$_2$ (**222**), and RuH{κ^2-*N*,*C*-(pz-C_6H_4)}(η^2-H_2)(P^iPr_3)$_2$ (**223**) (Scheme 27),[188,189] which are analogous to **217** and reminiscent of intermediates proposed for the insertion of olefins into aromatic C−H bonds located in the ortho position relative to a coordinating group, in agreement with the ability of the $RuH_2(\eta^2\text{-}H_2)_2$-compounds to catalyze the ortho alkylation of aromatic ketones.[55,190−192] Protonation of **220** and **222** yields cationic *cis*-hydride-dihydrogen derivatives containing the heterocycle coordinated through the heteroatom and a phenyl *ortho* CH bond.[193,194]

The tris(pyrazolyl)borate hydride-dihydrogen complex **149** activates 2-vinylpyridine. In toluene, the reaction initially gives the 1,2-dihydro-3-ruthenaindolizine Ru{κ^2-*N*,*C*-(py-CH_2CH_2)}Tp(P^iPr_3) (**224**), which aromatizes to afford the 3-ruthenaindolizine complex Ru{κ^2-*N*,*C*-(py-CHCH)}Tp(P^iPr_3) (**225**) by loss of a hydrogen molecule in the absence of any hydrogen acceptor (Scheme 28).[150]

Scheme 27. Chelate-Assisted C−H Activation Reactions Promoted by 58 and 63



Scheme 28. C−H Bond Activation of 2-Vinylpyridine Promoted by 149



It has been demonstrated that a coordinating functional group in an organic molecule does not direct the *ortho*-CH bond activation. On the contrary, it prevents the C−H bond addition to the metal center from a kinetic point of view. However, after the C−H bond cleavage, the coordinating group acts to trap the addition product.[195] The POP-pincer dihydride-dihydrogen complex **183** also activates acetophenone and benzophenone. The reactions afford the ruthenaisobenzofurans RuH{κ^2-*O*,*C*-[OC(R)C_6H_4]}{xant(P^iPr_2)$_2$} (R = Me (**226**), Ph (**227**)). Because the dihydride RuH_2{xant(P^iPr_2)$_2$} (**D**) reduces ketones, 2 equiv of substrate were used. It has been proposed that this reduction occurs via the intermediate **E** shown in Scheme 29. Thus, the elimination of alcohol should lead to the 14-valence electrons ruthenium(0) derivative **F**, which could undergo the oxidative addition of the second molecule of ketone. An alternative pathway would involve the direct heterolytic C−H bond activation of the second ketone molecule promoted by **E**, using the alkoxide ligand as a base. The participation of both mechanisms is consistent with the presence of about 0.5 deuterium atoms at the hydride position of the product resulting from the reaction of **183** with perdeuterated benzophenone. Furthermore, the metalated group contains 0.6 hydrogen atoms at the ortho-position with regard to the metal center (meta relative to the carbonyl) and about 0.2 hydrogen atoms at the ortho-position with regard to the carbonyl group. This indicates that the activation of the *meta*-C−H bonds of the ketone is kinetically favored over the *ortho*-C−H bonds and proves that the *ortho*-C−H bond cleavage is not chelated directed.[196]

Complex **183** favors the C−H bond activation over the C−F bond cleavage. Thus, the reaction of 2-fluoroacetophenone

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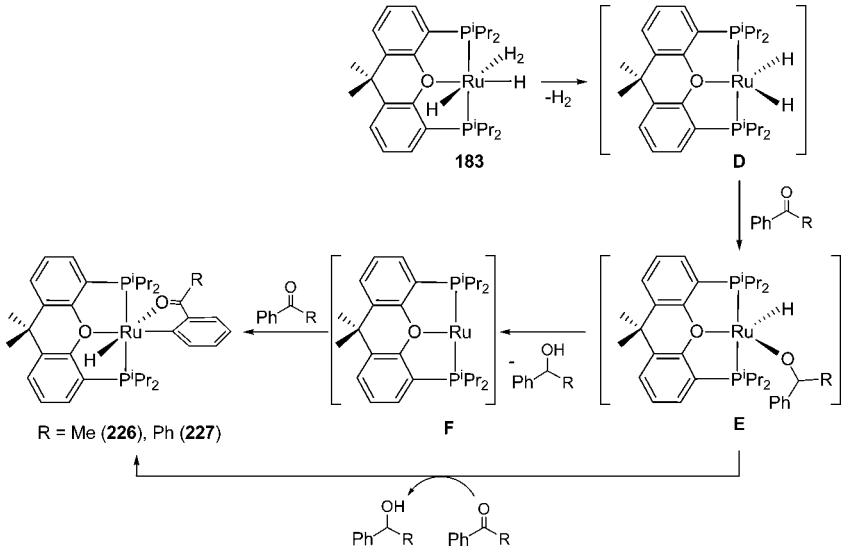
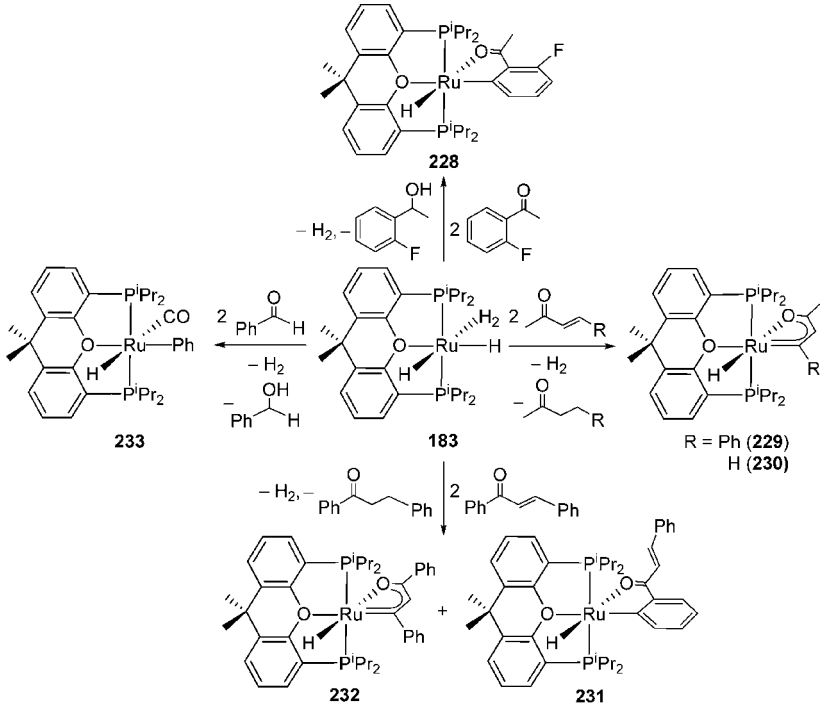
Scheme 29. C−H Bond Activation Reactions of Aromatic Ketones Promoted by 183.[a]



[a]Adapted from ref 196. Copyright 2015 American Chemical Society.

Scheme 30. C−H Bond Activation Reactions of Fluorinated Aromatic Ketones, α,β-Unsaturated Ketones, and Benzaldehyde Promoted by 183



leads to the C−H bond activation product RuH{κ^2-*O*,*C*-[OC(Me)C_6H_3F]}{xant(P^iPr_2)$_2$} (**228**). This complex also promotes the C_β−H bond activation of benzylideneacetone and methyl vinyl ketone to afford the ruthenafurans RuH{κ^2-*O*,*C*-[OC(Me)CHCR]}{xant(P^iPr_2)$_2$} (R = Ph (**229**), H (**230**)). The analogous reaction with benzylideneacetophenone yields a 1:1 mixture of the corresponding products resulting from the *ortho*-CH bond, RuH{κ^2-*O*,*C*-[OC(CH═CHPh)C_6H_4]}{xant(P^iPr_2)$_2$} (**231**), and C_β−H bond, RuH{κ^2-*O*,*C*-[OC(Ph)CHCPh]}{xant(P^iPr_2)$_2$} (**232**), activations. In aromatic aldehydes, the OC−H bond activation is favored over the cleavage of an *ortho*-CH bond. Thus, the reaction of **183** with benzaldehyde leads to RuH(Ph)(CO){xant(P^iPr_2)$_2$} (**233**), as a result of the phenyl deinsertion in an acyl intermediate (Scheme 30).[196]

The arene C−H bond activation without the need for chelate-assistance has been scarcely studied with this type of precursors. The PNP-pincer dihydride-dihydrogen complex **182** promotes the deuteration of a wide range of arenes and olefins, under mild conditions, using benzene-d_6 or D_2O as a deuterium source. The incorporation provides products with site-selectivity for C−H bond cleavage that depends upon steric factors (Scheme 31). Thus, for instance, the deuterium incorporation to toluene occurs mainly at meta (87%) and

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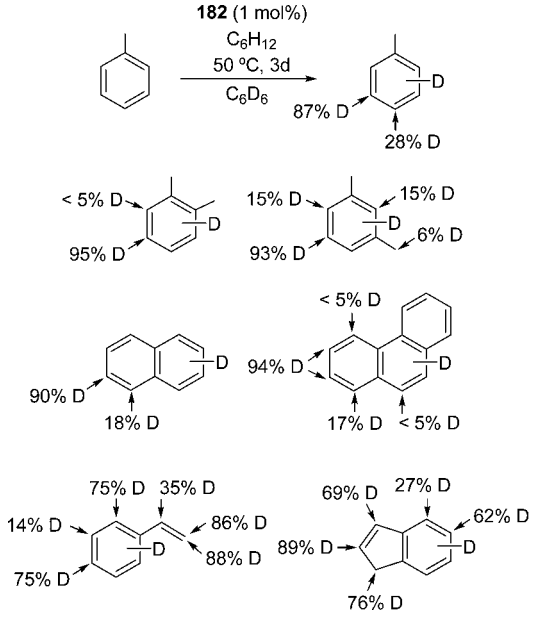
Scheme 31. Catalytic Deuteration of Arenes Promoted by 182

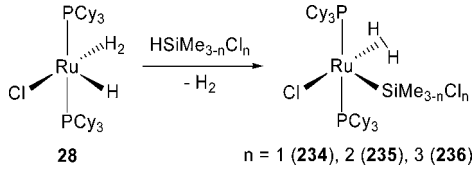


considerably less at para (28%); *ortho*-xylene undergoes deuteration almost exclusively at the β-positions to the methyl groups (95%); and naphthalene is preferably β-deuterated (90%), with a lower amount of α-deuteration (18%).[162,197]

2.6.3. Si−H Bond Activation. The ruthenium-promoted Si−H bond activation reactions were reviewed by Sabo-Etienne in 2006.[25] A continuum exists between the two extremes, leading either to η^2-Si−H coordination or oxidative addition. The tendency of silicon to be hypervalent seems to favor such a continuum by creating secondary interactions, which play a significant role for the stabilization of unusual structures and intermediates in exchange processes. In order to evaluate the degree of silane activation, J_{Si-H} values, IR bands, and Si−H and Ru−Si distances would not be used alone. J_{Si-H} values should be set up to 65 Hz for a secure criterion of a η^2-Si−H bond. Observation of a broad and intense IR band in the range of 1650−1800 cm^{-1} is also a good indication of η^2-coordination. Furthermore, one can consider that a Si−H distance between 1.7 and 1.8 Å is indicative of the formation of a η^2-silane complex, whereas separations between 1.9 and 2.4 Å are an alert of the presence of secondary interactions. The Ru−Si bond strength depends on the silicon-attached substituents, but a short bond length is a first evidence of an advanced oxidative addition process. Several interesting stoichiometric and catalytic findings involving the Si−H bond activation of, mainly, chlorosilanes have been reported since 2006. In addition, chelate-assisted Si−H bond coordination and activation have received special attention.

The hydride-dihydrogen complex **28** activates the Si−H bond of chlorosilanes $HSiMe_{3-n}Cl_n$ (n = 1−3) to form the corresponding silyl-elongated dihydrogen derivatives $RuCl(SiMe_{3-n}Cl_n)(\eta^2\text{-}H_2)(PCy_3)_2$ (n = 1 (**234**), 2 (**235**), 3 (**236**)). Substitution of the coordinated hydrogen molecule of **28** by the silanes to afford η^2-Si−H intermediates, which undergo hydride-promoted heterolytic activation, seems to be a plausible mechanism. The square pyramidal geometry proposed for these compounds, with the silyl ligand in the apex (Scheme 32), has been confirmed by means of the X-ray diffraction structure of

Scheme 32. Si−H Bond Activation Reactions of Chlorosilanes Promoted by 28

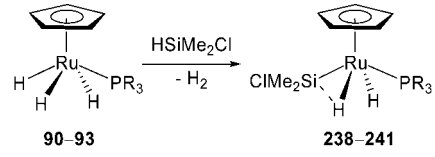


28 n = 1 (**234**), 2 (**235**), 3 (**236**)

235. The J_{H-D} values reveal that the sequential replacement of methyl substituents by chlorides shortens the dihydrogen ligand, from 1.21 Å in **234** to 1.05 Å in **236**. The trend, which is in agreement with an increase of the acidity of the silyl group in the same sequence, has been corroborated by DFT calculations. Complexes **235** and **236** do not react with ethylene. However, the ethylene species $RuHCl(\eta^2\text{-}C_2H_4)(PCy_3)_2$ (**237**) is formed in the case of **234**. The strong silyl trans influence may prevent the coordination in the vacant site of **235** and **236**, whereas for **234**, the interaction between the silicon atom and one hydrogen of the elongated dihydrogen seems to favor the silane elimination.[198] In contrast to **28**, the dihydride-bis(dihydrogen) complex **63** catalyzes the silylation of ethylene with $HSiMe_2Cl$ and $HSiMeCl_2$. Dehydrogenative silylation leading to the formation of vinylsilanes competes with hydrosilylation. The rate and selectivity of the reactions are influenced by the number of chloro substituents.[199]

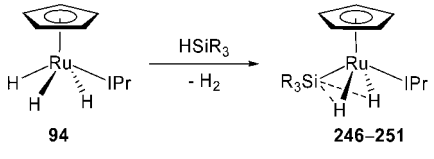
The half-sandwich trihydride complexes **90**−**93** also activate the Si−H bond of $HSiMe_2Cl$. The reactions give the dihydride-silyl derivatives $RuH_2(SiMe_2Cl)(\eta^5\text{-}C_5H_5)(PR_3)$ (PR_3 = PPh_3 (**238**), P^iPrPh_2 (**239**), P^iPr_2Ph (**240**), P^iPr_3 (**241**)), in good yields, and H_2. The related compounds $RuH_2(SiMe_2Cl)(\eta^5\text{-}C_5H_5)(PR_3)$ (PR_3 = P^iPr_2Me (**242**), PMe_2Ph (**243**)) have been also prepared, starting from the corresponding chloride complexes $RuCl(\eta^5\text{-}C_5H_5)(PR_3)_2$ (PR_3 = P^iPr_2Me (**244**), PMe_2Ph (**245**)). These ruthenium(IV) dihydride-silyl species exhibit hydride−silicon hypervalent interactions, whose strength decreases with the decreasing basicity of the phosphine coligand.[200] The reactions of the NHC-supported trihydride $RuH_3(\eta^5\text{-}C_5H_5)(IPr)$ (**94**) with hydrosilanes $HSiR_3$ afford the dihydride-silyl complexes $RuH_2(SiR_3)(\eta^5\text{-}C_5H_5)(IPr)$ (SiR_3 = $SiCl_3$ (**246**), $SiMeCl_2$ (**247**), $SiMe_2Cl$ (**248**), SiH_2Ph (**249**), SiHMePh (**250**), $SiMe_2Ph$ (**251**)) with nonclassical Si···H interligand interactions (Scheme 33). The comparison of the X-

Scheme 33. Si−H Bond Activation Reactions Promoted by $RuH_3(\eta^5\text{-}C_5H_5)L$ Complexes



90–**93** **238**–**241**

PR_3 = PPh_3 (**90**, **238**), P^iPrPh_2 (**91**, **239**), P^iPr_2Ph (**92**, **240**), P^iPr_3 (**93**, **241**)



94 **246**–**251**

SiR_3 = $SiCl_3$ (**246**), $SiMeCl_2$ (**247**), $SiMe_2Cl$(**248**), SiH_2Ph (**249**), SiHMePh (**250**), $SiMe_2Ph$ (**251**)

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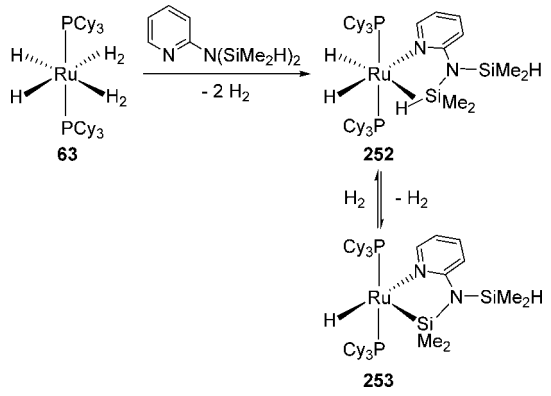
ray structures of **241** and **246**−**251** suggests that the replacement of the phosphine by the NHC ligand in the fragment Ru(η^5-C_5H_5)(P^iPr_3) results in the strengthening of the RuH···Si interactions.[137]

The dihydride-bis(dihydrogen) complex **63** promotes pyridyl-chelate-assisted Si−H bond activation (Scheme 34).

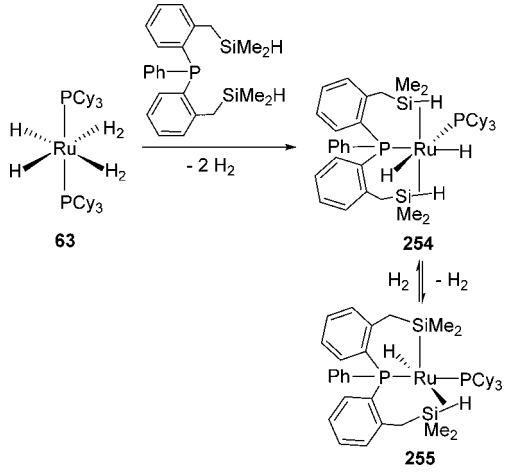
Scheme 34. Pyridyl-Chelate-Assisted Si−H Bond Activation Promoted 63



2-Pyridinetetramethyldisilazane displaces the coordinated hydrogen molecules of **63** to initially give $RuH_2\{(\eta^2\text{-}HSiMe_2)\text{-}N(\kappa\text{-}N\text{-}C_5H_4N)(SiMe_2H)\}(PCy_3)_2$ (**252**) by means of the coordination to the ruthenium atom of the pyridyl group and one of the Si−H bonds, as demonstrated by deuterium-labeling experiments. Heating **252**, at 70 °C under vacuum for 24 h, produces the loss of H_2 and the formation of the unsaturated compound $RuH\{(SiMe_2)N(\kappa\text{-}N\text{-}C_5H_4N)(SiMe_2H)\}(PCy_3)_2$ (**253**), as a result of the cleavage of the coordinated Si−H bond. The reaction is fully reversible under dihydrogen atmosphere.[201]

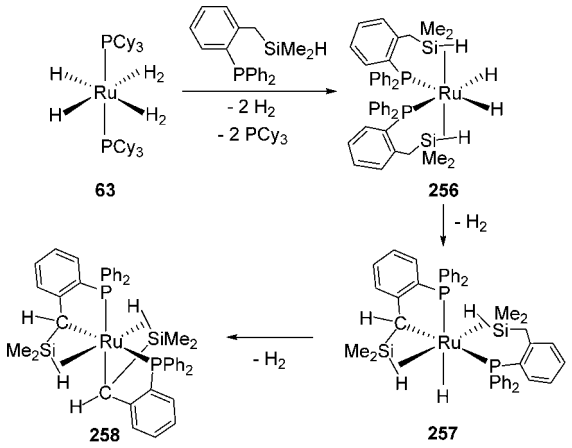
The phosphinodi(benzylsilane) $PhP(C_6H_4\text{-}o\text{-}CH_2SiMe_2H)_2$, in contrast to 2-pyridinetetramethyldisilazane, acts as a pincer-type ligand capable of adopting different coordination modes at ruthenium through different extent of Si−H bond activation (Scheme 35). This phosphine reacts with **63**, in toluene, at room temperature to give $RuH_2\{[\eta^2\text{-}(HSiMe_2)CH_2\text{-}o\text{-}C_6H_4]_2PPh\}(PCy_3)$ (**254**), as a result of the substitution of both coordinated hydrogen molecules and one tricyclohexylphosphine ligand by the phosphinodi(benzylsilane), which coordinates the phosphorus atom and both Si−H bonds in a *mer* disposition. This compound, which is involved in thermal hydride-SiH exchange processes, undergoes reversible loss of molecular hydrogen leading to the unsaturated species $RuH\{[\eta^2\text{-}(HSiMe_2)CH_2\text{-}o\text{-}C_6H_4]PPh[C_6H_4\text{-}o\text{-}CH_2SiMe_2]\}(PCy_3)$ (**255**),[202] most probably through a hydride-dihydrogen intermediate resulting from the hydride-promoted heterolytic cleavage of one of the coordinated Si−H bonds.

Scheme 35. Reactions of 63 with a Phosphinodi(benzylsilane)



Six-membered heterometalarings as that of **255** are less stable than the five-membered ring resulting of the C−H bond activation of the methylene linker between the silane and the aromatic group. The reactions shown in Scheme 36 are a strong demonstration of this. Complex **63** reacts with the phosphinobenzylsilane $Ph_2P(C_6H_4\text{-}o\text{-}CH_2SiMe_2H)$ to give $RuH_2\{[(\eta^2\text{-}HSiMe_2)CH_2\text{-}o\text{-}C_6H_4]PPh_2\}_2$ (**256**), as a result of the substitution of the dihydrogen and tricyclohexylphosphine ligands by two phosphinobenzylsilanes, which act as chelating groups through the phosphorus atom and the Si−H bond. This compound loses two hydrogen molecules, as a consequence of the sequential C−H bond activation of the methylene group of the phosphine in the presence of the Si−H bonds, to yield first $RuH\{[CH(\eta^2\text{-}HSiMe_2)\text{-}o\text{-}C_6H_4]PPh_2\}\{[(\eta^2\text{-}HSiMe_2)CH_2\text{-}o\text{-}C_6H_4]PPh_2\}$ (**257**) and subsequently $Ru\{[CH(\eta^2\text{-}HSiMe_2)\text{-}o\text{-}C_6H_4]PPh_2\}_2$ (**258**).[203]

Scheme 36. Reactions of 63 with Phosphinobenzylsilanes



The tendency shown by the RuH(η^2-H−Si)-complexes to undergo hydride-SiH exchange processes is consistent with the reactivity discussed for **63** and its ability, and that of the related dihydride-bis(dihydrogen) **66**, for promoting the deuteration of a diverse array of silanes, including alkyl-, aryl-, alkoxy-, and chlorosilanes, siloxane and silazane, under a molecular deuterium atmosphere.[204]

2.6.4. N−H and O−H Bond Activations. The dihydride-bis(dihydrogen) complex **63** reacts with pyridine, acridine, and pyrrole to afford compounds containing the heterocycles coordinated in different modes (Scheme 37). Pyridine produces the displacement of a dihydrogen ligand and coordinates the nitrogen atom, generating the dihydride-dihydrogen $RuH_2(\eta^2\text{-}H_2)(py)(PCy_3)_2$ (**259**). In contrast to pyridine, acridine displaces both dihydrogen ligands coordinating one of the terminal aromatic rings in a η^4-mode to form $RuH_2(\eta^4\text{-}C_{13}H_{19}N)(PCy_3)_2$ (**260**), whereas pyrrole undergoes the activation of its N−H bond to yield the half-sandwich derivative $RuH(\eta^5\text{-}C_4H_4N)(PCy_3)_2$ (**261**).[205]

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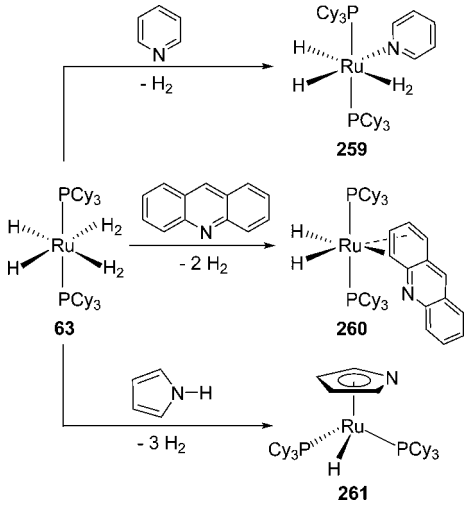
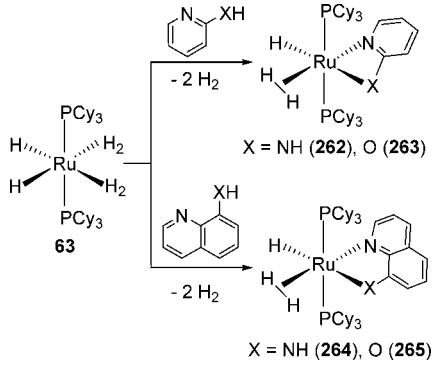
Scheme 37. Reactions of 63 with N-Heterocycles



Complex **63** also promotes the chelate-assisted cleavage of a N−H bond of 2-aminopyridine and 8-aminoquinoline and the O−H bond of 2-hydroxypyridine and 8-hydroxyquinoline (Scheme 38). These chelate-assisted activations lead to the

Scheme 38. Chelate-Assisted N−H and O−H Bond Activations Promoted by 63

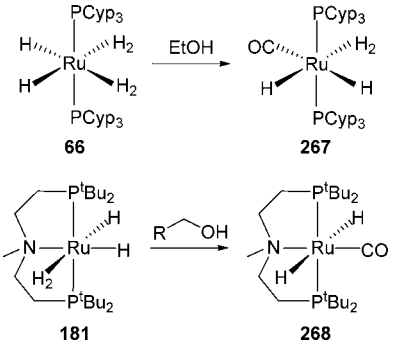


hydride-elongated dihydrogen derivatives RuH{κ^2-*N,X*-(py-2-X)}(η^2-H_2)(PCy_3)$_2$ (X = NH (**262**), O (**263**)) and RuH{κ-*N,X*-(quin-8-X)}(η^2-H_2)(PCy_3)$_2$ (X = NH (**264**), O (**265**)). The elongated character of the dihydrogen ligand of these compounds is supported by the J_{H-D} values, which allow for calculation of the separations between its hydrogen atoms of about 1.27 Å.[206] NMR studies on **262** and **263** have also shown that hydrogen bond donors, such as substituted phenols and hexafluoro-2-propanol, interact with the hydride ligand of the second one, whereas for **262**, an equilibrium with the cation [RuH(η^2-H_2){κ-*N,N*-(py-2-NH_2)}(PCy_3)$_2$]$^+$ (**266**) is attained.[207]

The related tricyclopentylphosphine dihydride-bis(dihydrogen) complex **66** dehydrogenates primary alcohols, which subsequently undergo decarbonylation. Thus, the carbonyl-dihydride-dihydrogen $RuH_2(CO)(\eta^2\text{-}H_2)(PCyp_3)_2$ (**267**) has been isolated from the reaction with ethanol.[208] A similar behavior has been reported for the PNP-pincer compound **181**, which affords the carbonyl-dihydride $RuH_2(CO)\{(^tBu_2PCH_2CH_2)_2NMe\}$ (**268**) (Scheme 39).[209]

Complex **268** is an efficient catalyst precursor for the direct conversion of primary alcohols into carboxylic acids with the

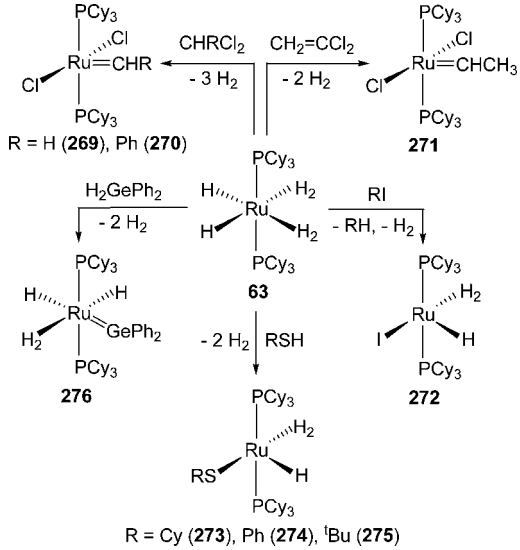
Scheme 39. Reactions of 66 and 181 with Alcohols



use of water as an oxygen source, whereas the triisopropylphosphine counterpart of **267**, complex **41**, catalyzes the hydrogen transfer from 2-propanol to ketones[210] and α,β-unsaturated ketones.[211] A preferential selective reduction to saturated ketones is observed for the α,β-unsaturated ketones case. The Tp^{Me2}-complex **160** also shows good catalytic activity for the reduction of unsaturated ketones by dihydrogen and by hydrogen transfer from alcohols in basic media.[212]

2.6.5. Other σ-Bond Activations. The dihydride-bis(dihydrogen) complex **63** is an exceptional tool to carry out the cleavage of σ-bonds. In addition to the previously mentioned activation reactions, it is capable of performing the activation of C−Cl, C−I, S−H, and Ge−H bonds (Scheme 40). Complex **63** serves as a formal source of the zerovalent

Scheme 40. C−Cl, C−I, S−H, and Ge−H Bond Activation Reactions Promoted by 63



species $Ru(PCy_3)_2$, which undergoes the addition of both C−Cl bonds of dichloromethane to a single metal center, providing a convenient synthesis of the alkene metathesis catalyst $RuCl_2(=CH_2)(PCy_3)_2$ (**269**).[213] The reaction with $CHPhCl_2$ affords $RuCl_2(=CHPh)(PCy_3)_2$ (**270**), whereas $CH_2=CCl_2$ gives $RuCl_2(=CHCH_3)(PCy_3)_2$ (**271**) due to the hydrogenation of the C−C double bond of the presumed vinylidene, primary product, by released H_2. Hydrogenation of **269** and **270** leads to CH_3R (R = H, Ph, respectively), HCl, and the chloride-hydride-dihydrogen **28**.[214] The iodide counterpart RuHI(η^2-H_2)(PCy_3)$_2$ (**272**) has been generated

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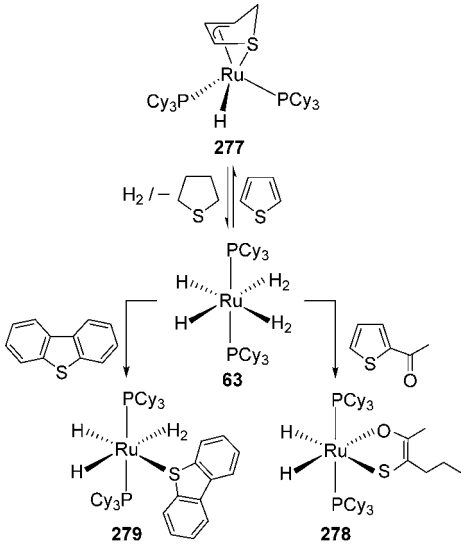
through the C−I bond activation of CH_3I or PhI.[215] Its formation probably involves a $RuI(R)(PCy_3)_2$ intermediate, which undergoes a double hydrogenation with R−H elimination. In a consistent manner with this, Macgregor, Grushin, and co-workers have recently reported that the dihydride-dihydrogen **42** reacts with PhX (X = I, Br, Cl) in the presence of styrene to give ethylbenzene, benzene, and the five-coordinate monohydrides $RuHX(PPh_3)_3$.[216] Similarly to RI (R = Me, Ph), complex **63** reacts with thiols to give the thiolate derivatives $RuH(SR)(\eta^2\text{-}H_2)(PCy_3)_2$ (R = Cy (**273**), Ph (**274**), ^{t}Bu (**275**)).[217] The reaction of **63** with Ph_2GeH_2 yields the dihydride-dihydrogen-germylene derivative $RuH_2(\eta^2\text{-}H_2)(=GePh_2)(PCy_3)_2$ (**276**).[218]

Complex **63** also has an interesting reactivity with *S*-heteroaromatic compounds (Scheme 41). Stoichiometric

Scheme 41. Reactions of 63 with *S*-Heteroaromatic Compounds



reaction with thiophene leads to the η^4-thioallyl complex $RuH\{\kappa^4\text{-}S,C,C,C\text{-}(SC_4H_5)\}(PCy_3)_2$ (**277**). This compound easily regenerates **63** upon treatment with molecular hydrogen and, in this way, can be successfully used as a catalyst precursor in thiophene hydrogenation to 2,3,4,5-tetrahydrothiophene. The reaction of **63** with 2-acetylthiophene produces a regioselective 1,5-C−S bond splitting with formal hydrogenation of two double C−C bonds and coordination of a 2-hexen-2-olate-3-thiolate ligand in a $\kappa^2(O,S)$ mode to form $RuH_2\{\kappa^2\text{-}O,S\text{-}(C_6H_{10}OS)\}(PCy_3)_2$ (**278**). In addition to thiophene, complex **63** is an effective catalyst precursor for the hydrogenation of 2-methylthiophene to 2-methyltetrahydrothiophene, 2-acetylthiophene to 1-(2-thienyl)ethanol, 2-thiophenecarboxaldehyde to 2-thiophenemethanol, and benzo[*b*]thiophene to 2,3-dihydrobenzo[*b*]thiophene. However, dibenzo[*b*,*d*]thiophene is not reduced due to the formation of $RuH_2(\eta^2\text{-}H_2)\{\kappa^1\text{-}S\text{-}(C_{12}H_8S)\}(PCy_3)_2$ (**279**).[219]

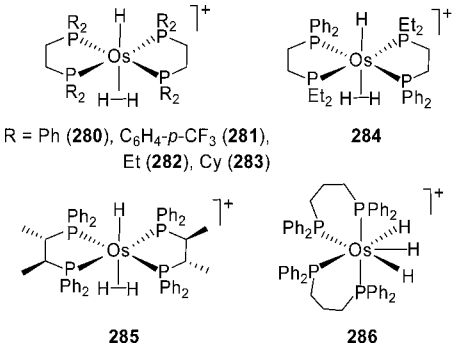
3. OSMIUM

3.1. Phosphine Complexes

Osmium favors classical structures with the metal in high oxidation state (4 and 6) and strong $M(\eta^2\text{-}H_2)$ bonds because of its reducing character and marked π-back bonding ability. As a consequence, osmium polyhydrides show a wider range of stoichiometries and structures than in the ruthenium case.

A variety of *trans*-hydride-elongated dihydrogen complexes $[OsH(\eta^2\text{-}H_2)(diphosphine)_2]^+$ (diphosphine = $R_2P(CH_2)_2PR_2$, R = Ph (**280**), C_6H_4-*p*-CF_3 (**281**), Et (**282**), Cy (**283**); diphosphine = $Ph_2P(CH_2)_2PEt_2$ (**284**), (*S*,*S*)-chiraphos (**285**)), analogous to the ruthenium-diphosphine complexes **1**−**11** have been reported (Chart 7).[58,59,64,65,69,220−222] The separation

Chart 7. $[OsH(\eta^2\text{-}H_2)(diphosphine)_2]^+$ and $[OsH_3(diphosphine)_2]^+$ Cations



between the hydrogen atoms of the elongated dihydrogen ligand, calculated from J_{H-D} and T_1(min) values, is in the range of 1.0−1.2 Å depending upon the phosphine substituents. A classical trihydride character (d_{H-H} = 1.6 Å) has been proposed however for complex $[OsH_3\{Ph_2P(CH_2)_3PPh_2\}_2]^+$ (**286**).[223] The comparison of spectroscopic features and some properties of these compounds with those of the triade analogous reveals several interesting trends. In accordance with the terminal hydride stretching mode ν(M−H), the strength of the M−H bond increases in the sequence Fe < Ru < Os, as expected for isostructural species. However, indicators of dihydrogen versus dihydride character show that ruthenium is out of plane in the periodic order. Analysis of J_{H-D} and T_1(min) values suggests that the overall ordering of increasing H−H distance is Ru ≈ Fe < Os, whereas the lability of dihydrogen as judged by the qualitative H_2/D_2 rates of exchange increases as Os < Fe < Ru (i.e., the strength of the $M(\eta^2\text{-}H_2)$ bond increases as Ru < Fe < Os). The hydride and dihydrogen ligands undergo thermally activated site exchange, which likely proceeds via the homolytic cleavage of the dihydrogen ligand. The $\Delta G^{\ddagger}$ values for the process decrease as Ru > Fe > Os and $Ph_2P(CH_2)_2PPh_2$ > $Ph_2P(CH_2)_2PEt_2$.[64] Changing the metal from Ru to Os has the effect of increasing the acidity of the dihydrogen ligand even though the osmium complexes are more reducing than the ruthenium compounds. This appears to be due to a higher H−H bond dissociation energy for the ruthenium complexes.[69]

Complexes $[OsH(\eta^2\text{-}H_2)\{PPh_2(OR)\}_4]^+$ (R = Me (**287**), Et (**288**), ^{i}Pr (**289**)), $[OsH(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]^+$ (**290**), and $[OsH(\eta^2\text{-}H_2)\{P(OR)_3\}_4]^+$ (R = Me (**291**), Et (**292**)) containing four monodentate phosphonite, phosphinite, and phosphite ligands, respectively, are also *trans*-hydride-elongated dihydrogen species.[75,224] However, complexes $[OsH_3(PR_3)_4]^+$ (R = Me (**293**), Et (**294**), Ph (**295**)), with basic phosphines, have been described as classical trihydride derivatives. The trimethylphosphine compound **293** seems to be a pentagonal bipyramidal trihydride in equilibrium with a hydride-capped tetrahedral structural form. Complexes **294** and **295** are

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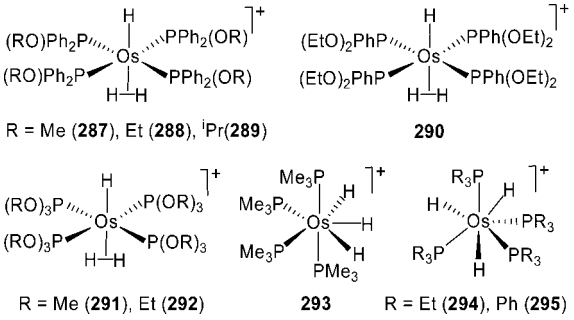
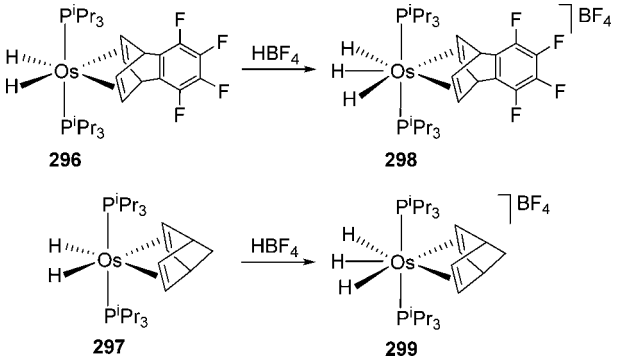
exclusively represented by the latter structural type (Chart 8).[77,225−227]

Chart 8. $[OsH(\eta^2\text{-}H_2)(PR_3)_4]^+$ and $[OsH_3(PR_3)_4]^+$ Cations



Protonation of the dihydrides $OsH_2(diolefin)(P^iPr_3)_2$ (diolefin = tetrafluorobenzobarrelene (TFB; **296**), 2,5-norbornadiene (NBD; **297**)), containing a chelating π-acid and two basic monodentate ligands, with $HBF_4{\cdot}OEt_2$ leads to $[OsH_3(diolefin)(P^iPr_3)_2]BF_4$ (diolefin = TFB (**298**), NBD (**299**)), which, in contrast to **280**−**285** and **287**−**292**, are classical trihydrides. On the basis of spectroscopic data, the pentagonal bipyramidal geometry shown in Scheme 42 has

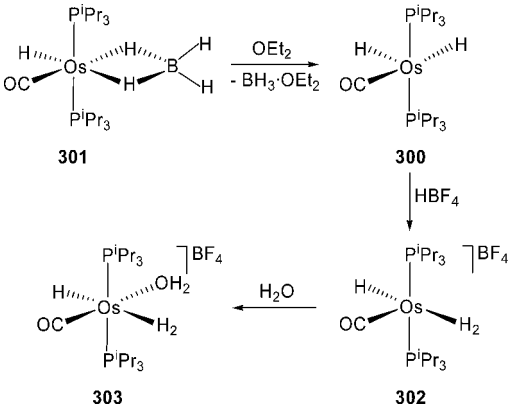
Scheme 42. Protonation of 296 and 297



been proposed for these compounds. The hydride ligands undergo thermally activated site exchange. Furthermore, they show quantum mechanical exchange coupling. Taking *a* as the separation between the hydride ligands calculated from the T_1(min) values, 1.7 Å for **298** and 1.8 Å for **299**, the phenomenon has been quantified by means of eq 1 and the following parameters J_{mag}, λ, and ν have been obtained: 6 Hz, 1.1 Å, and 484 cm^{-1} for **298** and 10 Hz, 1.0 Å, and 496 cm^{-1} for **299**.[228]

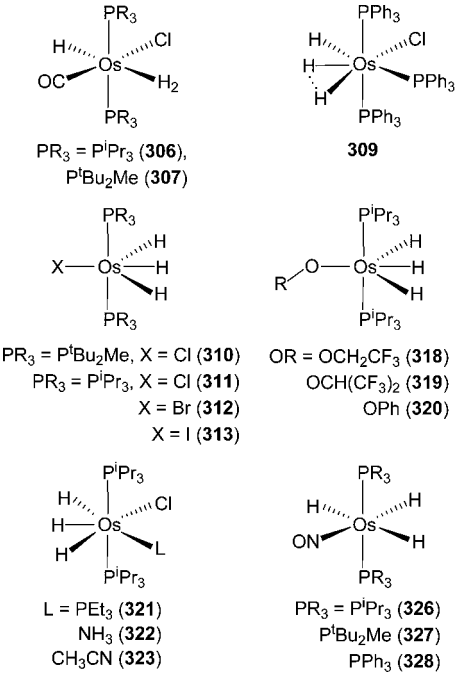
Most commonly BH_3 is abstracted from coordinated tetrahydrideborate ligands with Lewis bases capable of forming $H_3B{-}L$ adducts. This property of borane has been used to generate in situ the five-coordinate dihydride species $OsH_2(CO)(P^iPr_3)_2$ (**300**) by means of solution of the hydride-tetrahydrideborate $OsH(\kappa^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ (**301**) in diethyl ether. The protonation of this dihydride with $HBF_4{\cdot}OEt_2$ gives rise to the surprising cationic five-coordinate *trans*-hydride-dihydrogen derivative $[OsH(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2]BF_4$ (**302**),[229] which has been a useful starting material to carry out C−C coupling reactions.[230] In the presence of water, it affords the six-coordinate *trans*-hydride-dihydrogen $[OsH(\eta^2\text{-}H_2)(CO)(H_2O)(P^iPr_3)_2]BF_4$ (**303**), with three different heavy monodentate coligands (Scheme 43).

Scheme 43. Preparation of 302



Several types of neutral OsH_3-species have been described (Chart 9). Reactions of complexes $OsHCl(CO)(PR_3)_2$ (PR_3 =

Chart 9. Several Types of Neutral OsH_3-Species



P^iPr_3 (**304**), P^tBu_2Me (**305**)) with molecular hydrogen give the *trans*-hydride-dihydrogen derivatives $OsHCl(\eta^2\text{-}H_2)(CO)(PR_3)_2$ (PR_3 = P^iPr_3 (**306**), P^tBu_2Me (**307**)).[231,232] A H−H distance of 0.8 Å in the dihydrogen ligand of **306** has been determined from variable-temperature ^1H T_1 measurements. DFT calculations have revealed the existence of a *cis*-hydride-dihydrogen isomer with a relative energy of 13.8 kcal mol^{-1}.[233] The equilibrium between these trans and cis isomers appears to play a main role in the hydrogenation of benzylideneacetone to the saturated ketone catalyzed by the five-coordinate complexes **304** and **305**.[234] The five-coordinate dichloride complex $OsCl_2(PPh_3)_3$ (**308**) also reacts with molecular hydrogen. In the presence of NEt_3, the reaction leads to the *cis*-hydride-compressed dihydride $OsHCl(H{\cdots}H)(PPh_3)_3$ (**309**),[235] which has been characterized by neutron diffraction analysis.[236] The

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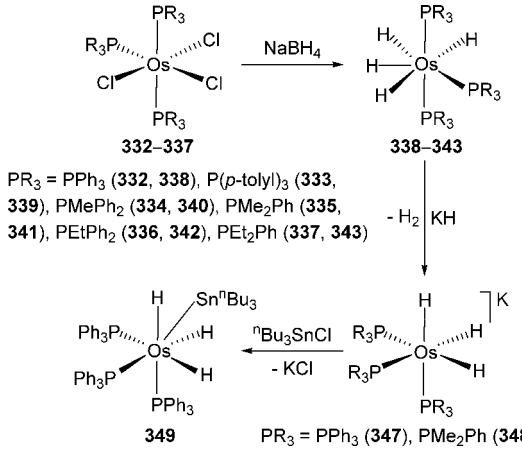
results confirm the presence of the compressed dihydride with a H···H separation of 1.48(2) Å. The molecule is substantially distorted from an ideal octahedral geometry. The hydride is located trans to a phosphine, separated by 1.67(2) Å from the compressed dihydride, which sits essentially trans to the chloride. Bulky phosphines stabilize related six-coordinate species $OsH_3X(PR_3)_2$ (PR_3 = P^tBu_2Me, X = Cl (**310**);[85] PR_3 = P^iPr_3, X = Cl (**311**), Br (**312**), I (**313**)[237]), which have been prepared by reaction of the corresponding $OsH_2X_2(PR_3)_2$ (PR_3 = P^tBu_2Me, X = Cl (**314**); PR_3 = P^iPr_3, X = Cl (**315**), Br (**316**), I (**317**)) complexes with molecular hydrogen in the presence of NEt_3. These compounds are neutral species showing spectacular quantum mechanical exchange coupling, which is sensitive to halide identity.[238,239] Starting from **311**, metathesis reactions with TlOR or NaOPh afford the alkoxide derivatives $OsH_3(OR)(P^iPr_3)_2$ (OR = OCH_2CF_3 (**318**), $OCH(CF_3)_2$ (**319**), OPh (**320**)). Complex **320** has been characterized by X-ray diffraction analysis. The structure has essentially C_{2v} symmetry with *trans* phosphines and the oxygen atom of the phenoxy group, the metal center, and the hydrides lying in the plane perpendicular to the P−Os−P direction.[240] The H−Os−H angles (58.1(5)° and 62.1(15)°) markedly deviate from 90°. It is well-known that the octahedral geometry is not favorable for heavy metal d^4 complexes, which prefer to be diamagnetic. These compounds undergo a distortion that destabilizes one orbital from the t_{2g} set and simultaneously stabilizes the occupied ones. The distortion partially cancels the electron deficiency at the metal, which receives additional electron density from the hydrides via stronger σ-bonds and from one lone pair of X or OR via π-bond. These compounds have a useful chemistry including reactions of hydroosmiation of unsaturated organic substrates,[241] as precursors of C−C coupling processes,[242] and as starting materials for the preparation of half-sandwich complexes.[243] The addition of Lewis bases, such as PEt_3, NH_3, and CH_3CN, to **311** affords seven-coordinate $OsH_3Cl(L)(P^iPr_3)_2$ (L = PEt_3 (**321**), NH_3 (**322**), CH_3CN (**323**)) species. These complexes are assigned to pentagonal bipyramidal geometry with axial phosphines and the Lewis base L *cisoid* disposed to the chloride, in the perpendicular plane along with the hydride ligands. This geometry is the most favorable thermodynamically because it minimizes steric interactions by putting bulky phosphines in trans positions and avoids placing hydride ligands, the strongest σ-donors, in trans or pseudo-trans positions, and kinetically because it places the incoming ligand in the position predicted by the LUMO of the unsaturated trihydride complex. Under excess NH_3 and CH_3CN, the Lewis bases displace chloride to form the cationic compounds $[OsH_3L_2(P^iPr_3)_2]Cl$ (L = NH_3 (**324**), CH_3CN (**325**)), related to **298** and **299**, but containing two monodentate N-donor ligands instead of a diolefin. The X-ray diffraction structure of **324** confirmed the *cis*-disposition of the L ligands in these compounds (N−Os−N = 81.5(2)°).[237] Neutral d^6 *mer*-trihydrides $OsH_3(NO)(PR_3)_2$ (PR_3 = P^iPr_3 (**326**), P^tBu_2Me (**327**), PPh_3 (**328**)) have been also prepared via $NaBH_4$/MeOH reduction of the corresponding *cis,trans*-$OsH_2Cl(NO)(PR_3)_2$ (PR_3 = P^iPr_3 (**329**), P^tBu_2Me (**330**), PPh_3 (**331**)) compounds.[91]

Reaction of $OsCl_3(PR_3)_3$ (PR_3 = PPh_3 (**332**), P(*p*-tolyl)$_3$ (**333**), $PMePh_2$ (**334**), PMe_2Ph (**335**), $PEtPh_2$ (**336**), PEt_2Ph (**337**)) with $NaBH_4$ in ethanol leads to the classical[92,94,244,245] tetrahydride complexes $OsH_4(PR_3)_3$ (PR_3 = PPh_3 (**338**), P(*p*-tolyl)$_3$ (**339**), $PMePh_2$ (**340**), PMe_2Ph (**341**), $PEtPh_2$ (**342**), PEt_2Ph (**343**)).[246−249] The structure of **341** has been determined by neutron diffraction. The complex can be described as a distorted pentagonal bipyramid with two axial phosphines, whereas the hydrides and the other phosphine lie in the perpendicular plane to the P−Os−P direction.[250] The formation of these d^4-tetrahydrides probably takes place via hydride-tetrahydrideborate intermediates. In agreement with this proposal, it has been observed that complexes **304** and **305** react with $NaBH_4$ to initially give the hydride-tetrahydridoborate intermediates **301** and $OsH(\kappa^2\text{-}H_2BH_2)(CO)(P^tBu_2Me)_2$ (**344**), which evolve into the dihydride-dihydrogen derivatives $OsH_2(\eta^2\text{-}H_2)(CO)(PR_3)_2$ (PR_3 = P^iPr_3 (**345**), P^tBu_2Me (**346**)) in methanol.[251,252] The presence of a carbonyl group in these compounds instead of one of the phosphines of **338**−**343** is a determinant for the nonclassical interaction. Tetrahydrides **338** and **341** have been deprotonated with KH in tetrahydrofuran. The resulting anionic *fac*-trihydrides $[OsH_3(PR_3)_3]^-$ (PR_3 = PPh_3 (**347**),[253] PMe_2Ph (**348**)[254]) are very unstable in solution and easily revert to the starting tetrahydrides. However, they can be stabilized by addition of 18-crown-6, which forms $[K(THF)(18\text{-crown-}6)][OsH_3(PR_3)_3]$. The X-ray structure of the PPh_3-adduct has revealed cation−anion contacts achieved through three Os−H···K moieties. In the absence of stabilizer, the tetrahydrofuran solutions of **347** react with $^nBu_3SnCl$ to produce $OsH_3(Sn^nBu_3)(PPh_3)_3$ (**349**). This compound possesses a covalent Os−Sn bond in a seven-coordinate *fac*-$OsH_3(PPh_3)_3$ arrangement with the Sn^nBu_3 group capping the OsH_3 face (Scheme 44).[253] The addition of $(\eta^5\text{-}C_5H_5)_2ZrXCl$

Scheme 44. Preparation and Deprotonation of $OsH_4(PR_3)_3$ Complexes



(X = H, Cl) to tetrahydrofuran solutions of **348** leads to the bimetallic complexes $(\eta^5\text{-}C_5H_5)_2XZr(\mu\text{-}H)_3Os(PMe_2Ph)_3$ (X = H (**350**), Cl (**351**)), containing three bridging hydrides.[255]

The related carbonyl complex $[OsH_3(CO)(P^iPr_3)_2]^-$ (**352**) has been similarly prepared to its ruthenium counterpart **53**, starting from **304**, according to the reaction summarized by the general eq 2, and isolated as $[K(Q)][OsH_3(CO)(P^iPr_3)_2]$ (Q = 18-crown-6, 1-aza-18-crown-6, 2.2.2-crypt).[104] In agreement with eq 2, treatment of tetrahydrofuran solutions of the dihydride-dichloride **315** with excess potassium hydride, in the presence of 1 equiv of crown ether Q, and under 1 atm of H_2 affords the pentahydride $[K(Q)][OsH_5(P^iPr_3)_2]$ (Q = 18-crown-6 (**353a**), 1-aza-18-crown-6 (**353b**), 1,10-diaza-18-crown-6 (**353c**)). The X-ray structure of **353c** indicates that intermolecular short proton−hydride interactions between the hydrides of the anion and the NH moieties of the cation cause

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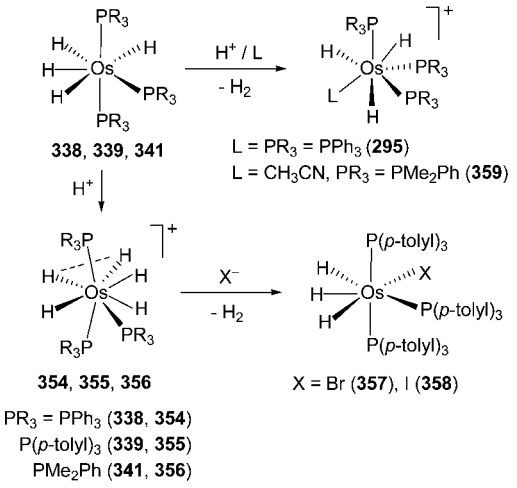
the self-assembly of one-dimensional networks of pentagonal bipyramidal anions and cations. The X-ray structure of **353b** reveals that this salt also forms one-dimensional chains due to Os−H···HN and weak Os−H···HC interactions between the hydrides of the anion and the NH and methylene CH of the cation.[105]

$$MH_xX_yL_z + (y+1)\,KH + Q \xrightarrow{H_2} [K(Q)][MH_{x+y+1}L_z] + y\,KX \quad (2)$$

Tetrahydrides **338**, **339**, and **341** have been protonated (Scheme 45).[256] The addition yields the pentahydride cations

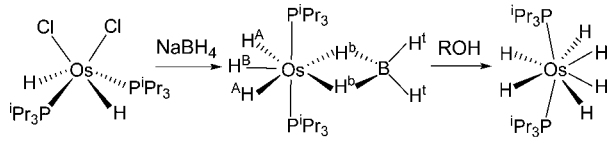
Scheme 45. Protonation Reactions of $OsH_4(PR_3)_3$ Complexes



$[OsH_5(PR_3)_3]^+$ (PR_3 = PPh_3 (**354**), P(*p*-tolyl)$_3$ (**355**), PMe_2Ph (**356**)). The BF_4^- salt of **356** has been characterized by neutron diffraction. The coordination geometry around the metal center of the cation can be rationalized as being derived form a distorted dodecahedron, which is defined by two intersecting BAAB orthogonal trapezoidal planes. One of them contains two phosphines and two hydrides and the other one a phosphine and three hydrides. The phosphines occupy the more spacious B sites of the dodecahedron. It should be also mentioned that the separation between the H_B and H_A hydrides in the trihydride plane is short (1.49(4) Å), and therefore, these species can be defined as trihydride-compressed dihydrides. Complex **356** catalyzes the hydrogenation of ethylene, cyclohexene, and 1,5-cyclooctadiene.[257,258] In the presence of bromide and iodide, complex **355** affords the neutral trihydrides $OsH_3X\{P(p\text{-tolyl})_3\}_3$ (X = Br (**357**), I (**358**)),[256] whereas the protonations of **338** and **341** in the presence of triphenylphosphine[227] and acetonitrile,[259] respectively, give the cationic trihydrides $[OsH_3L(PR_3)_3]^+$ (L = PR_3 = PPh_3 (**295**); L = CH_3CN, PR_3 = PMe_2Ph (**359**)).

Complexes $OsH_6(PR_3)_2$ (PR_3 = PMe_2Ph (**360**), P^iPr_2Ph (**361**), $PCyp_3$ (**362**)) with six hydrogen atoms attached to the metal center are also known. They have been generally prepared by reaction of the corresponding adducts $OsCl_2O_2(PR_3)_2$ with $LiAlH_4$ or $NaBH_4$.[248,260] In contrast to ruthenium, these compounds are classical hexahydrides. This fact has been confirmed by means of the neutron diffraction structure of **361**. The geometry of the inner coordination sphere can be rationalized as an irregular dodecahedron defined by two orthogonal (87.5°) BAAB trapezoidal planes. One of them contains the phosphorus atoms at B sites and two hydrides at A sites, whereas the remaining hydrides lie in the other one.[261] Like the tetrahydrides **338**−**343**, these hexahydride derivatives are generated via tetrahydrideborate intermediates. In favor of this, it has been observed that complex **315** reacts with $NaBH_4$ to give the trihydride-tetrahydrideborate intermediate $OsH_3(\kappa^2\text{-}H_2BH_2)(P^iPr_3)_2$ (**363**), which evolves into $OsH_6(P^iPr_3)_2$ (**364**) in alcohols (Scheme 46).[262]

Scheme 46. Preparation of the Hexahydride 364 via the Trihydride-Tetrahydrideborate Intermediate 363

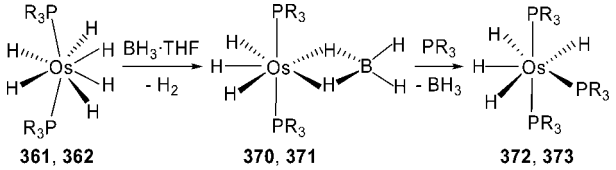


The P^tBu_2Me-counterpart $OsH_6(P^tBu_2Me)_2$ (**365**) has been similarly prepared starting from **314** and $NaBH_4$.[263] The same methodology has been used for the preparation of $OsH_6(P^iPr_2R)_2$ (R = CH_2CH_2OMe (**366**), CH_2CO_2Me (**367**), CH_2CO_2Et (**368**)), bearing functionalized phosphines, and the mixed phosphine derivative $OsH_6(P^iPr_3)\{P(CH_2CH_2NMe_2)^iPr_2\}$ (**369**).[264] Variable-temperature ^1H NMR studies and DFT calculations on **363** have revealed that this type of compounds undergo three different intramolecular rearrangements in solution. The lowest energy barrier is associated with the H^A−H^B hydride-exchange and goes through a dihydrogen transition state. The second lowest energy barrier corresponds to the hydride-tetrahydrideborate H^A−H^b exchange. In this case, the process goes through a seven-coordinate intermediate containing an η^2-H−BH_2 ligand. The highest energy barrier is associated with the exchange between the bridging (H^b) and terminal (H^t) hydrogens of the tetrahydrideborate group. This rearrangement goes via a dissociative mechanism, involving a transition state with a monodentate BH_4 ligand.[265]

Borane displaces a hydrogen molecule of **361** and **362** and is added to one of the remaining hydride ligands to quantitatively form the trihydride-tetrahydrideborate derivatives $OsH_3(\kappa^2\text{-}H_2BH_2)(PR_3)_2$ (PR_3 = P^iPr_2Ph (**370**), PCyp (**371**)). These compounds react with the corresponding PR_3 phosphine to give the tetrahydride complexes $OsH_4(PR_3)_3$ (PR_3 = P^iPr_2Ph (**372**), PCyp (**373**)), related to **338**−**343** (Scheme 47).[266]

The dissociation energy of a hydrogen molecule from the hexahydride complexes $OsH_6(PR_3)_2$ is not too high. Thus, the triisopropylphosphine derivative **364** reacts with diphenylphosphine in toluene at 80 °C to give H_2 and the tetrahydride

Scheme 47. Transformation of d^2-Hexahydride into d^4-Tetrahydride-Osmium Complexes via Trihydride-Tetrahydrideborate Intermediates



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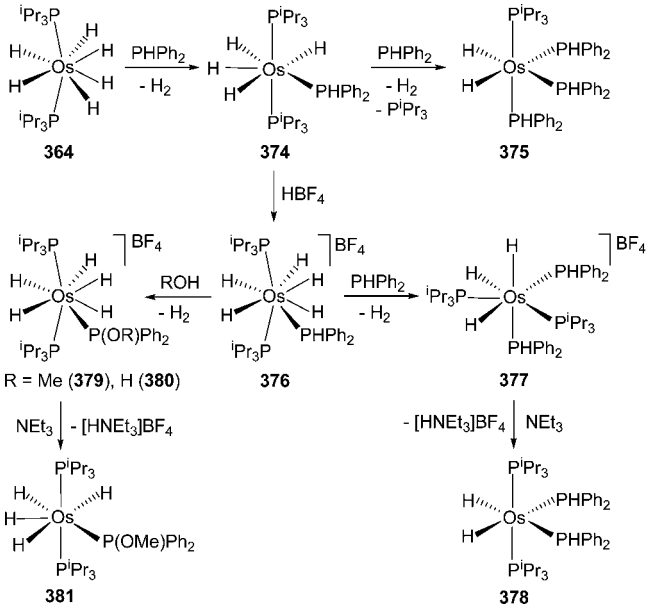
$OsH_4(PHPh_2)(P^iPr_3)_2$ (**374**) after 1 h. The dissociation of molecular hydrogen from complex **374** requires higher energy, which is similar to that necessary to break an Os−P bond. In contrast to **364**, the reaction of **374** with diphenylphosphine needs 3 days and gives rise to $OsH_2(PHPh_2)_3(P^iPr_3)$ (**375**), as a result of the loss of one molecule of hydrogen and the replacement of one of the triisopropylphosphine ligands. The selective substitution of molecular hydrogen in **374** requires its previous acidolysis with $HBF_4{\cdot}OEt_2$ (Scheme 48), which leads

Scheme 48. Mixed Triisopropylphosphine-Diphenylphosphine-Osmium(II), Osmium(IV), and Osmium(VI) Complexes

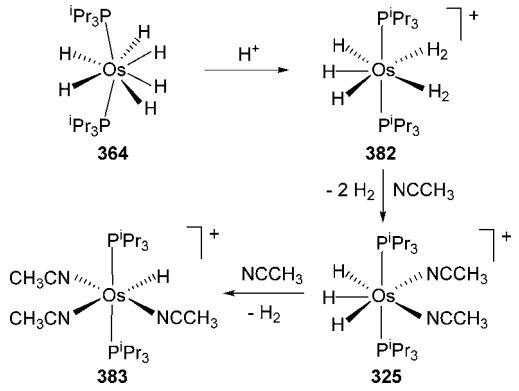


to $[OsH_5(PHPh_2)(P^iPr_3)_2]BF_4$ (**376**). In contrast to **374**, the addition of diphenylphosphine to **376** produces the selective substitution of H_2 to form $[OsH_3(PHPh_2)_2(P^iPr_3)_2]BF_4$ (**377**), which by deprotonation with NEt_3 affords $OsH_2(PHPh_2)_2(P^iPr_3)_2$ (**378**). Complex **376** also reacts with methanol and water to give $[OsH_5\{P(OMe)Ph_2\}(P^iPr_3)_2]BF_4$ (**379**) and $[OsH_5\{P(OH)Ph_2\}(P^iPr_3)_2]BF_4$ (**380**), respectively. The deprotonation of **379** with NEt_3 leads to $OsH_4\{P(OMe)Ph_2\}(P^iPr_3)_2$ (**381**).[267]

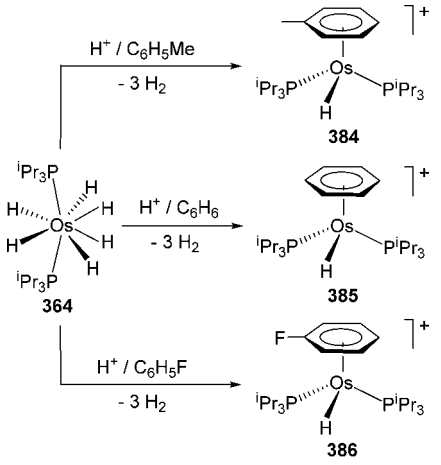
The acidolysis of **364** with $HBF_4{\cdot}OEt_2$ in diethyl ether produces the instantaneous precipitation of the trihydride-bis(dihydrogen) derivative $[OsH_3(\eta^2\text{-}H_2)_2(P^iPr_3)_2]BF_4$ (**382**), a rare case of OsH_7-species. In acetonitrile, complex **382** undergoes loss of the coordinated hydrogen molecules, which are replaced by solvent molecules to give the trihydride-bis(solvento) cation **325**. Further reaction with acetonitrile leads to the monohydride $[OsH(CH_3CN)_3(P^iPr_3)_2]BF_4$ (**383**) and H_2 (Scheme 49).[268]

Complex **383** is the result of the trapping of the 12-valence electrons monohydride cation $[OsH(P^iPr_3)_2]^+$ by the acetonitrile solvent. This "functional equivalent" can be also trapped by aromatic solvents such as toluene, benzene, or fluorobenzene (Scheme 50). Thus, the addition of 1.5 equiv of $HBF_4{\cdot}OEt_2$ to the solutions of **364** in these aromatic solvents leads to the half-sandwich compounds $[OsH(\eta^6\text{-arene})(P^iPr_3)_2]BF_4$ (arene = C_6H_5Me (**384**), C_6H_6 (**385**), C_6H_5F (**386**)), as a result of initial protonation of the hexahydride, the subsequent release of

Scheme 49. Acidolysis of 364 in Acetonitrile



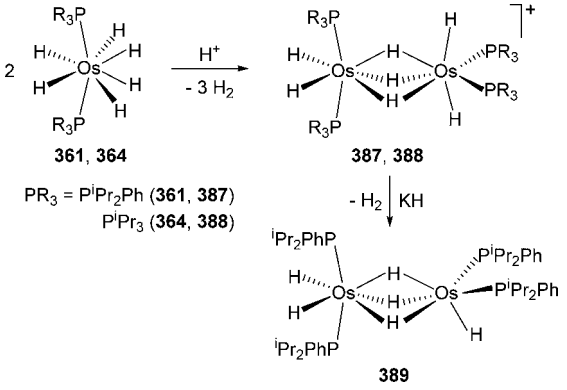
Scheme 50. Acidolysis of 364 in Aromatic Solvents



three hydrogen molecules from the intermediate **382**, and the arene coordination to the 12-valence electrons monohydride.[269]

This type of monohydride cations can also be trapped by the own hexahydrides (Scheme 51). Thus, the protonation of **361**

Scheme 51. Transformation of Hexahydride-Osmium Complexes into Dimer Species



and **364** with 0.5 equiv of acid yields the heptahydride dimers $[\{OsH_2(PR_3)_2\}_2(\mu\text{-}H)_3]^+$ (PR_3 = P^iPr_2Ph (**387**),[270] P^iPr_3 (**388**)[269]). Deprotonation of **387** with potassium hydride gives the neutral hexahydride dimer $(P^iPr_2Ph)_2H_2Os(\mu\text{-}H)_3OsH(P^iPr_2Ph)_2$ (**389**).

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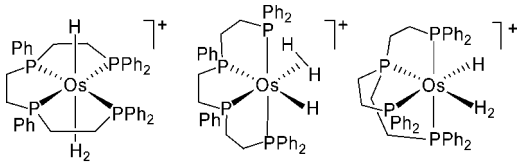
3.2. Complexes with Tetrapodal Phosphine Ligands

Polyhydrides stabilized with ligands of this type are rare in the osmium chemistry (Chart 10). The abstraction of the chloride

Chart 10. Complexes with Tetrapodal Phosphine Ligands

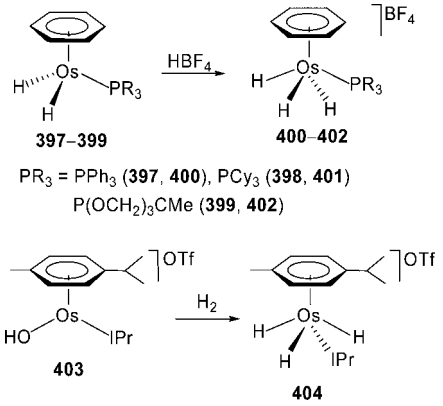


ligand of *trans*-OsHCl(*meso*-tetraphos-1) (**390**) with $NaBPh_4$ under hydrogen atmosphere yields the *trans*-hydride-dihydrogen $[OsH(\eta^2\text{-}H_2)(meso\text{-tetraphos-1})]BPh_4$ (**391**; d_{H2} = 0.95–0.99 Å),[132] whereas the protonation of *cis*-α-OsH_2(*rac*-tetraphos-1) (**392**) with $HBF_4{\cdot}OEt_2$ leads to the *cis*-hydride-elongated dihydrogen $[OsH(\eta^2\text{-}H_2)(rac\text{-tetraphos-1})]BF_4$ (**393**; d_{H-H} = 1.25–1.6 Å).[271] The related *cis*-hydride-dihydrogen $[OsH(\eta^2\text{-}H_2)\{P(CH_2CH_2PPh_2)_3\}]BPh_4$ (**394**; $d_{H2} \approx 0.95$ Å) has been prepared by displacement of the coordinated nitrogen molecule of $[OsH(\eta^2\text{-}N_2)\{P(CH_2CH_2PPh_2)_3\}]BPh_4$ (**395**) by H_2 or by protonation of the dihydride $OsH_2\{P(CH_2CH_2PPh_2)_3\}$ (**396**) with HOTf and subsequent addition of $NaBPh_4$. The mutually *trans*-disposition of the hydride and a terminal phosphorus atom in **394** has been established by X-ray diffraction analysis.[272]

3.3. Half Sandwich Compounds

Complexes of this type include a few cationic trihydride compounds containing arene ligands (Scheme 52). Protonation

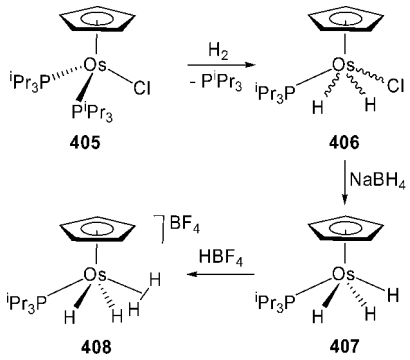
Scheme 52. Preparation of $[OsH_3(\eta^6\text{-arene})L]^+$ Cations



of the dihydride complexes $OsH_2(\eta^6\text{-}C_6H_6)(PR_3)$ (PR_3 = PPh_3 (**397**), PCy_3 (**398**), $P(OCH_2)_3CMe$ (**399**)) with $HBF_4{\cdot}OEt_2$ in dichloromethane leads to $[OsH_3(\eta^6\text{-}C_6H_6)(PR_3)]BF_4$ (PR_3 = PPh_3 (**400**), PCy_3 (**401**), $P(OCH_2)_3CMe$ (**402**)),[273] whereas the hydrogenation of the cationic 16-valence electrons hydroxo [Os(OH)(η⁶-*p*-cymene)(IPr)]OTf (**403**) affords the NHC-derivative $[OsH_3(\eta^6\text{-}p\text{-cymene})(IPr)]OTf$ (**404**).[274] The hydride ligands of these compounds undergo quantum mechanical exchange coupling with temperature-dependent values of J_{obs} between 70 and 370 Hz in the temperature range of 213–173 K.

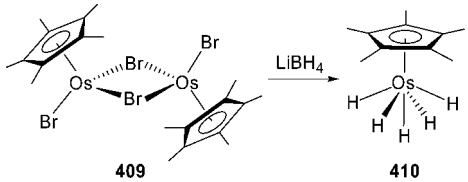
One of the phosphine ligands of the Cp-complex $OsCl(\eta^5\text{-}C_5H_5)(P^iPr_3)_2$ (**405**) can be displaced by molecular hydrogen to give $OsH_2Cl(\eta^5\text{-}C_5H_5)(P^iPr_3)$ (**406**), which is isolated as a mixture of isomers *transoid*- and *cisoid*-dihydride. The reaction of the mixture with $NaBH_4$ and methanol leads to the neutral trihydride $OsH_3(\eta^5\text{-}C_5H_5)(P^iPr_3)$ (**407**). Although the *cisoid* hydride ligands of this compound are involved in a thermally activated site exchange process, in contrast to **400**–**402** and **404**, they do not undergo quantum mechanical exchange coupling.[275] The addition of $HBF_4{\cdot}OEt_2$ to diethyl ether solutions of **407** produces the precipitation of the dihydride-elongated dihydrogen derivative $[OsH_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(P^iPr_3)]BF_4$ (**408**), for which a separation between the hydrogen atoms of the elongated dihydrogen ligand of about 1.1 Å has been calculated from the J_{H-D} value (Scheme 53).[276]

Scheme 53. Cyclopentadienyl-Osmium Complexes



Girolami reported in 1994 the preparation of the osmium(III) dimer $Os_2Br_4(\eta^5\text{-}C_5Me_5)_2$ (**409**) in high yield,[277] which has been the entry to an interesting osmium-polyhydride chemistry. This dimer reacts with $LiBH_4$ in tetrahydrofuran to give the osmium(VI) pentahydride $OsH_5(\eta^5\text{-}C_5Me_5)$ (**410**) in 85% yield (Scheme 54).[278] Complex **410** adopts a pseudo-C_{4v}

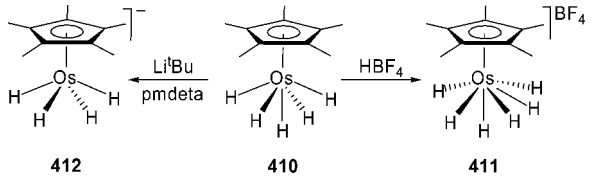
Scheme 54. Preparation of the Half-Sandwich Pentahydride 410



geometry with one axial and four equatorial hydride ligands.[279] A pseudo second-order Jahn–Teller distortion of this *pseudo*-octahedral geometry, where the equatorial hydride ligands bend away from the Cp*-ring at a large angle, explains the diamagnetic nature of this d^2 species.[280]

Complex **410** reacts with strong Brønsted acids and bases (Scheme 55). The addition of $HBF_4{\cdot}OEt_2$ to diethyl ether solutions of the pentahydride leads to the hexahydride

Scheme 55. Protonation and Deprotonation Reactions of 410



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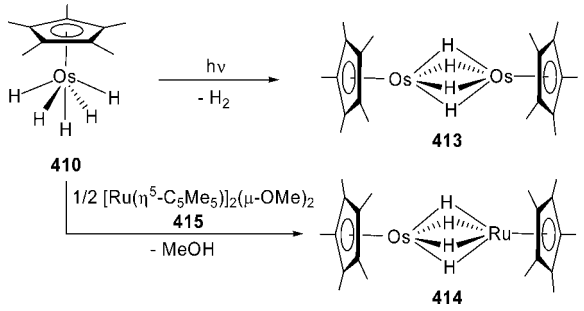
$[OsH_6(\eta^5\text{-}C_5Me_5)]BF_4$ (**411**). It is a classical polyhydride, which adopts a *pseudo*-pentagonal bipyramidal geometry with one axial and five equatorial hydride ligands. Treatmemt of **410** with *tert*-butyllithium in pentane in the presence of *N,N,N′,N″,N″*-pentamethyldiethylenediamine (pmdeta) produces its deprotonation and the formation of the salt $[Li(pmdeta)][OsH_4(\eta^5\text{-}C_5Me_5)]$ (**412**). The osmium(IV) tetrahydride anion adopts a four-legged piano-stool structure.[281]

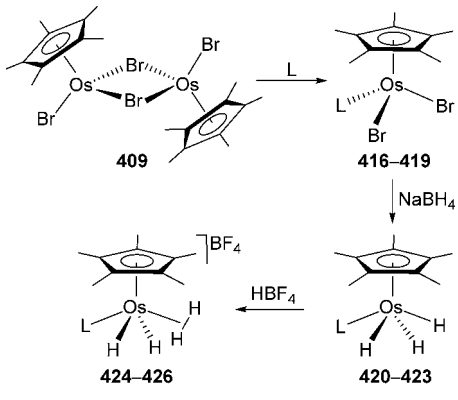
The pentahydride complex **410** loses molecular hydrogen under photolysis in benzene to give the tetrahydride dimer $[Os(\eta^5\text{-}C_5Me_5)]_2(\mu\text{-}H)_4$ (**413**).[277,281] The heterobimetallic osmium−ruthenium counterpart $(\eta^5\text{-}C_5Me_5)Os(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$ (**414**) has been prepared by reaction of the ruthenium dimer $[Ru(\eta^5\text{-}C_5Me_5)]_2(\mu\text{-}OMe)_2$ (**415**) with **410** (Scheme 56).[278]

Scheme 56. Pentahydride 410 as Starting Material of Homo- and Heterometallic Compounds



Addition of Lewis bases to **409** in ethanol affords the mononuclear osmium(III) complexes $OsBr_2(\eta^5\text{-}C_5Me_5)L$ (L = $AsPh_3$ (**416**), PPh_3 (**417**), PCy_3 (**418**), PEt_3 (**419**)).[282] These paramagnetic compounds react with $NaBH_4$ in ethanol to give the osmium(IV)-trihydrides $OsH_3(\eta^5\text{-}C_5Me_5)L$ (L = $AsPh_3$ (**420**), PPh_3 (**421**), PCy_3 (**422**), PEt_3 (**423**)), which are Cp*-counterparts of **407**. Like the latter, these compounds show no evidence of quantum mechanical exchange coupling. Protonation of **420**−**422** with $HBF_4{\cdot}OEt_2$ in diethyl ether leads to the precipitation of the respective dihydride-elongated dihydrogen derivatives $[OsH_2(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}H_2)L]BF_4$ (L = $AsPh_3$ (**424**), PPh_3 (**425**), PCy_3 (**426**)), related to the Cp-compound **408** (Scheme 57).[283,284] These compounds have

Scheme 57. Preparation of $OsH_3(\eta^5\text{-}C_5Me_5)L$ and $[OsH_2(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}H_2)L]^+$ Complexes

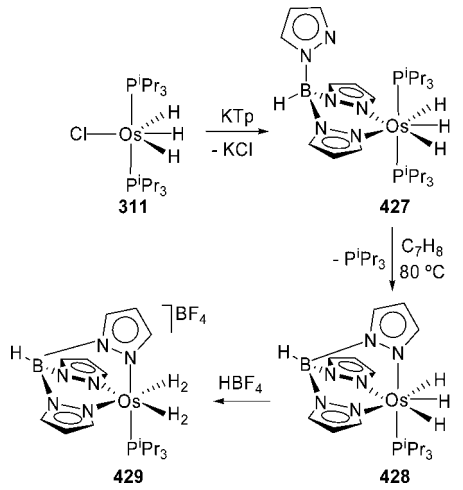


been characterized by single-crystal neutron diffraction. The coordination around the metal center can be described as four-legged piano-stool geometries in which the L ligand is transoid to the elongated dihydrogen ligand. For **424** and **425**, the coordinated hydrogen molecule is oriented with its H−H vector nearly parallel to the Os-Cp* direction, while in **426**, the elongated dihydrogen ligand is perpendicular. Not only the orientation of the elongated dihydrogen ligand but also the H−H bond length depends upon L. The H−H distance is 1.08(1) and 1.01(1) Å for **424** and **425**, respectively, but 1.31(3) Å for **426**.[285] In solution, the H−H distances determined from the corresponding T_1(min) and J_{H-D} values (1.15, 1.07, and 1.12 Å, respectively) are slightly shorter than in the solid state.[283,284]

3.4. Complexes with Tris(pyrazoyl)borate and Related Ligands

Tris(pyrazolyl)borate osmium complexes remain less explored than those of most *d*-block elements. As a consequence, polyhydride compounds with this type of ligands are scarce. The chloride-trihydride complex **311** reacts with KTp, in tetrahydrofuran, at room temperature to give $OsH_3(\kappa^2\text{-}Tp)(P^iPr_3)_2$ (**427**). In toluene at 80 °C, this κ^2-Tp complex is transformed to the κ^3-Tp derivative $OsH_3(\kappa^3\text{-}Tp)(P^iPr_3)$ (**428**), in quantitative yield after 7 h, as a result of the dissociation of one of the phosphines and the coordination of the free pyrazolyl group of **427** (Scheme 58). Protonation of

Scheme 58. Osmium-Tris(pyrazolyl)borate Complexes



428 with $HBF_4{\cdot}OEt_2$ in diethyl ether affords the bis-(dihydrogen) compound $[OsTp(\eta^2\text{-}H_2)_2(P^iPr_3)]BF_4$ (**429**).[286] In acetone, complex **429** releases the coordinated hydrogen molecules in a sequential manner. At room temperature, the dihydrogen solvate complex $[OsTp(\eta^2\text{-}H_2)(OCMe_2)(P^iPr_3)]BF_4$ (**430**) is formed, while at 56 °C the loss of both hydrogen molecules gives rise to the bis-solvento derivative $[OsTp(OCMe_2)_2(P^iPr_3)]BF_4$ (**431**). The bis-dihydrogen complex **429** reacts with ethylene under 2 atm to afford ethane and $[OsTp(CH_2CH_2P^iPr_3)(\eta^2\text{-}CH_2{=}CH_2)_2]BF_4$ (**432**), which promotes the C−H bond activation of fluorobenzene and 1,3-difluorobenzene by σ-bond metathesis.[287]

Complexes **427**−**429** have been characterized by X-ray diffraction analysis and DFT calculations. The geometry around the osmium atom of the trihydrides **427** and **428** can be rationalized as a distorted pentagonal bipyramid with the hydride ligands adopting a disposition of local C_{2v} symmetry,

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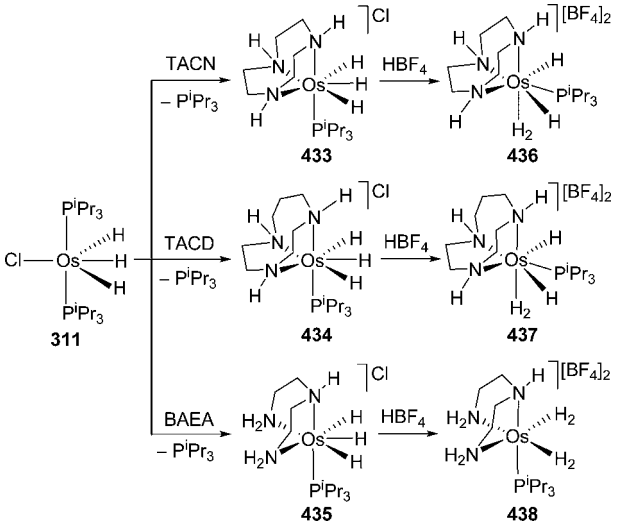
separated by about 1.61 Å. The bis(dihydrogen) complex **429** adopts an octahedral geometry, where the coordinated hydrogen molecules are cis disposed with a H−H bond length of 0.906 Å. The comparison of these structures with those of their Cp-counterparts **407** and **408** reinforces the idea that Tp avoids the piano-stool structures and enforces dispositions allowing N−M−N angles close to 90°, which favor the nonclassical interactions.[286]

The chloride-trihydride complex **311** is also the entry to polyhydride compounds with cyclic and acyclic triamine ligands (Scheme 59). Treatment of toluene solution of **311** with

Scheme 59. Osmium Complexes with Cyclic and Acyclic Triamine Ligands



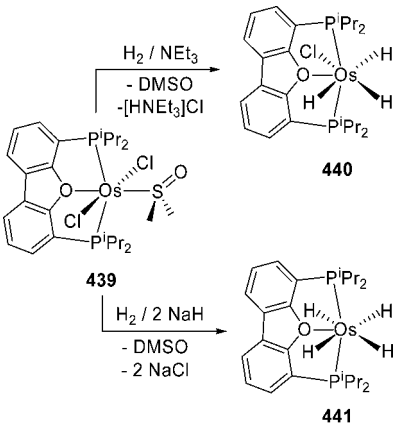
TACN, 1,4,7-triazacyclodecane (TACD), and bis(2-aminoethyl)amine (BAEA) at 60 °C affords the corresponding salts $[OsH_3(L_3)(P^iPr_3)]Cl$ (L_3 = TACN (**433**), TACD (**434**), BAEA (**435**)). Like their Tp-counterpart **428**, these compounds have structures that can be rationalized as pentagonal bipyramids with a nitrogen atom in the axial position and the other two lying in the equatorial plane along with the hydrides. The $N_{meridional}$−Os−$N_{meridional}$ angle of the bipyramids determines the behavior of these species. As previously mentioned, the neutral Tp-complex **428**, with an angle of 83.17(12)°, reacts with HBF_4 to give the monocationic bis(dihydrogen) **429**. However, the reactions of the TACN- and TACD-trihydrides **433** and **434**, which have angles close to 78°, with HBF_4 lead to the dicationic dihydride-dihydrogen compounds $[OsH_2(\eta^2\text{-}H_2)(L_3)(P^iPr_3)][BF_4]_2$ (L_3 = TACN (**436**), TACD (**437**)), analogous to the Cp-complex **408**, but with a shorter H−H dihydrogen distance (0.87−1.03 Å). In contrast to the trihydrides containing cyclic triamines, the BAEA trihydride **435**, with an angle similar to that of the Tp-complex **428**, 82.5(3)°, reacts with HBF_4 similarly to the latter to afford the dicationic bis(dihydrogen) $[Os(BAEA)(\eta^2\text{-}H_2)_2(P^iPr_3)][BF_4]_2$ (**438**).[288]

The systematical comparison of the structural features of the L_3-complexes and those of the Tp- and Cp-counterparts suggests that the charge of the complexes has less influence on the interactions between the atoms of the OsH_n units than certain structural parameters.

3.5. Complexes with Pincer Ligands

Complex $OsCl_2\{dbf(P^iPr_2)_2\}(\kappa^1\text{-DMSO})$ (**439**, $dbf(P^iPr_2)_2$ = 4,6-bis(diisopropylphosphine)dibenzofuran) reacts with molecular hydrogen in the presence of a Brønsted base. The products of the reaction depend upon the base (Scheme 60).

Scheme 60. Reactions of 439 with Molecular Hydrogen in the Presence of Bases



Triethylamine removes a chloride ligand. Thus, the reaction gives the trihydride $OsH_3Cl\{dbf(P^iPr_2)_2\}$ (**440**). On the other hand, NaH extracts both chloride ligands, to afford the tetrahydride $OsH_4\{dbf(P^iPr_2)_2\}$ (**441**). Both **440** and **441** have been characterized by X-ray diffraction analysis. The geometry around the osmium atom of **440** can be rationalized as a distorted pentagonal bipyramid, with the P^iPr_2 groups occupying axial positions and the chloride situated between the oxygen atom of the pincer and one of the hydrides. The structure of the tetrahydride **441** is as that of **440** with a hydride in the position of the chloride.[289]

The behavior of the $xant(P^iPr_2)_2$-counterpart, $OsCl_2\{xant\text{-}(P^iPr_2)_2\}(\kappa^1\text{-DMSO})$ (**442**), is similar. In the presence of triethylamine, the reaction of **442** with molecular hydrogen leads to the trihydride $OsH_3Cl\{xant(P^iPr_2)_2\}$ (**443**), which has also been prepared by addition of the diphosphine to toluene solutions of **311**. Sodium hydride removes both chloride ligands, and furthermore, a hydrogen molecule displaces the oxygen atom of the diphosphine to give the hexahydride $OsH_6\{xant(P^iPr_2)_2\}$ (**444**), containing a κ^2-diphosphine. In methanol, under argon atmosphere, complex **444** slowly loses a hydrogen molecule, and the diphosphine coordinates the oxygen atom to the metal center to form the tetrahydride $OsH_4\{xant(P^iPr_2)_2\}$ (**445**), which can also be prepared by addition of $xant(P^iPr_2)_2$ to the hexahydride **364** (Scheme 61). Like in the latter, the geometry around the osmium center of **444** can be described as a distorted dodecahedron. However, in this case, the phosphorus atoms occupy a B-site at each trapezoidal plane.[290]

The tetrahydride **445** is a strong reductor, which is able to promote the reduction of H^+ (Scheme 62), in spite of the high oxidation state of the metal center. Thus, the addition of 4 equiv of triflic acid to its dichloromethane solutions gives H_2 and the dihydride-elongated dihydrogen cation $[OsH_2(OTf)(\eta^2\text{-}H_2)\{xant(P^iPr_2)_2\}]^+$ (**446**). In agreement with the ^1H NMR spectrum, the DFT-optimized structure of this species shows two groups of two equivalent hydrogen atoms, one of them in the P,H,H,P-trapezoidal plane and the other one in the

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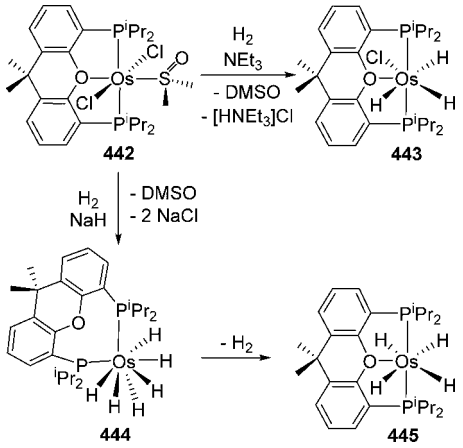
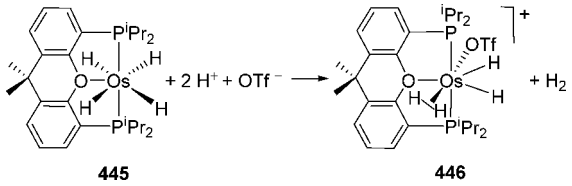
Scheme 61. Neutral Compounds with the xant(P^iPr_2)$_2$ Ligand



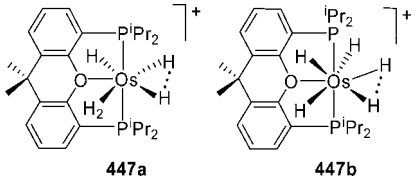
Scheme 62. Reduction of H^+ Promoted by 445



O,H,H,O-trapezoidal plane. In the first plane, the hydrogen atoms are separated by 1.545 Å, whereas in the second one, the H−H distance is 1.250 Å.

The redox reaction occurs in two stages. Initially complex **445** adds a proton to afford $[OsH_5\{xant(P^iPr_2)_2\}]^+$ (**447**), which reacts with HOTf to give H_2 and **446**. DFT calculations reveal that **447** (Chart 11) has two tautomers very close in

Chart 11. $[OsH_5\{xant(P^iPr_2)_2\}]^+$ Species

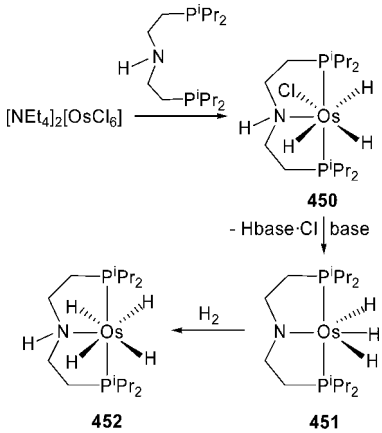


energy (<3 kcal mol^{-1}): a hydride-compressed dihydride-dihydrogen (**447a**) and a trihydride-compressed dihydride (**447b**). In **447a**, the dihydrogen ligand is disposed almost parallel to the P−Os−P direction with a H−H bond length of 0.87 Å, whereas the compressed dihydride (1.40 Å) lies in the perpendicular plane along with the oxygen atom of the diphosphine. In **447b**, the disposition of the hydrogen atoms is the same as in **447a** with the hydrogen atoms in the P,H,H,P plane separated by 1.762 Å.

Acetonitrile displaces the coordinated trifluoromethanesulfonate anion of **446** to afford the dication compressed dihydride-dihydrogen $[OsH_2(\eta^2\text{-}H_2)(CH_3CN)\{xant(P^iPr_2)_2\}]^{2+}$ (**448**). The dihydrogen ligand of this compound is situated in the perpendicular plane to the P−Os−P direction, with the hydrogen atoms separated by 0.898 Å, while the compressed dihydride lies in the trapezoidal plane containing the phosphorus atoms with the hydrogens separated by 1.475 Å. The treatment of **448** with NEt_3 causes its deprotonation and the formation of the trihydride $[OsH_3(CH_3CN)\{xant(P^iPr_2)_2\}]^+$ (**449**). The reaction is reversible, the addition of HOTf to **449** regenerates **448** (Scheme 63).

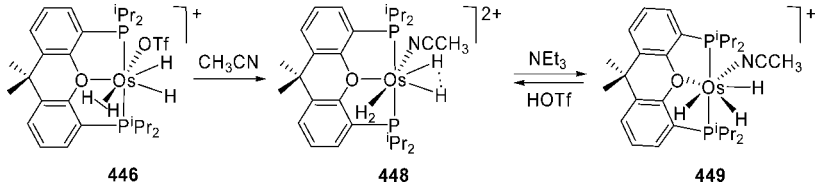
A small family of PNP complexes has been also reported. Ligand $(^iPr_2PCH_2CH_2)_2NH$ reacts with $[NEt_4]_2[OsCl_6]$ in 2-propanol or 2-pentanol to give the trihydride $OsH_3Cl\{(^iPr_2PCH_2CH_2)_2NH\}$ (**450**). Upon reaction with strong bases, such as KO^{t}Bu or NaN(SiMe$_3$)$_2$, complex **450** undergoes dehydrochlorination to give the 16-valence electrons d^4-amido-trihydride $OsH_3\{(^iPr_2PCH_2CH_2)_2N\}$ (**451**). This diamagnetic ML_6 d^4-complex has a structure similar to those of complexes $OsH_3X(PR_3)_2$ (**310**−**313** and **318**−**320**) with the nitrogen atom at the X-site. Under hydrogen atmosphere, complex **451** gives the tetrahydride $OsH_4\{(^iPr_2PCH_2CH_2)_2NH\}$ (**452**), as a result of the addition of H_2 to the Os−N bond of **451** (Scheme 64).[291]

Scheme 64. PNP-Osmium Complexes



P(olefin)P-Pincer complexes have been reported by Lin, Lau, Jia, and co-workers. Treatment of the hydride-compressed dihydride **309** with (*E*)-$Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2$ leads to $OsHCl(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}$ (**453**), which reacts with HOTf to give the elongated dihydrogen $[OsCl(\eta^2\text{-}H_2)(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}]OTf$ (**454**; d_{H-H} = 1.18 Å). Under molecular hydrogen atmosphere, the latter does not undergo the hydrogenation of the C−C double bond but a molecule of hydrogen chloride is removed to form the hydride-dihydrogen

Scheme 63. Other POP-Osmium Complexes



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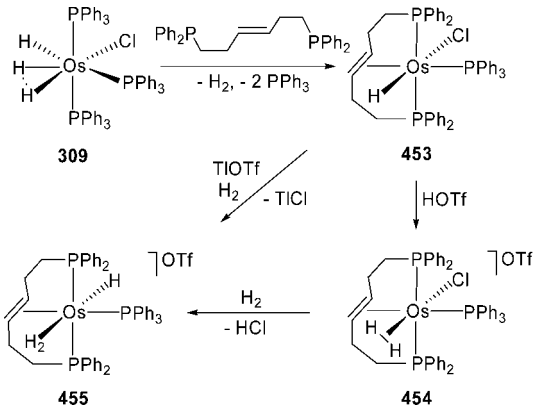
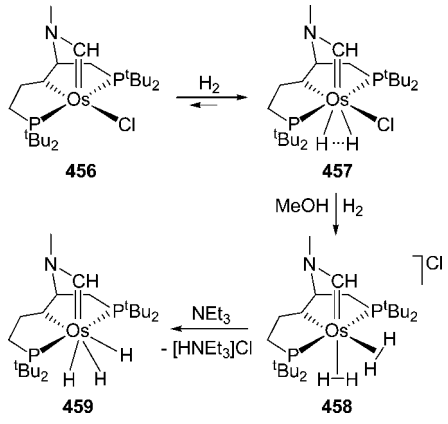
$[OsH(\eta^2\text{-}H_2)(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}]OTf$ (**455**; d_{H2} = 0.97 Å), which can be directly prepared from **453**, by reaction with TlOTf under hydrogen atmosphere (Scheme 65). DFT calculations suggest that although the hydrogenation of the olefin of **454** is thermodynamically feasible, it is kinetically unfavorable.[292]

Scheme 65. P(olefin)P-Osmium Complexes



Gusev and co-workers have reported chiral polyhydride complexes stabilized by a PC(sp^3)P-pincer ligand with an additional Fisher-type carbene arm.[293] Reaction of $[OsCl_6]^{2-}$ with the chiral ligand (*S*)-^{t}Bu$_2$PCH$_2$CH(NMe$_2$)(CH$_2$)$_3$P^{t}Bu$_2$ affords the square-pyramidal 16-valence electrons carbene derivative OsCl(PGP) (**456**, PGP = κ^4-^{t}Bu$_2$PCH$_2$CH{N(Me)-CH=}CH(CH$_2$)$_2$P^{t}Bu$_2$) in excellent yield. In toluene, at room temperature, under an atmosphere of hydrogen, complex **456** is in equilibrium with the chloride-compressed dihydride $OsH_2Cl(PGP)$ (**457**; $d_{H\cdots H}$ = 1.40–1.43 Å). This compound has a labile chloride ligand, which is rapidly and quantitatively displaced by H_2 in methanol or in the presence of $NaBPh_4$ in tetrahydrofuran to give the bis(elongated dihydrogen) complex $[Os(\eta^2\text{-}H_2)_2(PGP)]BPh_4$ (**458**), with two equal H–H bonds of 1.11 Å. Complex **458** can be deprotonated with NEt_3 to give the trihydride $OsH_3(PGP)$ (**459**), according to Scheme 66.

Scheme 66. Chiral Polyhydride Complexes Stabilized by a PC(sp^3)P-Pincer Ligand with an Additional Fisher-type Carbene Arm



3.6. Osmium-Polyhydride Complexes Involved in σ-Bond Activation Reactions

3.6.1. B–H Bond Activation Reactions. The previously mentioned behavior of the trihydride **311** is consistent with a marked tendency of this compound to release molecular hydrogen and to form the 14-valence electrons species OsHCl(P^{i}Pr$_3$)$_2$ (**G**), which can also be generated from the dichloride-dihydride **315** by means of the elimination of HCl. This unsaturated species activates the B–H bond of boronic esters and amine-boranes to afford compounds with unusual bonding situations (Scheme 67). The reaction of **G** with HBpin leads to the borinium derivative $OsH_2Cl(\eta^2\text{-}HBOCMe_2CMe_2OBpin)(P^iPr_3)_2$ (**460**).[294] This compound is formed via the intermediate bis(σ-borane) $OsHCl(\eta^2\text{-}HBpin)_2(P^iPr_3)_2$ (**H**), resulting from the coordination of two molecules of HBpin to **G**. Once coordinated, the heterolytic B–H activation of one of them, using an oxygen atom of the other one as an external base, gives **460**. In contrast to HBpin, the H–B bond of HBcat undergoes homolytic cleavage to initially afford the dihydride-boryl intermediate $OsH_2Cl(Bcat)(P^iPr_3)_2$ (**461**), which gives the hydride-bis(boryl) derivative $OsHCl(Bcat)_2(P^iPr_3)_2$ (**462**) and H_2 by reaction with an additional molecule of HBcat. As expected for a ML_6 d^4-species, complex **462** experiences a strong distortion from the octahedral geometry, adopting a similar structure to **311** where the boryl groups occupy two equivalent sites at the perpendicular plane to the P–Os–P direction.[295] Amine-boranes undergo dehydrogenation in the presence of **G** to form aminoboranes. The hydride transfer from the aminoboranes to **G** yields the corresponding aminoborinium complexes $OsH_2Cl(\eta^2\text{-}HBNRR')(P^iPr_3)_2$ (NRR′ = NMe$_2$ (**463**), NH^{t}Bu (**464**)) via bis(σ-B–H) intermediates $OsHCl(\eta^2,\eta^2\text{-}H_2BNRR')(P^iPr_3)_2$ (**I**).[294] DFT calculations suggest that the major contribution to the interaction between the metal fragment and this type of ligands is electrostatic (57%). This indicates a high degree of polarization for the osmium–borinium bond, which agrees well with the high electronegativity of the osmium atom and suggests a significant positive partial charge on the ligand. Although **463** has been described as an α-agostic boryl species,[177] the high degree of polarization for the Os–B bond in these compounds and the calculated hybridization at the boron atom ($sp^{1.3-1.6}$) is fully consistent with the borinium denomination. The orbital term of the interaction is the result of three contributions: two σ-interactions and a π-interaction. The most important σ-interaction involves to the boron atom and the metal center. The other one takes place between the doubly occupied σ(B–H) bond molecular orbital and the metal fragment.[296]

Cooperative heterolysis of the B–H bond can be performed with a soft base coordinated to an electrophilic osmium center. When the complex also contains a hydride ligand, in addition to the B–H heterolysis, the heterolytic H–H formation is also feasible (Scheme 68). The five-coordinate hydride-hydrogensulfide complex OsH(SH)(CO)(P^{i}Pr$_3$)$_2$ (**465**) reacts with HBpin, HBcat, and (HBbn)$_2$ to give the hydride-dihydrogen-borylthiolate compounds $OsH(SBR_2)(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ (BR_2 = Bpin (**466**), Bcat (**467**), Bbn (**468**)) as a result of the B–H heterolysis and a proton transfer from the sulfur atom to the metal center. DFT calculations suggest that the rupture of the B–H bond initially affords the *trans*-dihydride intermediates $OsH_2(SHBR_2)(CO)(P^iPr_3)_2$ (**J**), which evolve into **466**–**468** through a η^2-H–SBR$_2$ transition state. On the basis of T_1(min) and J_{H-D} values, a separation between the

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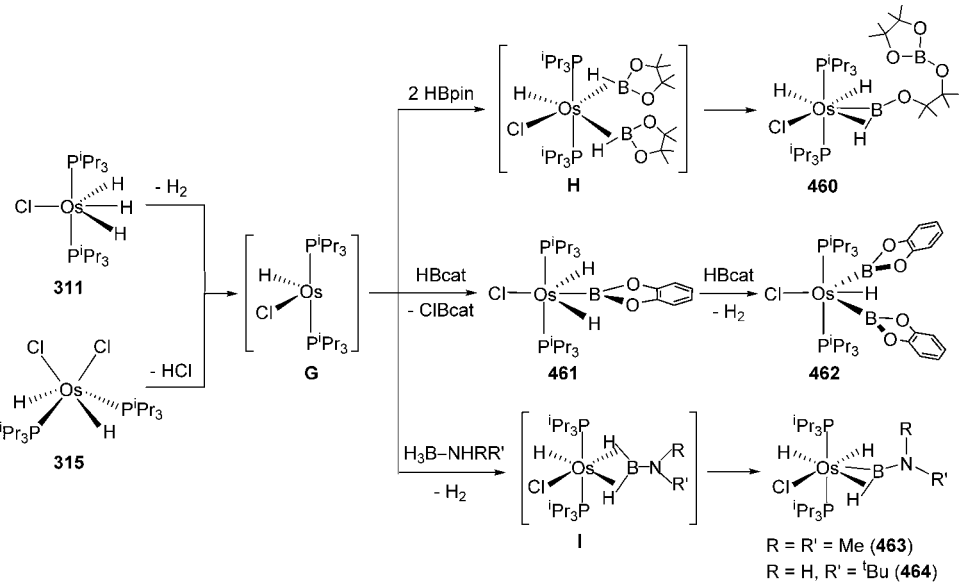
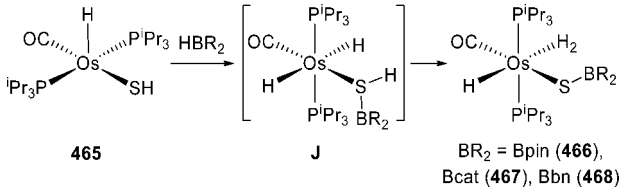
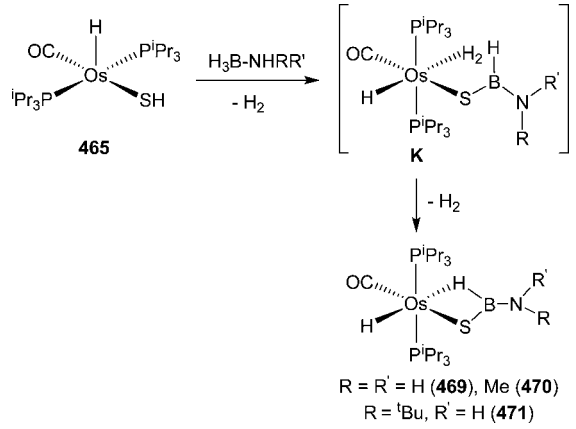
Scheme 67. B−H Bond Activation Reactions Promoted by the 14-Valence Electrons Species $OsHCl(P^iPr_3)_2$



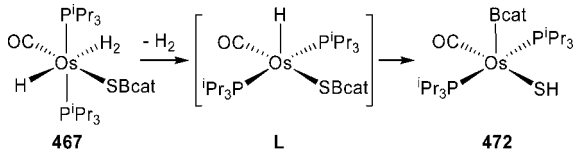
Scheme 68. B−H Heterolysis and Heterolytic H−H Formation



Scheme 69. Amine-Borane Dehydrogenation and Capture of the Resulting Aminoborane Monomers



Scheme 70. Intramolecular Hydride-Boryl Exchange



hydrogen atoms of the dihydrogen ligand of about 0.9 Å has been calculated for these compounds.[297]

Amine-boranes undergo catalytic dehydrogenation in the presence of the hydride-hydrogensulfide complex **465**. At low concentrations of substrate, the hydrogensulfide ligand captures the resulting aminoborane monomers, before their coupling, to initially form the hydride-dihydrogen species $OsH(SBHNRR')(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ (**K**), analogous to **466**−**468**, which release H_2 to give the hydrogenaminothioborate derivatives $OsH\{\kappa^2\text{-}H,S\text{-}[HB(S)(NRR')]\}(CO)(P^iPr_3)_2$ (NRR′ = NH_2 (**469**), NMe_2 (**470**), NH^tBu (**471**)), according to Scheme 69.[298]

Complex **466** is stable enough to be characterized by X-ray diffraction analysis. However, the Bcat-counterpart **467** has a marked tendency to lose molecular hydrogen. The resulting hydride-borylthiolate intermediate $OsH(SBcat)(CO)(P^iPr_3)_2$ (**L**) undergoes a fast intramolecular hydride-boryl exchange process (Scheme 70). As a consequence, complex **467** rapidly evolves into the boryl-hydrogensulfide $Os(Bcat)(SH)(CO)(P^iPr_3)_2$ (**472**) in toluene.[297] The formation of **467** via intermediate **J** and its transformation into **472** demonstrate that the hydrogensulfide group of **465** is a cooperating ligand in the heterolytic activation of the H−B bond of HBcat to give H_2 and **472**.

The hydride-dihydrogen-borylthiolate complex **466** exchanges borylthiol by HBpin. The exchange process leads to the dihydride-(σ-borane) derivative $OsH_2(\eta^2\text{-}HBpin)(CO)(P^iPr_3)_2$ (**473**). This compound and the HBcat-counterpart $OsH_2(\eta^2\text{-}HBcat)(CO)(P^iPr_3)_2$ (**474**) are properly prepared by coordination of the boranes to the unsaturated dihydride **300**, which can be generated in situ by means of the olefin dissociation from $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$ (**475** in Scheme 71). The hydrogen atoms bonded to the metal center of **473** and **474** undergo two thermally activated site-exchange processes, involving the hydride positions and that of the B−H site. The hydride−hydride site exchange, which needs an activation energy lower than the hydride-BH site exchange, appears to take place via dihydrogen species, whereas the hydride-BH site exchange seems to proceed through trihydride-boryl intermediates.[299]

Dihydride **300**, generated from **475** by dissociation of the olefin, promotes the release of 1 equiv of H_2 from ammonia-borane and the formation of polyaminoborane (eq 3) with a catalytic rate law given by eq 4.

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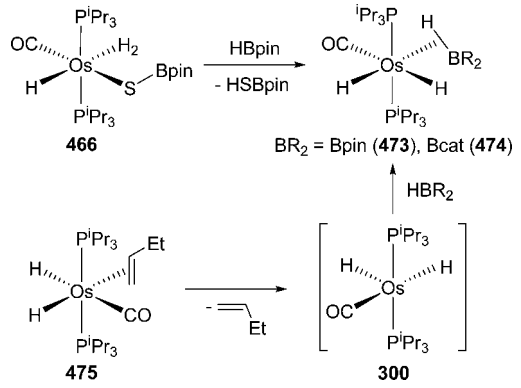
Scheme 71. Dihydride-(σ-borane)-Osmium Complexes

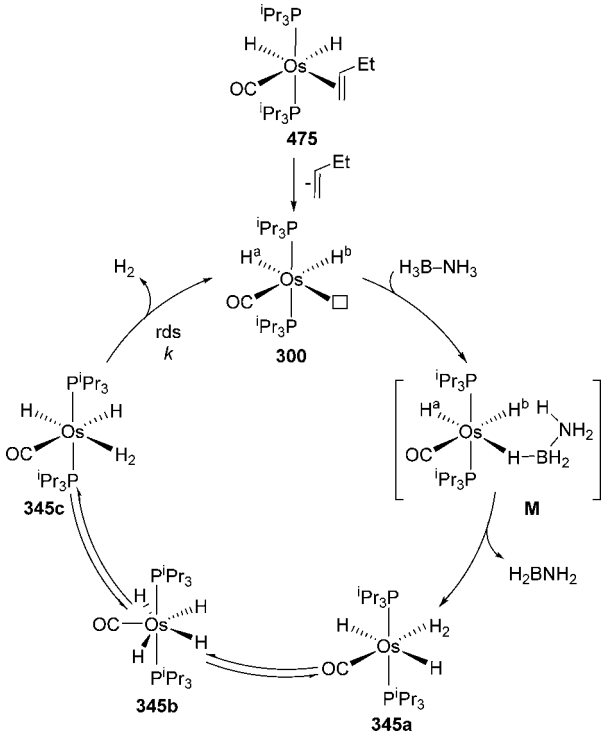


$$n\ H_3B-NH_3 \xrightarrow{[475]} n\ H_2 + [BH_2NH_2]_n \quad (3)$$

$$d[H_2]/dt = k[\mathbf{475}] \quad (4)$$

Scheme 72 summarizes the mechanism proposed for this process, which is strongly supported by kinetic results,

Scheme 72. Catalytic Cycle for the Dehydrogenation of Ammonia-Borane Catalyzed by 300[a]

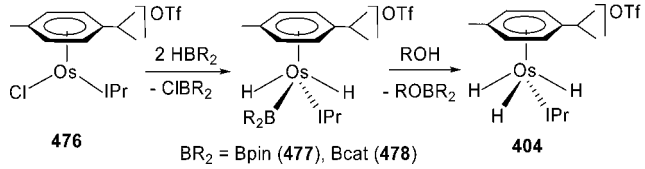


[a]Adapted from ref 300. Copyright 2015 American Chemical Society.

spectroscopic observations performed on the catalytic solution, and DFT calculations.[300] The coordination of ammonia-borane to the *cis*-dihydride **300**, in a Shimoi manner, gives the intermediate $OsH_2(\kappa^1\text{-}H_3BNH_3)(CO)(P^iPr_3)_2$ (**M**). This intermediate releases BH_2NH_2, which undergoes off-metal polymerization, after transferring the coordinated HB-hydrogen to the metal center and a NH-hydrogen to the hydride H^b, through a concerted process. The transition state can be described as a $\eta^1\text{-}H^b{-}H^N$ species, where the asymmetric dihydrogen ($H^b{-}H^N$ = 0.865 Å) is stabilized by interaction with the NH_2 group of the boron ligand. The hydrogen transfer from ammonia-borane leads to the *trans*-dihydride-dihydrogen derivative **345a**, which isomerizes via the tetrahydride **345b** into the *cis*-dihydride isomer **345c**. This transformation is barrierless. The coplanar *cis*-disposition of the dihydrogen ligand with regard to both hydrides in **345a** and the protic nature of one of the hydrogen atoms of the dihydrogen ligand could also facilitate the isomerization without the participation of the tetrahydride **345b**. The dissociation of H_2 from **345c** regenerates **300**.

The half-sandwich complex $[OsCl(\eta^6\text{-}p\text{-cymene})(IPr)]OTf$ (**476**) also promotes the B−H bond activation of HBpin and HBcat. Treatment of this five-coordinate compound with the boranes leads to the dihydride-boryl derivatives $[OsH_2(BR_2)(\eta^6\text{-}p\text{-cymene})(IPr)]OTf$ (BR_2 = Bpin (**477**), Bcat (**478**)) and $ClBR_2$. In the presence of OH groups, these compounds undergo hydrolysis or alcoholysis to afford the trihydride complex **404** (Scheme 73).[301]

Scheme 73. Alcoholysis of Half-Sandwich Dihydride-Boryl-Osmium(IV) Complexes



3.6.2. Direct C−H Bond Activation. Unsaturated **G** type species are also determinant in direct C−H bond activation processes promoted by trihydrides **310** and **311** (Scheme 74). For instance, these compounds react with vinyl ethers to initially form the five-coordinate hydride-carbene derivatives $OsHCl\{=C(OR')CH_3\}(PR_3)_2$ (PR_3 = P^tBu_2Me, R′ = Ph (**479**), Et (**480**); PR_3 = P^iPr_3, R′ = Ph (**481**), Et (**482**)), as a result of **G**-assisted olefin-carbene isomerization processes. Complexes **479**−**482** are unstable, even at room temperature, and evolve into the five-coordinate hydride-vinylidene or six-coordinate hydride-alkylidyne species depending upon the phosphine and OR′-substituent attached to the carbene carbon atom. Complexes **480** and **482** give ethanol and the vinylidenes $OsHCl(=C=CH_2)(PR_3)_2$ (PR_3 = P^tBu_2Me (**483**), P^iPr_3 (**484**)), whereas complex **481** affords $OsHCl(OPh)(\equiv CCH_3)(P^iPr_3)_2$ (**485**).[302] The substituted vinylidene $OsHCl(=C=CHSiMe_3)(P^iPr_3)_2$ (**486**) and $CH_2{=}CHSiMe_3$ have been obtained by reaction of **311** and 2 equiv of the alkyne.[86,88] The 14-valence electrons fragment **G** (PR_3 = P^iPr_3) also promotes the double dehydrogenation of the α-CH_2 of tetrahydrofuran to give $OsHCl\{=C(CH_2)_3O\}(P^iPr_3)_2$ (**487**).[303]

In contrast to **G**, the five-coordinate dihydride **300**, generated by dissociation of H_2 from the dihydride-dihydrogen **345**, reacts with terminal alkynes to give the alkynyl-hydride-dihydrogen derivatives $OsH(C\equiv CR)(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ (R = Ph (**488**), $SiMe_3$ (**489**)).[304] The reactions of these compounds with a second molecule of alkyne leads to the bis(alkynyl)derivatives $Os(C\equiv CR)_2(CO)(P^iPr_3)_2$ (R = Ph (**490**), $SiMe_3$ (**491**)) and H_2 (Scheme 75).[305]

Jia and co-workers have developed two methodologies for the preparation of half-sandwich osmium complexes by using a PPh_3-functionally equivalent to **G** (Scheme 76). The first approach involves the reactions of hydride-compressed dihydride **309** with indene and cyclopentadienes. Thus, the

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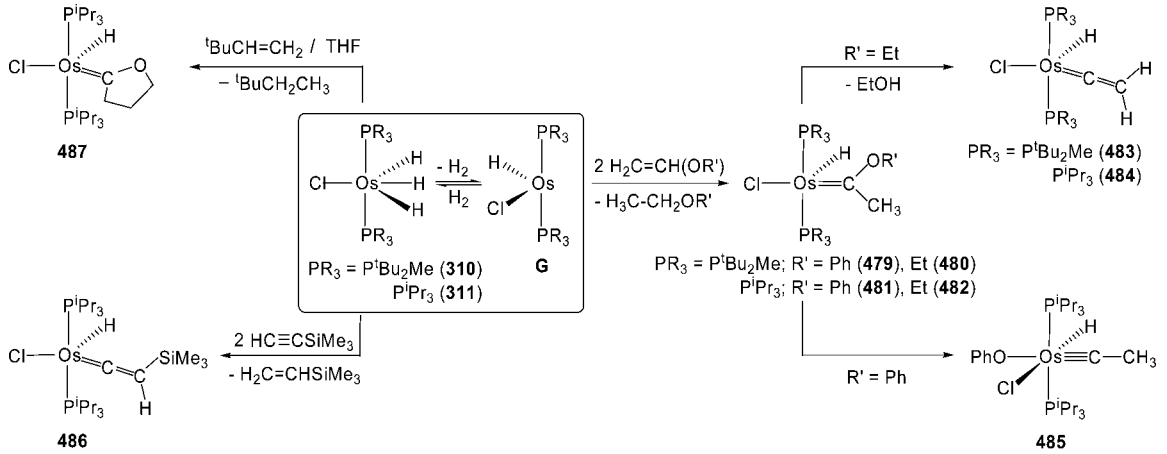
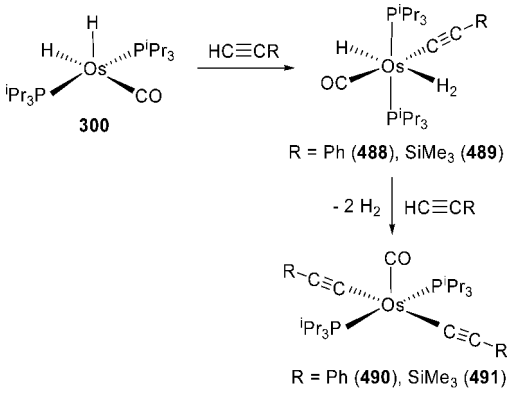
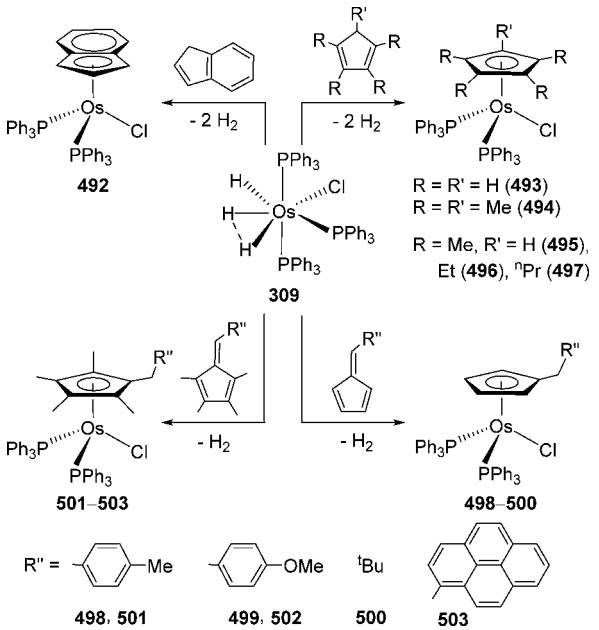
Scheme 74. Direct C−H Bond Activation Reactions Promoted by 14-Valence Electrons $OsHCl(PR_3)_2$ Species



Scheme 75. Addition of Terminal Alkynes to 300



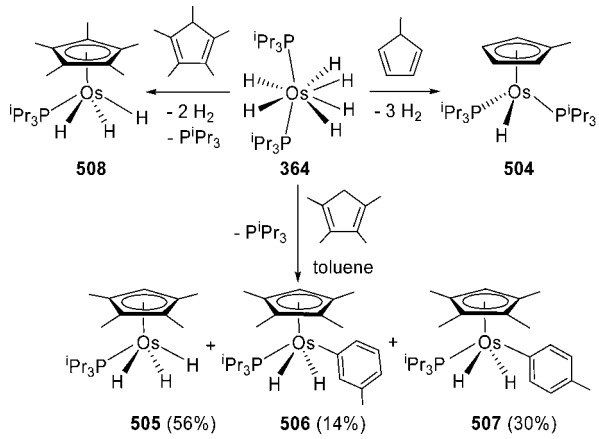
Scheme 76. Formation of Half-Sandwich Complexes by C−H Bond Activation and Insertion Reactions



treatment of **309** with this type of cyclic olefins leads to $Os(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2$ (**492**), $Os(\eta^5\text{-}C_5R_5)Cl(PPh_3)_2$ (R = H (**493**), Me (**494**)), and $Os(\eta^5\text{-}C_5Me_4R')Cl(PPh_3)_2$ (R′ = H (**495**), Et (**496**), ^{n}Pr (**497**)), depending upon the substrate, as a consequence of the $C(sp^3)$−H bond activation of the olefin and the release of two hydrogen molecules. The second approach involves the use of fulvenes. The reactions of **309** with C6-substituted fulvenes lead to $Os(\eta^5\text{-}C_5H_4CH_2R'')Cl(PPh_3)_2$ (R″ = C_6H_4-*p*-Me (**498**), C_6H_4-*p*-OMe (**499**), ^{t}Bu (**500**)) and a hydrogen molecule, whereas C6-substituted-1,2,3,4-tetramethylfulvenes give $Os(\eta^5\text{-}C_5Me_4CH_2R'')Cl(PPh_3)_2$ (R″ = C_6H_4-*p*-Me (**501**), C_6H_4-*p*-OMe (**502**), pyrenyl (**503**)) under the same conditions. The formation of **498**−**503** is the result of the Markovnikov insertion of the exocyclic carbon−carbon double bond of the fulvenes into the Os−H bond of **G** (PR_3 = PPh_3).[306]

The hexahydride **364** is also a useful starting material to prepare half-sandwich complexes by means of C−H bond activation of cyclopentadienes, in this case hydride derivatives. The product of the reaction depends upon the substituents of the diolefin (Scheme 77). The reaction of **364** with

Scheme 77. C−H Bond Activation Reactions of Cyclopentadienes and Toluene Promoted by 364



methylcyclopentadiene leads to the monohydride $OsH(\eta^5\text{-}C_5H_4Me)(P^iPr_3)_2$ (**504**). Treatment of toluene solutions of **364** with tetramethylcyclopentadiene gives a mixture of the trihydride $OsH_3(\eta^5\text{-}C_5HMe_4)(P^iPr_3)$ (**505**, 56%) and the dihydride-tolyl derivatives $OsH_2(m\text{-tolyl})(\eta^5\text{-}C_5H_4Me)(P^iPr_3)$ (**506**; 14%) and $OsH_2(p\text{-tolyl})(\eta^5\text{-}C_5HMe_4)(P^iPr_3)$ (**507**, 30%). However, in *n*-octane the trihydride **505** is formed in 85% yield. In contrast to tetramethylcyclopentadiene, pentam-

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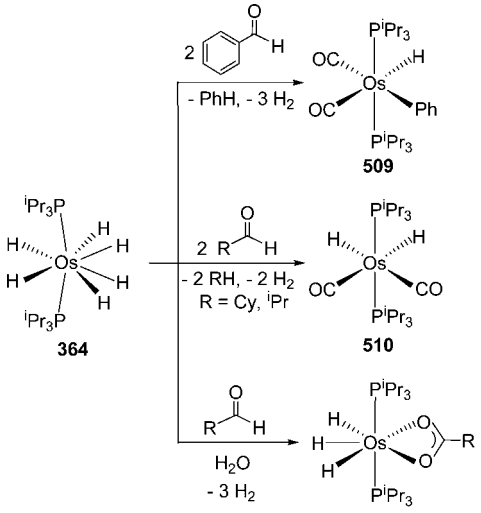
ethylcyclopentadiene reacts with **364** in toluene to give selectively the trihydride $OsH_3(\eta^5\text{-}C_5Me_5)(P^iPr_3)$ (**508**),[240] the P^iPr_3 counterpart of the Girolami's complexes **420**–**423**.

The hexahydride **364** also activates the OC–H bond of aldehydes (Scheme 78). In toluene under reflux, the reactions

Scheme 78. C–H Bond Activation Reactions of Aldehydes Promoted by 364

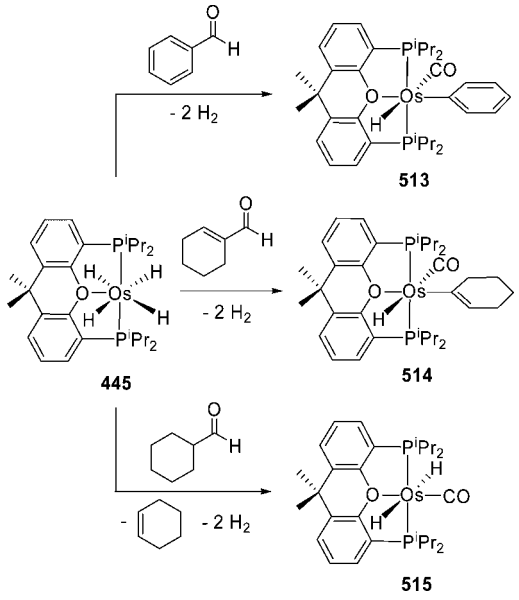


with benzaldehyde, cyclohexanecarboxaldehyde, and isobutyraldehyde lead to products resulting from OC–H bond activation and decarbonylation tandem processes. The reaction with benzaldehyde gives the hydride-phenyl-*cis*-dicarbonyl derivative $OsH(Ph)(CO)_2(P^iPr_3)_2$ (**509**) and benzene, while cyclohexanecarboxaldehyde and isobutyraldehyde yield the *cis*-dihydride-*cis*-dicarbonyl compound $OsH_2(CO)_2(P^iPr_3)_2$ (**510**) and the corresponding alkane. In the presence of water, the reactions of **364** with cyclohexanecarboxaldehyde and isobutyraldehyde afford the carboxylate-trihydride $OsH_3(\kappa^2\text{-}O_2CR)(P^iPr_3)_2$ (R = Cy (**511**), ^{i}Pr (**512**)). Complexes **364**, **510**, and **511** are active catalyst precursors for classical Tishchenko dimerization of cyclohexanecarboxaldehyde. Complexes **364** and **510** are also active catalyst precursors for the classical Tishchenko dimerization of benzaldehyde and for the homo aldo-Tishchenko trimerization of isobutyraldehyde.[307]

The tetrahydride pincer-complex **445** also activates the OC–H bond of aldehydes. The reaction with benzaldehyde yields $OsH(Ph)(CO)\{xant(P^iPr_2)_2\}$ (**513**), a $xant(P^iPr_2)_2$-counterpart of **509**. The decarbonylation of the substrate is also observed with α,β-unsaturated aldehydes. Thus, the reaction of **445** with 1-cyclohexene-1-carboxaldehyde gives $OsH(C_6H_9)(CO)\{xant(P^iPr_2)_2\}$ (**514**), although in this case the OC–H activation-deinsertion product is contaminated with the dihydride-carbonyl derivative $OsH_2(CO)\{xant(P^iPr_2)_2\}$ (**515**), which is generated as a consequence of the release of 1,3-cyclohexadiene from **514**. The dehydrogenation of the substituent of the aldehyde is favored for alkyl with regard to alkenyl. Thus, complex **515** is obtained as a pure organometallic species, along with cyclohexene, from the reaction of **445** with cyclohexanecarboxaldehyde (Scheme 79).[196]

The hexahydride **364** reacts with pyridine, 3-methylpyridine, and 4-methylpyridine to give the classical tetrahydride derivatives $OsH_4(R\text{-}py)(P^iPr_3)_2$ (R-py = py (**516**), 3-Mepy (**517**), 4-Mepy (**518**)). In benzene-d_6, these compounds release

Scheme 79. C–H Bond Activation Reactions of Aldehydes Promoted by the POP-Pincer Tetrahydride 445



the heterocycle, and the resulting $OsH_4(P^iPr_3)_2$ species catalyzes the deuteration of the heterocycles by means of H/D exchanges with the solvent. The deuteration rates of the pyridinic C–H bonds depend upon their positions in the substrates. For pyridine, they increase as the C–H bonds are separated from the heteroatom. A methyl substituent has a marked negative effect on the deuteration of its adjacent C–H bonds. The kinetic analysis of the deuteration reveals that the rate-determining step for the H/D exchange is the C–H bond activation of the bond that is deuterated. DFT calculations show that this step is formed by two elemental stages: the direct coordination of the C–H bond and its subsequent rupture. Thus, the relationship between the deuteration rates of the different positions is determined by the relative stability of the η^2-C–H intermediates and the activation energies for the rupture of the coordinated C–H bonds. For pyridine, the stability of the η^2-C–H intermediates increases in the sequence positions 2,6 < position 4 < positions 3,5, while the necessary energy for the rupture of the C–H bond diminishes in the sequence positions 3,5 > positions 2,6 > position 4.[308] The behavior of 2-methylpyridine is significantly different to that of 3- and 4-methylpyridine (Scheme 80). The reaction of **364** with 2-methylpyridine, in contrast to 3- and 4-methylpyridine, leads to the κ^2-*C*,*N*-pyridyl derivative $OsH_3\{\kappa^2\text{-}C,N\text{-}(NC_5H_3Me)\}(P^iPr_3)_2$ (**519**), as a result of the activation of the C–H bond at position 6. In dichloromethane, complex **519** undergoes the selective chlorination of the hydride ligand *cisoid* disposed to the nitrogen atom to give $OsH_2Cl\{\kappa^2\text{-}C,N\text{-}(NC_5H_3Me)\}(P^iPr_3)_2$ (**520**).[309]

3.6.3. Chelate-Assisted C–H Bond Activation. The bis(phosphine)-hexahydride complex **364** as well as the half-sandwich dihydride-elongated dihydrogen derivative **408** and the tetrahydride pincer compound **445** promote the activation of C(sp^3)–H and olefinic- and aromatic-C(sp^2)–H bonds of a wide range of organic molecules. The presence of a coordinating group (imine, ketone, phosphine, or *N*-heterocycle) in the substrates has allowed the stabilization of different types of hydride and polyhydride compounds, including interesting organometallic compounds, which in some cases

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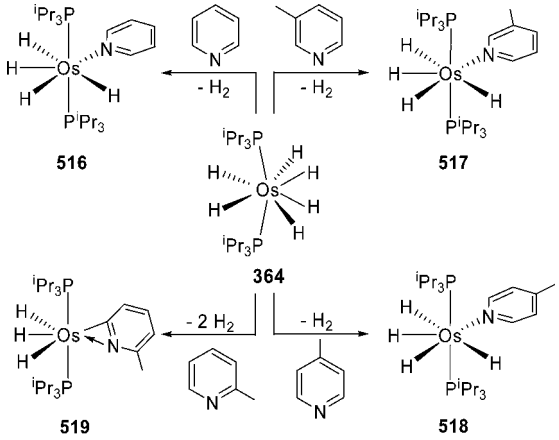
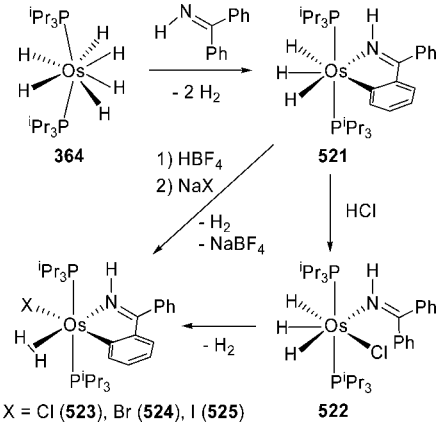
Scheme 80. Reactions of 364 with Pyridine and Substituted Pyridines

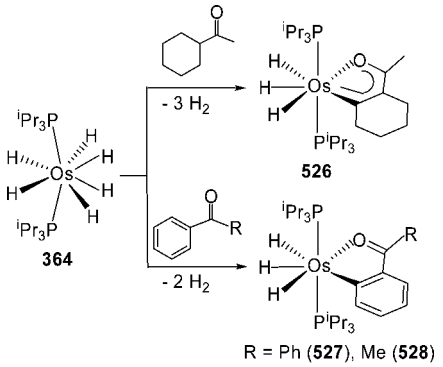


Scheme 81. C−H Bond Activation of Benzophenone Imine Promoted by 364 and Related Reactions



Like the hydride ligands of **521** and **526**, in solution, the hydride ligands of **527** and **528** undergo two thermally activated site-exchange processes. In these cases, the exchange of lower activation energy involves the hydride ligand disposed *cisoid* to the carbonyl ligand and the central one, which also show quantum exchange coupling (Scheme 82).[312]

Scheme 82. C−H Bond Activation of Cyclohexyl Methyl Ketone and Aromatic Ketones Promoted by 364



are reminiscent species of proposed intermediates of catalytic reactions relevant in organic synthesis.

The hexahydride **364** reacts with benzophenone imine to give the trihydride derivative $OsH_3\{\kappa^2\text{-}N,C\text{-}[NH{=}C(Ph)\text{-}C_6H_4]\}(P^iPr_3)_2$ (**521**). The hydride ligands and the bidentate group are situated in the equatorial plane of a pentagonal-bipyramidal arrangement of ligands around the metallic center. In solution, the hydride ligands undergo two thermally activated site-exchange processes, with different activation energies. The slower process involves the hydride ligand *transoid* to the N atom and the central hydride, whereas the faster one takes place between the latter and the hydride *transoid* to the aryl ring. DFT calculations suggests that the exchanges occur via dihydrogen species, being the relative energy between them the determining factor for the difference in rates, since once the dihydrogen structure has been reached, the energies associated with their rotations are similar. Treatment of **521** with a toluene solution of HCl leads to $OsH_3Cl(NH{=}CPh_2)(P^iPr_3)_2$ (**522**), which evolves into the elongated dihydrogen (d_{H-H} = 1.31 Å) $OsCl\{\kappa^2\text{-}N,C\text{-}[NH{=}C(Ph)C_6H_4]\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**523**), in methanol, as a result of the release of molecular hydrogen. This compound and the related derivatives $OsX\{\kappa^2\text{-}N,C\text{-}[NH{=}C(Ph)C_6H_4]\}(\eta^2\text{-}H_2)\text{-}(P^iPr_3)_2$ (X = Br (**524**), I (**525**)) can also be prepared by protonation of **521** with $HBF_4{\cdot}OEt_2$ in dichloromethane and subsequent treatment of the resulting solution with a methanol solution of NaX (Scheme 81).[310]

The hexahydride **364** is also able to produce a triple $C(sp^3)$−H bond activation in the cyclohexyl ring of cyclohexyl methyl ketone to give the trihydride-osmafuran derivative $OsH_3\{\kappa^2\text{-}O,C\text{-}[OC(Me)C_6H_8]\}(P^iPr_3)_2$ (**526**). The reaction probably occurs in two steps; initially the activation of a C_β−H bond of the six-membered ring generates an $Os\{\kappa^2\text{-}O,C\text{-}[OC(Me)\text{-}C_6H_{10}]\}$ intermediate which releases molecular hydrogen to afford the osmafuran.[311] The aromatic character of the latter should be the driving force for the dehydrogenation, in a similar manner to the formation of the 3-ruthenaindolizine complex **225**. In solution, the hydride ligands of **526** also undergo two thermally activated site-exchange processes. However, in contrast to **521**, both processes have similar activation energies. Reactions of **364** with benzophenone and acetophenone lead to the osmaisobenzofuran derivatives $OsH_3\{\kappa^2\text{-}O,C\text{-}[OC(R)\text{-}C_6H_4]\}(P^iPr_3)_2$ (R = Ph (**527**), Me (**528**)) as a result of the *ortho*-CH bond activation of the aromatic group of the ketones.

The half-sandwich dihydride-elongated dihydrogen **408** reacts with acetophenone and α,β-unsaturated ketones to give the osmaisobenzofuran complex $[OsH(\eta^5\text{-}C_5H_5)\{\kappa^2\text{-}O,C\text{-}[OC(Me)C_6H_4]\}(P^iPr_3)]BF_4$ (**529**) and the osmafuran derivatives $[OsH(\eta^5\text{-}C_5H_5)\{\kappa^2\text{-}O,C\text{-}[OC(Me)CHC(R)]\}(P^iPr_3)]BF_4$ (R = H (**530**), Ph (**531**)), respectively. Complex **408** favors the vinylic C−H bond activation with regard to the aromatic C−H bond cleavage in substrates with both types of bonds. Thus, the reaction with benzylideneacetophenone exclusively gives the osmafuran $[OsH(\eta^5\text{-}C_5H_5)\{\kappa^2\text{-}O,C\text{-}[OC(Ph)CHC(Ph)]\}\text{-}(P^iPr_3)]BF_4$ (**532**). These reactions generate molecular hydrogen and 1-phenylethanol or saturated ketones as side products (Scheme 83). This is consistent with a three step process involving the displacement of the coordinated hydrogen molecule by the substrates, their subsequent hydrogenation, and finally the C−H bond addition to the $[Os(\eta^5\text{-}C_5H_5)\text{-}(P^iPr_3)]^+$ metal fragment.[276]

The dehydrogenation of the metallic center is also a determinant in the reactions of **408** with alkynes. In acetone, this compound reacts with 1-phenyl-1-propyne and 2-butyne to give γ-(η^3-allyl)-α-alkenylphosphine derivatives $[OsH(\eta^5\text{-}$

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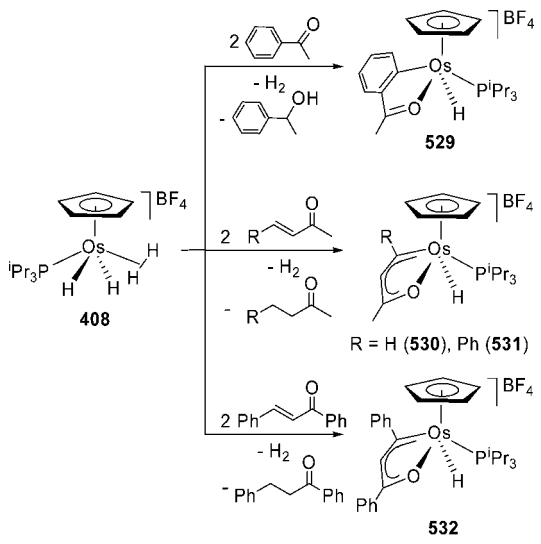
Scheme 83. C−H Bond Activation Reactions of Aromatic and α,β-Unsaturated Ketones Promoted by 408

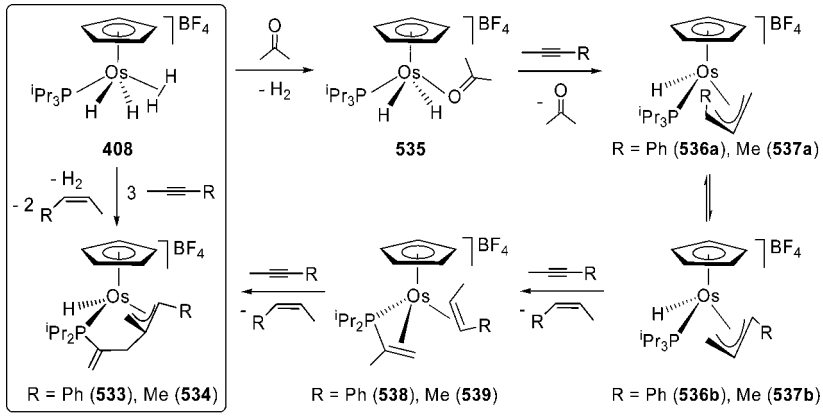


C_5H_5){κ^4-*P,C,C,C*-$CH_2C[CH_2C(=CH_2)P^iPr_2]CHR$}]$BF_4$ (R = Ph (**533**), Me (**534**)), in addition to molecular hydrogen and 2 equiv of the corresponding olefin (Scheme 84). The formation of **533** and **534** takes place by means of a one-pot tandem process of four reactions, including two C−H bond activations of an isopropyl substituent of the phosphine. In acetone, complex **408** dissociates the dihydrogen ligand and coordinates the solvent to afford [$OsH_2(\eta^5$-$C_5H_5)(OCMe_2)(P^iPr_3)$]BF_4 (**535**), which reacts with a molecule of alkyne to form [$OsH(\eta^5$-$C_5H_5)(\eta^3$-$CH_2CHCHR)(P^iPr_3)$]BF_4 (R = Ph (**536**), Me (**537**)). The reactions of **536** and **537** with a second molecule of alkyne lead to the corresponding *Z*-olefins and [$Os(\eta^5$-$C_5H_5)$){η^2-(*Z*)−$CH(CH_3)$=CHR}{κ^3-*P,C,C*-[CH_2=$C(CH_3)$]P^iPr_2}]BF_4 (R = Ph (**538**), Me (**539**)). A third alkyne molecule displaces the olefin of these compounds and couples with the isopropenyl group of the phosphine to give **533** and **534**.[313] In contrast to 1-phenyl-1-propyne and 2-butyne, the reaction of **408** with phenylacetylene leads to the allenylcarbene derivative [$OsH(\eta^5$-$C_5H_5)$){=C(Ph)(η^2-CH=C=CHPh)}(P^iPr_3)]BF_4 (**540**).[314]

The metallic center of the tetrahydride pincer compound **445** does not necessitate that it undergoes a complete dehydrogenation for promoting the C−H bond activation of aromatic and α,β-unsaturated ketones. Thus, its reactions do not need the presence of additional sacrificial substrate, in contrast to its ruthenium counterpart **183** and the half-sandwich derivative **408**. Treatment of toluene solutions of **445** with 1 equiv of acetophenone and benzophenone under reflux leads to the osmaisobenzofuran pincer derivatives OsH{κ^2-*O,C*-[OC(R)C_6H_4]}{xant($P^iPr_2)_2$} (R = Me (**541**), Ph (**542**)). Isotopic labeling experiments, using perdeuterated benzophenone as a substrate, demonstrate that the selectivity of the *ortho*-C−H bond activation is thermodynamic in origin, while the activation of the C−H bonds at meta and para positions are kinetically preferred. Furthermore, they suggest that the C−H bond activation takes place on an unsaturated OsH_4-species containing a bidentate phosphine. Thus, a heterolytic C−H bond cleavage using a hydride as internal base could generate trihydride intermediates related to **527** and **528**, with a bidentate diphosphine, which would evolve into **541** and **542** by means of the release of H_2 and the coordination of the phosphine oxygen atom, in a similar manner to the transformation of the hexahydride **444** into **445**. This precursor favors the C−H bond activation over the C−F bond cleavage in fluorinated aromatic ketones. Thus, the fluorinated osmaisobenzofurans OsH{κ^2-*O,C*-[OC(Me)C_6H_3F]}{xant($P^iPr_2)_2$} (**543**) and OsH{κ^2-*O,C*-[OC($C_6H_3F_2$)C_6H_4]}{xant($P^iPr_2)_2$} (**544**) are obtained from the reactions with 2-fluoroacetophenone and 2,6-difluorobenzophenone, respectively. Complex **445** also activates benzylideneacetone and methyl vinyl ketone to afford the osmafurans OsH{κ^2-*O,C*-[OC(Me)CHC(R)]}{xant($P^iPr_2)_2$} (R = Ph (**545**), H (**546**)). In contrast to the half-sandwich complex **408**, the reaction of **445** with benzylideneacetophenone yields a mixture of OsH{κ^2-*O,C*-[OC(CH=CHPh)C_6H_4)]}{xant($P^iPr_2)_2$} (**547**) and OsH{κ^2-*O,C*-[OC(Ph)CHC(Ph)]}{xant($P^iPr_2)_2$} (**548**) in a 2:1 molar ratio (Scheme 85).[196]

The hexahydride **364** reacts with 8-methylquinoline and 2-(dimethylamino)pyridine to give OsH_3){κ^2-*N,C*-(quin-8-CH_2)}($P^iPr_3)_2$ (**549**) and OsH_3){κ^2-*N,C*-[py-2-N(Me)CH_2]}($P^iPr_3)_2$ (**550**), respectively, as a result of the release of two hydrogen molecules and the *N*-heterocyclic-assisted C(sp^3)−H bond activation of a methyl group of the organic substrates. Treatment of the quinolyl derivative **549** with HBF_4·OEt_2 affords the hydride-elongated dihydrogen complex [$OsH(\eta^2$-$H_2)$(quin-8-CH_3)($P^iPr_3)_2$]BF_4 (**551**), with the methyl substituent of the quinolyl group coordinated in a η^3-H_2C fashion and a separation between the hydrogen atoms of the elongated dihydrogen ligand of about 1.2 Å. The reaction of the pyridyl

Scheme 84. Reactions of 408 with Internal Alkynes



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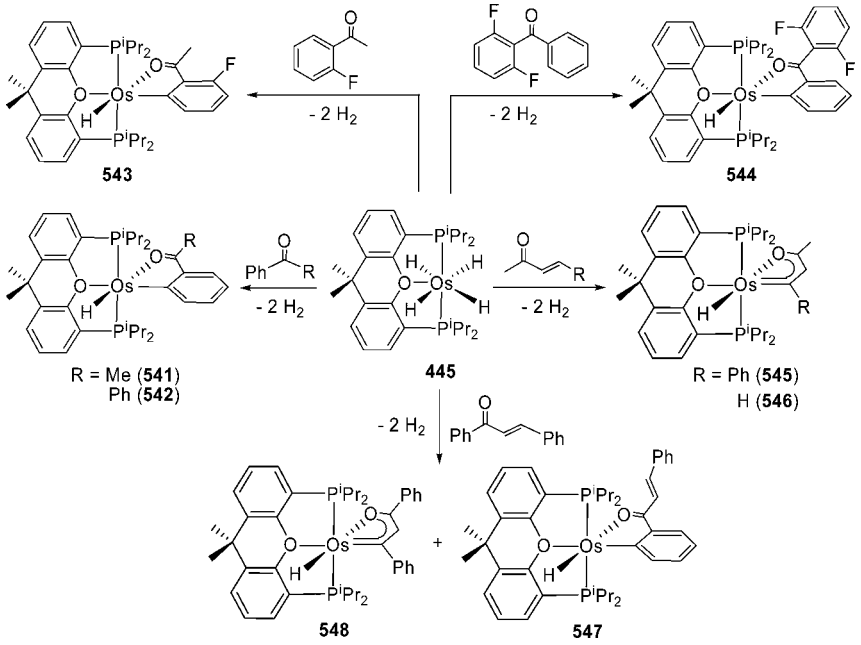
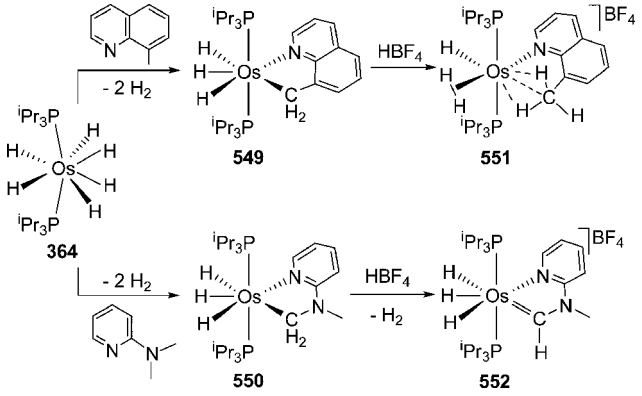
Scheme 85. C−H Bond Activation Reactions of Aromatic, Fluorinated Aromatic, and α,β-Unsaturated Ketones Promoted by 445



derivative **550** with $HBF_4{\cdot}OEt_2$ leads to the cyclic carbene compound $[OsH_3\{\kappa^2\text{-}C,N\text{-}[{=}CHN(Me)\text{-}2\text{-}py]\}(P^iPr_3)_2]BF_4$ (**552**), as a result of the release of a hydrogen molecule and a C(sp^3)−H bond activation of the methylene group (Scheme 86). In these systems, the activation energy for the rupture of a coordinated C(sp^3)−H bond appears to be similar to that for the cleavage of a coordinated H−H bond. Consequently, exchange processes between the hydrogen atoms bound to the metal center and a methyl group of the substrates occur in a competitive manner. The activation energies for the position exchanges between the hydrogen atoms attached to the metal center are not too sensitive to the coordination assistant. However, hydrogen exchanges between hydride and elongated dihydrogen ligands and the C(sp^3)−H bond of the susbtituent of the heterocycle show a noticeable dependence, since the coordination assistant seems to carry out a fine-tuning of the stabilities and activation energies involving the osmium-methyl unit. With regard to the quinolyl group, the 2-aminopyridine assistant provides lower activation energies for the C(sp^3)−H bond rupture and higher stabilities of the resulting alkyl derivative. Furthermore, it facilitates a second C(sp^3)−H bond activation.[315]

Scheme 86. Chelate-Assisted C(sp^3)−H Bond Activation Reactions Promoted by 364



The formation of **552** reveals that the pyridyl group is an efficient coordination assistant for the activation of methylene groups. In agreement with this, it has been observed that 2-vinylpyridine and *N*-methylene-2-pyridinamine react with the hexahydride **364** to give the osmaindolizine derivative $OsH_3\{\kappa^2\text{-}N,C\text{-}(pyCHCH)\}(P^iPr_3)_2$ (**553**) and the osmaimidazopyridine compound $OsH_3\{\kappa^2\text{-}N,C\text{-}(pyNCH)\}(P^iPr_3)_2$ (**554**), respectively, as a result of the pyridyl-assisted C(sp^2)−H bond activation of the terminal CH_2 group of the susbtituent of the heterocyclic substrates. Complex **554** is formed along with $OsH_3\{\kappa^2\text{-}N,N\text{-}(pyNCH_3)\}(P^iPr_3)_2$ (**555**; about 25%), resulting from the insertion of the N−C double bond of the substrate into a Os−hydride bond of the transitory species $OsH_4(P^iPr_3)_2$. In contrast to *N*-methylene-2-pyridinamine, (*E*)-*N*-(phenylmethylene)2-pyridinamine selectively affords the insertion product $OsH_3\{\kappa^2\text{-}N,N\text{-}(pyNCH_2Ph)\}(P^iPr_3)_2$ (**556**). The role of the phenyl group seems to be double. On one hand, it increases the electrophilic character of the carbon atom of the C−N double bond, favoring the migration of the hydride ligand; on the other, its steric hindrance prevents the coordination of the CPh group to the osmium atom (Scheme 87).[316] The formation of the insertion products **555** and **556** is strong evidence in favor of the participation of the unsaturated species $OsH_4(P^iPr_3)_2$ in the C−H bond activation reactions mediated by the hexahydride **364**. The 16-valence electrons of this species are consistent with no-directed C−H bond cleavage processes. To the contrary, the heterolytic rupture of the coordinated C−H bond, using a hydride ligand, should generate the necessary coordination vacancy for the entry of the coordination assistant in order to stabilize the activation product.

The addition of $HBF_4{\cdot}OEt_2$ to dichloromethane solutions of the osmaindolizine complex **553** leads to the hydride-elongated dihydrogen $[OsH(\eta^2\text{-}H_2)(pyCH{=}CH_2)(P^iPr_3)_2]BF_4$ (**557**),

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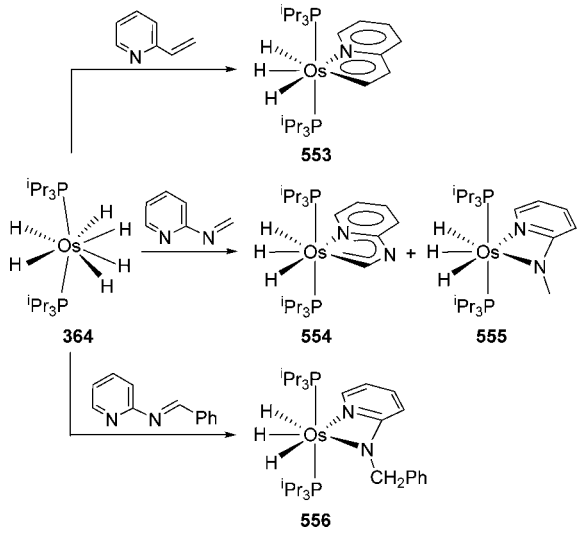
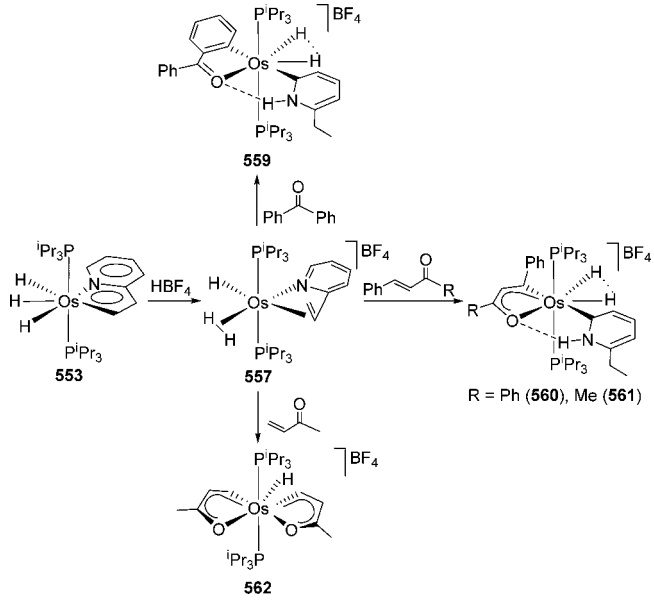
Scheme 87. Reactions of 364 with 2-Vinylpyridine and 2-Pyridinamines



Scheme 88. Formation and C−H Bond Activation Reactions of the Hydride-Elongated Dihydrogen 557



which catalyzes the hydrogenation of 2-vinylpyridine to 2-ethylpyridine in dichloromethane, although its durability is low due to the formation of the chloride-elongated dihydrogen $OsCl\{\kappa^2\text{-}N,C\text{-}(pyCHCH)\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**558**). The separation between the hydrogen atoms of the elongated dihydrogen ligand is similar in both compounds, about 1.32 Å. Treatment at 50 °C of **557** with benzophenone in the absence of the solvent gives $[OsH_2\{\kappa^2\text{-}O,C\text{-}[OC(Ph)C_6H_4]\}\{\kappa^1\text{-}C\text{-}(HNC_5H_3Et)\}(P^iPr_3)_2]BF_4$ (**559**), as a consequence of a one-pot process of three reactions: (i) hydrogenation of the vinyl substituent of the pyridine by means of the transfer of the elongated dihydrogen from the metal center to the C−C double bond; (ii) *ortho*-C−H bond activation of the ketone by the resulting monohydride; and (iii) C,*N*-1,2-H rearrangement of 2-ethylpyridine.[317] In the absence of solvent, **557** also reacts with benzylideneacetophenone and benzylideneacetone to give the related osmafuran-pyridylidene derivatives $[OsH_2\{\kappa^2\text{-}O,C\text{-}[OC(R)CHC(Ph)]\}\{\kappa^1\text{-}C\text{-}(HNC_5H_3Et)\}(P^iPr_3)_2]BF_4$ (R = Ph (**560**), Me (**561**)). The separation between the compressed hydrides of **559**−**561** is about 1.4 Å. In contrast to benzylideneacetophenone and benzylideneacetone, the reaction of **557** with methyl vinyl ketone leads to $[OsH\{\kappa^2\text{-}O,C\text{-}[OC(CH_3)CHCH]\}_2(P^iPr_3)_2]BF_4$ (**562**), which can be described as two osmafurans joined by the $[OsH(P^iPr_3)_2]^+$ fragment (Scheme 88).[318]

The pyridyl group is also an efficient coordination assistant for stabilizing products resulting from the activation of *ortho*-CH bonds of aryl groups attached at positions 2 and 6 of the heterocycle (Scheme 89). Thus, 2-phenylpyridine and 2,6-diphenylpyridine react with the hexahydride **364** to form $OsH_3\{\kappa^2\text{-}N,C\text{-}(pyC_6H_4)\}(P^iPr_3)_2$ (**563**) and $OsH_2\{\kappa^3\text{-}C,N,C\text{-}(C_6H_4pyC_6H_4)\}(P^iPr_3)_2$ (**564**), respectively. The reactions with 2,2′-diphenyl-4,4′-bipyridine and 2,2′,6,6′-tetraphenyl-4,4′-bipyridine lead to the respective dimers $(P^iPr_3)_2H_3Os\{\kappa^2\text{-}N,C\text{-}(pyC_6H_4)\text{-}(C_6H_4py)\text{-}C,N\text{-}\kappa^2\}OsH_3(P^iPr_3)_2$ (**565**) and $(P^iPr_3)_2H_2Os\{\kappa^3\text{-}C,N,C\text{-}(C_6H_4pyC_6H_4)\text{-}(C_6H_4pyC_6H_4)\text{-}C,N,C\text{-}\kappa^3\}OsH_2(P^iPr_3)_2$ (**566**). The use of 2,2′-diphenyl-4,4′-bipyridines containing an aryl, antranyl, or ethylidene spacer between the 2-phenylpyridine moieties has allowed for the preparation of related dinuclear species $(P^iPr_3)_2H_3Os\{\kappa^2\text{-}N,C\text{-}(pyC_6H_4)\text{-}X\text{-}(pyC_6H_4)\text{-}C,N\text{-}\kappa^2\}OsH_3(P^iPr_3)_2$ (X = C_6H_4 (**567**), $C_{14}H_8$ (**568**), CH_2CH_2 (**569**)). The spectroelectrochemical study of the dinuclear complexes **565**, **567**, and **568** has revealed significant changes in the emission spectra upon oxidation. While the transformation from Os(IV) to Os(V) produces small changes in the emission spectra of the complexes, the oxidation from Os(V) to Os(VI) produces a notable bathochromic shift of the emission band, accompanied by a moderate but significant increase in intensity.[319]

The interest in knowing the effect of the incorporation of the metal d electrons on the properties of helical structures has led to perform the reactions of the hexahydride **364** with 1-methyl-4-(2-pyridyl)-benzo[*g*]phenanthrene (HLpy) and 1-methyl-4-(2-pyrazinyl)-benzo[*g*]phenanthrene (HLpyz). Treatment of **364** with these substrates leads to the corresponding d^4-[6]-azaosmahelicene derivatives $OsH_3(Lpy)(P^iPr_3)_2$ (**570**) and $OsH_3(Lpyz)(P^iPr_3)_2$ (**571**), as a result of the *ortho*-CH bond activation of the substituted ring of the starting [4]-carbohelicene (Scheme 90). The participation of the d-orbitals of the metal in the helical π-backbone of the resulting [6]-azaosmahelicenes produces significant perturbations in the aromaticity of the six-membered rings compared to that in the starting [4]-carbohelicenes, which gives rise to notable differences between the optical properties of the [6]-azaosmahelicene products and the [4]-carbohelicene reagents.[320]

The ability of the hexahydride **364** for activating C−H bonds has allowed the preparation of novel aromatic systems, formed by a central six-membered cycle fused with nitrogen-containing osma-five-membered rings, by means of the 1,3-C−H bond activation of aromatic six-membered cycles with imino substituents *meta* disposed. Treatment of **364** with 0.5 equiv of 2,6-bis{1-[(4-methylphenyl)imino]ethyl}pyridine (H_2Ipy) and 1,3-bis{1-[(4-methylphenyl)imino]ethyl}benzene (H_2Iph) leads to the 1,7-diosma-2,4,6-triaza-*s*-indacene complex $(P^iPr_3)_2H_3Os(Ipy)OsH_3(P^iPr_3)_2$ (**572**) and the 1,7-diosma-pyrrolo[3,4,*f*]isoindole derivative $(P^iPr_3)_2H_3Os(Iph)\text{-}OsH_3(P^iPr_3)_2$ (**573**), respectively (Scheme 91). The orbital situation in the tricycles is fully consistent with the aromatic character of the compounds showing interaction of π- and δ-

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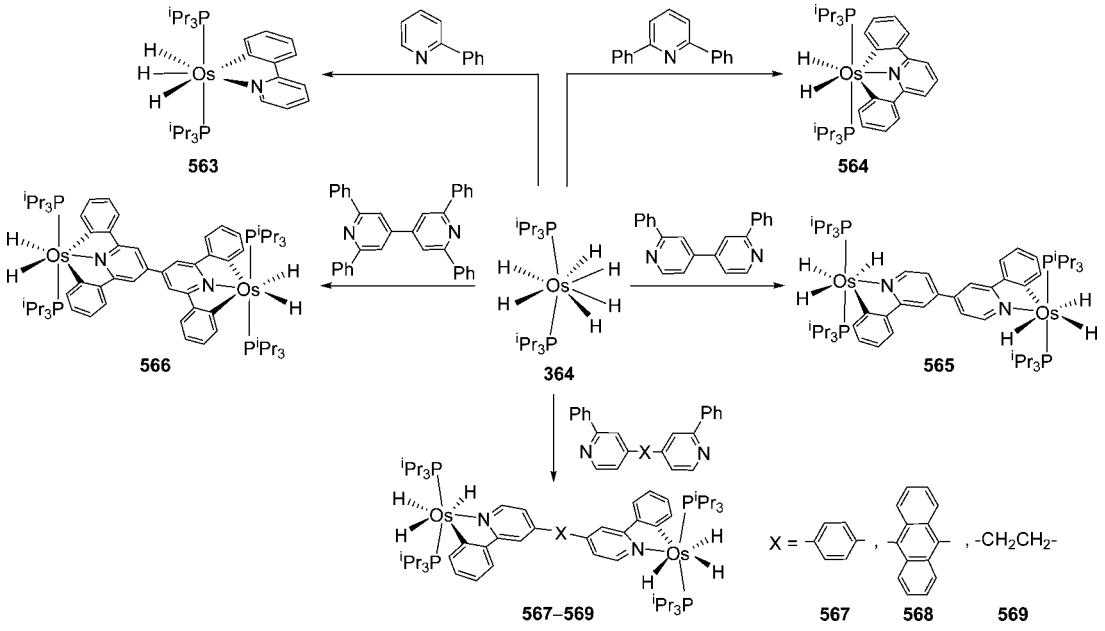
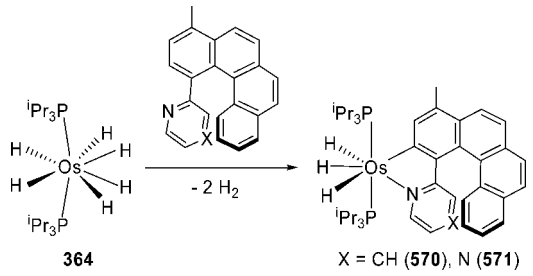
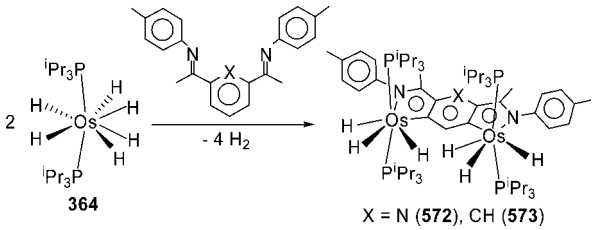
Scheme 89. Pyridyl-Chelate-Assisted Phenyl-*ortho*-CH Bond Activation Reactions Promoted by 364



Scheme 90. Formation of d^4-[6]-Azaosmahelicene Derivatives



Scheme 91. Formation of Aromatic Diosmatricyclic Nitrogen-Containing Derivatives



symmetry between the metal d_{xz} and d_{xy} orbitals and orbitals of the organic fragments.[321]

Polycyclic compounds of five and eight fused cycles, which have no counterpart in conventional organic chemistry, have been also formed by means of the reactions of **364** with 4,5-dimethyl-2,6-bis(4-methylphenyl)pyrimidine (H_2P_{Ph2}), 2,4,6-tris(4-methylphenyl)triazine (H_4T_{Ph3}), and 2,4,6-triphenylpyrimidine (H_4P_{Ph3}). The reactions of **364** with H_2P_{Ph2} give a mixture of the metalapolycyclic derivatives $OsH_3(HP_{Ph2})(P^iPr_3)_2$ (**574**) and $OsH_2(P_{Ph2})(P^iPr_3)_2$ (**575**). The reaction of **364** with H_4T_{Ph3} leads to a mixture of $OsH_2(H_2T_{Ph3})(P^iPr_3)_2$ (**576**) and $(P^iPr_3)_2H_2Os(T_{Ph3})OsH_2(P^iPr_3)_2$ (**577**), containing five and eight fused rings, respectively. Complex **364** reacts with H_4P_{Ph3} to afford $OsH_2(H_2P_{Ph3})(P^iPr_3)_2$ (**578**) and $(P^iPr_3)_2H_2Os(P_{Ph3})OsH_2(P^iPr_3)_2$ (**579**), which are related to **576** and **577**, respectively (Scheme 92).[322]

Sulfur donor compounds are considered soft bases, while nitrogen donor species are viewed as hard bases. In order to investigate the capacity of **364** to discern between soft and hard assistants for the chelate-assisted C−H bond activation, the reactions of this hexahydride with 2-phenylthiazole and 2-phenylbenzothiazole have been performed. Treatment of toluene solutions of **364** with these substrates under reflux leads to the trihydride derivatives $OsH_3\{\kappa^2\text{-}C,N\text{-}(C_6H_4\text{-thiazole})\}(P^iPr_3)_2$ (**580**) and $OsH_3\{\kappa^2\text{-}C,N\text{-}(C_6H_4\text{-benzothiazole})\}(P^iPr_3)_2$ (**581**), containing N-coordinated thiazole and benzothiazole assistants in spite of the soft nature of the late third row transition metals. Similarly, the reactions of **364** with 2-phenylimidazole and 2-phenylbenzimidazole afford $OsH_3\{\kappa^2\text{-}C,N\text{-}(C_6H_4\text{-imidazole})\}(P^iPr_3)_2$ (**582**) and $OsH_3\{\kappa^2\text{-}C,N\text{-}(C_6H_4\text{-benzimidazole})\}(P^iPr_3)_2$ (**583**), respectively (Scheme 93).[323]

3.6.4. C−H Bond Activation of Imidazolium and Benzimidazolium Salts: Formation of NHC Complexes. The hydride ligands of the hexahydride **364** are basic enough to promote the deprotonation of imidazolium salts. The treatment of tetrahydrofuran solutions of this compound with 1-mesityl-3-methylimidazolium tetraphenylborate and 1-mesityl-3-ethylimidazolium tetraphenylborate leads to the trihydride-elongated dihydrogen derivatives $[OsH_3(\eta^2\text{-}H_2)(1\text{-mesityl-3-methylimidazol-4-ylidene})(P^iPr_3)_2]BPh_4$ (**584**) and $[OsH_3(\eta^2\text{-}H_2)(1\text{-mesityl-3-ethylimidazol-4-ylidene})(P^iPr_3)_2]BPh_4$ (**585**), respectively, containing an abnormal NHC ligand (Scheme 94). The coordination geometry around the osmium atom of these eight-coordinate species is the expected dodecahedron, defined by two orthogonal trapezoidal planes. One of them contains the phosphorus atoms at B sites and two hydride ligands, whereas a hydride, the NHC group, and the hydrogen atoms of the elongated dihydrogen (d_{H-H} = 1.25(5) Å) lie in the other one. Although compounds **584** and **585** could be viewed as metal-imidazolium salts, the deprotonation of the OsH_5-unit is favored with regard to the N_2CH-proton. Thus, the addition of NaH to tetrahydrofuran solutions of **584** and

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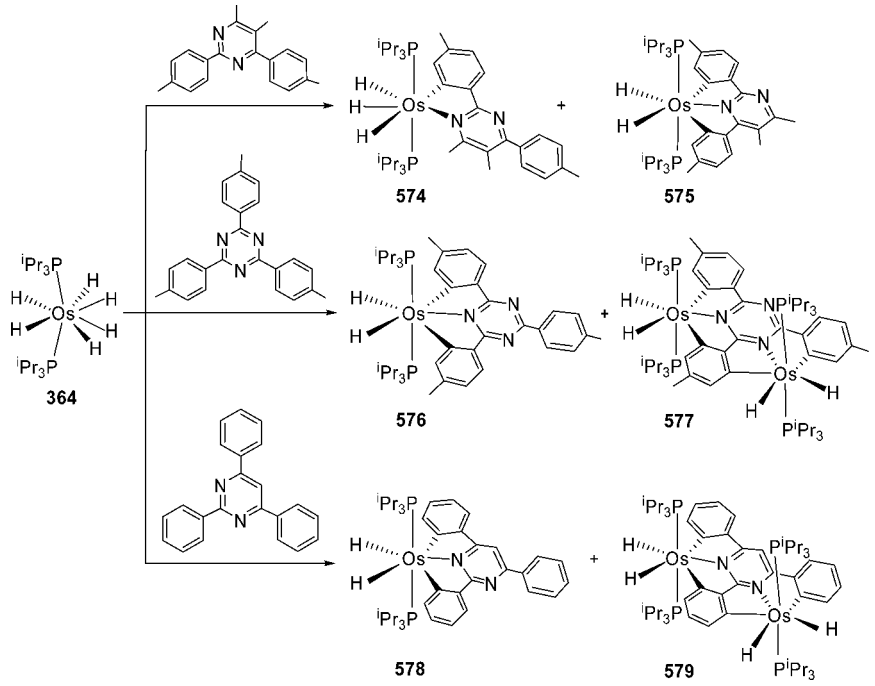
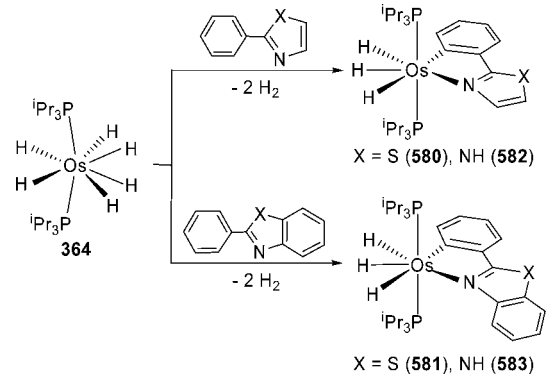
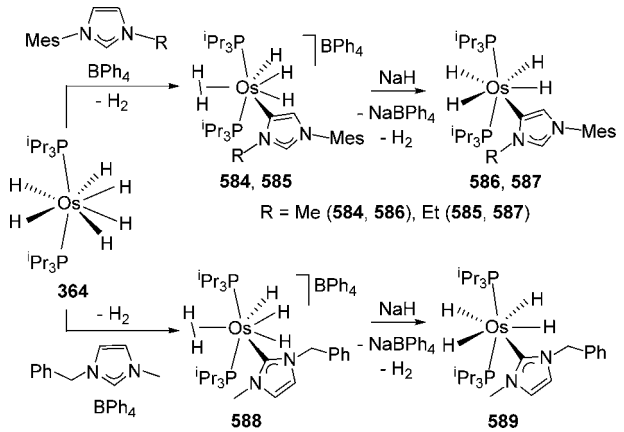
Scheme 92. Osmapolycyclic Compounds with Five and Eight Fused Cycles



Scheme 93. Other Chelate-Assisted Phenyl-*ortho*-CH Bond Activation Reactions Promoted by 364



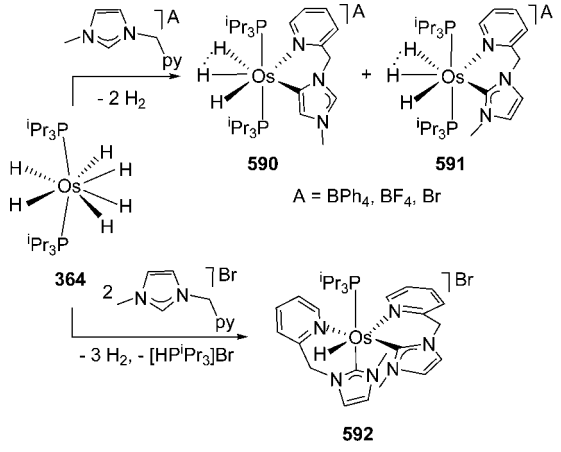
Scheme 94. Direct Metalation of Imidazolium Salts Promoted by 364



585 affords the classical tetrahydrides OsH_4(1-mesityl-3-methylimidazol-4-ylidene)$(P^iPr_3)_2$ (**586**) and OsH_4(1-mesityl-3-ethylimidazol-4-ylidene)$(P^iPr_3)_2$ (**587**). The replacement of the mesityl substituent by a benzyl group on the 1-mesityl-3-methylimidazolium cation diminishes the steric hindrance around the C2 carbon atom, increasing the accessibility of this atom. Thus, in contrast to 1-mesityl-3-methylimidazolium tetraphenylborate, the treatment of tetrahydrofuran solutions of **364** with 1-benzyl-3-methylimidazolium tetraphenylborate leads to the trihydride-elongated dihydrogen $[OsH_5$(1-benzyl-3-methylimidazol-2-ylidene)$(P^iPr_3)_2]BPh_4$ (**588**), containing a normal NHC-ligand. Similarly to **584** and **585**, the deprotonation of **588** affords the tetrahydride OsH_4(1-benzyl-3-methylimidazol-2-ylidene)$(P^iPr_3)_2$ (**589**).[324]

Pyridyl-assisted C−H bond activation of imidazolium salts has been also performed (Scheme 95). The reactions of **364** with 1 equiv of BPh_4^-, BF_4^-, and Br^- salts of 1-(2-pyridylmethyl)-3-methylimidazolium in tetrahydrofuran under reflux lead to mixtures of the abnormal $[OsH_3\{\kappa\text{-}C^5,N\text{-}[1\text{-}(2\text{-}$

Scheme 95. Pyridyl-Chelate-Assisted Metalation of Imidazolium Salts Promoted by 364



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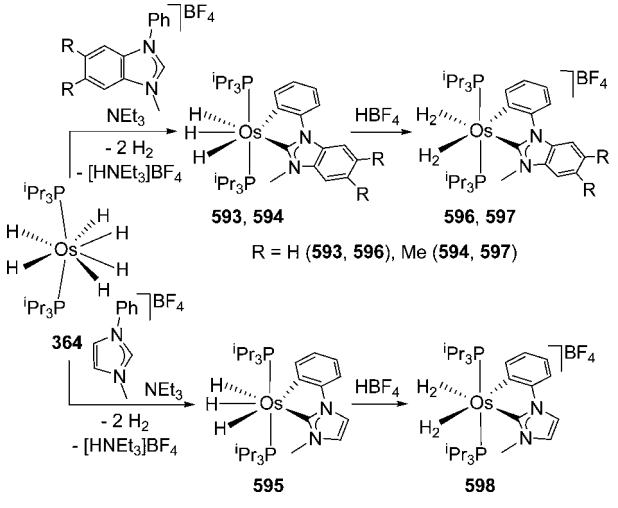
pyridylmethyl)-3-methylimidazol-5-ylidene]}(P^iPr_3)$_2$]A (A = BPh_4, BF_4, and Br; **590**) and normal [OsH_3{κ-C^2,N-[1-(2-pyridylmethyl)-3-methylimidazol-2-ylidene]}(P^iPr_3)$_2$]A (A = BPh_4, BF_4, and Br; **591**) species. The amount of normal isomer increases as the basicity of the anion of the salts increases (i.e., in the sequence BPh_4^- < BF_4^- < Br^-). The T_1(min) values of the OsH_3-resonances and the X-ray structure of the BPh_4-salt of **590** support a hydride-compressed dihydride formulation for these compounds, with a separation between the compressed hydrides of about 1.45 Å. Reaction of **364** with 2.0 equiv of 1-(2-pyridylmethyl)-3-methyl imidazolium bromide yields the bis(normal)-NHC monohydride [OsH{κ-C,N-[1-(2-pyridylmethyl)-3-methylimidazol-2-ylidene]}$_2$(P^iPr_3)]Br (**592**).[325]

N-heterocyclic carbene ligands are very useful to stabilize nonclassical H−H interactions due to their significant π-accepting capacity, which is higher than those of aryl groups and alkylphosphine ligands. Hexahydride **364** reacts with the BF_4-salts of 1-phenyl-3-methyl-1-*H*-benzimidazolium (H_2PhbI), 1-phenyl-3-methyl-1-*H*-5,6-dimetyl-benzimidazolium (H_2PhbIMe$_2$), and 1-phenyl-3-methyl-1-*H*-imidazolium (H_2PhI), in the presence of NEt_3, to give the respective trihydride derivatives OsH_3(κ^2-C_{aryl},C_{NHC})(P^iPr_3)$_2$ (C_{aryl},C_{NHC} = PhbI (**593**), PhbIMe$_2$ (**594**), PhI (**595**)), as a result of the N_2C−H bond activation of the benzimidazolium and imidazolium salts and the *ortho*-CH bond activation of the phenyl substituent (Scheme 96). The protonation of **593**−**595**

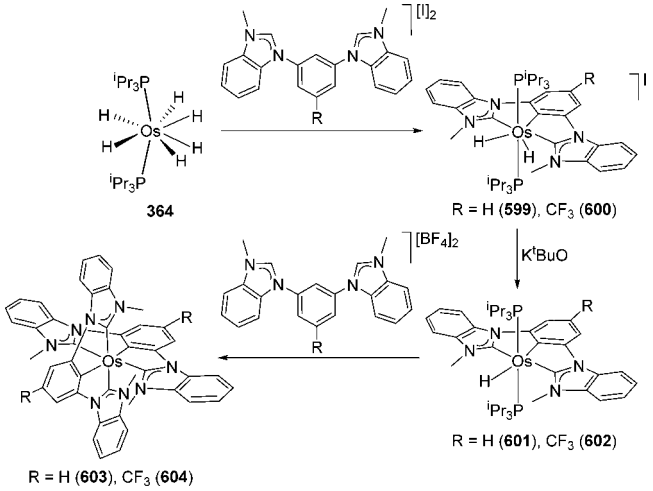
Scheme 96. Bis(dihydrogen)-Osmium(II) Complexes Stabilized by NHC Ligands



with HBF_4·OEt_2 leads to the bis(dihydrogen) derivatives [Os(κ^2-C_{aryl},C_{NHC})(η^2-H_2)$_2$(P^iPr_3)$_2$]BF_4 (C_{aryl},C_{NHC} = PhbI (**596**), PhbIMe$_2$ (**597**), PhI (**598**)). In accordance with the X-ray structure of **597**, the coordinated hydrogen molecule situated trans to the aryl group disposes its hydrogen atoms almost parallel to the P−Os−P direction, separated by about 0.9 Å, whereas the other one, trans disposed to the NHC unit, lies in the plane of the C,C′-chelate ligand with the hydrogen atoms also separated by about 0.9 Å. DFT calculations using AIM and NBO methods have revealed that the Os−NHC bond of the Os−chelate link tolerates a significant π-back-donation from a doubly occupied d_π(Os) atomic orbital to the p_z atomic orbital of the carbene carbon atom. The π-accepting capacity of the NHC unit enhances the electrophilicity of the metal center activating one of the coordinated hydrogen molecules toward the heterolysis. As a result, compounds **596**−**598** are strong Brønsted acids with pK_a^{water} values between 2.5 and 2.8, which compare well with the values of phosphoric acid and organic compounds such as bromoacetic acid or chloroacetic acid.[326]

The direct metalation of bis-benzimidazolium salts 1,3-attached to an aromatic group along with the *ortho*-CH bond activation of the latter, have been decisive for the recent **364**-mediated preparation of novel types of blue-green emissive neutral compounds, for organic light-emitting devices (Scheme 97). Complex **364** reacts with the iodide salts of 1,3-bis(3-

Scheme 97. Hexahydride 364 as Precursor of Os($C_{NHC}C_{aryl}C_{NHC}$)($C_{NHC}C_{R\text{-}aryl}C_{NHC}$) Blue-Green Emissive Compounds



methylbenzimidazolium-1-yl)benzene and 1,3-bis(3-methylbenzimidazolium-1-yl)-5-trifluoromethylbenzene to give the respective dihydrides [OsH_2($C_{NHC}C_{aryl}C_{NHC}$)(P^iPr_3)$_2$]I (**599**) and [OsH_2($C_{NHC}C_{CF3aryl}C_{NHC}$)($P^iPr_3$)$_2$]I (**600**). The subsequent deprotonation of these compounds with K^{t}BuO yields the monohydrides OsH($C_{NHC}C_{aryl}C_{NHC}$)(P^iPr_3)$_2$ (**601**) and OsH($C_{NHC}C_{CF3aryl}C_{NHC}$)($P^iPr_3$)$_2$ (**602**), which react with a second organic cation to afford the homoleptic derivatives Os($C_{NHC}C_{aryl}C_{NHC}$)$_2$ (**603**) and Os($C_{NHC}C_{CF3aryl}C_{NHC}$)$_2$ (**604**). The reactions of **601** with 1,3-bis(3-methylbenzimidazolium-1-yl)-5-trifluoromethylbenzene and of **602** with 1,3-bis(3-methylbenzimidazolium-1-yl)benzene lead to the heteroleptic counterpart Os($C_{NHC}C_{aryl}C_{NHC}$)($C_{NHC}C_{CF3aryl}C_{NHC}$) (**605**). Complexes **603**−**605** are emissive in the blue-green spectral region with high quantum yields in the solid state, which reach 0.62 for **604**.[327]

3.6.5. Si−H, Ge−H, and Sn−H Bond Activations. The unsaturated dihydride **300**, generated in situ from the tetrahydrideborate complex **301** or the olefin compound **475**, adds the Si−H bond of silanes, the Ge−H bond of germanes, and the Sn−H bond of stannanes to give the corresponding trihydride-silyl OsH_3(SiR_3)(CO)(P^iPr_3)$_2$ (SiR_3 = $SiHPh_2$ (**606**), $SiPh_3$ (**607**)), trihydride-germyl OsH_3(GeR_3)(CO)(P^iPr_3)$_2$ (GeR_3 = $GeHPh_2$ (**608**), $GePh_3$ (**609**), $GeEt_3$ (**610**)), and trihydride-stannyl OsH_3(SnR_3)(CO)(P^iPr_3)$_2$ (SnR_3 = $SnPh_3$ (**611**), Sn^nBu_3 (**612**)) derivatives. The reaction of **300** with H_3SiPh in methanol yields OsH_3{Si(OMe)$_2$Ph}(CO)(P^iPr_3)$_2$ (**613**). The behavior in solution of the four types of compounds is similar, suggesting that all of them have the same

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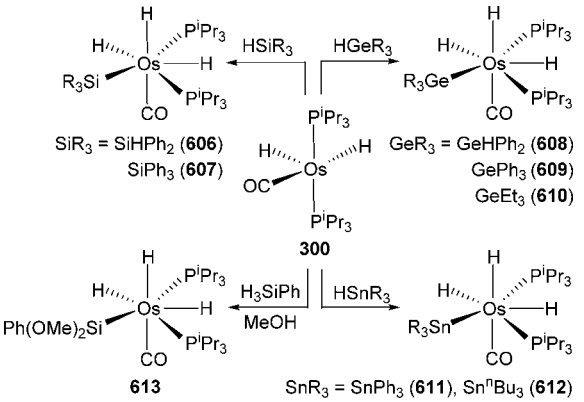
arrangement of ligands around the osmium atom. On the basis of the X-ray structure of **606** and DFT calculations on the model compound $OsH_3(SiH_3)(CO)(PH_3)_2$, the proposed coordination geometry around the metal center of these compounds has been described as a heavily distorted pentagonal bipyramid with a hydride ligand and the carbonyl group in the axial positions. The two other hydride ligands lie in the equatorial plane, one between the phosphines and the other between the ER_3 (E = Si, Ge, and Sn) group and a phosphine (Scheme 98).[328]

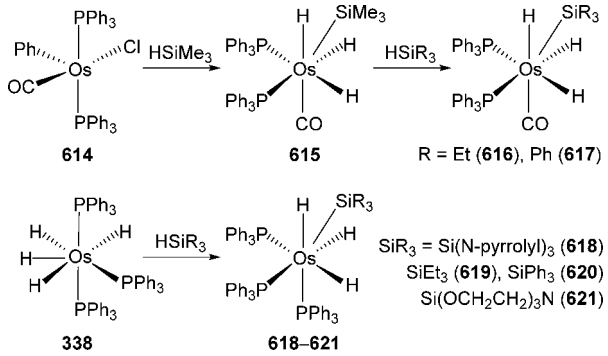
Scheme 98. Reactions of Activation of Si−H, Ge−H, and Sn−H Bonds Promoted by 300



Reaction of the carbonyl-bis(triphenylphosphine) complex $OsPhCl(CO)(PPh_3)_2$ (**614**) with $HSiMe_3$ leads to $OsH_3(SiMe_3)(CO)(PPh_3)_2$ (**615**). Treatment of the latter with $HSiEt_3$ and $HSiPh_3$ affords $OsH_3(SiEt_3)(CO)(PPh_3)_2$ (**616**) and $OsH_3(SiPh_3)(CO)(PPh_3)_2$ (**617**), respectively. Although these compounds are PPh_3-counterparts of **606** and **607**, there are marked structural differences between them because of the cone angles of the phosphine, which have a significant influence on the coordination geometry around the osmium atom. The P−Os−P angle decreases from 146.06(7)° in **606** to 98.85(2)° in **615**. Consequently, and in contrast to the P^iPr_3-complexes, the arrangement of ligands around the osmium atom of the PPh_3-compounds has been described as an approximately tetrahedral disposition of silyl, CO, and phosphine ligands with the three classical hydride ligands located *trans* to the CO and phosphine groups. This structure resembles that of complex **349** with the silyl in the Sn^nBu_3 position and a carbonyl group instead of a phosphine.[329] The reactions of the tetrahydride-tris(triphenylphosphine) complex **338** with $HSiR_3$ lead to the corresponding trihydride-silyl-tris(triphenylphosphine) analogous $OsH_3(SiR_3)(PPh_3)_3$ (SiR_3 = Si(N-pyrrolyl)$_3$ (**618**), $SiEt_3$ (**619**), $SiPh_3$ (**620**), Si$(OCH_2CH_2)_3N$ (**621**)). These compounds have the same structure as **615**−**617**, with a phosphine in the position of the carbonyl group (Scheme 99). The methylation and protonation of the nitrogen atom of **621** give the salts $[OsH_3\{Si(OCH_2CH_2)_3NMe\}(PPh_3)_3]I$ (**622**) and $[OsH_3\{Si(OCH_2CH_2)_3NH\}(PPh_3)_3]OTf$ (**623**), respectively.[330,331]

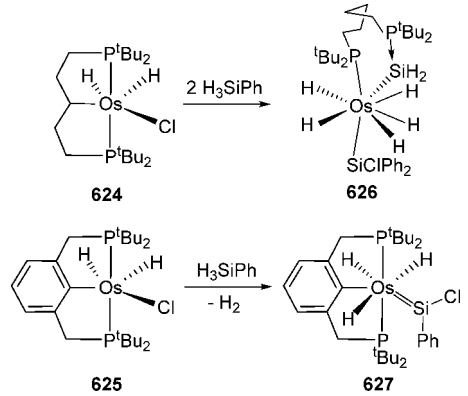
Gusev, Zargarian, and co-workers have reported novel silyl and silylene compounds resulting from reactions of H_3SiPh with the pincer complexes $OsH_2Cl\{CH(C_2H_4P^tBu_2)_2\}$ (**624**) and $OsH_2Cl\{2,6\text{-}(CH_2P^tBu_2)C_6H_3\}$ (**625**). Addition of 2 equiv of H_3SiPh to toluene solutions of **624** gives $OsH_5(SiPh_2Cl)\{\kappa^2\text{-}Si,P\text{-}[SiH_2P^tBu_2(CH_2)_5P^tBu_2]\}$ (**626**). During the process,

Scheme 99. Si−H Bond Activation Reactions Promoted by Triphenylphosphine-Osmium Complexes



complex **624** and the two molecules of silane undergo a series of redistribution reactions culminating in the net hydrogenation of the Os−C(sp^3) bond and the generation of a silyl, one base-stabilized silylene, and five hydride ligands. The donor atoms around the metal center define a dodecahedron consisting of two orthogonal trapezoidal planes. One of them contains the Si-silyl atom and the coordinated phosphorus atom of the phosphine at B sites and two hydrides, whereas the other plane contains three hydrides and the Si atom of the base-stabilized silylene. The reaction of H_3SiPh with **625**, which has a pincer ligand with a more rigid backbone, leads to the trihydride-silylene $OsH_3(=SiClPh)\{2,6\text{-}(CH_2P^tBu_2)C_6H_3\}$ (**627**) and molecular hydrogen (Scheme 100).[332]

Scheme 100. Si−H Bond Activation Reactions Promoted by PCP-Pincer Osmium Complexes



The activation of the Sn−H bond of $HSnPh_3$ by the dichloride-dihydride complex **315** has been the starting point to the development of an interesting family of stannyl and bis(stannyl)-polyhydride compounds, including pentahydride, tetrahydride, trihydride, and compressed dihydride species (Scheme 101). Complex **315** reacts with two equiv of $HSnPh_3$ to give the tetrahydride-stannyl $OsH_4Cl(SnPh_3)(P^iPr_3)_2$ (**628**) and $ClSnPh_3$. The structure of **628** is the expected dodecahedron with the bulky ligands at B sites of the orthogonal trapezoidal planes.[333] This compound reacts with other two equivalents of $HSnPh_3$ to afford the tetrahydride-bis(stannyl) derivative $OsH_4(SnPh_3)_2(P^iPr_3)_2$ (**629**) and $ClSnPh_3$. Complex **629** is a rare example of bis(stannyl) compound with the transition metal in a high oxidation state. A distinguishing feature of the structure of this compound is the P−Os−Sn angle in both orthogonal trapezoidal planes (B−

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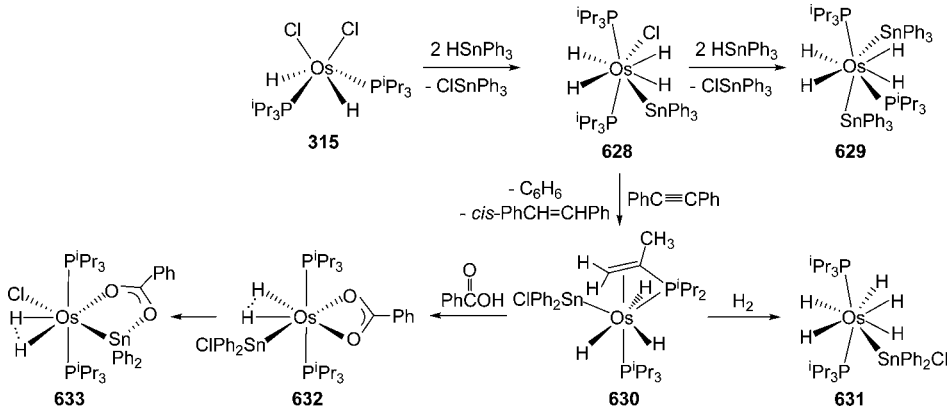
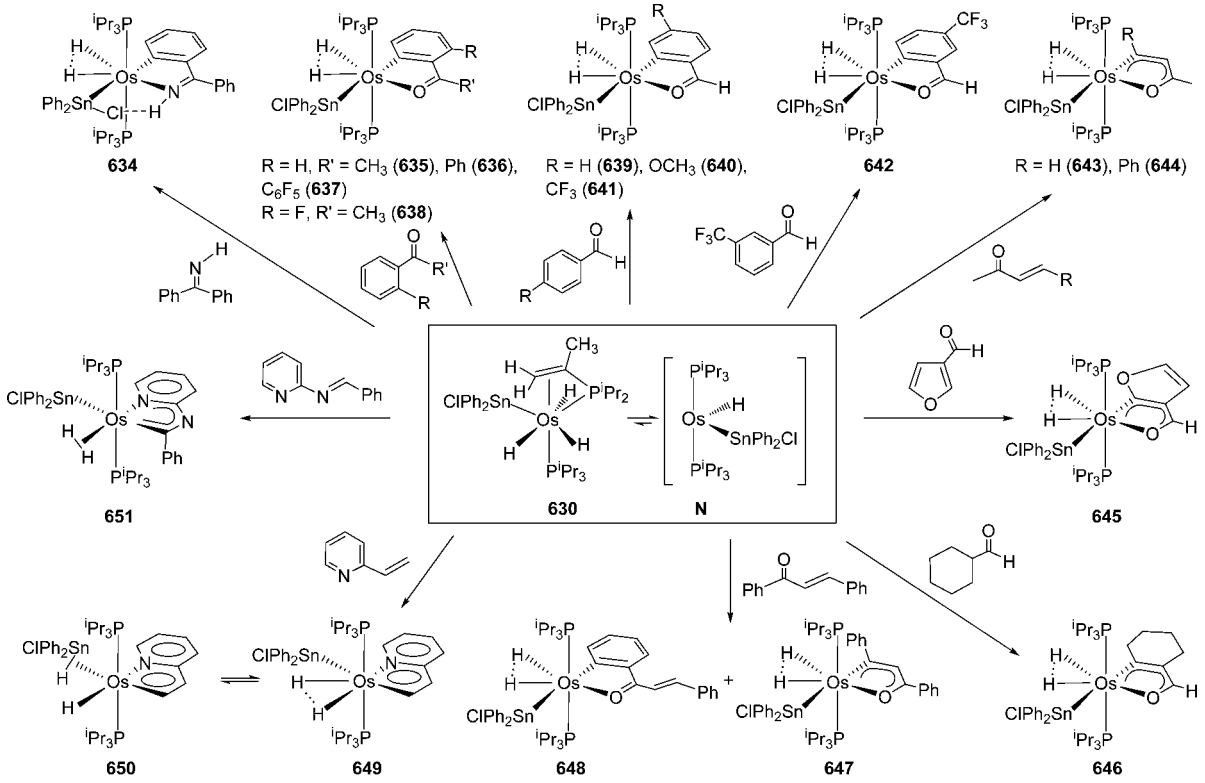
Scheme 101. Formation of Osmium-Polyhydrides via Sn−H Bond Activation Reactions



Scheme 102. C−H Bond Activation Reactions Promoted by 630



Os−B) of 122.56(3)°, which is significantly smaller than the related angle in other eight-coordinate osmium polyhydride complexes (145−156°). This seems to be a consequence of the steric hindrance experienced by the phosphine and stannyl ligands of different planes.[334] In the presence of diphenylacetylene, complex **628** gives the trihydride-stannyl $OsH_3(SnClPh_2)\{\kappa^3\text{-}P,C,C\text{-}[CH_2{=}C(CH_3)]P^iPr_2\}(P^iPr_3)$ (**630**), *cis*-stilbene, and benzene. In the solid state, its structure has been determined by X-ray diffraction analysis and can be described as a very distorted pentagonal bypiramid, with the phosphorus atoms of the triisopropylphosphine ligand and the midpoint of the olefinic bond of the isopropenyl group of the dehydrogenated phosphine occupying axial positions. The formation of **630** is a one-pot synthesis of multiple complex reactions. Four different processes are assembled to afford this compound: (i) dehydrogenation of one isopropyl group of one phosphine, (ii) reduction of diphenylacetylene to give *cis*-stilbene, (iii) hydrogenolysis of a phenyl group of the triphenylstannyl ligand, and (iv) migration of the chloride from the transition metal to the tin atom. The elemental steps of this synthesis appear to occur with the participation of radical-like species as intermediates. Thus, the formation of **630** is inhibited in the presence of hydroquinone. Complex **630** reacts with molecular hydrogen to form the pentahydride-stannyl $OsH_5(SnClPh_2)(P^iPr_3)_2$ (**631**), as a result of the hydrogenation of the coordinated olefinic bond and a d^4−d^2 oxidative addition of hydrogen. The donor atoms adopt the expected dodecahedral disposition around the metal center with the bulky ligand at the B sites of the trapezoidal planes.[333] Complex **630** also undergoes protonation-addition of benzoic acid to initially give the compressed dihydride-stannyl derivative $OsH_2(SnClPh_2)(\kappa^2\text{-}O_2CPh)(P^iPr_3)_2$ (**632**; $d_{H\cdots H}$ = 1.50 Å). In solution, the tin atom exchanges with the transition metal on the chloride ligand by one of the oxygen atoms of the

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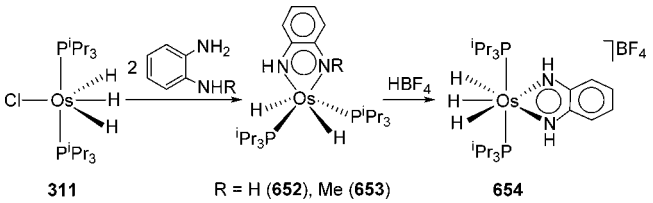
carboxylate group to afford $OsH_2Cl\{\kappa^2$-*O*,*Sn*-[OC(Ph)-$OSnPh_2]\}(P^iPr_3)_2$ (**633**; $d_{H\cdots H}$ = 1.50 Å).[335]

The formation of **631** and **632** is consistent with the previous transformation of **630** into the 14-valence electrons monohydride $OsH(SnClPh_2)(P^iPr_3)_2$ (**N**), which adds two molecules of H_2 or one molecule of benzoic acid. This functionally equivalent promotes the chelate-assisted C(sp^2)−H bond activation of aromatic imines, ketones, and aldehydes; α,β-unsaturated ketones and aldehydes; 2-vinylpyridine, and (*E*)-*N*-(phenylmethylene)-2-pyridinamine to afford compressed dihydrides (Scheme 102). The reaction with benzophenone imine leads to $OsH_2(SnClPh_2)\{\kappa^2$-*N*,*C*-$[NHC(Ph)C_6H_4]\}(P^iPr_3)_2$ (**634**), whereas acetophenone and benzophenone give $OsH_2(SnClPh_2)\{\kappa^2$-*O*,*C*-$[OC(R)C_6H_4]\}(P^iPr_3)_2$ (R = Me (**635**), Ph (**636**)). The functionally equivalent **N** is certainly the key species for the activation; in agreement with this, the reaction of **630** with 1 equiv of perdeuterated benzophenone affords the hydride-deuteride $Os(H)(D)(SnClPh_2)\{\kappa^2$-*O*,*C*-$[OC(C_6D_5)C_6D_4]\}(P^iPr_3)_2$ (**636-d_{10}**). The *ortho*-CH bond activation is preferred over the *ortho*-CF bond activation. Thus, the reactions with 2,3,4,5,6-pentafluorobenzophenone and 2-fluoroacetophenone yield $OsH_2(SnClPh_2)\{\kappa^2$-*O*,*C*-$[OC(C_6F_5)-C_6H_4]\}(P^iPr_3)_2$ (**637**) and $OsH_2(SnClPh_2)\{\kappa^2$-*O*,*C*-$[OC(Me)-C_6FH_3]\}(P^iPr_3)_2$ (**638**), respectively.[336] The *ortho*-CH activation is also preferred with regard to the OC−H bond activation in benzaldehydes. Reactions of **630** with benzaldehyde and substituted benzaldehydes give the corresponding *ortho*-metalated compounds $OsH_2(SnClPh_2)\{\kappa^2$-*O*,*C*-$[OC(H)-C_6RH_3]\}(P^iPr_3)_2$ (R = H (**639**), *p*-OCH_3 (**640**), *p*-CF_3 (**641**), *m*-CF_3 (**642**)).[337] α,β-Unsaturated ketones and aldehydes generate osmafuran derivatives, methyl vinyl ketone and benzylidenacetone give $OsH_2(SnClPh_2)\{\kappa^2$-*O*,*C*-$[OC-(CH_3)CHCR]\}(P^iPr_3)_2$ (R = H (**643**), Ph (**644**)),[338] whereas 3-furaldehyde and 1-cyclohexene-1-carboxaldehyde form $OsH_2(SnClPh_2)\{\kappa^2$-*O*,*C*-$[OCHC_4(O)H_2]\}(P^iPr_3)_2$ (**645**) and $OsH_2(SnClPh_2)\{\kappa^2$-*O*,*C*-$(OCHC_6H_8)\}(P^iPr_3)_2$ (**646**), respectively.[337] As expected, the functionally equivalent **N** activates both β-olefinic- and *ortho*-CH bonds of benzylideneacetophenone to give the osmafuran $OsH_2(SnClPh_2)\{\kappa^2$-*O*,*C*-$[OC(Ph)-CHCPh]\}(P^iPr_3)_2$ (**647**) and the osmaisobenzofuran $OsH_2(SnClPh_2)\{\kappa^2$-*O*,*C*-$[OC(CH{=}CHPh)C_6H_4]\}(P^iPr_3)_2$ (**648**). The activation of the C−H bond of the olefinic moiety is kinetically favored with regard to the *ortho*-CH bond activation of the phenyl group. However, complex **648**, resulting from the *ortho*-CH bond activation, is thermodynamically more stable than **647**. The activation of 2-vinylpyridine affords $OsH_2(SnClPh_2)\{\kappa^2$-*N*,*C*-(pyCHCH)$\}(P^iPr_3)_2$ (**649**) in equilibrium with the tautomer $OsH\{\kappa^2$-*N*,*C*-(pyCHCH)$\}(\eta^2-HSnClPh_2)(P^iPr_3)_2$ (**650**), where the stannane is bonded to the transition metal by an Os−H−Sn three-center bond (J_{H-Sn} = 183 Hz). The activation of (*E*)-*N*-(phenylmethylene)-2-pyridinamine leads to $Os(SnClPh_2)\{\kappa^2$-*N*,*C*-(pyNCPh)$\}(\eta^2-H_2)(P^iPr_3)_2$ (**651**). In this compound, the separation between the hydrogen atoms of the OsH_2 unit of 1.32 Å is slightly shorter than in the other members of the family (1.4−1.5 Å). So, it is better described as an elongated dihydrogen species.[338]

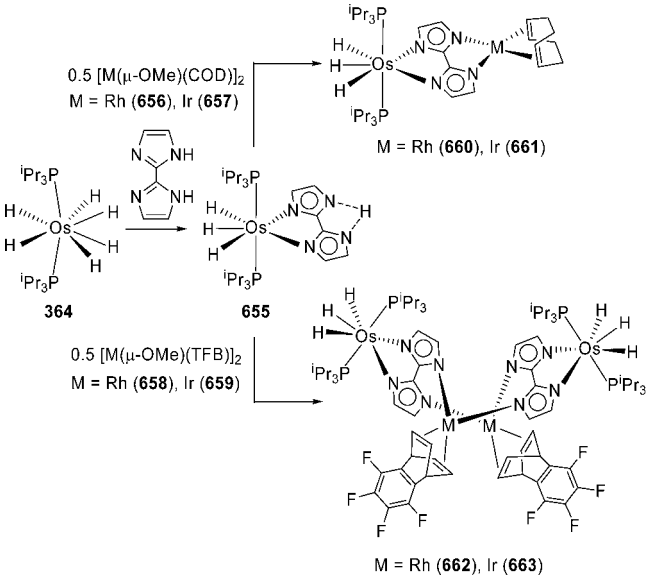
3.6.6. N−H and O−H Bond Activations. Trihydride **311** activates one N−H bond of each NHR group of 1,2-phenylenediamine and *N*-methyl-1,2-phenylenediamine to give the six-coordinate d^4-dihydrides $OsH_2\{\kappa$-*N*,*N*-(*o*-NH-C_6H_4−NR)$\}(P^iPr_3)_2$ (R = H (**652**), Me (**653**)),[339] containing an osmabenzimidazolium core. The planarity and the length equalization of the bicycle of these compounds along with negative NICS values calculated for both rings and the aromatic MO delocalization suggest that, as the organic counterparts, the osmabenzimidazolium moiety of **652** and **653** is aromatic. The frontier HOMO−1 of the $[OsH_2(P^iPr_3)_2]^{2+}$ fragment remains nonbonding. In agreement with this, the addition of $HBF_4\cdot OEt_2$ to diethyl ether solutions of **652** produces its protonation to afford the trihydride $[OsH_3\{\kappa$-*N*,*N*-(*o*-NH-C_6H_4−NH)$\}-(P^iPr_3)_2]BF_4$ (**654**), in high yield (Scheme 103).[340]

Scheme 103. Formation of Compounds Containing an Osmabenzimidazolium Core by Means of N−H Bond Activation of 1,2-Phenylenediamines



Abstraction of a NH-hydrogen atom of 2,2′-biimidazole (H_2biim) by the hexahydride **364** has been the entry to heterometallic Os(μ-biim)Rh and Os(μ-biim)Ir complexes (Scheme 104). The abstraction leads to the classical trihydride

Scheme 104. Fomation of Heterobimetallic Compounds by Means of the Double N−H Bond Activation of 2,2′-Biimidazole



derivative $OsH_3(Hbiim)(P^iPr_3)_2$ (**655**).[341] Treatment of this compound with the dimers $[M(\mu$-OMe)$(\eta^4$-COD)$]_2$ (M = Rh (**656**), Ir (**657**)) and $[M(\mu$-OMe)$(\eta^4$-TFB)$]_2$ (M = Rh (**658**), Ir (**659**)) produces the methoxy-mediated abstraction of the second NH-hydrogen atom of the heterocycle to afford the dinuclear complexes $(P^iPr_3)_2H_3Os(\mu$-biim)$M(\eta^4$-COD) (M = Rh (**660**), Ir (**661**)) and the tetranuclear compounds $[(P^iPr_3)_2H_3Os(\mu$-biim)$M(\eta^4$-TFB)$]_2$ (M = Rh (**662**), Ir (**663**)), respectively.[342] In solution, the hydride ligands of these species undergo quantum exchange coupling.

Hexahydride **364** also activates the N−H bond of 2-phenylbenzimidazole,[323] pyrazole (Hpz),[341] and pyrrole[240] (Scheme 105). Refluxing toluene solution of **364** with 0.5

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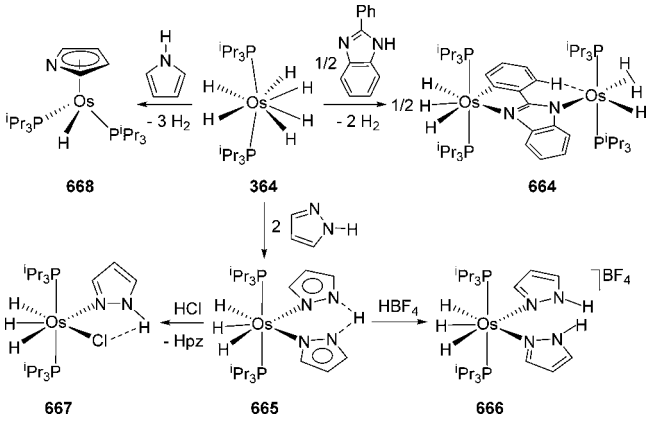
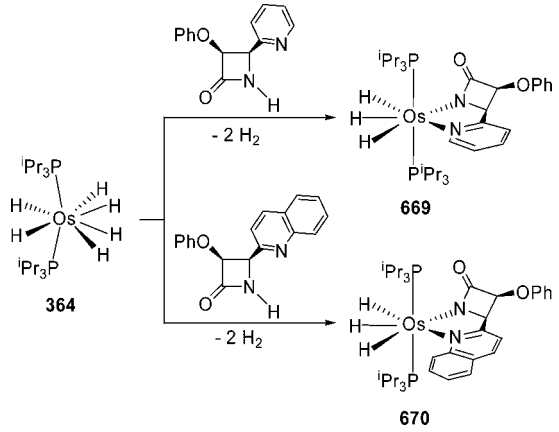
Scheme 105. N−H Bond Activation of Heterocycles Promoted by 364



equiv of 2-phenylbenzimidazole leads to the dinuclear compound $(P^iPr_3)_2H_3Os(C_6H_4\text{-benzimidazolate})OsH(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**664**). The formation of this complex can be rationalized as the hexahydride-mediated N−H bond activation of the C_6H_4-benzimidazole ligand of **583**. The N−H activation results in the release of two hydrogen molecules, which generates a coordination vacancy that is saturated by agostic coordination of the remaining *ortho*-CH bond of the metalated phenyl group of **583**. Furthermore, two classical hydrides are converted into an elongated dihydrogen (d_{H-H} = 1.29(1) Å). The spectroscopic data and electrochemical behavior of **664** indicate that the mutual influence between the metal centers is negligible.[323] The reaction of **364** with pyrazole gives $OsH_3(pz)(Hpz)(P^iPr_3)_2$ (**665**), which affords $[OsH_3(Hpz)_2(P^iPr_3)_2]BF_4$ (**666**) and $OsH_3Cl(Hpz)(P^iPr_3)_2$ (**667**) by reaction with HBF_4 and HCl, respectively.[341] Treatment of **364** with pyrrole yields the half-sandwich derivative $OsH(\eta^5\text{-}C_5H_4N)(P^iPr_3)_2$ (**668**).

Chelate-assisted N−H bond activation of 2-azetidinones promoted by **364** has been investigated in the search for new inhibitors of β-lactamases (Scheme 106). This hexahydride reacts with 3-phenoxy-4-(pyridin-2-yl)- and 3-phenoxy-4-(quinol-2-yl)-azetidin-2-one (HAzpy and HAzquin, respectively) to give the osmatrinems $OsH_3(Azpy)(P^iPr_3)_2$ (**669**) and $OsH_3(Azquin)(P^iPr_3)_2$ (**670**), containing a seven-coordinate d^4-metal fragment in their skeletons. The X-ray structure

Scheme 106. Formation of Osmatrinems via N−H Bond Activation of 2-Azetidinones[a]

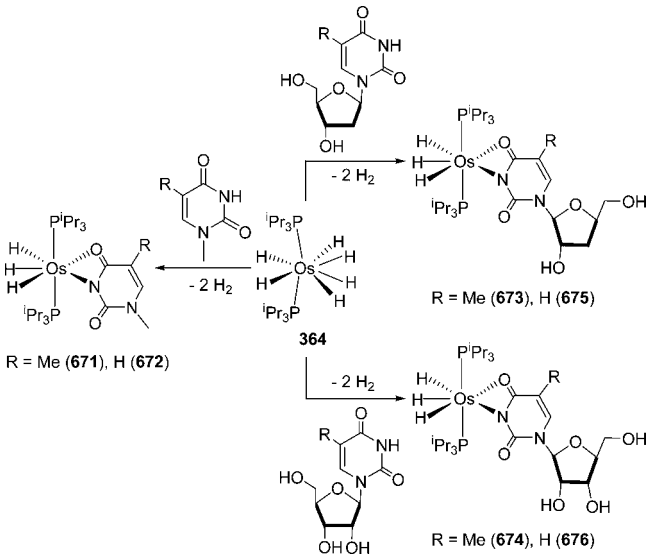


[a]Adapted from ref 343. Copyright 2014 American Chemical Society.

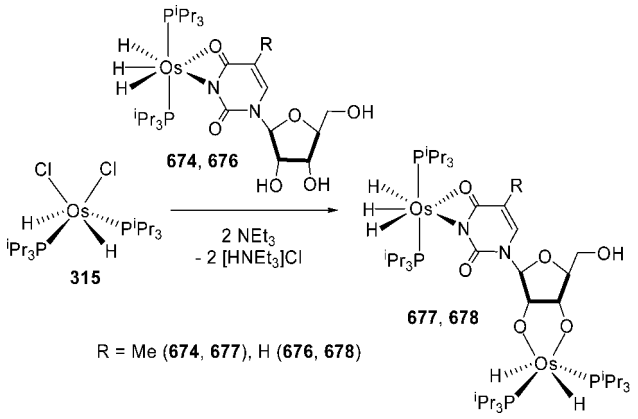
of **669** has revealed that the dihedral angle between the five-membered metalacycle and the four-membered lactamic ring is 45.0°.[343]

The N−H bond activation of pyrimidinic *N*-methyl nucleobases and nucleosides promoted by **364** has also been investigated in the search for model osmium anticancer drugs (Schemes 107 and 108).[344]

Scheme 107. N−H Bond Activation Reactions of Pyrimidinic *N*-Methyl Nucleobases and Nucleosides Promoted by 364



Scheme 108. Dinuclear Compounds Containing Nucleosides Derived from Ribose



Treatment of **364** with 1-methylthymine and 1-methyluracil leads to $OsH_3(1\text{-methylthyminate})(P^iPr_3)_2$ (**671**) and $OsH_3(1\text{-methyluracilate})(P^iPr_3)_2$ (**672**), respectively. The reactions of **364** with thymidine, 5-methyluridine, deoxyuridine, and uridine afford $OsH_3(thymidinate)(P^iPr_3)_2$ (**673**), $OsH_3(5\text{-methyluridinate})(P^iPr_3)_2$ (**674**), $OsH_3(deoxiuridinate)(P^iPr_3)_2$ (**675**), and $OsH_3(uridinate)(P^iPr_3)_2$ (**676**), respectively (Scheme 107). Treatment of **674** and **676**, containing nucleosides derived from ribose, with **315** in the presence of NEt_3 yields the dinuclear species $OsH_3(P^iPr_3)_2(nucleobase')(ribose)OsH_2(P^iPr_3)_2$ (**677** and **678**, respectively) formed by two different metal fragments (Scheme 108).

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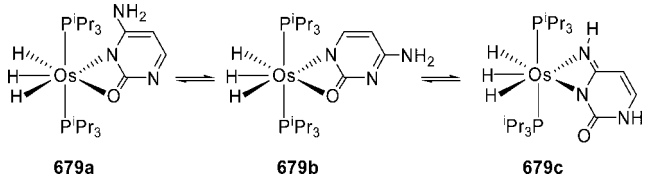
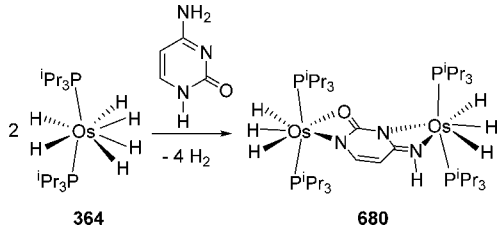
Reactions of **364** with cytosine, deoxycytosine, and cytidine have also been studied.[345] Complex **364** deprotonates cytosine to give the d^4-trihydride derivative OsH_3(cytosinate)$(P^iPr_3)_2$ (**679**), which in solution exists as a mixture of isomers containing κ^2-N1,O (**679a**) and κ^2-N3,O (**679b**) amino-oxo and κ^2-N3,N4 (**679c**) imino-oxo tautomers (Scheme 109).

Scheme 109. Coordination Modes of the Cytosinate Anion



Complex **364** is also able to perform the double deprotonation of cytosine to afford the dinuclear derivative $(P^iPr_3)_2H_3Os(\mu$-cytosinate′$)OsH_3(P^iPr_3)_2$ (**680**), where the anion is coordinated κ^2-N1,O and κ^2-N3,N4 to two different $OsH_3(P^iPr_3)_2$ moieties (Scheme 110). Deprotonations of deoxycytidine and

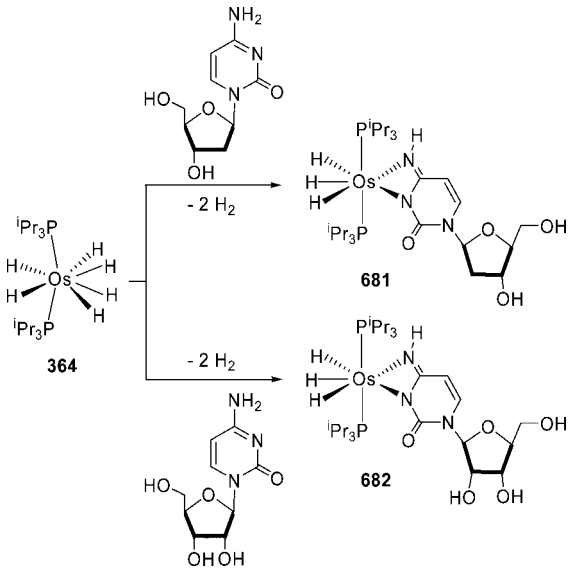
Scheme 110. Double N−H Bond Activation of Cytosine Promoted by 364



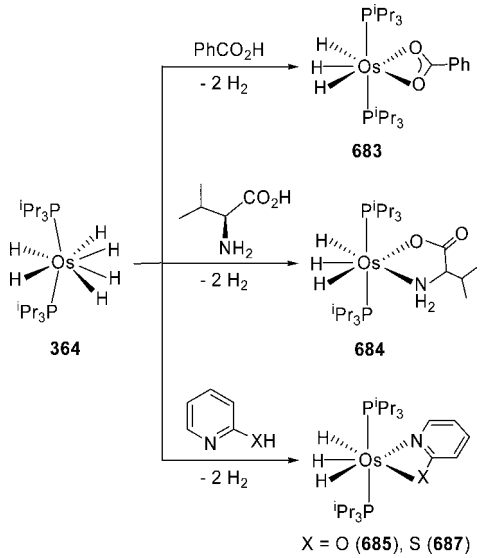
cytidine lead to OsH_3(deoxycytidinate)$(P^iPr_3)_2$ (**681**) and OsH_3(cytidinate)$(P^iPr_3)_2$ (**682**), respectively, containing the anion κ^2-N3,N4 coordinated (Scheme 111).

Hexahydride **364** also promotes the cleavage of O−H bonds of a wide range of organic molecules, including benzoic acid, *L*-valine, and 2-hydroxypyridine (Scheme 112). The reactions

Scheme 111. Formation of Deoxycytidinate and Cytidinate Derivatives



Scheme 112. O−H Bond Activation Reactions Promoted by 364



lead to the corresponding classical trihydride derivatives $OsH_3(\kappa^2$-$O_2CPh)(P^iPr_3)_2$ (**683**),[307] $OsH_3\{\kappa^2$-*N,O*-[OC(O)-$CH(CHMe_2)NH_2]\}(P^iPr_3)_2$ (**684**), and $OsH_3\{\kappa^2$-*N,O*-(py-2-O)$\}(P^iPr_3)_2$ (**685**).[342] The acetate counterpart of **683**, $OsH_3(\kappa^2$-$O_2CMe)(P^iPr_3)_2$ (**686**), has been prepared by reaction of the dichloride-dihydride $OsH_2Cl_2(P^iPr_3)_2$ (**315**) with KO_2CMe in methanol.[346] Similarly to 2-hydroxypyridine, 2-thiolpyridine reacts with **364** to afford the pyridylthiolate derivative $OsH_3\{\kappa^2$-*N,S*-(py-2-S)$\}(P^iPr_3)_2$ (**687**).[342]

Hexahydride **364** promotes the imidazolium metalation and alcohol dehydrogenation of alcohol-functionalized imidazolium salts and the N-bound to C-bound transformation along with the alcohol deprotonation-dehydrogenation of alcohol-functionalized imidazoles. In the first case, NHC-keto-trihydride compounds are formed, whereas in the second case, NHC-enolate-trihydride derivatives bearing a N−H wingtip are obtained. The conversion between the respective NHC-keto and NHC-enolate is easily achieved by deprotonation-protonation reactions. As a proof of concept, the reactions shown in Scheme 113 have been reported.[347] Treatment of **364** with 3-benzyl-1-(2-hydroxy-2-phenylethyl)imidazolium tetrafluoroborate and 3-benzyl-1-(2-hydroxypropyl)imidazolium tetraphenylborate leads to the NHC-keto complexes $[OsH_3\{\kappa^2$-*C,O*-$[CN(CH_2Ph)CHCHNCH_2C(R)=O]\}$-$(P^iPr_3)_2]A$ (A = BF_4, R = Ph (**688**); A = BPh_4, R = Me (**689**)), as a consequence of the direct metalation of the heterocycle and the dehydrogenation of the alcohol substituent. Similarly to pyridine, 3- and 4-methylpyridine, 1-(2-hydroxy-2-phenylethyl)imidazole, and 1-(2-hydroxypropyl)imidazole react with **364** to give the classical tetrahydrides OsH_4(Rim)-$(P^iPr_3)_2$ (R = $CH_2CH(OH)Ph$ (**690**), $CH_2CH(OH)Me$ (**691**)), containing a N-bound imidazole ligand. In toluene under reflux, complexes **690** and **691** evolve into the C-bound imidazole derivatives $OsH_3\{\kappa^2$-*C,O*-$[CN(H)CHCHNCH{=}C$-$(R)O]\}(P^iPr_3)_2$ (R = Ph (**692**), Me (**693**)). The deprotonation-dehydrogenation process of the alcohol substituent is determinant for the N-bound to C-bound transformation. In contrast to **690** and **691**, 1-mesityl and 1-methylimidazole complexes OsH_4(MesIm)$(P^iPr_3)_2$ (**694**) and OsH_4(MeIm)-$(P^iPr_3)_2$ (**695**) do not undergo tautomerization. An intra-

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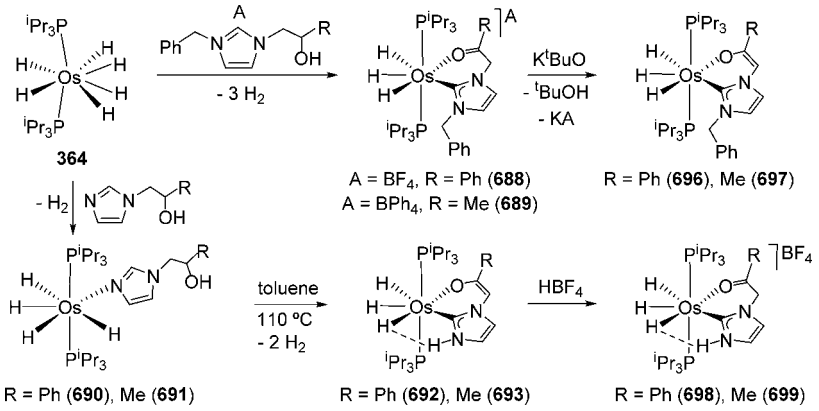
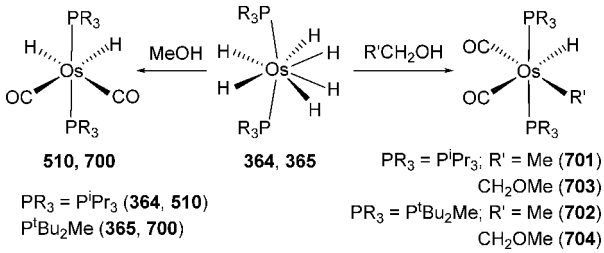
Scheme 113. Reactions of 364 with Alcohol-Functionalized-Imidazolium Salts and -Imidazoles



molecular hydrogen bond between a hydride and the NH-hydrogen atom of the C-bound heterocycle seems to contribute to the stabilization of **692** and **693**. The deprotonation of **688** and **689** with K^{t}BuO affords the corresponding enolate compounds $OsH_3\{\kappa^2$-*C,O*-$[CN(CH_2Ph)CHCHNCH{=}C(R)O]\}(P^iPr_3)_2$ (R = Ph (**696**), Me (**697**)), whereas the protonation of **692** and **693** with $HBF_4{\cdot}OEt_2$ yields the keto derivatives $[OsH_3\{\kappa^2$-*C,O*-$[CN(H)CHCHNCH_2C(R){=}O]\}(P^iPr_3)_2]BF_4$ (R = Ph (**698**), Me (**699**)).

Hexahydride **364** and its P^tBu_2Me-counterpart **365** also show a marked tendency to promote the direct O−H bond activation of primary alcohols. The reactions initially afford alkoxide species, which evolve by *β*-hydrogen elimination and via aldehyde intermediates into carbonyl compounds. As a consequence, these polyhydrides are unstable in solvents such as methanol, ethanol, and 2-methoxyethanol (Scheme 114).[348]

Scheme 114. O−H Bond Activation Reactions of Primary Alcohols Promoted by d^2-Hexahydride-Osmium Complexes

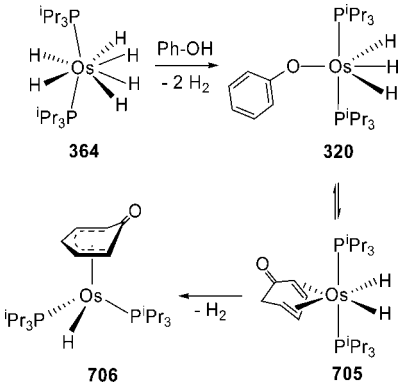


In methanol, these compounds give the dihydride-dicarbonyl complexes $OsH_2(CO)_2(PR_3)_2$ (PR_3 = P^iPr_3 (**510**), P^tBu_2Me (**700**)). In contrast to methanol, ethanol affords the hydride-methyl-dicarbonyl derivatives $OsH(CH_3)(CO)_2(PR_3)_2$ (PR_3 = P^iPr_3 (**701**), P^tBu_2Me (**702**)). 2-Methoxyethanol behaves similarly to ethanol and yields $OsH(CH_2OMe)(CO)_2(PR_3)_2$ (PR_3 = P^iPr_3 (**703**), P^tBu_2Me (**704**)).

Phenol is a particularly acidic alcohol having no geminal hydrogen atoms. However, it contains a coordinating aromatic ring. The activation of its O−H bond by **364** leads to the trihydride **320**. In toluene, the latter undergoes a reductive elimination-tautomerization process to afford $OsH_2(\eta^4$-2,4-cyclohexadien-1-one$)(P^iPr_3)_2$ (**705**). Subsequently, the equilibrium mixture of **320** and **705** evolves into $OsH(\eta^5$-$C_6H_5O)(P^iPr_3)_2$ (**706**) with loss of H_2 (Scheme 115).[240]

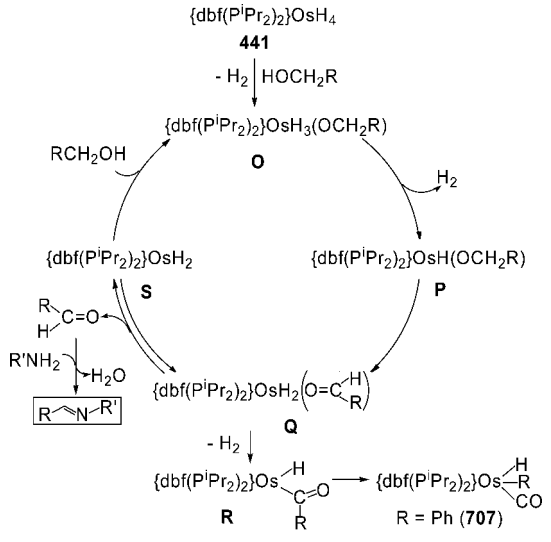
The POP-pincer tetrahydride **441** also shows a marked tendency to activate the O−H bond of primary alcohols. In

Scheme 115. O−H Bond Activation of Phenol Promoted by 364



agreement with **364** and **365**, complex **441** reacts with benzyl alcohol to afford the hydride-aryl-carbonyl derivative $OsH(Ph)(CO)\{dbf(P^iPr_2)_2\}$ (**707**). Its formation has been rationalized through the intermediates **O**−**R** shown in Scheme 116. The O−H bond activation of the alcohol by **441** could initially afford **O**, which should give the unsaturated species **P** by

Scheme 116. Catalytic Cycle for the 441-Mediated Formation of Imines from Alcohols and Amines[a]



[a]Adapted from ref 289. Copyright 2011 American Chemical Society.

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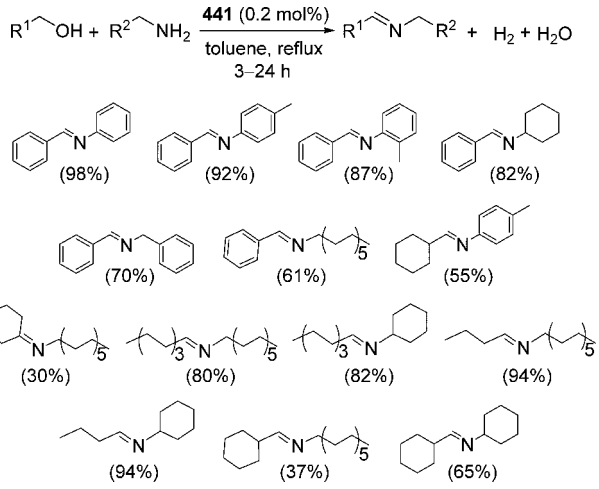
dissociation of H_2. A β-elimination reaction in the alkoxide group could lead to the dihydride-aldehyde **Q**, wich should generate the acyl intermediate **R**. Finally, the deinsertion of the phenyl group should give **707**.

Intermediate **Q** dissociates the aldehyde to afford an equilibrium mixture with the unsaturated dihydride **S**. Thus, when the reaction is carried out in the presence of a primary amine, the corresponding imine is formed. Because the addition of the O−H bond of the alcohol to **S** regenerates **O**, complex **441** catalyzes the selective formation of a variety of imines from alcohols and amines with liberation of H_2, under an argon atmosphere (Scheme 117). The reactions include the formation of aliphatic imines, which are inherently more challenging due to their instability.[289]

Scheme 117. Scope of the 441-Mediated Formation of Imines from Alcohols and Amines

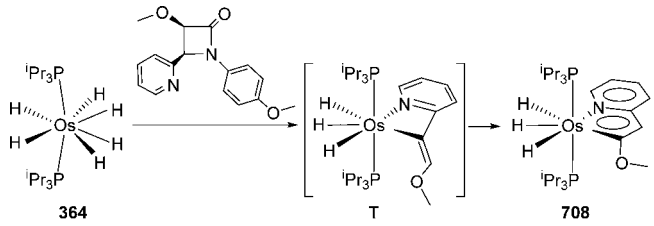


The PNP-pincer tetrahydride **452** couples primary alcohols and primary amines to afford secondary amines, in contrast to **441**. In addition, it operates as an efficient catalyst for reactions of dehydrogenative coupling of primary alcohols to symmetrical esters and for the hydrogen transfer from 2-propanol to acetophenone and cyclohexanone.[291] The *cis*-hydride-dihydrogen **394** is an efficient catalyst precursor for the hydrogen transfer from 2-propanol to α,β-unsaturated ketones. In contrast to its ruthenium counterpart, complex **71**, the reduction leads to the saturated ketone via isomerization of the initially produced allylic alcohol.[131] The equilibrium mixture of the dihydride **300** and the dihydride-dihydrogen **345** catalyzes the hydrogen transfer from 2-propanol to α,β-unsaturated ketones to afford the saturated alcohol via the saturated ketone.[210,211]

3.6.7. Other σ-Bond Activations. Hexahydride **364** is probably the transition metal-polyhydride with the highest capacity to break σ-bonds. As a consequence, it has been used to achieve less common ruptures, including the B-type fragmentation of the four-membered core of β-lactams, the cleavage of an exocyclic N−C bond of nucleobases, a C−OR bond activation, and the selective *ortho*-CF bond activation of aromatic ketones in the presence of weaker *ortho*-CH bonds.

The thermal B-type fragmentation of the four-membered ring of a β-lactam, involving the breakage of the N1−C4 and C2−C3 bonds is a difficult reaction with an energy barrier of more than 40 kcal mol^{-1}. It is a concerted asynchronous [2 + 2] cycloreversion, which takes place with complete retention of the stereochemistry to afford a C3−C4 olefin and a N1−C2−O isocyanate. The replacement of the NH-hydrogen atom of 4-(2-pyridyl)azetidin-2-ones by aryl protects the nitrogen atom against the metal center of **364**, which is directed toward the C4−H bond of the four-membered ring. The addition of this bond to the metal center allows the active participation of an osmium lone pair in the B-type β-lactam fragmentation process. The breakage of the N1−C4 and C2−C3 bonds is now thermally accessible through a stepwise process, which implies a much lower barrier than the concerted asynchronous mechanism of the fragmentation without metal. As a consequence, instead of osmatrinems related to **669** and **670**, the reaction of **364** with (±)-*cis*-1-(4-methoxyphenyl)-3-methoxy-4-(pyridine-2-yl)azetidin-2-one leads to $OsH_3\{\kappa^2\text{-}N,C\text{-}(py\text{-}2\text{-}CHCOMe)\}(P^iPr_3)_2$ (**708**) after the expansion of the four-membered heterometalaring of the resulting intermediate $OsH_3\{\kappa^2\text{-}N,C\text{-}[py\text{-}2\text{-}C{=}C(OMe)H]\}(P^iPr_3)_2$ (**T** in Scheme 118), which involves 1,2-metal and -hydrogen shifts.[349]

Scheme 118. B-Type Fragmentation of the Four-Membered Ring of (±)-*cis*-1-(4-methoxyphenyl)-3-methoxy-4-(pyridine-2-yl)azetidin-2-one Promoted by 364



The arene C−H bond activation is thermodynamically and kinetically favored with regard to the alkane C−H bond activation. This fact has allowed the preparation of novel C,C′,N-pincer complexes by means of the replacement of the methoxy substituent at the 3-position of the lactamic four-membered ring by a phenoxy group (Scheme 119). Reactions of **364** with (±)-*cis*-1-(4-methoxyphenyl)-3-phenoxy-4-(pyridine-2-yl)azetidin-2-one, (±)-*cis*-1-(4-methoxyphenyl)-3-phenoxy-4-(isoquinolin-2-yl)azetidin-2-one, and (±)-*cis*-1-(4-methoxyphenyl)-3-phenoxy-4-(quinolin-2-yl)azetidin-2-one lead to the compressed dihydrides $OsH_2\{\kappa^3\text{-}C,C,N\text{-}(C_6H_4OCCH\text{-}2\text{-}L)\}(P^iPr_3)_2$ (L = py (**709**), isoquin (**710**), quin (**711**)), containing a dianionic C,C′,N-pincer ligand, as a result of the degradation of the azetidinones and the additional *ortho*-CH bond activation of the phenoxy group. Complexes **709**−**711** add HBF_4 to yield $[OsH_2\{\kappa^3\text{-}C,C,N\text{-}(C_6H_4OCCH_2\text{-}2\text{-}L)\}(P^iPr_3)_2]BF_4$ (L = py (**712**), isoquin (**713**), quin (**714**)) as a consequence of the protonation of the dianionic C,C′,N-pincer ligand. The hydride ligands of **709**−**714** undergo quantum mechanical exchange coupling, which has been quantified according to eq 1. The comparison of the results reveals that the phenomenon is particularly intense for cations **712**−**714**. Furthermore, in these compounds the separation between the hydrides is ∼0.1 Å shorter than in the respective neutral species **709**−**711**, whereas the hydride hard sphere radius increases by ∼10% and the ν value decreases by ∼20%.[350]

Hexahydride **364** also promotes the cleavage of the N−Me bond of the ligands 1-methylthyminate and 1-methyluracilate of **671** and **672** to give the dinuclear species $[OsH_3(P^iPr_3)_2]_2(\mu\text{-thyminate})$ (**715**) and $[OsH_3(P^iPr_3)_2]_2(\mu\text{-uracylate})$ (**716**)

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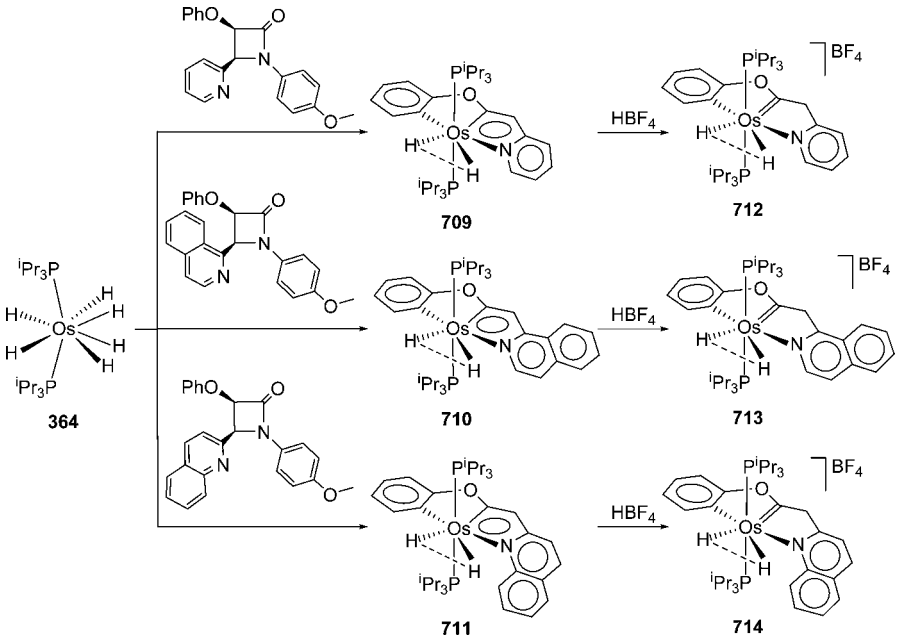
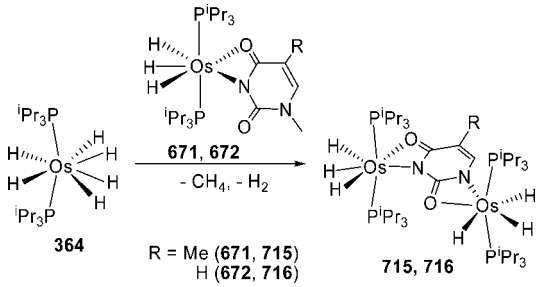
Scheme 119. Fomation of CCN-Pincer Complexes



with the nucleobase skeleton κ^2-N,O-coordinated to both metal fragments (Scheme 120).[344]

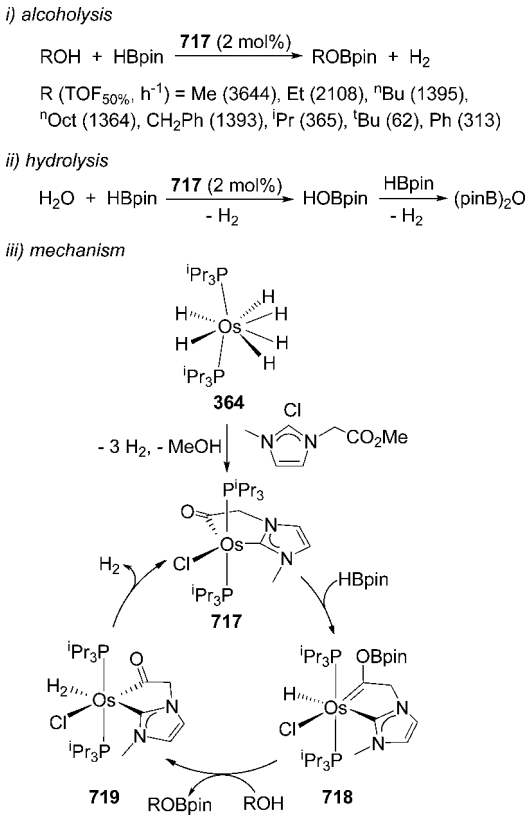
Scheme 120. Cleavage of the N−Me Bond of 1-Methyl-Thyminate and 1-Methyluracilate



Catalysts based on cooperative ligands are having great relevance in reactions associated with conversion and storage of regenerative energy. These ligands cooperate with the metal center by participating directly in the σ-bond activation stage and by performing the reversible structural change in the process of product formation. A problem for the use of NHC ligands in metal−ligand cooperating catalysis is to keep the cooperation capacity between the Lewis base tethered to the imidazole moiety and the metal center, after the carbene coordination. Hexahydride **364** activates the C−OMe bond of 1-(2-methoxy-2-oxoethyl)-3-methylimidazolium chloride, in addition to promoting the direct metalation of the imidazolium group, to afford the five coordinate complex $OsCl\{C(O)CH_2Im\}(P^iPr_3)_2$ (**717**), which is a metal ligand cooperating catalyst for the generation of molecular hydrogen by means of both the alcoholysis and the hydrolysis of HBpin (Scheme 121), via intermediates $OsHCl\{C(OBpin)CH_2Im\}(P^iPr_3)_2$ (**718**) and $OsCl\{C(O)CH_2Im\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**719**).[351]

Hexahydride **364** activates *ortho*-CF bonds of aromatic ketones, in addition to *ortho*-CH bonds (Scheme 122). Thus, the reactions of this polyhydride with pentafluoroacetophenone, decafluorobenzophenone, and 2,6-difluoroacetophenone

Scheme 121. C−OMe Bond Activation of 1-(2-Methoxy-2-oxoethyl)-3-methylimidazolium Promoted by 364: Formation of 717 and its Catalytic Properties



give HF and the trihydride derivatives $OsH_3\{\kappa^2\text{-}O,C\text{-}[OC(R)C_6F_4]\}(P^iPr_3)_2$ (R = Me (**720**), C_6F_5 (**721**)) and $OsH_3\{\kappa^2\text{-}O,C\text{-}[OC(Me)C_6H_3F]\}(P^iPr_3)_2$ (**722**), respectively. Complexes **720** and **722** are also obtained from the reactions of **364** with 2,3,4,5-tetrafluoroacetophenone and 2-fluoroacetophenone, respectively, indicating that for ketones with only one aromatic

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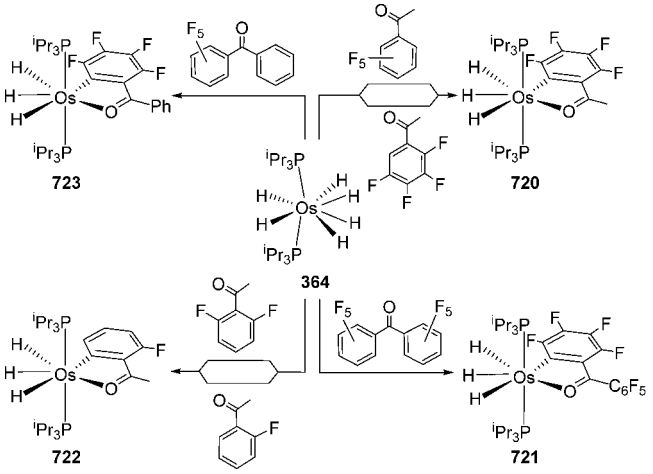
Scheme 122. Reactions of 364 with Fluorinated Aromatic Ketones: *ortho*-CF Cleavage versus *ortho*-CH Bond Activation



ring, the *ortho*-CH bond activation is preferred over the *ortho*-CF bond activation. However, the *ortho*-CF activation is preferred over the *ortho*-CH bond activation for 2,3,4,5,6-pentafluorobenzophenone. The reaction of **364** with this ketone leads to $OsH_3\{\kappa^2\text{-}O,C\text{-}[OC(C_6H_5)C_6F_4]\}(P^iPr_3)_2$ (**723**). DFT calculations suggest that the hexahydride promoted C−F bond activation of aromatic ketones is thermodynamically favored over the C−H bond activation, due to the formation of HF. So, the preferred C−H activation of 2-fluoroacetophenone and 2,3,4,5-tetrafluoroacetophenone appears to have kinetic origin, which has been related with the preferred anti arrangement of the F−C−C−C═O unit of the starting ketones.[312]

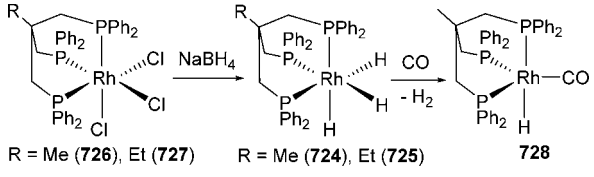
4. RHODIUM

Rhodium hydride complexes have acquired great importance in homogeneous catalysis because of their hydrogenating properties. However, rhodium polyhydrides are rare as a consequence of the oxidizing character of this metal, which prevents high oxidation states. Thus, the majority of them show nonclassical interactions between the hydrogen atoms coordinated to the metal center and play a relevant role in processes associated with the storage of molecular hydrogen.

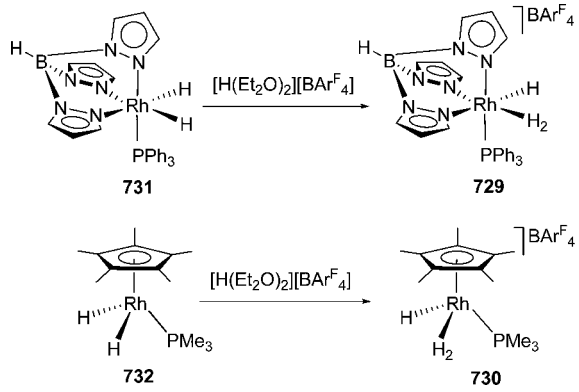
Classical trihydride complexes $RhH_3(triphos^R)$ ($triphos^R$ = $MeC(CH_2PPh_2)_3$) (**724**) and ($EtC(CH_2PPh_2)_3$) (**725**)) have been prepared by replacement of chloride by hydride from $RhCl_3(triphos^R)$ (R = Me (**726**), Et (**727**)). In agreement with the trend of rhodium(III) to undergo reduction, complex **724** reacts with CO to give the carbonyl derivative $RhH(CO)(triphos^{Me})$ (**728** in Scheme 123).[352]

In contrast to **724** and **725**, the Tp- and Cp*-complexes $[RhHTp(\eta^2\text{-}H_2)(PPh_3)][BAr^F{}_4]$ (**729**)[353] and $[RhH(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}H_2)(PMe_3)][BAr^F{}_4]$ (**730**)[354] are hydride-dihydrogen derivatives. In both compounds the separation between the hydrogen atoms of the coordinated hydrogen molecule is about 0.9 Å, whereas the barrier ($\Delta G^{\ddagger}$) for the exchange of hydride with dihydrogen sites is less than ca. 5 kcal mol^{-1}. The Tp complex **729**, which is stable in solution up to 250 K, is generated by addition of 1 equiv of $[H(Et_2O)_2][BAr^F{}_4]$ to dichloromethane solutions of the dihydride $RhH_2Tp(PPh_3)$ (**731**). The protonation of the Cp*-dihydride $RhH_2(\eta^5\text{-}C_5Me_5)(PMe_3)$ (**732**) gives **730** (Scheme 124), with

Scheme 123. Rhodium Complexes Containing Tripodal Phosphine Ligands



Scheme 124. Hydride-Dihydrogen−Rhodium(III) Complexes with Tris(pyrazolyl)borate and Pentamethylcyclopentadienyl Ligands



concomitant formation of the side dimer $[\{RhH(\eta^5\text{-}C_5Me_5)(PMe_3)\}_2(\mu\text{-}H)][BAr^F{}_4]$ (**733**). A free energy of activation of 9.1 kcal mol^{-1} was measured for the exchange of terminal and bridging hydrides in this complex.

Rhodium complexes with four coordinated hydrogen atoms are dihydride-dihydrogen species. The protonation of the classical trihydride **724** at 210 K gives $[RhH_2(triphos^{Me})(\eta^2\text{-}H_2)]^+$ (**734**; $d_{H2} \approx 0.9$ Å), which is thermally unstable. Above 240 K, it dissociates the coordinated hydrogen molecule. The resulting dihydride is trapped by coordinating solvents, such as THF, to afford the solvento complex $[RhH_2(triphos^{Me})(THF)]^+$ (**735**). In dichloromethane, the dimerization of the unsaturated dihydride leads to $[\{RhH(triphos^{Me})\}(\mu\text{-}H)_2]^{2+}$ (**736**), as a mixture of cis and trans isomers that are transformed into the corresponding bridging chloride dimers $[\{RhH(triphos^{Me})\}(\mu\text{-}Cl)_2]^{2+}$ (**737**) at room temperature (Scheme 125).[355] The Tp^{Me2}-derivative $RhH_2Tp^{Me2}(\eta^2\text{-}H_2)$ (**738**) is, however, stable in the solid state.[356,357] DFT calculations have confirmed the dihydride-dihydrogen structure, which presents a near octahedral arrangement of the ligands around the metal center.[358] The barrier for the rotation of the dihydrogen ligand and the separation between the hydrogen atoms, calculated from data of inelastic neutron scattering spectroscopy, are 0.56(2) kcal mol^{-1} and 0.94 Å, respectively.[359]

The salt $[Rh\{Ph_2P(CH_2)_2PPh_2\}\{PCyp_2(\eta^2\text{-}C_5H_7)\}][BAr^F{}_4]$ (**739**), which is quantitatively formed by reaction of $NaBAr^F{}_4$ with $RhCl\{Ph_2P(CH_2)_2PPh_2\}(PCyp_3)$ (**740**), is easily hydrogenated under 1 atm of H_2 to give the dihydride-dihydrogen complex $[RhH_2(\eta^2\text{-}H_2)\{Ph_2P(CH_2)_2PPh_2\}(PCyp_3)][BAr^F{}_4]$ (**741**; $d_{H2} \approx 0.9$ Å), according to Scheme 126.[360]

The hydrogenation of the Osborn-type complexes $[Rh(\eta^4\text{-}NBD)(PR_3)_2][BAr^F{}_4]$ (PR_3 = PCy_3 (**742**), P^iPr_3 (**743**), $PCyp_3$ (**744**)), under 4 atm of H_2, at 298 K affords the dihydride-

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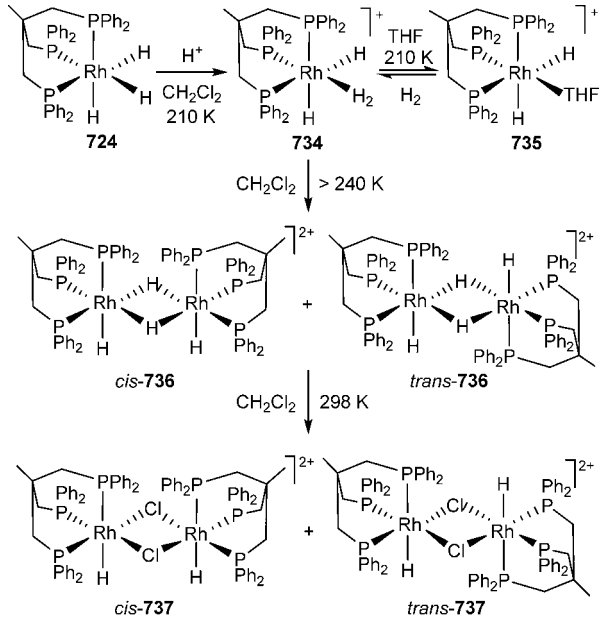
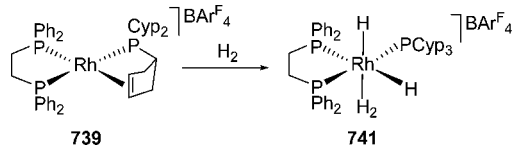
Scheme 125. Formation and Reactions of the Dihydride-Dihydrogen-Rhodium(III) Cation 734

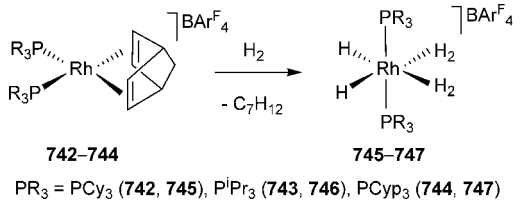


Scheme 126. Formation of the Dihydride-Dihydrogen-Rhodium(III) Cation 741



bis(dihydrogen) derivatives $[RhH_2(\eta^2\text{-}H_2)_2(PR_3)_2][BAr^F_4]$ (PR_3 = PCy_3 (**745**), P^iPr_3 (**746**),[361] $PCyp_3$ (**747**)[360]). DFT calculations support the d^6-dihydride-bis(dihydrogen) formulation, with *cis*-hydride ligands and H−H distances between the hydrogen atoms of the dihydrogen ligands of about 0.8 Å (Scheme 127). At room temperature, complexes **745** and **746**

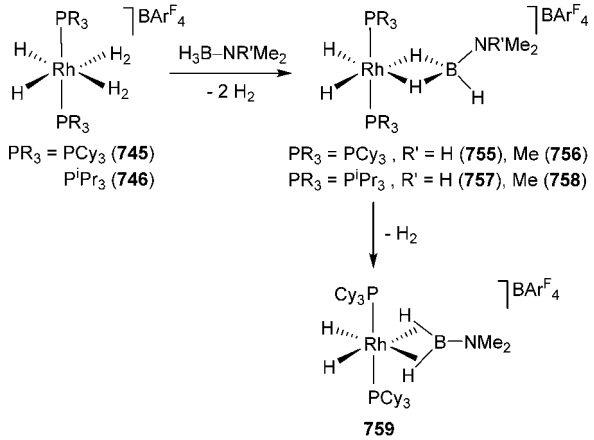
Scheme 127. Formation of Dihydride-bis(Dihydrogen)-Rhodium(III) Complexes



lose $[HPR_3][BAr^F_4]$ and H_2 to give the dicationic cluster compounds $[Rh_6(PR_3)_6(\mu\text{-}H)_{12}][BAr^F_4]_2$ (PR_3 = PCy_3 (**748**), P^iPr_3 (**749**)), in moderate yields. The 12 hydride ligands bridge each Rh−Rh edge of a regular octahedron. Both clusters reversibly take up two molecules of hydrogen to generate $[Rh_6(PR_3)_6H_{16}][BAr^F_4]_2$ (PR_3 = PCy_3 (**750**), P^iPr_3 (**751**)), with 16 hydrogen atoms surrounding the metal core. The uptake of H_2 is a consequence of two low-lying unoccupied molecular orbitals that readily accept two electron pairs.[362] The hydrogenation of **743** in the presence of $[Rh(\eta^4\text{-NBD})_2][BAr^F_4]$ (**752**) leads to an inseparable mixture of $[Rh_7(P^iPr_3)_6H_{18}][BAr^F_4]_2$ (**753**) and $[Rh_8(P^iPr_3)_6H_{16}][BAr^F_4]_2$ (**754**).[363]

The dihydrogen ligands of the dihydride-bis(dihydrogen) complexes **745** and **746** can be displaced by amine-boranes to give the dihydride-(amine-borane) derivatives $[RhH_2(\kappa^2\text{-}H_2BHNR'Me_2)(PR_3)_2][BAr^F_4]$ (PR_3 = PCy_3, R′ = H (**755**), Me (**756**); PR_3 = P^iPr_3, R′ = H (**757**), Me (**758**)), which can also be obtained by oxidative addition of H_2 to the corresponding bis(phosphine)-rhodium(I)-(amine-borane) precursors. In 1,2-difluorobenzene, these compounds undergo three H/H exchange processes with activation barriers increasing in the sequence B−H bridging/terminal < Rh−H/external H_2 < Rh−H/B−H.[364] Furthermore, they are only moderately stable. In agreement with this, it has been observed that the amine-borane ligand of **755** slowly loses H_2 to afford the aminoborane derivative $[RhH_2(\eta^2,\eta^2\text{-}H_2BNMe_2)(PCy_3)_2][BAr^F_4]$ (**759** in Scheme 128).[365] Related (amine-borane)- and

Scheme 128. Reactions of 745 and 746 with Amine-Boranes



(aminoborane)-rhodium(III) complexes containing NHC ligands instead of PR_3 groups have been prepared from the unsaturated $RhH_2Cl(IMes)_2$ starting material in the presence of $Na[BAr^F_4]$.[366,367]

These types of compounds have been proposed as relevant intermediates in the rhodium-promoted kinetically controlled dehydrocoupling of ammonia-borane and secondary amine-boranes.[368−371] The mechanism appears to be very dependent on the substrate. Lloyd-Jones, Weller, and co-workers have recently shown a remarkable diversity in mechanisms. Their study suggests a number of key processes, including dehydrogenation by catalytic cycles that can involve a change in oxidation state at rhodium or have a constant oxidation state; autocatalysis; parallel catalysis; B−N bond cleavage; and dehydrocyclization.[365]

5. IRIDIUM

5.1. Phosphine Complexes

Phosphine ligands stabilize a wide range of polyhydrides, which include complexes with three, four, five, and six hydrogen atoms directly bound to the metal center.

The five-coordinate iridium(III) complexes $IrHX_2(PR_3)_2$ (X = Cl, PR_3 = P^iPr_3 (**760**), PCy_3 (**761**), P^tBu_2Ph (**762**); X = Br, PR_3 = P^iPr_3 (**763**)) rapidly react with H_2 to set up an equilibrium with *trans*-$IrHX_2(\eta^2\text{-}H_2)(PR_3)_2$ (X = Cl, PR_3 = P^iPr_3 (**764a**), PCy_3 (**765a**), P^tBu_2Ph (**766a**); X = Br, PR_3 = P^iPr_3 (**767a**)) where the elongated dihydrogen ligand binds

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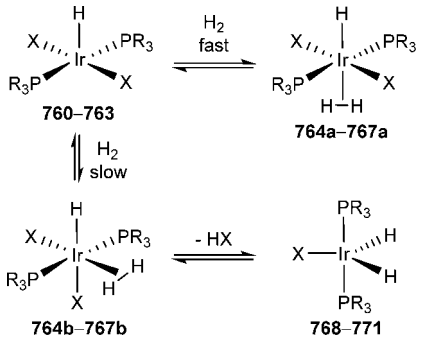
trans to the original hydride. A second slower reaction forms the corresponding cis-isomers **764b–767b**, where the cis disposition of the halides, and also H cis to H_2, has been demonstrated by means of the neutron diffraction structure of **764b**. Interestingly, the iridium–hydride bond length of 1.584(3) Å is not significantly different from the separation of the iridium atom to the hydrogen atoms of the elongated dihydrogen (1.537(19) and 1.550(17) Å), indicating a strong binding of the latter. Consistently with this conclusion, the H–H distance within the dihydrogen is long, 1.11(3) Å. In contrast to the *trans* isomers, the *cis*-isomers show rapid site exchange between coordinated hydride and elongated dihydrogen. The *cis*-isomers can also be induced to lose HX to form the corresponding unsaturated iridium(III)-dihydride derivatives $IrH_2X(PR_3)_2$ (X = Cl, PR_3 = P^iPr_3 (**768**), PCy_3 (**769**), P^tBu_2Ph (**770**); X = Br, PR_3 = P^iPr_3 (**771**) in Scheme 129).[372−374]

Scheme 129. Formation of $IrHX_2(\eta^2\text{-}H_2)(PR_3)_2$ Complexes



X = Cl; PR_3 = P^iPr_3 (**760**, **764**, **768**), PCy_3 (**761**, **765**, **769**), P^tBu_2Ph (**762**, **766**, **770**)

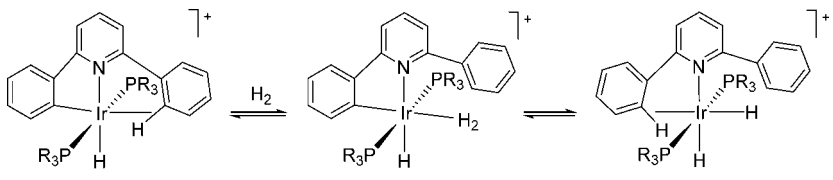
X = Br; PR_3 = P^iPr_3 (**763**, **767**, **771**)

The formation of **768–771** can be rationalized as an inner-sphere process of heterolytic H–H bond activation. The outer sphere heterolytic activation of the coordinated hydrogen molecule, promoted by an external base at a cooperating ligand, has also been described (Scheme 130).[375] Molecular hydrogen rapidly and reversibly displaces the Ir–H–C agostic interaction between the metal center and an *ortho*-CH bond of the phenyl substituent of the orthometalated 2,6-diphenylpyridine in $[IrH\{\kappa^2\text{-}N,C\text{-}(Ph\text{-}py\text{-}C_6H_4)\}(PR_3)_2]SbF_6$ (PR_3 = PPh_2Me (**772**), P^nBu_3 (**773**)) and the water molecule of $[IrH(bq)(H_2O)(PR_3)_2]SbF_6$ (PR_3 = PPh_3 (**774**), PCy_3 (**775**)) and $[IrH(bq\text{-}NH_2)(H_2O)(PR_3)_2]BF_4$ (bq-NH_2 = 2-amino-7,8-benzoquinolinate; PR_3 = PPh_3 (**776**), PCy_3 (**777**)) to give the *cis*-hydride-dihydrogen derivatives $[IrH\{\kappa^2\text{-}N,C\text{-}(Ph\text{-}py\text{-}C_6H_4)\}(\eta^2\text{-}H_2)(PR_3)_2]SbF_6$ (PR_3 = PPh_2Me (**778**), P^nBu_3 (**779**)),[376] $[IrH(bq)(\eta^2\text{-}H_2)(PR_3)_2]SbF_6$ (PR_3 = PPh_3 (**780**), PCy_3 (**781**)),[377] and $[IrH(bq\text{-}NH_2)(\eta^2\text{-}H_2)(PR_3)_2]BF_4$ (PR_3 = PPh_3 (**782**), PCy_3 (**783**)),[378] respectively, with a H–H distance between the hydrogen atoms of the dihydrogen ligand of about 0.9 Å. At 0 °C, complexes **778** and **779** reach an equilibrium with the hydrogenolysis dihydride products $[IrH_2(pyPh_2)(PR_3)_2]SbF_6$ (PR_3 = PPh_2Me (**784**), P^nBu_3 (**785**)) through a typical inner-sphere process. On the other hand, a free pendant 2-amino group at the benzoquinolinate ligand bound to the Ir(III) center promotes the heterolytic rupture of the coordinated hydrogen molecule. Thus, complexes **782** and **783** evolve into $[IrH_2(bq\text{-}NH_3)(PR_3)_2]BF_4$ (PR_3 = PPh_3 (**786**), PCy_3 (**787**)).

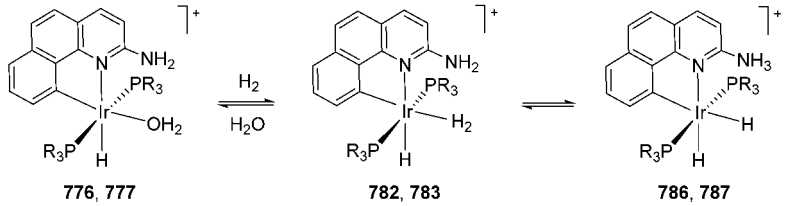
Intermolecular heterolytic H–H bond activation promoted by external N-heterocycles plays a main role in the hydrogenation of these substrates via a stepwise outer-sphere mechanism involving sequential proton and hydride transfers. The iridium(I) complex $[Ir(\eta^4\text{-}COD)(1,3\text{-dimethylbenzimidazol-2-ylidene})(PPh_3)]PF_6$ (**788**) reacts with molecular hydrogen in the presence of 1 equiv of PPh_3 and 1 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to give the neutral meridional trihydride $IrH_3(1,3\text{-dimethylbenzimidazol-2-ylidene})(PPh_3)_2$ (**789**) and $[HDBU]PF_6$. The addition of 1 equiv of a strong acid to this compound affords the dihydride-dihydrogen derivative $[IrH_2(\eta^2\text{-}H_2)(1,3\text{-dimethylbenzimidazol-2-ylidene})(PPh_3)_2]^+$ (**790**; $d_{H2} \approx 0.9$ Å). Complex **790** readily converts to the unsaturated dihydride $[IrH_2(1,3\text{-dimethylbenzimidazol-2-ylidene})(PPh_3)_2]^+$ (**791**) on applying a vacuum. The reaction is reversible under 1 atm of H_2. Complex **791** can be directly formed from the reaction of **788** with PPh_3 and H_2, without the need for any base (Scheme 131).

Complexes **789–791** have been proposed as active intermediates in the hydrogenation of quinolines to the corresponding 1,2,3,4-tetrahydroquinolines, under mild conditions, catalyzed by the precursor **788**.[379] The cationic

Scheme 130. Heterolytic Activation of Hydrogen via Hydride-Dihydrogen-Iridium(III) Cations



PR_3 = PPh_2Me (**772**, **778**, **784**), P^nBu_3 (**773**, **779**, **785**)



PR_3 = PPh_3 (**776**, **782**, **786**), PCy_3 (**777**, **783**, **787**)

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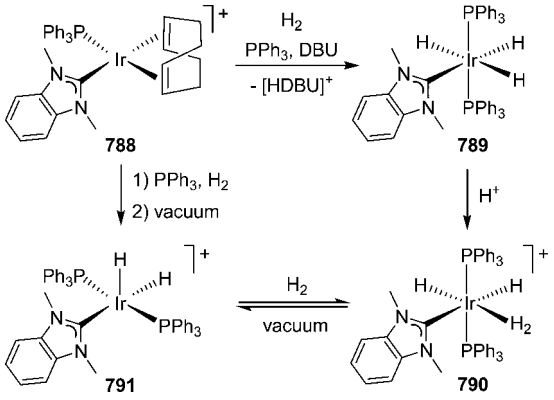
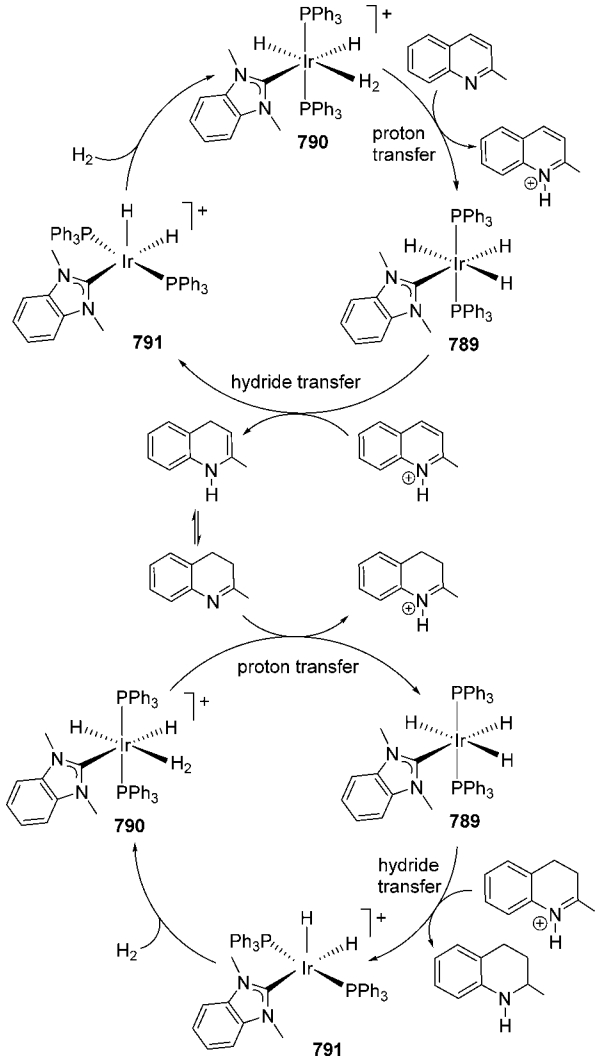
Scheme 131. Intermolecular Heterolytic H−H Bond Activation Promoted by DBU: Formation of 789−791



dihydride-dihydrogen complex **790** first transfers a proton to the substrate, resulting in the neutral trihydride **789** and a protonated substrate. Hydride transfer to the protonated substrate in a later step results in the formation of the unsaturated dihydride **791**, which then coordinates H_2 and completes the catalytic cycle (Scheme 132). The related tris(phosphine) derivative $[IrH_2(\eta^2\text{-}H_2)(PMe_2Ph)_3]^+$ (**792**; T_1(min) = 20 ms (360 MHz)) has been shown to be an efficient catalyst precursor for the hydrogenation of ethylene and butyne via the unsaturated dihydride $[IrH_2(PMe_2Ph)_3]^+$ (**793**).[380−383]

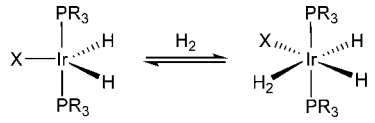
The behavior of the five-coordinate dihydride complexes $IrH_2X(PR_3)_2$ (**768−771**; X = Cl, $PR_3 = P^tBu_3$ (**794**), P^tBu_2Me (**795**); X = I, $PR_3 = P^iPr_3$ (**796**)) under hydrogen atmosphere is reminiscent of that of their monohydride counterparts (Scheme 133). Thus, the metal center coordinates the hydrogen molecule to establish an equilibrium with the corresponding dihydride-dihydrogen derivatives $IrH_2X(\eta^2\text{-}H_2)(PR_3)_2$ (X = Cl, $PR_3 = P^iPr_3$ (**797**), PCy_3 (**798**), P^tBu_2Ph (**799**), P^tBu_3 (**800**), P^tBu_2Me (**801**); X = Br, $PR_3 = P^iPr_3$ (**802**); X = I, $PR_3 = P^iPr_3$ (**803**)), which undergo a rapid hydride-dihydrogen site exchange. The activation energy of this intramolecular process is similar to the barrier for the rotation motion of the dihydrogen ligand, suggesting that both fenomena are coupled to some extent.[384−391] The dihydrogen ligand lies trans to a hydride in the ground state. This is corroborated by the neutron diffraction structure of the iodide complex **803**.[392] Although the dihydrogen ligand is situated cis to the other hydride, as in the hydride-dihydrogen **764b**, a *cis*-hydride stabilization is not observed in this case. Thus, in contrast to **764b**, the iridium−hydride bond lengths of 1.579(6) and 1.589(6) Å are significantly shorter than the iridium−dihydrogen distances of 1.764(7) and 1.748(7) Å. This verifies a weaker iridium−dihydrogen interaction, which is evident in the short H−H separation of 0.856(9) Å. The thermodynamic stability of these dihydrogen complexes depends upon the halide, decreasing in the sequence I > Br > Cl.[387] The ordering of halides is reversed in the five (**768−771** and **794−796**) and the six-coordinate (**797−803**) sides and correlates with the fact that the X-ligand lone pairs do not simply stabilize the H_2-loss transition state, but they destabilize the H_2-adduct ground state, by filled/filled repulsions with the filled d_π-iridium orbitals.[389] In addition to dissociation, the dihydrogen ligand of these compounds is activated toward heterolytic cleavage, releasing HX. Complex **797** uses this

Scheme 132. Proposed Mechanism for the Hydrogenation of Quinolines through 789−791[a]



[a]Adpated from ref 379. Copyright 2011 American Chemical Society.

Scheme 133. Formation of $IrH_2X(\eta^2\text{-}H_2)(PR_3)_2$ Complexes



768−771, 794−796 **797−803**

X = Cl, $PR_3 = P^iPr_3$ (**768**, **797**), PCy_3 (**769**, **798**), P^tBu_2Ph (**770**, **799**), P^tBu_3 (**794**, **800**), P^tBu_2Me (**795**, **801**)

X = Br, $PR_3 = P^iPr_3$ (**771**, **802**)

X = I, $PR_3 = P^iPr_3$ (**796**, **803**)

property to catalyze the hydrogenation of benzylideneacetone via the unsaturated trihydride $IrH_3(P^iPr_3)_2$.[393]

The five-coordinate monohydrides **760** and **762** and the dihydrides **768**, **770**, **794**, and **795**, containing bulky phosphines, react with $NaBH_4$ to give the dihydride-tetrahydrideborate derivatives $IrH_2(\kappa^2\text{-}H_2BH_2)(PR_3)_2$ ($PR_3 = P^iPr_3$ (**804**), P^tBu_2Ph (**805**), P^tBu_3 (**806**), P^tBu_2Me (**807**)).[394,395] These compounds are stable in aprotic solvents but rapidly decompose on heating in alcohols to give the

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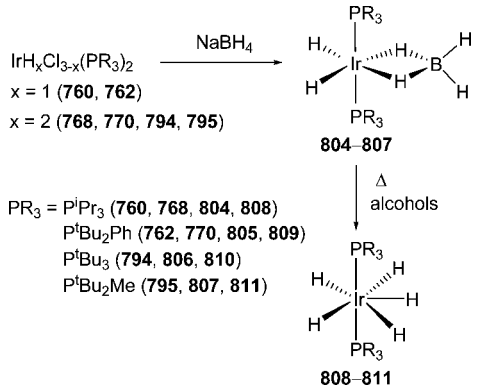
pentahydride derivatives $IrH_5(PR_3)_2$ (PR_3 = P^iPr_3 (**808**), P^tBu_2Ph (**809**), P^tBu_3 (**810**), P^tBu_2Me (**811**)) according to Scheme 134. Several alternative methods have been developed

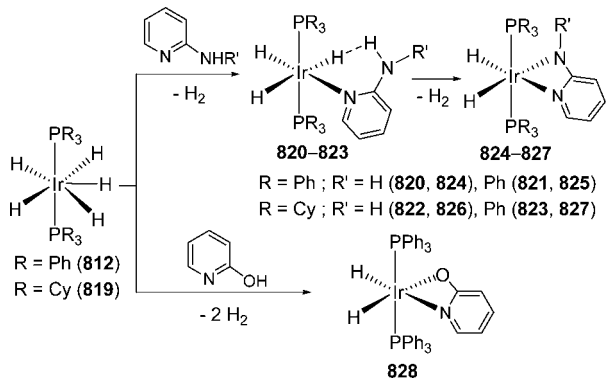
Scheme 134. Preparation of $IrH_5(PR_3)_2$



to obtain different members of this family,[98,396] in particular those containing phosphines of small cone angle. Thus, complexes $IrH_5(PR'_3)_2$ (PR'_3 = PPh_3 (**812**), $P(p\text{-}F\text{-}C_6H_4)_3$ (**813**), PPh_2Me (**814**), $PPhMe_2$ (**815**), PMe_3 (**816**), PEt_3 (**817**), PEt_2Ph (**818**)) can be prepared by reaction of the corresponding square-planar precursors $[Ir(\eta^4\text{-}COD)(PR'_3)_2]^+$ with H_2 in the presence of a base. Complex $IrH_5(PCy_3)_2$ (**819**) has been similarly synthesized starting from $[Ir(\eta^4\text{-}COD)(py)(PCy_3)]^+$ and PCy_3.[397] The neutron diffraction structure of **808** has revealed that the core of these molecules is a pentagonal bipyramid with five equatorial hydrogen atoms. The average Ir−H distance of 1.603(9) Å and the average H−H separation of 1.87(1) Å prove the classical character of these polyhydrides.[398] Distinctive features of these complexes include their ability to serve as hydrogen reservoirs and the accessibility of vacant coordination sites in unsaturated trihydrides, which are trapped with neutral Lewis bases to form saturated $IrH_3L(PR_3)_2$ species.[399,400] These properties make such complexes particularly effective as catalysts for the hydrogenation of organic substrates[396] as well as for transfer hydrogenation reactions.[401,402]

The pentahydride complexes promote the chelated-assisted heteroatom−H bond activation to yield dihydride derivatives (Scheme 135).[403−405] The reactions take place via trihydride intermediates, which show moderately strong intramolecular Ir−H···H−X hydrogen bonds.[406] Treatment of the pentahydrides **812** and **819** with 2-aminopyridines in benzene at 80 °C leads to the H-bonded derivatives $IrH_3(py\text{-}2\text{-}NHR')(PR_3)_2$ (PR_3 = PPh_3, R′ = H (**820**), Ph (**821**); PR_3 = PCy_3, R′ = H (**822**), Ph (**823**)). On warming, these species lose H_2 to form the chelate amido compounds $IrH_2\{\kappa^2\text{-}N,N\text{-}(py\text{-}2\text{-}NR')\}(PR_3)_2$ (PR_3 = PPh_3, R′ = H (**824**), Ph (**825**); PR_3 = PCy_3, R′ = H (**826**), Ph (**827**)). The reaction of **812** with 2-hydroxypyridine directly gives $IrH_2\{\kappa^2\text{-}N,O\text{-}(py\text{-}2\text{-}O)\}(PPh_3)_2$ (**828**).

Scheme 135. Reactions of Pentahydrides 812 and 819 with 2-Functionalized Pyridines



The pentahydride complexes are weak Brønsted acids, which can be deprotonated by superbases.[407,408] Thus, the treatment of **808**, **812**, and **819** with KH in THF in the presence of a slight excess of the appropriate crown ether or cryptand (Q) yields the tetrahydride compounds $[K(Q)][IrH_4(P^iPr_3)_2]$ (Q = 18-crown-6 (**829a**), 1-aza-18-crown-6 (**829b**), 1,10-diaza-18-crown-6 (**829c**), cryptand-2.2.2 (**829d**)), $[K(Q)][IrH_4(PPh_3)_2]$ (Q = 18-crown-6 (**830a**), 1,10-diaza-18-crown-6 (**830c**)), and $[K(Q)][IrH_4(PCy_3)_2]$ (Q = 18-crown-6 (**831a**), 1,10-diaza-18-crown-6 (**831c**), cryptand-2.2.2 (**831d**)), respectively. In THF solution, the stereochemistry of the anion of the salts is sensitive to the countercation: either *trans*-phosphines as the potassium cryptand-2.2.2 salts (**829d**, **831d**) or exclusively *cis*-phosphines as the crown- and azacrown-potassium salts (**830**, **831a,c**) or a mixture of cis and trans (**829a−829c**). The contribution of four factors appears to explain these facts: (i) potassium-hydride interactions in the ion pairs that favor the *cis* isomer, (ii) protonic-hydridic bonding that could contribute to a strengthening of the cation−anion interaction, (iii) the high trans influence of the hydride ligand that favors the cis arrangement, and (iv) the interligand repulsions in the anion, expected to increase with the Tolman cone angle of the phosphine and that can explain why the stereochemistry is trans in the absence of potassium-hydride interaction. The potassium-hydride interactions have been confirmed by the X-ray structures of the salts **829a**, **829b**, and **830a**, which show a cis-disposition of the phosphine ligands, whereas three facially arranged hydrides and the potassium atom form a tetrahedron. The salts **829c** and **830c** have been also characterized by X-ray diffraction analysis. The phosphine ligands are trans-disposed in the first of them, whereas they lie *cis* in the second one.

The pentahydride complexes also act as Brønsted bases.[377,409] Thus, they react with acids to afford dihydride-bis(dihydrogen) derivatives of formula $[IrH_2(\eta^2\text{-}H_2)_2(PR_3)_2]^+$, which are the species involved in the catalytic hydrogenation of unsaturated organic molecules promoted by the cationic iridium precursors $[Ir(\eta^4\text{-}COD)(PR_3)_2]^+$ in noncoordinating solvents.[410] The protonation is reversible, the treatment of these species with a base such as NEt_3 gives back the pentahydrides. In agreement with the weak binding of the dihydrogen ligand to the metal center, Lewis bases displace the hydrogen molecules.[377,409,411] The dihydride-bis(dihydrogen)-derivatives can also be prepared starting from the five-coordinate dihydrides $IrH_2X(PR_3)_2$ (**768−771** and **794−796**). For instance, abstraction of the chloride ligand of **770** by $Na[BAr^F{}_4]$ in fluorobenzene leads to the solvent−ligand-free cationic iridium(III) complex $[IrH_2(P^tBu_2Ph)_2][BAr^F{}_4]$ (**832**). Under 1 atm of hydrogen, this compound is in equilibrium with the mono- and bis-dihydrogen derivatives $[IrH_2(\eta^2\text{-}H_2)(P^tBu_2Ph)_2][BAr^F{}_4]$ (**833**) and $[IrH_2(\eta^2\text{-}H_2)_2(P^tBu_2Ph)_2][BAr^F{}_4]$ (**834**) (Scheme 136). The formation of the monodihydrogen **833** is favored by decreasing temperature.[412,413]

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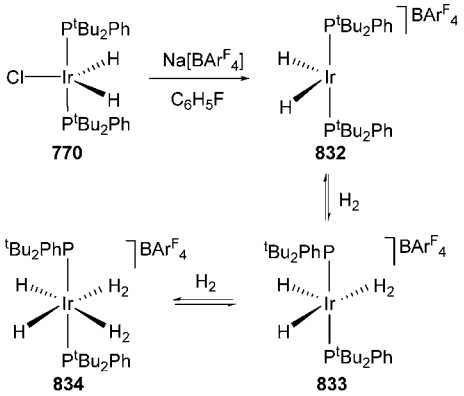
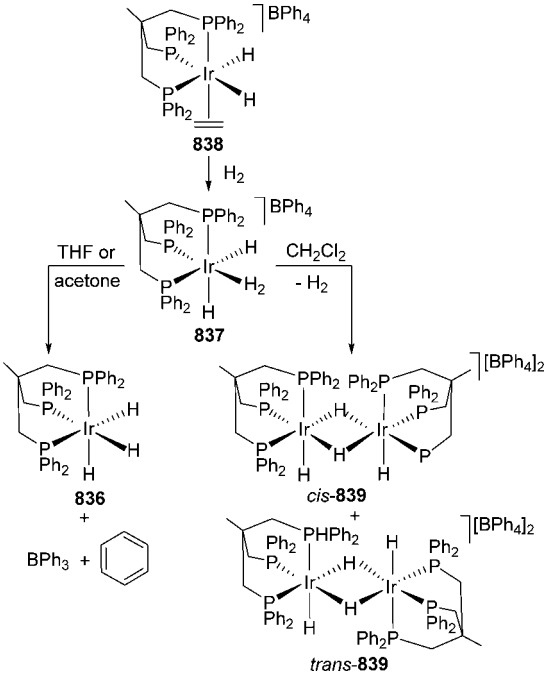
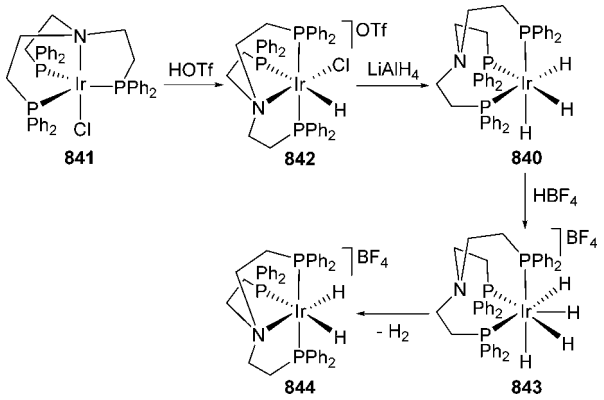
Scheme 136. Formation of the Dihydride-bis(Dihydrogen)-Iridium(III) Cation 834



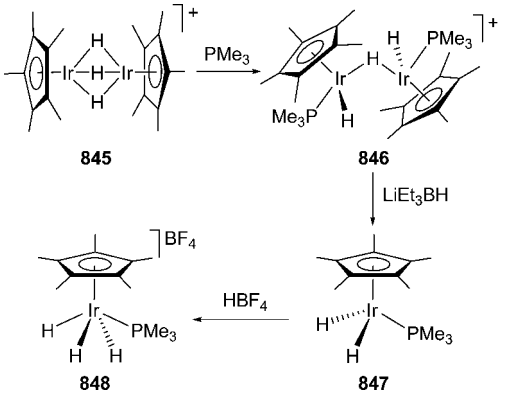
Scheme 137. Iridium-Polyhydrides Containing the Triphos^{Me} Ligand



Scheme 138. NP_3–Iridium Complexes



Scheme 139. Trimethylphosphine-Iridium-Pentamethylcyclopentadienyl Complexes



5.2. Complexes with Tripodal Phosphine Ligands

A few polyhydride–iridium complexes with the tripodal phosphines triphos^{Me} and NP_3 have been reported.

Treatment of tetrahydrofuran solutions of $IrCl_3$(triphos^{Me}) (**835**) with diethyl ether solutions of $LiAlH_4$ produces the replacement of the chloride ligands by hydrides to afford the trihydride IrH_3(triphos^{Me}) (**836**),[414] which yields the cation $[IrH_2(\eta^2\text{-}H_2)(\text{triphos}^{Me})]^+$ (**837**) by protonation. The $[BPh_4]$-salt of **837** has been prepared by hydrogenation of the coordinated ethylene molecule of the dihydride complex $[IrH_2(\eta^2\text{-}C_2H_4)(\text{triphos}^{Me})][BPh_4]$ (**838**) in either the solid state ($P_{H2} \geq 1$ atm) or dichloromethane ($P_{H2} \geq 3$ atm). The $[BPh_4]$-salt of **837** is unstable in solution; in dichloromethane, it loses H_2 converting to a mixture of the dimers *cis*- and *trans*-$[\{IrH(\text{triphos}^{Me})\}(\mu\text{-}H)_2][BPh_4]_2$ (**839**), whereas in tetrahydrofuran and acetone it evolves into **836**, BPh_3, and benzene. The last process involves the formal heterolytic splitting of H_2 with the concomitant protonolysis of the counteranion and formation of a metal–hydride bond (Scheme 137).[415−417]

The NP_3-counterpart of **836**, $IrH_3(\kappa^3\text{-}P,P,P\text{-}NP_3)$ (**840**), has been prepared according to Scheme 138, starting from the iridium(I) precursor $IrCl(\kappa^4\text{-}NP_3)$ (**841**) via the intermediate $[IrHCl(\kappa^4\text{-}NP_3)]^+$ (**842**). The protonation of **840** yields the expected cation $[IrH_4(\kappa^3\text{-}P,P,P\text{-}NP_3)]^+$ (**843**). However, in contrast to **837**, its structure is not clear. Discrimination between classical and nonclassical polyhydride cannot be made on the basis of DFT results of the naked cation, since both dihydride-dihydrogen and tetrahydride forms are located on an extremely low flat energy surface. On the other hand, in the presence of the $[(CF_3)_2CHO\cdots HOCH(CF_3)_2]^-$ counteranion, only the dihydride-dihydrogen isomer seems to be relatively stable. The final protonation product at room temperature is the dihydride $[IrH_2(\kappa^4\text{-}NP_3)]^+$ (**844**), resulting from the loss of a hydrogen molecule.[418]

5.3. Half Sandwich Compounds

The trihydride complex $[\{Ir(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}H)_3]PF_6$ (**845**) adds trimethylphosphine. The reaction leads to the monohydride-bridged dimer $[\{IrH(\eta^5\text{-}C_5Me_5)(PMe_3)\}_2(\mu\text{-}H)]PF_6$ (**846**). Reaction of this compound with $LiEt_3BH$ affords the mononuclear dihydride $IrH_2(\eta^5\text{-}C_5Me_5)(PMe_3)$ (**847**), which gives the trihydride $[IrH_3(\eta^5\text{-}C_5Me_5)(PMe_3)]BF_4$ (**848**) by protonation with $HBF_4\cdot OEt_2$ (Scheme 139).[419] Similarly, the protonation of the dihydrides $IrH_2(\eta^5\text{-}C_5Me_5)(PR_3)$ (PR_3 = P^iPr_3 (**849**), PCy_3 (**850**), PPh_3 (**851**), PPh_2Me (**852**)) and $IrH_2(\eta^5\text{-}C_5H_5)(ER_3)$ (ER_3 = PMe_3 (**853**), P^iPr_3 (**854**), PCy_3 (**855**), PPh_3 (**856**), $AsPh_3$ (**857**)) generates the corresponding trihydrides $[IrH_3(\eta^5\text{-}C_5Me_5)(PR_3)]BF_4$ (PR_3 = P^iPr_3 (**858**), PCy_3 (**859**), PPh_3 (**860**),[23] PPh_2Me (**861**)[420]) and $[IrH_3(\eta^5\text{-}$

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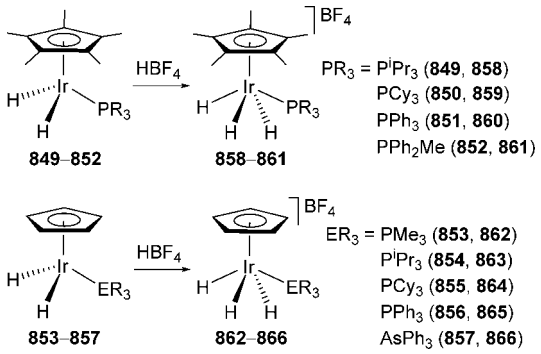
$C_5H_5)(ER_3)]BF_4$ (ER_3 = PMe_3 (**862**), P^iPr_3 (**863**), PCy_3 (**864**), PPh_3 (**865**), $AsPh_3$ (**866**)),[421] according to Scheme 140. The hydride ligands of these trihydride derivatives

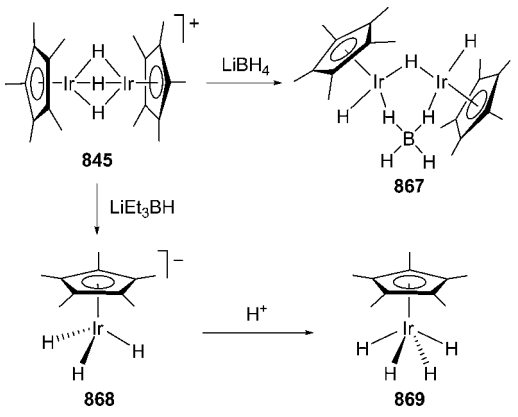
Scheme 140. $[IrH_3(\eta^5\text{-}C_5R_5)L]BF_4$ Complexes



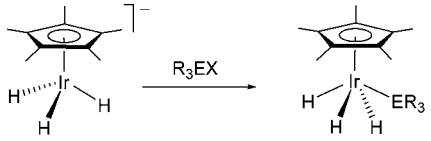
undergo thermally activated position exchange. The activation barriers for the rearrangement of the hydrides are higher for the Cp* complexes **848** and **858**–**860** than for the Cp derivatives **862**–**866**. Furthermore, they show quantum mechanical exchange coupling, which has been quantified according to eq 1. The values for a do not vary appreciably between the Cp* and Cp systems. However, the value of λ for the Cp* species (1.1 Å) is larger than for the Cp derivatives (0.9 Å), whereas the values of ν follow an opposite trend (i.e., they are smaller for the Cp* complexes than for the corresponding Cp counterparts). Thus, the variation in the magnitude of exchange coupling from **848** and **858**–**860** to **862**–**866** is apparently caused by differences in λ and ν, which are attributed to the differences in Cp* versus Cp.[23]

The cation of the salt **845** also adds the tetrahydrideborate anion. The addition gives the tetrahydrideborate-bonded dimer $[IrH(\eta^5\text{-}C_5Me_5)]_2(\mu\text{-}H)(\mu\text{-}H_2BH_2)$ (**867**). In contrast to $[BH_4]^-$, the reaction with the more nucleophilic reducing agent $LiEt_3BH$ leads to the anion $[IrH_3(\eta^5\text{-}C_5Me_5)]^-$ (**868**), which affords the neutral tetrahydride-iridium(V) derivative $IrH_4(\eta^5\text{-}C_5Me_5)$ (**869**), by hydrolysis or methanolysis (Scheme 141). Silyl- and stannylation of **868** occur with $Me_3SiO_3SCF_3$ and Me_3SnCl and Ph_3SnBr to form the complexes $IrH_3(\eta^5\text{-}C_5Me_5)(SiMe_3)$ (**870**), $IrH_3(\eta^5\text{-}C_5Me_5)(SnMe_3)$ (**871**), and $IrH_3(\eta^5\text{-}C_5Me_5)(SnPh_3)$ (**872**), respectively (Scheme 142).[422]

Scheme 141. Reactions of the Dimer 845: Iridium-Polyhydrides Stabilized by Pentamethylcyclopentadienyl



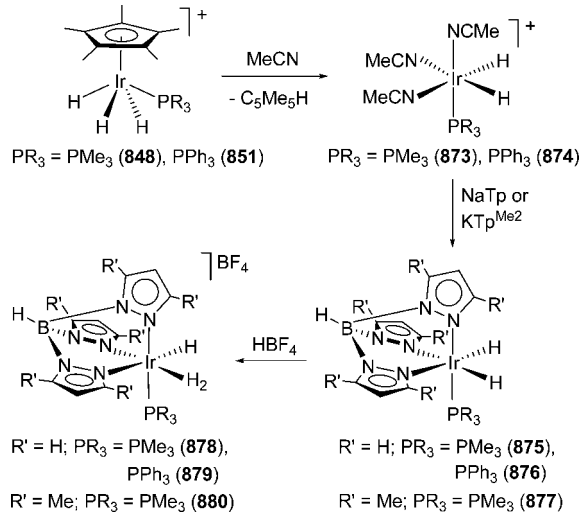
Scheme 142. Trihydride-Silyl and Trihydride-Stannyl-Iridium(V) Complexes



5.4. Complexes with Tris(pyrazolyl)borate and Related Ligands

The pentamethylcyclopentadienyl complexes **848** and **851** undergo reductive elimination of pentamethylcyclopentadiene in acetonitrile.[423] The reduction affords the tris(solvento) species $[IrH_2(CH_3CN)_3(PR_3)]^+$ (PR_3 = PMe_3 (**873**), PPh_3 (**874**)), which react with NaTp and KTp^{Me2} to give $IrH_2Tp(PR_3)$ (PR_3 = PMe_3 (**875**), PPh_3 (**876**)) and $IrH_2Tp^{Me2}(PMe_3)$ (**877**), respectively.[353] In contrast to their Cp* and Cp counterparts, the protonation of these dihydrides with $HBF_4{\cdot}OEt_2$ leads to the corresponding hydride-dihydrogen derivatives $[IrHTp(\eta^2\text{-}H_2)(PR_3)]BF_4$ (PR_3 = PMe_3 (**878**), PPh_3 (**879**)) and $[IrHTp^{Me2}(\eta^2\text{-}H_2)(PMe_3)]BF_4$ (**880**), in agreement with the high tendency of the Tp^R-ligands to stabilize nonclassical H–H interactions (Scheme 143). Partial

Scheme 143. Preparation of Iridium Complexes with Tp-Type Ligands



substitution of the IrH_3-positions with deuterium and tritium results in large temperature-dependent isotope shift, which is consistent with the preference of the heavy isotope to occupy the hydride site. The $J_{H\text{-}D}$ and T_1(min) values are consistent with a separation between the hydrogen atoms of the coordinated hydrogen molecule of about 1 Å.[353]

Tp^R-Counterparts of the tetrahydride **869** are also known. Complex IrH_4Tp^{Me2} (**881**) has been prepared in high yield by hydrogenation of $IrTp^{Me2}(\eta^2\text{-}C_2H_4)_2$ (**882**) under forcing conditions (C_6H_{12}, 90 °C, 2 atm, 3 days), whereas IrH_4Tp (**883**) has been obtained only in very low yield (10%) by a similar procedure starting from $IrTp(\eta^2\text{-}C_2H_4)_2$ (**884**).[424] On the basis of NMR spectroscopy, a ground-state C_{3v} structure in which a hydride ligand caps the face of the remaining hydrides has been proposed. However, DFT calculations suggest that

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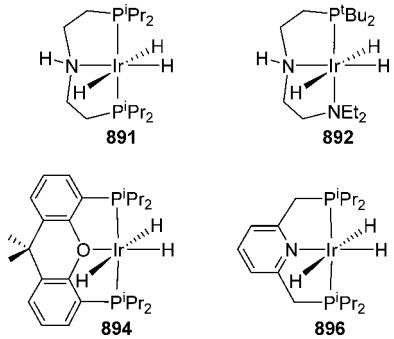
this structure is a local maximum, while a C_s edge-bridged octahedral structure (formally Ir(V)) and a C_1 dihydride-dihydrogen structure (formally Ir(III)) are local minima, nearly isoenergetic, which seem to coexist in a rapid equilibrium in solution.[425]

The hydrogenation of the cyclooctene ligand of the β-diiminate complex Ir(^{iPr}BDI)(η^2-COE)(N_2) (**885**, BDI = ArNC(Me)CHC(Me)CNAr, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$; COE = cyclooctene) under 4 atm of H_2 yields the related six-coordinate tetrahydride IrH_4(^{iPr}BDI) (**886**). X-ray diffraction and DFT studies have revealed a trigonal prismatic structure with close H···H contacts of about 1.25 and 1.30 Å.[426]

5.5. Complexes with Pincer Ligands

A few neutral trihydride compounds stabilized by pincer ligands have been isolated, characterized, and their catalytic potential investigated (Chart 12). Treatment of the dihydride PNP- and

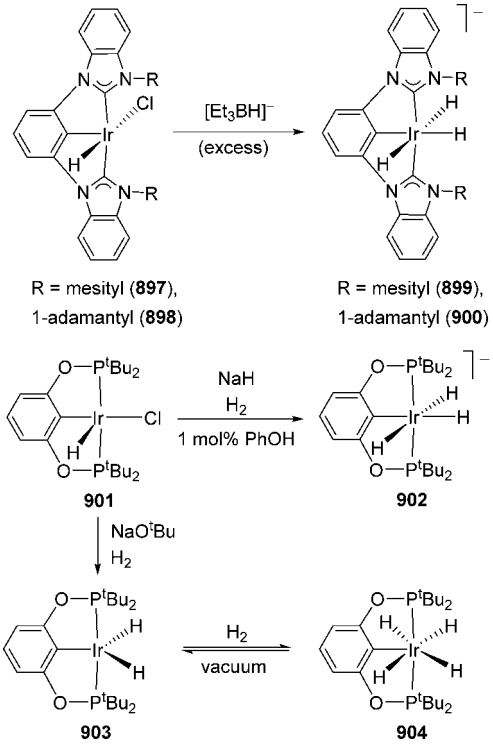
Chart 12. Neutral Trihydride Iridium(III) Compounds with Pincer Ligands



PNN-complexes $IrH_2Cl\{(^iPr_2PCH_2CH_2)_2NH\}$ (**887**) and $IrH_2Cl(^tBu_2PC_2H_4NHC_2H_4NEt_2)$ (**888**) with KO^{t}Bu produces the deprotonation of the amine and the abstraction of the chloride ligand from the metal center to afford the amidodihydride derivatives $IrH_2\{(^iPr_2PCH_2CH_2)_2N\}$ (**889**) and $IrH_2(^tBu_2PC_2H_4NC_2H_4NEt_2)$ (**890**), which give the trihydride derivatives $IrH_3\{(^iPr_2PCH_2CH_2)_2NH\}$ (**891**)[427] and $IrH_3(^tBu_2PC_2H_4NHC_2H_4NEt_2)$ (**892**),[428] respectively, by hydrogen transfer from 2-propanol, the first of them, and by hydrogenation with H_2, the second one. Stirring of IrHCl{xant(P^{i}Pr$_2$)[κ^2-*P*,*C*-^{i}PrPCH(Me)CH$_2$]} (**893**) in KOH solutions of 2-propanol leads to $IrH_3\{xant(P^iPr_2)_2\}$ (**894**).[429] The addition of an excess amount of NaH to THF solutions of IrH_2Cl(PpyP) (**895**, PpyP = 2,6-bis-(diisopropylphosphinomethyl)pyridine) yields IrH_3(PpyP) (**896**).[430] Complexes **891** and **892** are active catalysts for the hydrogen transfer from 2-propanol to ketones. Complex **891** is, furthermore, active for the reduction of ketones and aldehydes with H_2 in a wide range of solvents including dichloromethane and chloroform,[431] as well as for the hydrogenation of carboxylic acid esters.[432] Trihydride **896** catalyzes the hydrogenation of CO_2 to $HCOO^-$ in aqueous base.[430,433−438]

Anionic trihydride complexes stabilized by pincer ligands have been generated by addition of hydrides to unsaturated chloride-hydride species (Scheme 144). For instance, it has been observed that the treatment of the $C_{benzimidazolylidene}C_{aryl}C_{benzimidazolylidene}$ complexes $IrHCl(C^RCC^R)$ (R = mesityl (**897**), 1-adamantyl (**898**)) with an excess amount of $LiEt_3BH$ and $NaEt_3BH$, respectively, affords $[IrH_3(C^RCC^R)]^-$ (R = mesityl (**899**), 1-adamantyl (**900**)).[439]

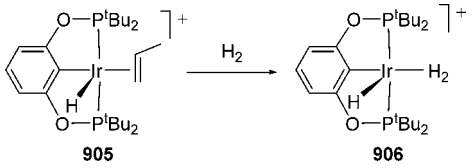
Scheme 144. Anionic Trihydride-Iridium(III) Complexes Stabilized by Pincer Ligands



The heterolytic cleavage of molecular hydrogen in the presence of a superbase is an alternative method. Thus, Brookhart and co-workers have reported that the treatment of $IrHCl\{C_6H_3$-2,6-$(OP^tBu_2)_2\}$ (**901**) with NaH or KH under an atmosphere of hydrogen in THF gives $[IrH_3\{C_6H_3$-2,6-$(OP^tBu_2)_2\}]^-$ (**902**). Addition of a catalytic amount of a mild Brønsted acid such as phenol or a Brønsted base such as NaO^{t}Bu greatly accelerates the reaction. On the other hand, the reaction of **901** with the stoichiometric amount of NaO^{t}Bu in aromatic solvents, under 1 atm of hydrogen, leads to the neutral dihydride $IrH_2\{C_6H_3$-2,6-$(OP^tBu_2)_2\}$ (**903**), which is in equilibrium with the tetrahydride $IrH_4\{C_6H_3$-2,6-$(OP^tBu_2)_2\}$ (**904**).[440]

The charge of the complexes certainly determines the nature of the IrH_3-unit. The hydrogenation of the propylene complex $[IrH\{C_6H_3$-2,6-$(OP^tBu_2)_2\}(\eta^2$-CH_2=CHMe)$][BAr^F{}_4]$ (**905**) in dichloromethane gives $[IrH\{C_6H_3$-2,6-$(OP^tBu_2)_2\}(\eta^2$-$H_2)]$-$[BAr^F{}_4]$ (**906**), which in contrast to **902** is a nonclassical hydride-dihydrogen species with a H−H separation between the hydrogen atoms of the dihydrogen ligand of about 0.9 Å (Scheme 145). This compound is quite stable in fluorobenzene, while slow decomposition occurs in chlorinated solvents.[441] Given the electron depletion of the metal center in these compounds, the dihydrogen ligand is activated toward its heterolytic cleavage. Thus, for instance, evidence for the key

Scheme 145. Preparation of 906



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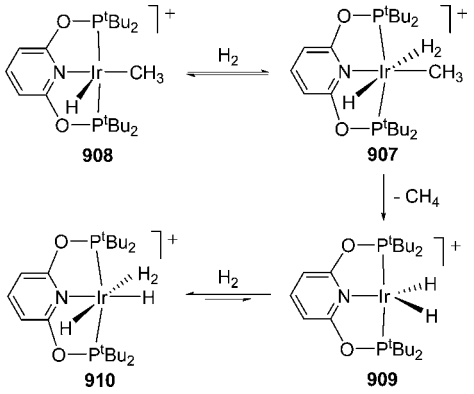
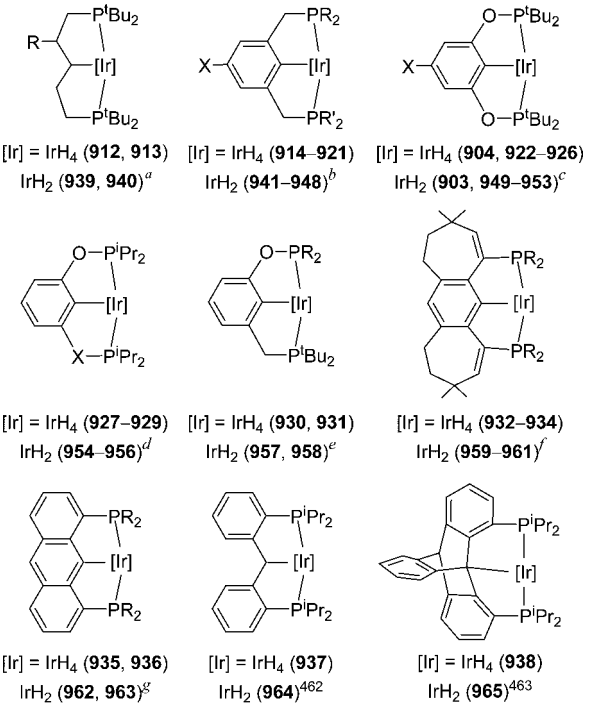
hydride-dihydrogen $[IrH(CH_3)(\eta^2\text{-}H_2)\{py\text{-}2,6\text{-}(OP^tBu_2)_2\}]^+$ (**907**) in the hydrogenolysis of the Ir−CH_3 bond of $[IrH(CH_3)\{py\text{-}2,6\text{-}(OP^tBu_2)_2\}]^+$ (**908**) has been obtained.[442] Deuterium-labeling experiments suggest the transformation of **907** into a σ-CH_4 complex prior to the release of methane. The loss of the alkane results in the formation of the dihydride $[IrH_2\{py\text{-}2,6\text{-}(OP^tBu_2)_2\}]^+$ (**909**), which under H_2 forms the dihydride-dihydrogen $[IrH_2(\eta^2\text{-}H_2)\{py\text{-}2,6\text{-}(OP^tBu_2)_2\}]^+$ (**910** in Scheme 146). The hydride-dihydrogen **907** has also been proposed as a key intermediate for the *trans*-addition of H_2 to $Ir(CH_3)\{py\text{-}2,6\text{-}(OP^tBu_2)_2\}$ (**911**) catalyzed by water or alcohols.[443]

Scheme 146. Formation of the Hydride-Dihydrogen 907 and the Dihydride-Dihydrogen 910



A significant number of neutral IrH_4-complexes containing anionic PCP-pincer ligands, related to **904**, are also known (Chart 13).[440,444−463] These IrH_4(PCP) (**904** and **912**−**938**) compounds have been generally prepared by reduction of the corresponding IrHCl(PCP) starting complexes under an atmosphere of hydrogen. The structure of **914** in the solid state has been determined by neutron diffraction analysis. The distribution of donor atoms around the metal center can be rationalized as a distorted pentagonal bipyramid with apical phosphorus atoms and the hydrides separated by more than 1.5 Å, in agreement with a compressed tetrahydride formulation. However, the J_{H-D} obtained from spectroscopic studies (22 ± 5 Hz) is consistent with at least a H−H distance of 1.06 ± 0.11 Å, which supports a dihydride-dihydrogen nature in solution. Similarly to **914**, complex **904** appears to have a dihydride-dihydrogen structure in solution with a H−H distance of 0.97 ± 0.09 Å, within the coordinated hydrogen molecule. Electronic structure calculations on both **904** and **914** indicate that global minima on the potential surfaces in the gas phase are tetrahydride structures. On the other hand, the dihydride-dihydrogen forms are only slightly higher in energy (1−3 kcal mol^{-1}) and the barriers to the interconversion between the tetrahydride and dihydride-dihydrogen species are almost negligible.[464] The 400 MHz T_1(min) values of 104 and 105 ms for **932** and **933**, respectively, suggest tetrahydride structures in solution. The solid state structure of **932**, determined by X-ray diffraction analysis, can be regarded as a dihydride-compressed dihydride ($d_{H\cdots H}$ = 1.50 Å).[460] These sometimes contradictory data have been explained by arguing that the IrH_4(PCP) complexes are not optimally characterized in terms of individual well-defined structures. Rather, extensive nuclear motions on exceptionally flat energy surfaces seem to offer the simplest and most appropriate description for these

Chart 13. IrH_4/IrH_2−Pairs Containing Anionic PCP-Pincer Ligands[a]



[a]R = H (**912**, **939**),[444,445] Me (**913**, **940**).[444] [b]X = H; R = R′ = ^{t}Bu (**914**, **941**),[446,447] ^{i}Pr (**915**, **942**),[447] 1-adamantyl (**916**, **943**).[448] X = H; PR_2 = P^tBu_2, PR'_2 = P^tBuMe (**917**, **944**),[449,450] PR_2 = PR'_2 = P^tBuMe (**918**, **945**).[450] X = C(O)OMe; R = R′ = ^{t}Bu (**919**, **946**).[451] X = OMe; R = R′ = ^{i}Pr (**920**, **947**),[452] R = R′ = ^{t}Bu (**921**, **948**).[451] [c]X = H (**904**, **903**), Me (**922**, **949**), OMe (**923**, **950**), F (**924**, **951**), C_6F_5 (**925**, **952**), 3,5-$(CF_3)_2C_6H_3$ (**926**, **953**).[440,453,454] [d]X = CH_2 (**927**, **954**),[455−457] O (**928**, **955**),[455] S (**929**, **956**).[458] [e]R = ^{t}Bu (**930**, **957**), ^{i}Pr (**931**, **958**).[459] [f]R = ^{i}Pr (**932**, **959**), Cy (**933**, **960**), Ph (**934**, **961**).[460] [g]R = ^{t}Bu (**935**, **962**),[455,461] ^{i}Pr (**936**, **963**).[455]

molecules.[464] This appears to be in agreement with the fact that complexes **904** and **912**−**938** lose H_2 under vacuum to afford the corresponding dihydrides IrH_2(PCP) (**903** and **939**−**965**). The process is reversible and, interestingly, increasing electron donation by the diphosphine disfavors the addition of H_2, in contradiction to the idea of such addition being oxidative.[451] IrH_4- and IrH_2-species catalyze the dehydrogenation of alkanes and related reactions. The use of IrH_4- species as catalyst precursors has never shown any significant difference from use of the corresponding dihydrides, other than requiring one additional mole of hydrogen acceptor in the case of transfer-dehydrogenation.[56]

A neutral IrH_4-compound containing an anionic CCC-pincer ligand has been also reported. This species, $IrH_2\{2,6\text{-}(CH_2NHC^{Mes})_2C_6H_3\}(\eta^2\text{-}H_2)$ (**966**, NHC^{Mes} = *N*-mesitylimidazol-2-ylidene), was described as a dihydride-dihydrogen on the basis of T_1(min), J_{H-D} analysis, and DFT calculations, although the data do not rule out the possibility of **966** existing as a mixture of Ir(III) and Ir(V) tautomers in solution. Complex **966** activates C−H bonds of arenes at room temperature, as demonstrated by isotope exchange reactions. However, under analogous conditions, no reaction was observed with alkanes.[465]

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5.6. Iridium-Polyhydride Complexes Involved in σ-Bond Activation Reactions

5.6.1. B−H Bond Activation. Several iridium polyhydride complexes have been employed to investigate the role of the metal center in the catalytic dehydrocoupling of amine-boranes, and some of them have been shown to play a main role in the kinetically controlled dehydrogenation of these substrates.

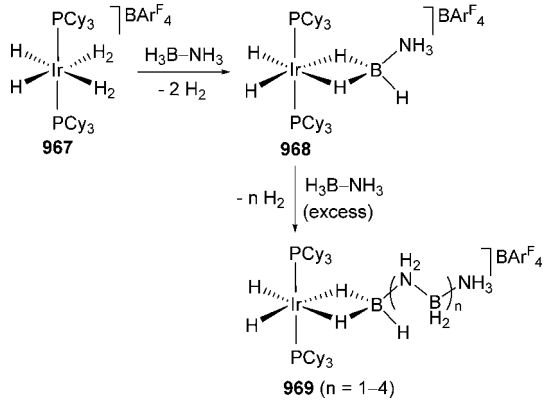
The dihydride-bis(dihydrogen) $[IrH_2(\eta^2\text{-}H_2)_2(PCy_3)_2][BAr^F{}_4]$ (**967**) has allowed the characterization of multiple metal-bound oligomers which are believed to participate in the on-metal dehydrocoupling of $H_3B{-}NH_3$. The coordinated hydrogen molecules of this compound are displaced by ammonia-borane to give $[IrH_2(\kappa^2\text{-}H_2BHNH_3)(PCy_3)_2][BAr^F{}_4]$ (**968**). The addition of further $H_3B{-}NH_3$ results in the formation of higher oligomers $[IrH_2\{\kappa^2\text{-}H_2BH(NH_2BH_2)_nNH_3\}(PCy_3)_2][BAr^F{}_4]$ (n = 1−4, **969** in Scheme 147). The identity of these species has been confirmed by the independent synthesis of some of them by means of the reaction of **967** with the preformed borazanes.[466] The primary amine-borane $H_3B{-}NMeH_2$ forms the simplest oligomeric species. Complex **967** reacts with this amine-borane to give the amine-borane counterpart of **968**, $[IrH_2(\kappa^2\text{-}H_2BHNMeH_2)(PCy_3)_2][BAr^F{}_4]$ (**970**), which is stable and does not undergo dehydrogenation. However, the addition of a further equivalent of amine-borane to **970** results in a relatively fast reaction to afford $[IrH_2\{\kappa^2\text{-}H_2BH(NMeHBH_2)NMeH_2\}(PCy_3)_2][BAr^F{}_4]$ (**971**) and H_2.[467]

The use of bulky primary, $H_3B{-}N^tBuH_2$, or secondary, $H_3B{-}NMe_2H$, amine-boranes has also given information about the dehydrocoupling, although this suggests an on-metal dehydrogenation and an off-metal coupling. The reaction of **967** with $H_3B{-}N^tBuH_2$ leads to $[IrH_2(\kappa^2\text{-}H_2BHN^tBuH_2)(PCy_3)_2][BAr_4]$ (**972**), which eliminates H_2 to afford the bis(σ-B−H) aminoborane derivative $[IrH_2(\eta^2,\eta^2\text{-}H_2BN^tBuH)(PCy_3)_2][BAr^F{}_4]$ (**973**). The release of the aminoborane, by addition of acetonitrile to **973**, gives rise to the formation of the cyclic borazine $[HBN^tBu]_3$.[176,468] Similarly, the addition of $H_3B{-}NMe_2H$ to **967** gives $[IrH_2(\kappa^2\text{-}H_2BHNMe_2H)(PCy_3)_2][BAr^F{}_4]$ (**974**). The dehydrogenation of the amine-borane leads to $[IrH_2(\eta^2,\eta^2\text{-}H_2BNMe_2)(PCy_3)_2][BAr^F{}_4]$ (**975**), which has also been prepared by addition of the cyclic dimer $[H_2BNMe_2]_2$ to **967** (Scheme 148).[469] Related NHC-complexes $[IrH_2(\eta^2,\eta^2\text{-}H_2BNR_2)(IMes)_2][BAr^F{}_4]$ (R = Me (**976**), ^{i}Pr (**977**), Cy (**978**)) have also been prepared by reaction of $IrH_2Cl(IMes)_2$ with the corresponding amine-borane in the presence of $Na[BAr^F{}_4]$.[366,367,470]

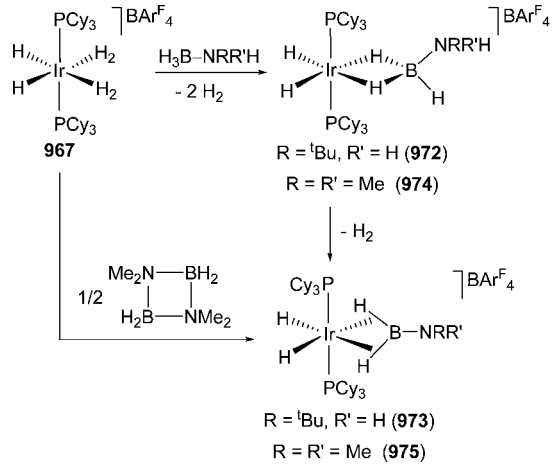
The bis(phosphinite) pincer-IrH_2/IrH_4-pair **903**/**904** catalyzes the release of hydrogen chemically stored in ammonia-borane under mild conditions,[471,472] forming polyaminoborane.[473,474] Although a side $IrH_2(\eta^2\text{-}HBH_2)\{\kappa^3\text{-}C_6H_3\text{-}1,3\text{-}(OP^tBu_2)_2\}$ (**979**) species is formed during the reaction,[39,475] the active intermediate **904** is efficiently regenerated in the presence of molecular hydrogen. DFT calculations[476] suggest that the mechanism of the catalysis is similar to that previously described for the bis(phosphine) OsH_2/OsH_4-system **300**/**345**.

The B−H bond activation is also a fundamental reaction in order to perform regiospecific functionalization of hydrocarbons, since it is one of the key steps in the direct borylation of arene and alkanes.[32−36] Thermolysis of the Ir(V) complex **869** with a small excess of HBpin at 80 °C for 50 h in octane forms the monoboryl trihydride $IrH_3(Bpin)(\eta^5\text{-}C_5Me_5)$ (**980**). Reaction of the latter with a large excess of HBpin for 50 h at 100 °C produces the dihydride-bis(boryl) derivative $IrH_2(Bpin)_2(\eta^5\text{-}C_5Me_5)$ (**981**). Reaction of the anion **868** with haloboranes provides an alternative route to monoboryl species. This method is more convenient to generate **980** and allows for the synthesis of $IrH_3(BR_2)(\eta^5\text{-}C_5Me_5)$ (BR_2 = Bcat (**982**), $BOC_6H_2\text{-}3,5\text{-}Me_2$ (**983**), BCy_2 (**984**)), according to Scheme 149. In benzene-d_6, complexes **980** and **982** afford $D_5C_6BR_2$ in 78% and 79% yield, respectively. Heating of an octane solution of **980** at 200 °C for 2 h forms the borylated

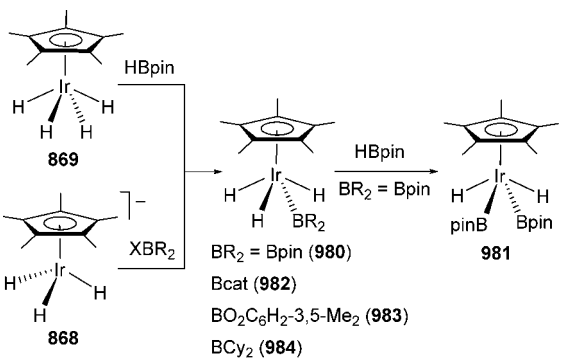
Scheme 147. Dehydrocoupling of Ammonia-Borane Promoted by 967



Scheme 148. Dehydrogenation of Amine-Boranes Promoted by 967



Scheme 149. B−H Bond Activation Reactions Promoted by Pentamethylcyclopentadienyl Complexes



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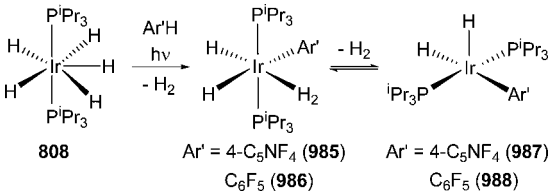
octane in 50% yield, whereas the reaction of **981** gives rise to 2 equiv of octylboronate ester in 45%.[477]

5.6.2. C−H Bond Activation. Several interesting stoichiometric and catalytic reactions involving Ir(polyhydride)-mediated activation of C−H bonds have been performed since 1985, after the revision of Hlatky and Crabtree.[54]

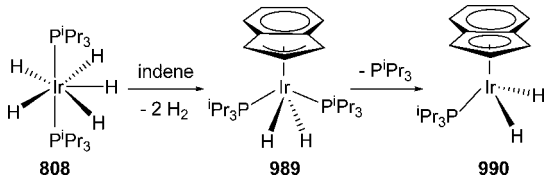
Irradiation of the pentahydride **808** with 2,3,5,6-tetrafluoropyridine and pentafluorobenzene in hexane or benzene affords the C−H bond activation products $IrH_2(Ar')(\eta^2\text{-}H_2)(P^iPr_3)_2$ (Ar′ = 4-C_5NF_4 (**985**), C_6F_5 (**986**)), which lose molecular hydrogen to give the square pyramidal complexes $IrH_2(Ar')(P^iPr_3)_2$ (Ar′ = 4-C_5NF_4 (**987**), C_6F_5 (**988**)), according to Scheme 150.[478]

Scheme 150. C−H Bond Activation of 2,3,5,6-Tetrafluoropyridine and Pentafluorobenzene Promoted by 808



Complex **808** also activates indene. At 60 °C, the reaction initially leads to $IrH_2(\eta^3\text{-}C_9H_7)(P^iPr_3)_2$ (**989**), which dissociates triisopropylphosphine to give the η^5-indenyl derivative $IrH_2(\eta^5\text{-}C_9H_7)(P^iPr_3)_2$ (**990** in Scheme 151).[479]

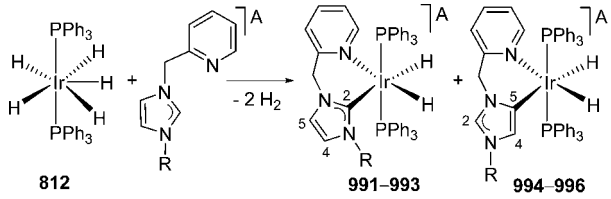
Scheme 151. C−H Bond Activation of Indene Promoted by 808



The iridium-pentahydride **812** promotes the pyridyl-assisted C−H bond activation of 2-pyridylmethylimidazolium salts. The activation is kinetically controlled and takes place at both C2 and C5 to give mixtures of the normal (**991**−**993**) and abnormal (**994**−**996**) NHC products. The molar ratio between them depends upon the anion of the salt and the bulkiness of the substituent at N3 (Scheme 152). The normal product is the thermodynamically favored species. Thus, the HBF_4/CH_2Cl_2 treatment of the mixtures, at room temperature, converts the abnormal products to the normal derivatives.[480−482]

DFT calculations suggest that the formation of the abnormal products involves C−H oxidative addition to Ir(III) to give Ir(V) intermediates with little anion dependence. The formation of the normal product, in contrast, goes by heterolytic C−H activation with proton transfer to the adjacent hydride. The transferred proton is accompanied by the counteranion in an anion-coupled proton transfer, leading to an anion dependence of the normal formation pathway and, therefore, of the normal/abnormal selectivity. Steric congestion favors abnormal carbene binding (R = ^{i}Pr, ^{n}Bu), while the less sterically demanding Me group promotes C2−H bond activation and formation of the normal carbene.[482] The pyridyl assistant does not play any role in the coordination mode of the

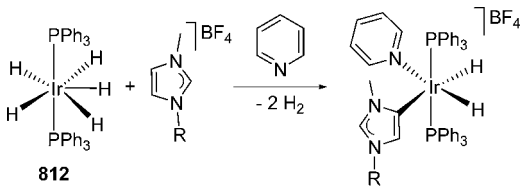
Scheme 152. Pyridyl-Chelate-Assisted C−H Bond Activation of 2-Pyridylmethylimidazolium Salts Promoted by 808: Normal vs Abnormal Metalation



R	Normal	Abnormal	A	Normal / Abnormal
Me	**991**	**994**	Br	91 / 9
			OAc	80 / 20
			OCOPh	50 / 50
			PF_6	50 / 50
			BF_4	45 / 55
			SbF_6	11 / 89
^{i}Pr	**992**	**995**	Br	84 / 16
			BF_4	0 / 100
^{n}Bu	**993**	**996**	BF_4	5 / 95

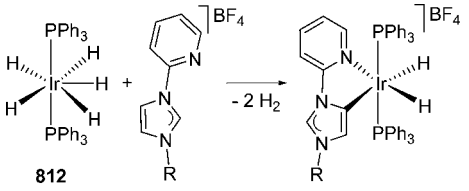
NHC group. The reactions of the tetrafluoroborate salts of 3-isopropyl- and 3-butyl-1-methylimidazolium with **812**, in the presence of free pyridine, also yield the corresponding abnormal derivatives $[IrH_2(^{ab}NHC^R)(py)(PPh_3)_2]BF_4$ (R = ^{i}Pr (**997**), ^{n}Bu (**998**)), according to Scheme 153.[483]

Scheme 153. Reactions of 812 with 3-Isopropyl- and 3-Butyl-1-methylimidazolium in the Presence of Pyridine



The ligand precursors tetrafluoroborate 2-pyridylimidazolium salts, without a methylene linker between the pyridyl and imidazolium moieties, favor the abnormal coordination. Thus, the reactions with **812** lead to $[IrH_2\{\kappa^2\text{-}C,N\text{-}(py\text{-}2\text{-}^{ab}NHC^R)\}(PPh_3)_2]BF_4$ (R = mesityl (**999**), ^{i}Pr (**1000**), ^{n}Bu (**1001**), Me (**1002**)). Their formation seems to take place via an intermediate bearing a hydrogenated imidazolium ring, resulting from the hydrogen transfer from the metal to the carbene. This hydrogen transfer proves reversible on reflux, and the abnormal complexes **999**−**1002** are obtained as final products (Scheme 154).[484] If abnormal binding is blocked, the normal coordination occurs. So, this is not forbidden for small-

Scheme 154. Reactions of 812 with 2-Pyridylimidazolium Salts



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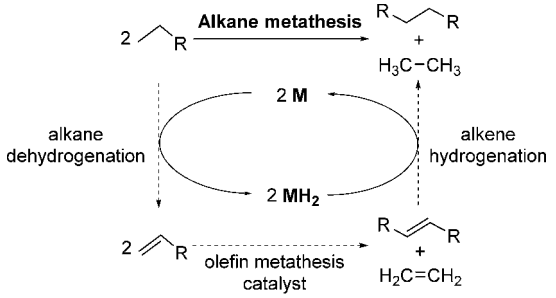
bite angle ligands. The reactions of **812** with benzimidazolium salts give the corresponding C2 carbene complexes.

The triphenylphosphine complex **812** is insoluble in the usual organic solvents. In contrast, its triisopropylphosphine counterpart **808** is very soluble. This high solubility has greatly facilitated the use of **808** as a homogeneous catalyst precursor for a wide range of interesting organic reactions. α,β-Ynones isomerize in the presence of **808** to give (*E*,*E*)- α,β:γ,δ-dienones in high yield with high regioselectivity.[485] Deuterium−hydrogen exchange between benzene-d_6 and 3,3-dimethylbutene is also catalyzed by **808** at room temperature.[486] In the presence of small amounts of this olefin, after its hydrogenation, complex **808** even catalyzes the deuterium−hydrogen exchange between benzene-d_6 and methane.[487] By using 3,3-dimethylbutene as the hydrogen acceptor, the catalytic dehydrogenations of *n*-hexane to 1-hexene, methylcyclohexane to methylenecyclohexane,[488] pinane to β-pinene,[489] and cyclooctane to cyclooctene[490] have been performed with **808** as the catalyst precursor. The regioselective functionalization of alkanes has been achieved by dehydrogenation in the presence of **808** followed by hydrozirconation of the resulting olefin.[491] The formation of vinyl ethers by dehydrogenative coupling of ethers and olefins is other catalytic process promoted by **808**.[492]

The IrH_4/IrH_2-pincer pairs have also shown to be efficient catalyst precursors for organic processes involving C−H bond activation reactions. The application of this type of systems to dehydrogenation and related reactions was reviewed by MacArthur, Brookhart, and Goldman in 2011.[56] Since then, several findings should be highlighted. The transfer dehydrogenation of ketones by the bis(phosphine) pair **914**/**941** (^{tBu2}PCP^{tBu2}) has been observed. Catalytic turnover was inhibited in most cases by the formation of stable metalacycles or the O−H oxidative addition of phenolic products. Catalytic transfer dehydrogenation of 3,3-dimethylcyclohexanone was achieved, giving the corresponding α,β-enone. The transfer dehydrogenation of cycloheptanone was found to generate a stable troponyl-iridium-hydride derivative, which catalyzes the dimerization of tropone to give a fused tricyclic dihydrodicycloheptafuranol.[493] Krogh-Jespersen, Goldman, and co-workers have reported the transfer-dehydrogenation of gas-phase alkanes, using ethylene or propene as hydrogen acceptor. In the solid phase, the pair **915**/**942** (^{iPr2}PCP^{iPr2}) is found to give extremely high rate and turnover numbers for *n*-alkane dehydrogenation and yields of α-olefin that are much higher than those obtained for solution-phase experiments. Experimental mechanistic studies and DFT calculations suggest that olefin isomerization, which limits yields of α-olefin, proceeds via two pathways. The more conventional pathway involves 2,1-insertion of the α-olefin into an Ir−H bond of **942**, followed by 3,2-β-H elimination. The use of ethylene as hydrogen acceptor, or high pressures of propene, precludes this pathway by rapid hydrogenation of these olefins. The other pathway proceeds via α-olefin C−H addition to the iridium center to afford an allyl species. The improved understanding of the factors controlling rates and selectivity has led to solution-phase systems that afford improved yields of α-olefins.[457] The pair **915**/**942** also catalyzes the conversion of *n*-alkanes to alkylaromatics using olefinic hydrogen acceptors. For instance, the reaction of *n*-octane affords up to 86% yield of aromatic products, primarily *o*-xylene and secondarily ethylbenzene. In the case of *n*-decane and *n*-dodecane, the resulting alkylarenes are exclusively unbranched, with selectivity for the corresponding *o*-(*n*-alkyl)toluene.[455] Huang and co-workers have reported that the hybrid thiophosphinite-phosphinite pair **929**/**956** (PSCOP) catalyzes the dehydrogenation of *n*-alkanes with high regioselectivity to the α-olefin and of heterocycles to heteroarenes, in the presence of 3,3-dimethylbutene.[458] With the same hydrogen acceptor, Yamamoto and co-workers have observed that the bis(phosphine) pincer pairs **932**/**959** and **934**/**961** bearing a 7−6−7 fused-ring skeleton are highly effective in the dehydrogenation of cyclooctane to cyclooctene. The initial rate at 230 °C is higher for **932**/**959** (^{iPr2}PCP^{iPr2}) than **934**/**961** (^{Ph2}PCP^{Ph2}). However, the turnover number of the overall process is higher for the latter (4600 versus 4820).[460]

Goldman, Brookhart, and co-workers have developed a highly productive tandem catalytic procedure for the metathesis of *n*-alkanes (Scheme 155). Each elemental reaction comprises

Scheme 155. Tandem Catalytic Procedure for the Metathesis of *n*-Alkanes



MH_2 = **903**, **941**, **957**, **958**

one molecular catalyst. IrH_4/IrH_2-pincer pairs effect alkane dehydrogenation and olefin hydrogenation whereas a Schrock-type molybdenum alkylidene derivative performs the olefin metathesis.[494] Both the pincer bis(phosphinite) **904**/**903** (^{tBu2}POCOP^{tBu2}) and bis(phosphine) **914**/**941** (^{tBu2}PCP^{tBu2}) cocatalyze alkane metathesis in tandem with olefin metathesis catalysts, but the two pairs have different resting states during the catalysis, suggesting that different steps are turnover-limiting in each case. In tandem with the olefin-metathesis catalyst Mo(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$, the hybrid phosphine-phosphinite pincer pairs **930**/**957** (^{tBu2}PCOP^{tBu2}) and **931**/**958** (^{tBu2}PCOP^{iPr2}) display significantly higher activity for the metathesis of *n*-hexane than does **904**/**903** and **914**/**941**.[459]

A tandem catalytic approach for the coupling of alkanes and alkenes has been recently developed by Labinger and Bercaw in order to upgrade light hydrocarbons into heavier fuel molecules. The procedure involves alkane dehydrogenation with a bis(phosphine) pincer- IrH_4/IrH_2-pair, for example **914**/**941** or **915**/**942**, and alkene dimerization by a Ta(η^5-C$_5$Me$_5$)Cl$_2$(η^2-alkene) catalyst (Scheme 156). The dual homogeneous system operates with up to 60/30 cooperative turnovers (Ir/Ta) in the dimerization of 1-hexene/*n*-heptane, giving C_{13}/C_{14} products in 40% yield. The system can also effect the catalytic dimerization of *n*-heptane with cooperative turnover number of 22/3 (Ir/Ta), using neohexene as hydrogen acceptor.[495,496]

Wendt and co-workers have reported an iridium pincer promoted intramolecular coupling reaction involving three unactivated C(sp^3)−H bonds to give a C−C double bond under the extrusion of dihydrogen.[497]

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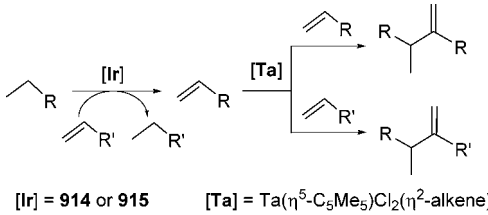
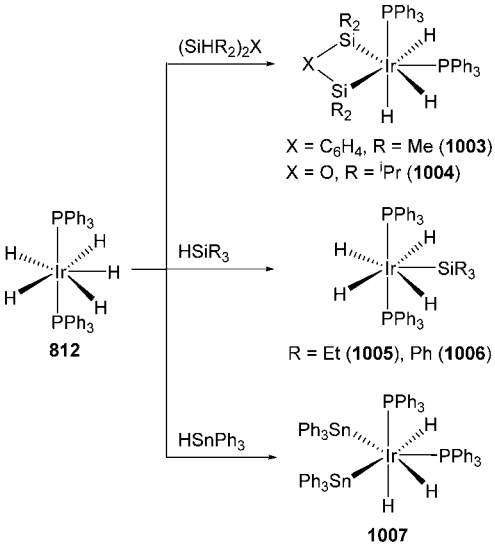
Scheme 156. Tandem Catalytic Approach for the Coupling of Alkanes and Alkenes



5.6.3. Si−H Bond Activation. Interesting polyhydride-iridium(V)-silyl compounds have been obtained by activation of Si−H bonds.

The bis(phosphine) pentahydride complex **812** reacts with disilanes with loss of molecular hydrogen to form the classical seven-coordinate distorted pentagonal bipyramidal trihydride-silyl derivatives $IrH_3(R_2SiXSiR_2)(PPh_3)_2$ (X = C_6H_4, R = Me (**1003**); X = O, R = ^{i}Pr (**1004**)). The reactions with monodentate silanes, $HSiR_3$, lead to the tetrahydride compounds $IrH_4(SiR_3)(PPh_3)_2$ (R = Et (**1005**), Ph (**1006**)), whereas with $HSnPh_3$ the trihydride-bis(stannyl) $IrH_3(SnPh_3)_2(PPh_3)_2$ (**1007**) is obtained (Scheme 157).[498]

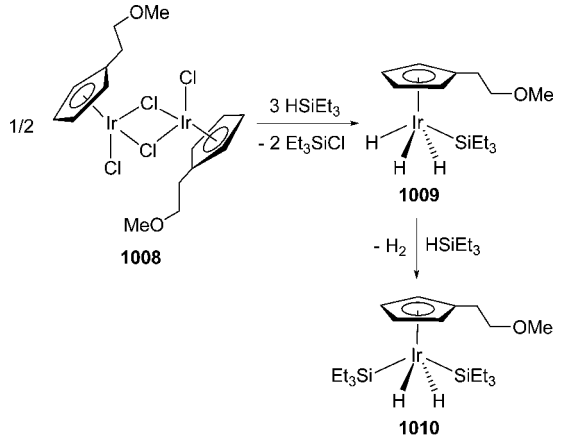
Scheme 157. Si−H and Sn−H Bond Activation Reactions Promoted by 812



The cyclopentadienyl-dimer complex $[Ir\{\eta^5\text{-}C_5H_4(CH_2)_2OMe\}Cl(\mu\text{-}Cl)]_2$ (**1008**) reacts with 3.0 equiv of $HSiEt_3$ per iridium to give the Ir(V) silyl-trihydride derivative $IrH_3(SiEt_3)\{\eta^5\text{-}C_5H_4(CH_2)_2OMe\}$ (**1009**), which in the presence of excess of $HSiEt_3$ is transformed into $IrH_2(SiEt_3)_2\{\eta^5\text{-}C_5H_4(CH_2)_2OMe\}$ (**1010**), according to Scheme 158. In benzene-d_6 at 80 °C, the selective deuteration of the hydride and cyclopentadienyl positions of **1009** takes place to afford $IrD_3(SiEt_3)\{\eta^5\text{-}C_5H_4(CH_2)_2OMe\}$ (**1009-d_3**) and $IrD_3(SiEt_3)\{\eta^5\text{-}C_5D_4(CH_2)_2OMe\}$ (**1009-d_7**). In benzene, the latter evolves into $IrH_3(SiEt_3)\{\eta^5\text{-}C_5D_4(CH_2)_2OMe\}$ (**1009-d_4**).[499]

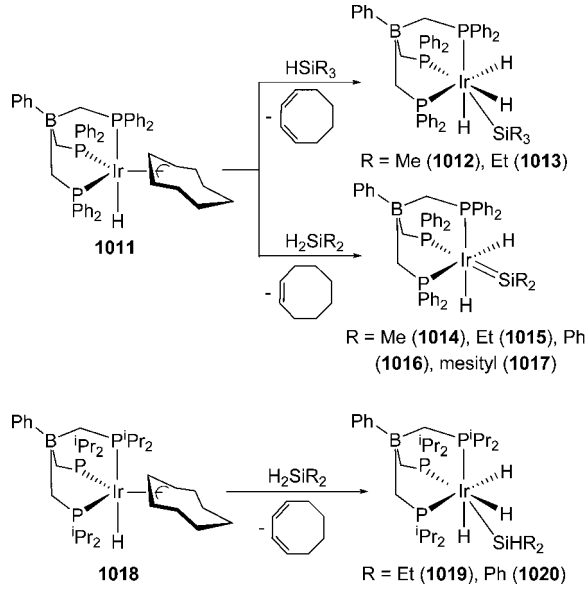
Complex $IrH(PhBP_3^{Ph})(\eta^3\text{-}C_8H_{13})$ (**1011**, $PhBP_3^{Ph}$ = PhB-$(CH_2PPh_2)_3$) reacts with tertiary silanes, $HSiR_3$, to give the silyl-capped trihydride derivatives $IrH_3(PhBP_3^{Ph})(SiR_3)$ (R = Me (**1012**), Et (**1013**)), with concomitant β-hydride elimination of 1,3-cyclooctadiene. However, the reactions of

Scheme 158. Si−H Bond Activation Reactions Promoted by Iridium-Cyclopentadienyl Complexes



1011 with secondary silanes, H_2SiR_2, lead to the corresponding dihydride-silylene species $IrH_2(PhBP_3^{Ph})(=SiR_2)$ (R = Me (**1014**), Et (**1015**), Ph (**1016**), mesityl (**1017**)) with elimination of cyclooctene. In contrast to **1011**, its ^{i}Pr-analogous $IrH(PhBP_3^{iPr})(\eta^3\text{-}C_8H_{13})$ (**1018**, $PhBP_3^{iPr}$ = PhB-$(CH_2P^iPr_2)_3$) does not induce the formation of silylene derivatives in the presence of secondary silanes. Thus, its reactions with H_2SiR_2 lead to the corresponding trihydride complexes $IrH_3(PhBP_3^{iPr})(SiHR_2)$ (R = Et (**1019**), Ph (**1020**)) and 1,3-cyclooctadiene (Scheme 159).[500,501] Complex **1019** has

Scheme 159. Si−H Bond Activation Reactions Promoted by 1011 and 1018



been shown to undergo H/D exchange with D_2 to incorporate deuterium into both the hydride and Si−H positions. A Tp^{Me2} complex $IrH_3(SiEt_3)Tp^{Me2}$ (**1021**) with a similar structure has been isolated and characterized by X-ray diffraction analysis.[424]

Brookhart and co-workers have proved that a trihydride-Ir(V)-silyl complex stabilized by the pincer ligand 2,6-bis(di-*tert*-butylphosphinito)phenyl is the silylating agent in the reduction of tertiary amides to amines with secondary silanes. The iridium(III) cation $[IrH(acetone)\{C_6H_3\text{-}2,6\text{-}(OP^tBu_2)_2\}]^+$ (**1022**) was shown to catalyze the reduction of tertiary amides

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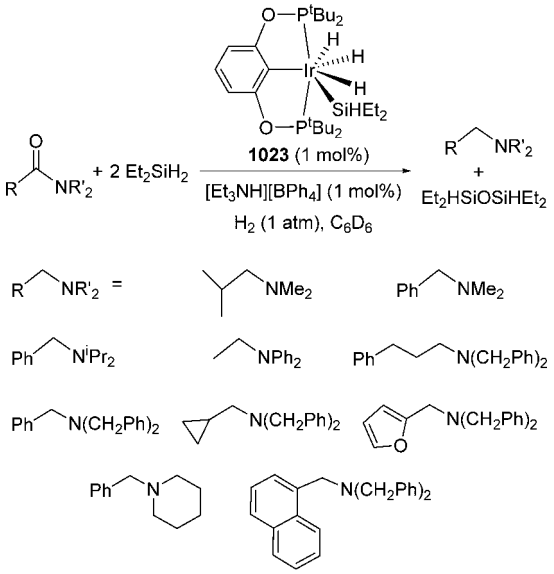
using diethylsilane as a reductant. Mechanistic studies established that complex $IrH_3(SiHEt_2)\{C_6H_3\text{-}2,6\text{-}(OP^tBu_2)_2\}$ (**1023**) was the active species. High concentrations of **1023** can be generated by treatment of the starting material $IrHCl\{C_6H_3\text{-}2,6\text{-}(OP^tBu_2)_2\}$ (**1024**) with *tert*-butoxide in the presence of Et_2SiH_2 under H_2. Thus, using this mixture in the presence of a trialkylammonium salt, a wide array of tertiary amides are efficiently reduced to amines (Scheme 160). This reaction

Scheme 160. Iridium-Mediated Reduction of Tertiary Amides to Amines with Secondary Silanes



works as follows: complex **1023** reduces the amide to the hemiaminal silyl ether that, in the presence of a trialkylammonium salt, is ionized to the iminium ion, which is then reduced to the tertiary amine by H_2SiEt_2. Good functional group compability is observed, and a high stability has provided turnover numbers as high as 10000.[502]

5.6.4. O−H Bond Activation. Several catalytic processes involving the IrH_n-mediated O−H bond activation of alcohols have been described.[56] The bis(triisopropylphosphine)-pentahydride complex **808** catalyzes the hydrogen transfer from 2-propanol to cyclohexanones, benzylideneacetone, styrene, and cyclohexadienes. The reduction of the carbon−carbon double bond of the α,β-unsaturated ketone is clearly preferred, and no unsaturated alcohol is formed. With 1,4-cyclohexadiene as a substrate, different reactions are observed. Initially, the rapid isomerization of the 1,4-isomer to the thermodynamically more stable 1,3-cyclohexadiene occurs. Subsequently, the disproportionation of the latter to cyclohexene and benzene takes place.[395] Complex **808** also catalyzes the isomerization of allylic secondary alcohols into ketones[503] and the isomerization of propargylic alcohols to α,β-enones. In toluene under reflux, the reactions proceed through the intramolecular hydrogen transfer from the alcohol function to the unsaturated carbon−carbon double bond. The significance of this type of process is demonstrated by the transformation of 3-hexyn-2,5-diol to 2,5-hexanedione.[504] In the absence of hydrogen acceptor, the catalyst promotes the generation of molecular hydrogen. Thus, in hexamethyldisiloxane at 100 °C, a wide range of secondary alcohols have been converted into the corresponding ketones, including allylic and homoallylic steroidal alcohols. In these cases, saturated ketones were also formed as a result of the competition of the hydrogen transfer reaction with the dehydrogenation.[505] The oxidative condensation of diols promoted by **808** leads to 5- and 6-ring lactones. The regioselective dehydrogenation of unsymmetrically substituted 1,4-diols gives β- or γ-substituted γ-lactones in high yields.[506]

6. GROUP 10

The relative stabilities of diatomic first and second row transition metal hydrides have been compared from a theoretical point of view and rationalized in terms of the electronic configuration ground state of the metal center.[507] Although the calculated dissociation energies for the M−H bond in the sequence Ru, Rh, and Pd do not seem to be very different (58.9, 64.1, and 51.1 kcal mol^{-1}, respectively),[508] the fact is that the chemistry of the polyhydrides of palladium is elusive in absolute terms, being confined to the salt $Na_2[PdH_4]$ (**1025**)[509] and a pair of dihydrogen adducts formed at low temperature in rare-gas matrices and characterized by vibrational spectroscopy.[510] The dihydrogen form is favored with regard to the dihydride tautomer because the intramolecular reductive elimination of hydrogen from palladium(II) appears to be exothermic, since palladium prefers to be d^{10}, in contrast to the reductive elimination from platinum(II) which is endothermic preferring platinum to be s^1d^9.[511] Thus, thermally evaporated and laser-ablated palladium atoms interact with molecular hydrogen in excess argon to yield the side-bonded $Pd(\eta^2\text{-}H_2)$ (**1026**). This species readily adds one and two more hydrogen molecules to afford $Pd(\eta^2\text{-}H_2)_2$ (**1027**) and $Pd(\eta^2\text{-}H_2)_3$ (**1028**), which are predicted by DFT calculations to have approximately D_{2d} and D_{3h} structures. The bonding situation in these dihydrogens has been analyzed using the electron localization function (ELF) topological method. The results suggest a predominant charge-transfer nature of the Pd−H_2 interaction with a minor amount of charge reorganization on the metal center in the cooperatively coupled donor−acceptor delocalization.[512]

Some polyhydride complexes of platinum are known, although their chemistry is extremely poor and is limited to PtH_3-derivatives, including square-planar *trans*-hydride-dihydrogen-platinum(II) cations and a few five-coordinate and octahedral trihydride-platinum(IV) complexes.

The *trans*-dihydride-bis(phosphine) complexes $PtH_2(PR_3)_2$ (PR_3 = P^tBu_3 (**1029**), P^iPr_3 (**1030**), PCy_3 (**1031**)) undergo protonation with CF_3SO_3H (**1029**) and $[H(OEt_2)_2]BAr^F{}_4$ (**1030** and **1031**), at low temperature (183−190 K), to afford *trans*-$[PtH(\eta^2\text{-}H_2)(PR_3)_2]^+$ (PR_3 = P^tBu_3 (**1032**), P^iPr_3 (**1033**), PCy_3 (**1034**)). A short separation between the hydrogen atoms of the dihydrogen ligand (0.8−0.9 Å) has been inferred from the large H−D coupling constant in the corresponding isotopomers (J_{H-D} = 31−35 Hz). Complexes **1032**−**1034** are stable in dichloromethane at low temperature. At room temperature, they dissociate the dihydrogen ligand to afford the solvento derivatives $[PtH(ClCH_2Cl)(PR_3)_2]^+$ (PR_3 = P^tBu_3 (**1035**), P^iPr_3 (**1036**), PCy_3 (**1037**)). The dissociation is reversible. Under hydrogen atmosphere, complexes **1035**−**1037** are in equilibrium with the hydride-dihydrogen derivatives **1032**−**1034** (Scheme 161).[513−515]

Conejero and Lledós have reported related bis(NHC) complexes. The cationic species $[Pt(NHC')(NHC)]^+$ (NHC = IPr (**1038**), 1,3-dimesityl-4,5-dimethylimidazol-2-ylidene (IMes*; **1039**)) containing a cyclometalated NHC ligand (NHC′), undergo hydrogenolysis under hydrogen atmosphere, at room temperature, to give the monohydrides [PtH-

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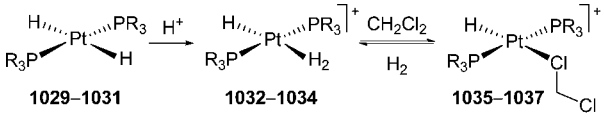
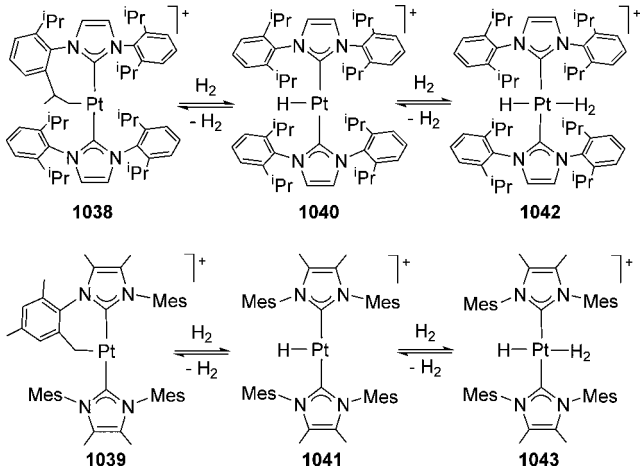
Scheme 161. Preparation of *trans*-$[PtH(\eta^2\text{-}H_2)(PR_3)_2]^+$ Complexes



$(NHC)_2]^+$ (NHC = IPr (**1040**), IMes* (**1041**)) in equilibrium with the respective *trans*-hydride-dihydrogen derivatives $[PtH(\eta^2\text{-}H_2)(NHC)_2]^+$ (NHC = IPr (**1042**), IMes* (**1043**)), which are the NHC counterparts of **1032**−**1034** (Scheme 162).[516] In

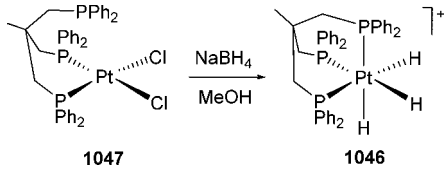
Scheme 162. Preparation of $[PtH(\eta^2\text{-}H_2)(NHC)_2]^+$ Complexes



contrast to **1042** and **1043**, the stannyl complexes $PtH_3(Sn^tBu_3)(I^tBu)$ (**1044**)[517] and $PtH_3(Sn^tBu_3)(IPr)$ (**1045**)[518] have been characterized as five-coordinate trihydride-platinum(IV) species.

The trihydride complex $[PtH_3(triphos^{Me})]^+$ (**1046**) is quantitatively formed upon treatment of $PtCl_2(\kappa^2\text{-}P,P\text{-}triphos^{Me})$ (**1047**) with $NaBH_4$ in methanol or methanol-dichloromethane according to Scheme 163.[519] The reaction is

Scheme 163. Prepartion of 1046



proposed to occur via the platinum(II) intermediate $PtH_2(\kappa^2\text{-}P,P\text{-}triphos^{Me})$ (**1048**), which undergoes protonation with MeOH. Treatment of $[PtPh(MeOH)(PR_3)_2]^+$ (PR_3 = PMe_3 (**1049**), PEt_3 (**1050**)) with $NaBH_4$ in methanol leads to a mixture of products containing a small amount (less than 10%) of the trihydrides *mer*-$PtH_3Ph(PR_3)_2$ (PR_3 = PMe_3 (**1051**), PEt_3 (**1052**)).[520]

Brookhart, Templeton, and co-workers have efficiently transformed the precursor PtH_2MeTp^{Me2} (**1053**) into the classical trihydride PtH_3Tp^{Me2} (**1054**), via the platinum(II) intermediate $PtHTp^{Me2}(CO)$ (**1055**). Under a CO atmosphere, the protonation of **1054** with $[H(OEt_2)_2][BAr^F{}_4]$ at 193 K, gives $[PtH_3(\kappa^2\text{-}HTp^{Me2})(CO)]BAr^F{}_4$ (**1056**), which loses H_2 to afford $[PtH(\kappa^2\text{-}HTp^{Me2})(CO)][BAr^F{}_4]$ (**1057**) in an almost quantitative yield (Scheme 164). The isotopic effect (2.2 ± 0.1) and the reaction entropy (24.5 ± 4 eu) are consistent with a mechanism involving reversible reductive coupling to form a dihydrogen intermediate followed by rate-limiting irreversible dissociation of H_2.[521,522]

7. CONCLUSION AND OUTLOOK

Osmium possesses the richest chemistry among the six platinum group metals. Thus, the widest range of complexes with different stoichiometries and structures is observed. Furthermore, its polyhydrides show a highly diverse reactivity which is dominated by C−H bond activation reactions. In the opposite side, palladium polyhydrides are largely unknown. This situation is due to three general precepts in coordination chemistry: (i) the transition metals situated at the center of the periodic table exhibit the widest range of oxidation states, and in this respect, ruthenium and osmium occupy a particularly privileged position; (ii) the oxidation state of the metal center determines the coordination number and the geometry of the complexes; and (iii) the stability of the highest oxidation states increases as going down in a triade.

Ruthenium and rhodium favor the formation of dihydrogen derivatives. Osmium and iridium however prefer to stabilize elongated dihydrogen species or compressed dihydrides, of the same stoichiometry. The comparison of the ruthenium-bis(diphosphine) complexes with their osmium counterparts is an overwhelming evidence of this asseveration. The question is what are truly elongated dihydrogens and compressed dihydrides, dihydrogens, or dihydrides? Section 3.5 shows some evidence that strongly supports the dihydride character of these ligands. In this context, it should be noted that 4d metals are more oxidizing than their triade 5d analogous. However, the 5d metals are more reducing. Elongated dihydrogen and compressed dihydrides should be viewed as dihydrides undergoing some nonclassical interaction, including quantum mechanical exchange coupling. So, elongated dihydrogen and compressed dihydrides should be properly called nonclassical dihydrides.

The dihydrogen or elongated dihydrogen nature of the $M(\eta^2\text{-}H_2)$ units mainly depends upon the electron richness of the metal center. However, the elongated dihydrogen or compressed dihydride character appears to be a consequence of the steric requirements of the heavy coligands, in the plane containing the coordinated hydrogen atoms. As a proof of concept, it has been observed that the hydrogen−hydrogen separation in the pincer compressed dihydrides in section 3.6.7 decreases as the steric requirements of the heterocyclic moiety of the pincers increase[350] (i.e., pyridine > isoquinoline > quinoline). The dihydrogen or elongated dihydrogen nature of the compounds is a consequence not only of the electron richness of the metal center but also of the geometry of the heavy coligands. The difference between half-sandwich and Tp complexes is clear evidence. Tp-type and BAEA ligands enforce dispositions allowing N−M−N angles close to 90° and in contrast to Cp and Cp*, which favor four-legged piano stool structures, stabilize dihydrogen derivatives.

The nonclassical or classical character of the polyhydrides is decisive in the reactivity of these compounds. First because it determines the dissociation energy of a hydrogen molecule, it is the necessary step for generating the unsaturated species which initiate the σ-bond activation processes. Second because it

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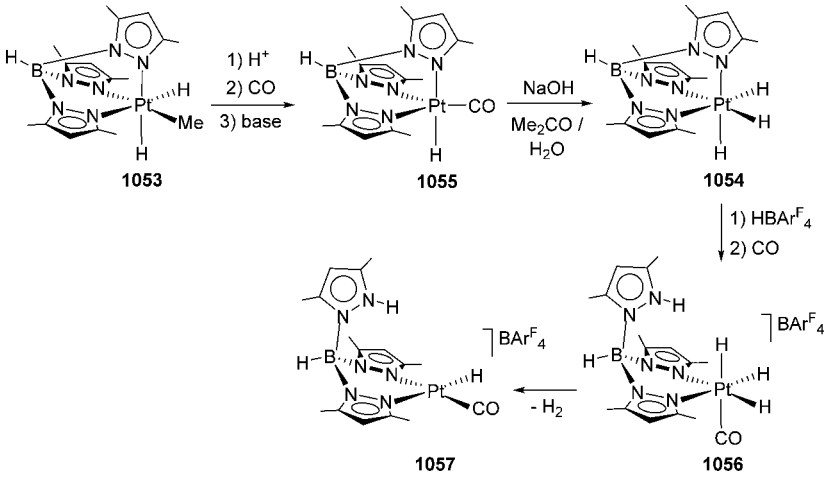
Scheme 164. Preparation of Classical Trihydride-Platinum(IV) Complexes Containing the Tp^{Me2} Ligand



reflects the richness of the metal center, which governs the basicity of the remaining hydrides and predetermines the nature of the interaction between the metal center and the σ-bond which, after its coordination, will be activated. In general, nonclassical polyhydrides promote the homolysis of the σ-bonds, since the metal center is able to reach low oxidation states, while classical polyhydrides favor heterolytic cleavages through intermediate oxidation states of the metal center.

The improvement of quality of the characterization techniques has been certainly crucial for the development of the field. In spite of this fact, the chemistry of polyhydrides remains laborious and complex from an experimental point of view and conceptually difficult. So, it is not foreseeable that the topic will be popularized. On the contrary, it will most probably continue being restricted to specialized laboratories. However, its survival is guaranteed by the ability of the polyhydrides of platinum group metals to activate σ-bonds. In this context, an increased interest should be expected due to the role that this type of compound can play in understanding and developing reactions associated with conversion and storage of regenerative energy. The importance of the C−H bond activation reactions in modern organic synthetic chemistry is another relevant factor that will contribute to the reinforcement of the field, although in this case, an improvement of the experimental procedures in some organic laboratories will be necessary, in order to fully exploit the potential of the polyhydrides. The possibility of generating metalatrinems, which can be a novel type of inhibitors of β-lactamases, by means of the N−H bond activation of 2-azetidinones opens the door of the drugs design to the polyhydrides. Additionally, in the search for models of new anticancer drugs, the activation of N−H, O−H, and N−C bonds of nucleobases promoted by osmium hexahydrides, as well as, the ability of some hydride ligands to form hydrogen bonds[523−525] envisages exciting new ground. Finally, it should also be mentioned the recent use of polyhydrides for the preparation of new types of compounds with notable applications in materials science.[526−528] So, the chemistry of the polyhydrides of the platinum group metals is still far from their full development. Unlike other more mature areas, it offers new exciting conceptual challenges and at the same time the possibility of interacting with other fields which foresee promising advances in the near future.

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Notes

The authors declare no competing financial interest.

Biographies

Miguel A. Esteruelas was born in Zaragoza and grew up in La Zaida, a small village situated on the banks of the Ebro. He attended University of Zaragoza where received his Diploma in Chemistry in 1981. He carried out his doctoral work in organometallics at University of Zaragoza under the direction of Professors Daniel Carmona and Luis A. Oro. After obtaining his Ph.D. in December 1983, he worked as a postdoctoral fellow in the laboratory of Prof. Helmut Werner at the University of Würzburg, for 18 months. In 1985, Esteruelas returned to the University of Zaragoza, where he was promoted to Professor of Inorganic Chemistry in 1988 and to Distinguished Professor in 2003. In 2007, he moved to the Spanish Research Council (CSIC), where he is currently Research Professor at the Instituto de Síntesis Química y Catálisis Homogénea (ISQCH). Esteruelas' research group focuses its interest in mechanistic, synthetic, and structural organometallic chemistry. Emphasis has been placed on the use of transition metal hydride complexes for the activation of σ-bonds, the generation of metal−carbon multiple bonds, and the catalytic formation of carbon−carbon and carbon−heteroatom bonds.

Ana M. López was born in Aranda de Duero, Spain, in 1962. She studied Chemistry at the University of Zaragoza where she obtained her Ph.D. in 1991 under the supervision of Professors M. Pilar García and Luis A. Oro. Then she joined the Prof. Esteruelas group. Since 2012, she has been full professor at the University of Zaragoza. Her research interests concern organometallic complexes of the platinum group metals and their applications in homogeneous catalysis.

Montserrat Oliván studied chemistry at the University of Zaragoza (Spain) and obtained her Ph.D. in 1995 working under the supervision of Profs. Miguel A. Esteruelas and Luis A. Oro. She then joined the group of Prof. Kenneth G. Caulton at Indiana University (Bloomington, IN) for a two-year postdoctoral stay. Thereafter, she returned to the University of Zaragoza. Since 2005, she has been "Científico Titular" at the Instituto de Síntesis Química y Catálisis Homogénea (Universidad de Zaragoza−CSIC). Her current research interests are mainly devoted to the study and reactivity of polyhydride and pincer derivatives of platinum group metal complexes as well as

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their applications in fields ranging from homogeneous catalysis to material science.

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DEDICATION

Dedicated to the memory of Prof. Rafael Usón (1926−2016) for his outstanding contribution to the development of organometallic chemistry.

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