Reactivity of Phosphane–Imidazolium Salts Towards [Ir(COD)Cl] 2 : Preparation of New Hydridoiridium(III) Complexes Bearing Abnormal Carbenes

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Reactivity of phosphane-imidazolium salts toward $[Ir(COD)Cl]_2$: preparation of new hydridoiridium(III) complexes bearing abnormal carbenes.[§]

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Keywords: Carbenes / Phosphane ligands / Iridium / Hydrides / C-H activation

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[§] Dedicated to Prof. W. A. Herrmann on the occasion of his 60th birthday.

Abstract

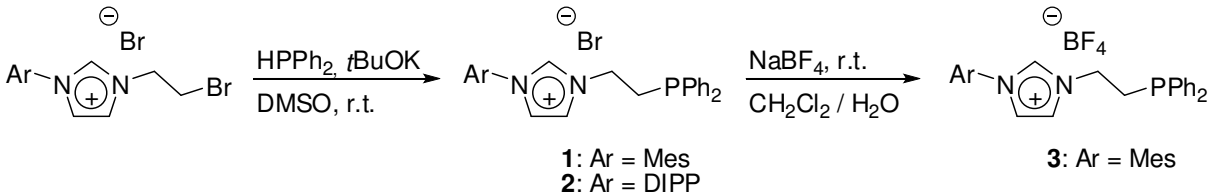
The unusual reactivity of chelating phosphine-imidazolium salts $MesImEtPPh_2^+Br^-$, $DIPP\text{-}ImEtPPh_2^+Br^-$ and $MesImEtPPh_2^+BF_4^-$ toward low oxidation state iridium complex $[Ir(COD)(\mu\text{-}Cl)]_2$ was studied. In the absence of a base, the C-H insertion at the C5 position of the imidazolium ring is the only reaction occurring, with no normal NHC observed, and lead to iridium(III) hydride complexes. This reactivity is independent of the nature of the imidazolium counteranion and of the substitution pattern of the aryl group.

Introduction

N-heterocyclic carbene (NHC) complexes are now widely used for catalytic applications[1]. This interest is particularly due to the production of more robust catalysts by coordination of NHCs on transition metals such as palladium, nickel, rhodium, ruthenium and iridium[2]. Over the last fifteen years, a number of bidentate as well as polydentate ligands incorporating NHCs[3] and other coordinating atoms[4-6],[7,8] have been developed and used successfully in catalysis.

More recently a different binding mode for NHCs has been described by Crabtree and co-workers:[9] instead of the normal C2 coordination, the metal can be bound to the C4 or C5 atom of an imidazolium salt. Since this discovery, only few examples of "abnormal" carbenes have been described, for example with iridium,[10-12] ruthenium,[13] osmium[14] and several other transition metals.[15] In the case of Crabtree's work with iridium precursor $IrH_5(PPh_3)_2$, it has been shown that the formation of classical or abnormal NHCs was anion-dependent: imidazolium salts bearing a halogen anion led preferentially to classical NHCs, whereas non-coordinating anions BF_4^- or PF_6^- gave mostly abnormal NHCs.[12] Monodentate ligands have then been used instead of bidentate NHCs, with similar results, showing no chelate effect.[11] Very recently, the group of Li has reported iridium^{III} hydride complexes bearing chelating phosphine-(abnormal)NHC ligands.[16] They did not observe any influence of the counter-anion on the product selectivity.

We are interested in the preparation of bifunctional imidazolium salts containing a coordinating heteroatom such as phosphorus or sulfur, and their use as ligands or ligand precursors for transition metals.[4-6] More particularly, we have recently described the use of phosphine-imidazolium salts to prepare zwitterionic Ni^{II} complexes and shown their excellent activities for Kumada-Tamao-Corriu cross coupling reactions.[4] We now report the unusual reactivity of these salts with $[IrCl(COD)]_2$. These results were obtained during attempts to synthesise new Ir^{I} pre-catalysts, following the same procedure that allowed us to access Ni^{II} and Pd^{II} analogues.[4,5]



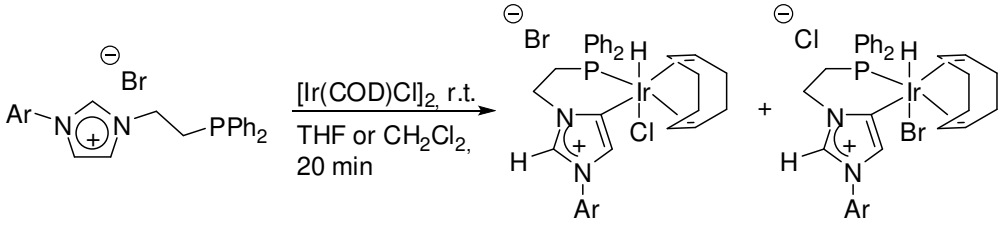
1: Ar = Mes
2: Ar = DIPP

3: Ar = Mes

Scheme 1. Synthesis of phosphine-imidazolium salts. Mes = mesityl or 2,4,6-trimethylphenyl; DIPP = 2,6-diisopropylphenyl.

Results and discussion

The phosphine-imidazolium salts were prepared according to previously reported procedures (Scheme 1).[4] The reaction of 1-(2-diphenylphosphinoethyl)-3-(2,4,6-trimethylphenyl) imidazolium bromide salt $MesImC_2H_4PPh_2^+Br^-$ **1** with $[Ir(COD)(\mu\text{-}Cl)]_2$ yields a mixture of two hydride complexes (**4a** and **4b**) in a 1:1 ratio (Scheme 2). The two complexes exhibit two almost equivalent ^{31}P NMR signals at δ -1.1 and -2.4 and two equivalent ^1H NMR hydride doublet resonances at δ -15.22 and -14.55, see figure 1a.



1: Ar = Mes
2: Ar = DIPP

4a: Ar = Mes
6a: Ar = DIPP

4b: Ar = Mes
6b: Ar = DIPP

4a + **4b**: 92%
6a + **6b**: 87%

Scheme 2. Mixture of isomers **4a+4b** from the reaction of ligand **1**, or isomers **6a+6b** from the reaction of ligand **2**, with $[Ir(COD)(\mu\text{-}Cl)]_2$.

We attribute this behavior to halogen exchange, induced by the bromide anion of **1**. This hypothesis is confirmed by the observation that using $MesImC_2H_4PPh_2^+BF_4^-$ **3** in place of **1** leads to a single product **5**, whose ^{31}P and ^1H (hydride) resonances match with those of **4a** (Scheme 3, figure 1b). Thus, both products **4a** and **5** contain a chloride ligand and a different counterion (Br^- for **4a** and BF_4^- for **5**), whereas the chloride and bromide ions are exchanged in **4b**.

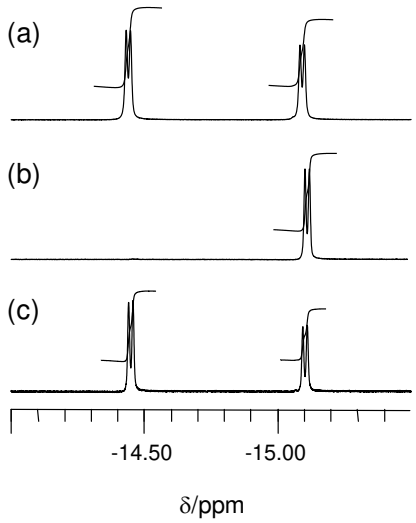
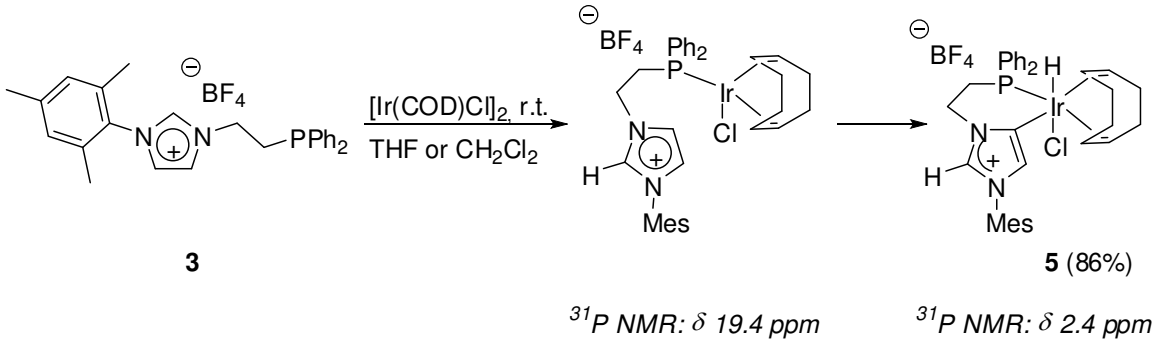


Figure 1. ^{1}H NMR spectra (500 MHz, 20°C) of complexes a) **4a/4b** ($CDCl_3$), b) **5** (CD_2Cl_2), c) **6a/6b** (CD_2Cl_2) (hydride resonances).



Scheme 3. Synthesis of complex **5** via an iridium(I) intermediate.

The ^{1}H NMR spectrum of the **4a/4b** mixture indicates C_1 symmetry and reveals three signals corresponding to the imidazole ring protons at δ 9.74, 6.24 and 6.18, with integration values of 1: 0.5: 0.5, whereas that of compound **5** exhibits two 1:1 resonances at δ 8.45 and 6.40, see Figure 2. Whereas the upfield imidazole ring ^{1}H resonances of **5** approximately matches with that of **4a**, the downfield one is quite anion dependent. Furthermore, 1:1 ^{13}C resonances for quaternary carbons are observed at δ 119.9 and 121.1, which is a typical region for aryl substituents and not for NHC ligands. These results indicate that the products are Ir^{III} complexes coordinated by a bidentate phosphine-abnormal carbene ligand (scheme 2). The shift of the downfield ^{1}H resonance is attributed to differences in H-bonding between the acidic imidazolium proton and the different counterion. Related iridium(III) hydride complexes, also featuring an abnormal carbene coordination, have been recently reported by Li *et al.* and show similar NMR features (complex **A**, figure 3).[16] Danopoulos *et al.* also obtained and crystallographically characterised a similar complex, Ir(COD)(Br){κ^2:*P*,*C5*-$Ph_2PCH_2CH_2(N_2C_3HMes)$} (**B** in figure 3), from the reaction of **1** with $[Ir(COD)(HCl)(\mu\text{-}Cl)_2]_2$. It is related to **4b** by elimination of HCl.[8]

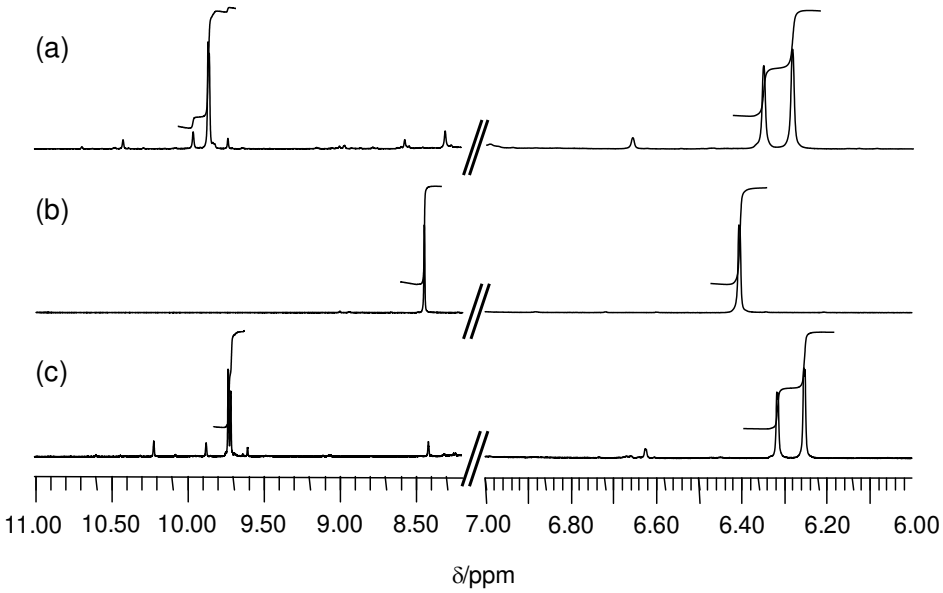


Figure 2. ^{1}H NMR spectra (500 MHz, 20°C) of complexes a) **4a/4b** ($CDCl_3$), b) **5** (CD_2Cl_2), c) **6a/6b** (CD_2Cl_2) (imidazolium resonances).

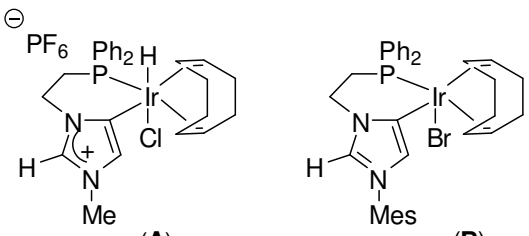


Figure 3. Related iridium complexes reported by Li *et al.* (**A**)[16] and Danopoulos *et al.* (**B**)[8].

Complex **5** has also been characterised by X-ray crystallography (figure 4, table 1). The Ir-C(2) distance [2.068(5) Å] and the Ir(1)-Cl(1) distance are in agreement with the data given by Li *et al.* for (**A**) (table 2).[16] The Ir(1)-P(1) distance, however, appears much shorter than in Li's compound, but is very close to the distance measured in Danopoulos' compound (**B**),[8] where the N(2) atom is also substituted with a bulky aryl group. The C(2)–Ir(1)–P(1) bite angle is also very close to that of Li's complex, with a large value of 92.70(13)°. The structure confirms the binding of the imidazole moiety through C5 (labeled as {C2} in the structure). It also shows the presence of a hydride *trans* to the chloride, with a Ir(1)-H(100) bond length of 1.586(19) Å, and a relative angle to the Cl atom of 164(2)°. The coordination is distorted octahedral at the iridium(III) center. All other characterisations (elemental analysis and mass spectrometry) confirmed the nature of these products.

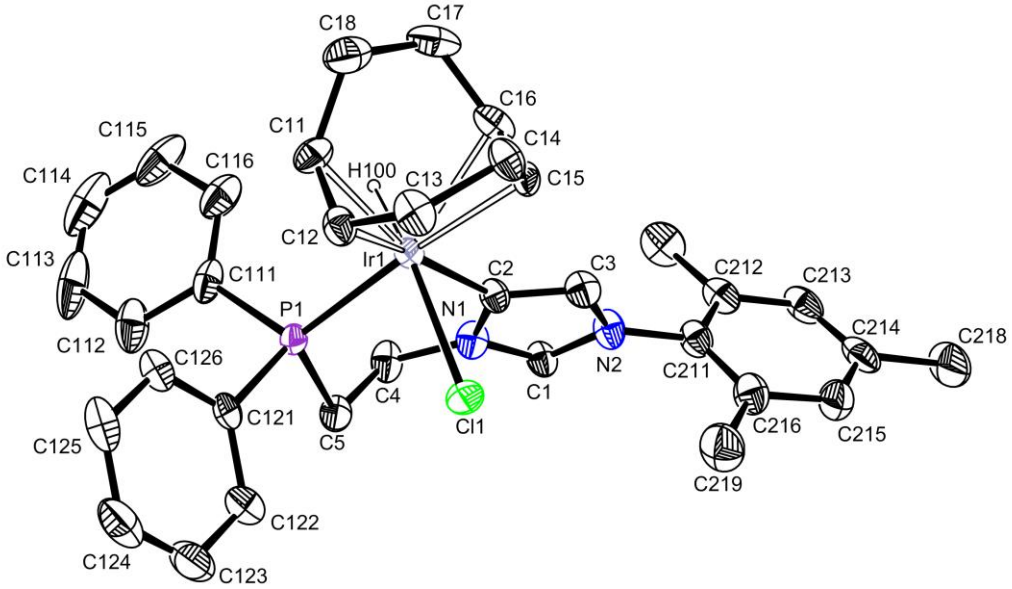


Figure 4. An ORTEP view of compound **5**. Ellipsoids are represented at the 30% probability level. Hydrogen atoms, except H100, cocrystallised solvent molecules and BF_4^- are omitted for clarity.

Table 1. Crystallographic data for compound **5**.

	5
Empirical formula	$C_{36}H_{44}BCl_5F_4IrN_2P$
Formula weight	991.96
Temperature (K)	180(2)
Crystal system	triclinic
Space group	P -1
a (Å)	10.071(5)
b (Å)	15.126(5)
c (Å)	15.988(5)
α (°)	68.528(5)
β (°)	74.532(5)
γ (°)	78.030(5)
Volume (Å^3)	2168.0(15)
Z	2
Density	1.520
Absorption coefficient. (mm^{-1})	3.468
F(0 0 0)	984
θ range for data collection	30.5> θ >1.4
Reflections collected	57426
Independent reflections	13227 [*R*(int) = 0.0612]
Godness-of-fit on F²	1.087
Final *R* indices [I>2σ(I)]	R_1 = 0.0481, wR_2 = 0.1217
R indices for all data	R_1 = 0.0628, wR_2 = 0.1267

Table 2. Comparison of the main structural parameters of **5** and of the iridium complexes described by Li *et al*. (**A**)[16] and Danopoulos *et al.* (**B**)[8].

	5	(**A**)	(**B**)
Bond distances (Å)			
Ir(1)–C(2)[a]	2.068(5)	2.065(6)	2.018(9)
Ir(1)–P(1)	2.2972(16)	2.585(1)	2.283(2)
Ir(1)–Cl(1)	2.4845(15)	2.5097(9)	–
Ir(1)-Br(1)	–	–	2.6865(11)
Ir(1)-H(100)	1.586(19)	–	–
Bond angles (°)			
C(2)–Ir(1)–P(1)	92.70(13)	92.24(16)	88.9(3)
C(2)-Ir(1)-Cl(1)	82.75(15)	85.50(16)	
P(1)–Ir–(1)–Cl(1)	86.81(5)	90.83(5)	–
C(2)-Ir(1)-H(100)	82(2)	–	–
P(1)-Ir(1)-H(100)	92(2)	–	–
Cl(1)-Ir(1)-H(100)	164(2)	–	–

[a] Labelled as C(9) in Li's complex (**A**).[16]

A ^{31}P NMR monitoring of the [Ir(COD)(μ-Cl)]$_2$/**3** reaction at room temperature revealed additional features. After five minutes, the ligand was completely consumed and two products were visible: the final product at 1.1 ppm, and an intermediate compound at 19.4 ppm which quickly disappeared (Scheme 3). Our hypothesis is that, in a first step, the phosphine coordinates to the iridium center, splitting the dimer. Subsequently, the CH insertion occurs at the C5 position of the imidazolium ring, possibly assisted by a chelating effect. This hypothesis is supported by the recent results obtained by Li *et al*.[16]

However, our observed reactivity is at variance with the results described by Danopoulos with a similar ligand, where the mesityl substituent is replaced by DIPP (2,6-diisopropylphenyl, compound **2**).[8] That contribution indicated that the interaction of [Ir(COD)(μ-Cl)]$_2$ with **2**, under unspecified reaction conditions, affords the simple addition product where the chloride ligand has however been exchanged with bromide, [Ir(COD)(Br)(PPh$_2$CH$_2$CH$_2$Im^{DIPP}), similar to the proposed intermediate of our reaction leading to **5**. In the interest of checking whether a simple change of aryl group would enforce such a big reactivity change, we decided to repeat the same reaction under conditions similar to those leading to **4a/4b**. The reactions were carried out in two

different solvents (CH_2Cl_2 or THF), always leading to complete conversion in 20 minutes at room temperature and leading to iridium complex bearing an abnormal carbene (mixture of isomers, **6a+6b**, Scheme 2). These compounds have been fully characterised by NMR and mass spectrometry, leaving no doubt about their nature. Indeed, the NMR spectra present many similar features to those of complexes **4a** and **4b**: the ^{1}H NMR spectrum shows four signals corresponding to the imidazole ring protons at δ 9.73, 9.71, 6.35 and 6.28, with integration values of 0.5 each, for the mixture of **6a** and **6b**. We can also observe two equivalent ^{1}H NMR hydride doublets at δ -15.07 and -14.41 (figure 1c) and two signals at δ -2.04 and -3.08 in the ^{31}P NMR spectrum, corresponding to the two isomers. Moreover, the mass spectrum clearly shows two peaks at *m/z* 777.9 and 821.8, corresponding respectively to cations $\mathbf{6a^+}$ and $\mathbf{6b^+}$.

Conclusions

In summary, we have described an unusual reactivity of chelating phosphine-imidazolium salts toward low oxidation state iridium complexes. In the absence of a base, we have shown that the C-H insertion at the C5 position of the imidazolium ring is the only occurring reaction, with no normal NHC observed. Contrary to related iridium chemistry previously reported by the Crabtree group,[12] this reactivity is independent of the nature of the imidazolium counteranion. It is also independent of the substitution pattern of the aryl group. In fact, the recent paper by Li *et al.*[16] shows identical chemistry for ligands bearing alkyl substituents (Me, *i*Pr) on the 3-N atom of the imidazolium ring. Thus, this reactivity pattern appears to be quite general.

Experimental Section

All reactions were carried out under a dry argon atmosphere using Schlenk glassware and vacuum line techniques. Solvents for syntheses were dried and degassed by standard methods before use. Elemental analyses were carried out by the analytical service of the "Laboratoire de Chimie de Coordination" in Toulouse. ^{1}H data were recorded on a Bruker AV-500 spectrometer, operating at 500 MHz. $^{13}C\{H, P\}$ and $^{31}P\{H\}$ NMR data were recorded on a Bruker AV-500 instrument, operating at 125.8 and 202.5 MHz, respectively. ^{19}F NMR data were recorded on a Bruker AC-200 instrument, operating at 188 MHz. The spectra were referenced internally using the signal from the residual protiosolvent (^{1}H) or the solvent signals (^{13}C), the signal of CF_3CO_2H (10%) in C_6D_6 (^{19}F) and externally using 85% H_3PO_4 for ^{31}P. Mass spectra were obtained from acetonitrile or methanol solutions on a TSQ7000 instrument from ThermoElectron (electrospray ionisation), and from DMSO or DMF solutions on a Nermag R10-10 instrument (FAB). $[Ir(COD)(\mu\text{-}Cl)]_2$ was from Strem and used as received. $MesImEtPPh_2^+Br^-$ **1**, $DIPP\text{-}ImEtPPh_2^+Br^-$ **2** and $MesImEtPPh_2^+BF_4^-$ **3** were prepared as previously described.[4]

General procedure for the synthesis of Ir^{III} complexes

In a Schlenk tube, CH_2Cl_2 was added to a phosphine-imidazolium salt and $[Ir(COD)Cl)]_2$ mixture and stirred for 30 minutes at room temperature. The solvent was removed under vacuum, the residue washed with diethyl ether until the ethereal phase remains colourless, then dried under vacuum.

These reactions can also be done in THF without any change in the results.

Iridium chloro-1,4-cyclooctadienyl-1-(2-(diphenylphosphinoethyl) -3-(2,4,6-trimethylphenyl) imidazol-5-ylidene bromide (4a+4b)

CH_2Cl_2 (3 mL), $MesImEtPPh_2^+Br^-$ **1** (60 mg, 125.4 µmol) and $[Ir(COD)Cl)]_2$ (46 mg, 68.5 µmol). A pale yellow, air-sensitive product was obtained. Yield 94 mg (92%).

$C_{34}H_{40}BrClIrN_2P$ (815.25) Calcd for $C_{34}H_{40}BrClIrN_2P.CHCl_3$: C 44.98, H 4.42, N 3.00; found C 45.01, H 4.35, N 2.80.

First isomer:

^{1}H NMR (500 MHz, $CDCl_3$, 20°C): δ = 9.74 (s, 1 H, NC*H*N), 7.88-7.98 (m, 2 H, *o*-C*H*(Ph^2)), 7.54-7.64 (m, 3 H, *m*,*p*-C*H*(Ph^2)), 7.32-7.51 (m, 5 H, *o*,*m*,*p*-C*H*(Ph^1)), 6.92 (br s, 2 H,

C*H*(Mes)), 6.18 (d, ^{3}J = 1.4 Hz, 1 H, MesNC*H*=), 5.74-5.83 (m, 1 H, NCH_2), 5.29-5.33 (m, 1 H, C*H*(COD)), 5.17-5.23 (m, 1 H, C*H*(COD), 4.61-4.69 (m, 1 H, C*H*(COD)), 3.83-3.91 (m, 1 H, NCH_2), 3.73-3.81 (m, 1 H, C*H*(COD)), 3.37-3.55 (m, 1 H, CH_2P), 3.01-3.12 (m, 1 H, CH_2(COD)), 2.65-2.80 (m, 4 H, CH_2(COD); CH_2P), 2.40-2.60 (m, 2 H, CH_2(COD)), 2.25-2.40 (m + s, 4 H, CH_2(COD); *p*-CH_3), 1.90-2.12 (m + s, 7 H, CH_2(COD); *o*-CH_3), -14.55 (d, $^{2}J_{P\text{-}H}$ = 8.1 Hz, 1 H, Ir-*H*). ^{13}C NMR (125.8 MHz, $CDCl_3$, 20°C): δ = 140.2 (s, *p*-*C*(Mes)), 137.1 (s, N*C*HN), 135.0; 134.1 (s, *o*-*C*(Mes)), 134.5 (d, $^{2}J_{C\text{-}P}$ = 10.4 Hz, *o*-*C*H(Ph^2)), 132.9 (d, $^{2}J_{C\text{-}P}$ = 7.8 Hz, *o*-*C*H(Ph^1)), 132.6 (d, $^{4}J_{C\text{-}P}$ = 2 Hz, *p*-*C*H(Ph^2)), 131.7 (d, $^{4}J_{C\text{-}P}$ = 2 Hz, *p*-*C*H(Ph^1)), 131.5 (s, N*C*(Mes)), 129.5 (d, $^{3}J_{C\text{-}P}$ = 15 Hz, *m*-*C*H(Ph^2)), 129.4; 129.3 (s, *C*H(Mes)), 128.6 (d, *ipso*-*C*(Ph^2)), 128.1 (d, $^{3}J_{C\text{-}P}$ = 10.6 Hz, *m*-*C*H(Ph^1)), 128.0 (d, *ipso*-*C*(Ph^1)), 123.8 (s, MesN*C*H=), 119.9 (d, $^{2}J_{C\text{-}P}$ = 7.9 Hz, Ir-*C*), 96.7 (d, $^{2}J_{C\text{-}P}$ = 16 Hz, *C*H(COD)), 93.3 (d, $^{2}J_{C\text{-}P}$ = 9.5 Hz, *C*H(COD)), 91.7; 82.4 (s, *C*H(COD)), 45.3 (s, N*C*H_2), 34.1; (d, $^{3}J_{C\text{-}P}$ = 2 Hz, *C*H_2(COD)), 31.6; 30.0 (s, *C*H_2(COD)), 29.7 (d, $^{3}J_{C\text{-}P}$ = 2 Hz, *C*H_2(COD)), 25.0 (d, $^{1}J_{C\text{-}P}$ = 40.1 Hz, *C*H_2P), 21.1 (s, *p*-*C*H_3(Mes)), 17.9; 17.7 (s, *o*-*C*H_3(Mes)). ^{31}P NMR (202.5 MHz, $CDCl_3$, 20°C): δ = -2.39 (s, *P*Ph_2).

Second isomer:

^{1}H NMR (500 MHz, $CDCl_3$, 20°C): δ = 9.74 (s, 1 H, NC*H*N), 7.88-7.98 (m, 2 H, *o*-C*H*(Ph^2)), 7.54-7.64 (m, 3 H, *m*,*p*-C*H*(Ph^2)), 7.32-7.51 (m, 5 H, *o*,*m*,*p*-C*H*(Ph^1)), 6.94 (br s, 2 H, C*H*(Mes)), 6.24 (d, ^{3}J = 1.4 Hz, 1 H, MesNC*H*=), 5.74-5.83 (m, 1 H, NCH_2), 5.35-5.41 (m, 1 H, C*H*(COD)), 5.06-5.11 (m, 1 H, C*H*(COD), 4.61-4.69 (m, 1 H, C*H*(COD)), 4.07-4.17 (m, 1 H, NCH_2), 3.63-3.69 (m, 1 H, C*H*(COD)), 3.37-3.55 (m, 1 H, CH_2P), 3.01-3.12 (m, 1 H, CH_2(COD)), 2.65-2.80 (m, 4 H, CH_2(COD); CH_2P), 2.40-2.60 (m, 2 H, CH_2(COD)), 2.25-2.40 (m + s, 4 H, CH_2(COD); *p*-CH_3), 1.90-2.12 (m + s, 7 H, CH_2(COD); *o*-CH_3), -15.22 (d, $^{2}J_{P\text{-}H}$ = 8.3 Hz, 1 H, Ir-*H*). ^{13}C NMR (125.8 MHz, $CDCl_3$, 20°C): δ = 140.2 (s, *p*-*C*(Mes)), 137.4 (s, N*C*HN), 134.8; 134.2 (s, *o*-*C*(Mes)), 134.4 (d, $^{2}J_{C\text{-}P}$ = 10.4 Hz, *o*-*C*H(Ph^2)), 132.8 (d, $^{2}J_{C\text{-}P}$ = 7.9 Hz, *o*-*C*H(Ph^1)), 133.3 (d, $^{4}J_{C\text{-}P}$ = 11 Hz, *p*-*C*H(Ph^2)), 131.6 (d, $^{4}J_{C\text{-}P}$ = 2 Hz, *p*-*C*H(Ph^1)), 131.5 (s, N*C*(Mes)), 129.6 (d, $^{3}J_{C\text{-}P}$ = 15 Hz, *m*-*C*H(Ph^2)), 129.4; 129.3 (s, *C*H(Mes)), 128.6 (d, *ipso*-*C*(Ph^2)), 128.2 (d, $^{3}J_{C\text{-}P}$ = 10.4 Hz, *m*-*C*H(Ph^1)), 128.0 (d, *ipso*-*C*(Ph^1)), 123.5 (s, MesN*C*H=), 121.1 (d, $^{2}J_{C\text{-}P}$ = 8.1 Hz, Ir-*C*), 98.6 (d, $^{2}J_{C\text{-}P}$ = 16.2 Hz, *C*H(COD)), 93.8 (d, $^{2}J_{C\text{-}P}$ = 9.1 Hz, *C*H(COD)), 93.9; 83.7 (s, *C*H(COD)), 45.6 (s, N*C*H_2), 35.5; 31.0 (s, *C*H_2(COD)), 29.6 (d, $^{3}J_{C\text{-}P}$ = 2 Hz, *C*H_2(COD)), 28.2; (d, $^{3}J_{C\text{-}P}$ = 2 Hz, *C*H_2(COD)), 24.9 (d, $^{1}J_{C\text{-}P}$ = 39.5 Hz, *C*H_2P), 21.1 (s, *p*-*C*H_3(Mes)), 17.8; 17.6 (s, *o*-*C*H_3(Mes)). ^{31}P NMR (202.5 MHz, $CDCl_3$, 20°C): δ = -1.14 (s, *P*Ph_2).

MS (FAB, mNBA matrix): *m/z* (%) = 627 (100) [$C_{26}H_{28}ClIrN_2P^+$], 671 (92) [$C_{26}H_{26}BrIrN_2P^+$], 735 (34) [$C_{34}H_{40}ClIrN_2P^+$], 779 (36) [$C_{34}H_{40}BrN_2IrP^+$].

Iridium chloro-1,4-cyclooctadienyl-1-(2-(diphenylphosphinoethyl) -3-(2,4,6- trimethylph enyl) imidazol-5-ylidene tetrafluoroborate (5)

CH_2Cl_2 (3 mL), $MesImEtPPh_2^+BF_4^-$ **3** (60 mg, 123 µmol) and $[Ir(COD)Cl)]_2$ (43 mg, 63 µmol). A cream-white, air-sensitive product was obtained (87 mg, 86%). Suitable X-ray crystals were obtained by layer diffusion of pentane into a CH_2Cl_2 solution at -20°C.

$C_{34}H_{40}BClF_4IrN_2P$ (822.15) Calcd for $C_{34}H_{40}BClF_4IrN_2P.0{,}5\ CH_2Cl_2$: C 47.93, H 4.78, N 3.24; found C 47.53, H 4.90, N 3.36.

^{1}H NMR (500 MHz, CD_2Cl_2, 20°C): δ = 8.45 (s, 1 H, N*C*HN), 7.99 (dd, ^3J = 7 Hz; $^3J_{P\text{-}H}$ = 11.5 Hz, 2 H, *o*-*C*H(Ph^2)), 7.63-7.72 (m, 3 H, *m*,*p*-*C*H(Ph^2)), 7.43-7.57 (m, 5 H, *o*,*m*,*p*-*C*H(Ph^1)), 7.04 (br s, 2 H, *C*H(Mes)), 6.40 (d, ^4J = 1 Hz, 1 H, MesN*C*H=), 5.47-5.54 (m, 1 H, *C*H(COD)), 5.14 (dddd, $^{2,3}J$ = 2.3; 7.6; 14.3 Hz; $^3J_{P\text{-}H}$ = 27.4 Hz, 1 H, N*C*H$_2$), 5.05-5.12 (m, 1 H, *C*H(COD), 4.73-4.77 (m, 1 H, *C*H(COD)), 4.12 (ddd, $^{2,3}J$ = 11; 12 Hz; $^3J_{P\text{-}H}$ = 19.6 Hz, 1 H, N*C*H$_2$), 3.62-3.69 (m, 1 H, *C*H(COD)), 3.49-3.58 (m, 1 H, *C*H$_2$P), 3.02-3.12 (m, 1 H, *C*H$_2$(COD)), 2.92-3.00 (m, 1 H, *C*H$_2$(COD)), 2.66-2.82 (m, 3 H, *C*H$_2$(COD); *C*H$_2$P), 2.47-2.58 (m, 2 H, *C*H$_2$(COD)), 2.32-2.42 (m + s, 4 H, *C*H$_2$(COD); *p*-*C*H$_3$), 2.00-2.15 (m + s, 7 H, *C*H$_2$(COD); *o*-*C*H$_3$), -15.12 (d, $^2J_{P\text{-}H}$ = 8.3 Hz, 1 H, Ir-*H*). ^{13}C NMR (125.8 MHz, CD_2Cl_2, 20°C): δ = 140.6 (s, *p*-*C*(Mes)), 135.9 (s, N*C*HN), 134.8; 134.4 (s, *o*-*C*(Mes)), 134.3 (d, $^2J_{C\text{-}P}$ = 7.3 Hz, *o*-*C*H(Ph^2)), 132.8 (d, $^2J_{C\text{-}P}$ = 8 Hz, *o*-*C*H(Ph^1)), 132.6 (d, $^4J_{C\text{-}P}$ = 2.3 Hz, *p*-*C*H(Ph^2)), 131.4 (d, $^4J_{C\text{-}P}$ = 2.6 Hz, *p*-*C*H(Ph^1)), 131.3 (s, N*C*(Mes)), 129.5 (d, $^3J_{C\text{-}P}$ = 10.6 Hz, *m*-*C*H(Ph^2)), 129.4 (br s, *C*H(Mes)), 128.8 (d, $^1J_{C\text{-}P}$ = 58.7 Hz, *ipso*-*C*(Ph^1)), 128.6 (d, $^1J_{C\text{-}P}$ = 58.7 Hz, *ipso*-*C*(Ph^2)), 128.1 (d, $^3J_{C\text{-}P}$ = 10.5 Hz, *m*-*C*H(Ph^1)), 124.5 (s, MesN*C*H=), 121.4 (d, $^2J_{C\text{-}P}$ = 9.2 Hz, Ir-*C*), 98.7 (d, $^2J_{C\text{-}P}$ = 15.6 Hz, *C*H(COD)), 94.6 (d, $^3J_{C\text{-}P}$ = 9.4 Hz, *C*H(COD)), 94.1; 84.4 (s, *C*H(COD)), 45.7 (s, N*C*H$_2$), 35.6; 30.7 (s, *C*H$_2$(COD)), 29.6 (d, $^3J_{C\text{-}P}$ = 2.1 Hz, *C*H$_2$(COD)), 28.0 (d, $^3J_{C\text{-}P}$ = 3.8 Hz, *C*H$_2$(COD)), 25.1 (d, $^1J_{C\text{-}P}$ = 39.7 Hz, *C*H$_2$P), 20.8 (s, *p*-*C*H$_3$(Mes)), 17.1; 17.0 (s, *o*-*C*H$_3$(Mes)). ^{31}P NMR (202.5 MHz, CD_2Cl_2, 20°C): δ = 2.42 (s, *P*Ph$_2$). ^{19}F NMR (188 MHz, CD_2Cl_2, 20°C): δ = -76.2 (s, B*F*$_4$). MS (ESI, positive mode) *m/z* (%) = 627.1 (10) [$C_{26}H_{28}ClIrN_2P^+$], 735.1 (100) [$C_{34}H_{40}ClIrN_2P^+$]. MS (ESI, negative mode) *m/z* (%) = 87 (100) [BF_4^-].

Iridium chloro-1,4-cyclooctadienyl-1-(2-(diphenylphosphinoethyl) -3-(2,6-diisopropylphe nyl) imidazol-5-ylidene bromide (6a+6b)

CH_2Cl_2 (3 mL), DIPP-ImEtPPh$_2$$^+Br^-$ **2** (82 mg, 157 µmol) and [Ir(COD)Cl)]$_2$ (53 mg, 79 µmol). A pale yellow, air-sensitive product was obtained (118 mg, 87%).

$C_{37}H_{46}BrClIrN_2P$ (857.33). Calcd for $C_{37}H_{46}BrClIrN_2P.CH_2Cl_2$: C 48.44, H 5.13, N 2.97; found C 48.41, H 5.13, N 2.92.

First isomer:

^{1}H NMR (500 MHz, CD_2Cl_2, 20°C): δ = 9.73 (d, ^4J = 1.1 Hz, 1 H, NC*H*N), 8.02-8.05 (m, 2 H, *o*-C*H*(Ph^2)), 7.63-7.69 (m, 3 H, *m*,*p*-C*H*(Ph^2)), 7.39-7.55 (m, 5 H, *o*,*m*,*p*-C*H*(Ph^1)), 7.32 (d, ^3J = 6.5 Hz, 1 H, *m*-C*H*(DIPP)), 7.31 (d, ^3J = 6.6 Hz, 1 H, *m*-C*H*(DIPP)), 6.28 (d, ^3J = 1.6 Hz, 1 H, (DIPP)NC*H*=), 5.70-5.78 (m, 1 H, NCH_2), 5.31-5.36 (m, 1 H, C*H*(COD)), 5.16-5.20 (m, 1 H, C*H*(COD), 4.67-4.75 (m, 1 H, C*H*(COD)), 3.89-3.97 (m, 1 H, NCH_2), 3.66-3.74 (m, 1 H, C*H*(COD)), 3.54-3.61 (m, 1 H, CH_2P), 3.00-3.09 (m, 1 H, CH_2(COD)), 2.66-2.91 (m, 3 H, CH_2(COD); CH_2P), 2.54-2.63 (m, 1 H, CH_2(COD)), 2.32-2.52 (m, 4 H, CH_2(COD); C*H*(CH$_3$)$_2$), 1.90-2.12 (m, 1 H, CH_2(COD)), 1.16-1.26 (m, 12 H,CH(CH_3)$_2$), -14.41 (d, $^2J_{P\text{-}H}$ = 8.2 Hz, 1 H, Ir-*H*). ^{13}C NMR (125.8 MHz, CD_2Cl_2, 20°C): δ = 146.0; 145.3 (s, *o*-*C*(DIPP)), 137.4 (s, N*C*HN), 134.6 (d, $^2J_{P\text{-}C}$ = 10.5 Hz, *o*-*C*H(PPh$_2$)), 133.0 (s, $^2J_{P\text{-}C}$ = 6.7 Hz, *o*-*C*H(PPh$_2$)), 132.5 (d, $^4J_{P\text{-}C}$ = 2.6 Hz, *p*-*C*H(PPh$_2$)), 131.4 (d, $^4J_{P\text{-}C}$ = 2.7 Hz, *p*-*C*H(PPh$_2$)), 131.2 (s, N*C*(Mes)), 131.0 (s, *p*-*C*H(DIPP)), 129.4 (d, $^3J_{P\text{-}C}$ = 10.5 Hz, *m*-*C*H(PPh$_2$)), 127.9 (s d, $^3J_{P\text{-}C}$ = 10.5 Hz, *m*-*C*H(PPh$_2$)), 125.5 (d, $^3J_{C\text{-}P}$ = 8.5 Hz, (DIPP)N*C*H=), 124.3; 124.1 (s, *m*-*C*H(DIPP)), 120.1 (d, $^2J_{C\text{-}P}$ = 8.4 Hz, Ir-*C*), 96.8 (d, $^2J_{P\text{-}C}$ = 16.2 Hz, *C*H(COD)), 93.8 (d, $^2J_{P\text{-}C}$ = 9.0 Hz, *C*H(COD)), 91.7; 82.7 (s, *C*H(COD), 45. 4 (s, N*C*H$_2$), 33.7 (d, $^3J_{P\text{-}C}$ = 2.1 Hz, *C*H$_2$(COD)), 31.9 (s, *C*H$_2$(COD)), 29.9 (d, $^3J_{P\text{-}C}$ = 4.3 Hz, *C*H$_2$(COD)), 29.7 (d, $^3J_{P\text{-}C}$ = 2.2 Hz, *C*H$_2$(COD)), 28.5; 28.4 (s, *C*H(CH$_3$)$_2$), 25.0 (d, $^1J_{C\text{-}P}$ = 40.3 Hz, *C*H$_2$P), 24.3; 24.2; 24.1; 24.0 (s, CH (*C*H$_3$)$_2$). ^{31}P NMR (202.5 MHz, CD_2Cl_2, 20°C): δ = -3.08 (s, *P*Ph$_2$).

Second isomer:

^{1}H NMR (500 MHz, CD_2Cl_2, 20°C): δ = 9.71 (d, ^4J = 1.2 Hz, 1 H, NC*H*N), 7.98-8.01 (m, 2 H, *o*-C*H*(Ph^2)), 7.63-7.69 (m, 3 H, *m*,*p*-C*H*(Ph^2)), 7.39-7.55 (m, 5 H, *o*,*m*,*p*-C*H*(Ph^1)), 7.36 (d, ^3J= 7.9 Hz, 1 H, *m*-C*H*(DIPP)), 7.35 (d, ^3J = 7.9 Hz, 1 H, *m*-C*H*(DIPP)), 6.35 (d, ^3J = 1.5 Hz, 1 H, (DIPP)NC*H*=), 5.70-5.78 (m, 1 H, NCH_2), 5.37-5.43 (m, 1 H, C*H*(COD)), 5.10-5.17 (m, 1 H, C*H*(COD), 4.67-4.75 (m, 1 H, C*H*(COD)), 4.20-4.27 (m, 1 H, NCH_2), 3.76-3.83 (m, 1 H, C*H*(COD)), 3.38-3.43 (m, 1 H, CH_2P), 3.00-3.09 (m, 1 H, CH_2(COD)), 2.66-2.91 (m, 3 H, CH_2(COD); CH_2P), 2.54-2.63 (m, 1 H, CH_2(COD)), 2.32-2.52 (m, 4 H, CH_2(COD); C*H*(CH$_3$)$_2$), 1.90-2.12 (m, 1 H, CH_2(COD)), 1.16-1.26 (m, 12 H,CH(CH_3)$_2$), -15.07 (d, $^2J_{P\text{-}H}$ = 8.1 Hz, 1 H, Ir-*H*). ^{13}C NMR (125.8 MHz, CD_2Cl_2, 20°C): δ = 145.9; 145.4 (s, *o*-*C*(DIPP)), 137.6 (s, N*C*HN), 134.4 (d, $^2J_{P\text{-}C}$ = 10.5 Hz, *o*-*C*H(PPh$_2$)), 132.9 (s, $^2J_{P\text{-}C}$ = 8.0 Hz, *o*-

*C*H(PPh$_2$)), 132.5 (d, $^4J_{P\text{-}C}$ = 2.4 Hz, *p*-*C*H(PPh$_2$)), 131.4 (d, $^4J_{P\text{-}C}$ = 2.5 Hz, *p*-*C*H(PPh$_2$)), 131.1 (s, N*C*(Mes)), 131.0 (s, *p*-*C*H(DIPP)), 129.4 (d, $^3J_{P\text{-}C}$ = 10.5 Hz, *m*-*C*H(PPh$_2$)), 128.1 (s d, $^3J_{P\text{-}C}$ = 10.6 Hz, *m*-*C*H(PPh$_2$)), 125.3 (d, $^3J_{C\text{-}P}$ = 8.5 Hz, (DIPP)N*C*H=), 124.3; 124.2 (s, *m*-*C*H(DIPP)), 120.2 (d, $^2J_{C\text{-}P}$ = 8.6 Hz, Ir-*C*), 98.7 (d, $^2J_{P\text{-}C}$ = 15.7 Hz, *C*H(COD)), 94.2 (d, $^2J_{P\text{-}C}$ = 9.3 Hz, *C*H(COD)), 93.9; 84.2 (s, *C*H(COD), 45.8 (s, N*C*H$_2$), 35.2 (d, $^3J_{P\text{-}C}$ = 2.1 Hz, *C*H$_2$(COD)), 32.2 (s, *C*H$_2$(COD)), 29.4 (d, $^3J_{P\text{-}C}$ = 2.1 Hz, *C*H$_2$(COD)), 28.6; 28.5 (s, *C*H(CH$_3$)$_2$), 28.3 (d, $^3J_{P\text{-}C}$ = 3.9 Hz, *C*H$_2$(COD)), 25.1 (d, $^1J_{C\text{-}P}$ = 39.6 Hz, *C*H$_2$P), 24.3; 24.2; 24.1; 24.0 (s, CH(*C*H$_3$)$_2$). ^{31}P NMR (202.5 MHz, CD$_2$Cl$_2$, 20°C): δ = -2.04 (s, *P*Ph$_2$).
MS (ESI, positive mode) *m/z* (%) = 777.9 (100) [$C_{37}H_{46}ClIrN_2P^+$], 821.8 (33) [$C_{37}H_{46}BrIrN_2P^+$].

Crystallographic Data

A single crystal was mounted under inert perfluoropolyether on the tip of a glass fibre and cooled in the cryostream of an Bruker APEX2 diffactometer. Data were collected using the monochromatic Mo Kα radiation (λ = 0.71073). The final unit cells parameters were obtained by the least-squares refinement of a large number of selected reflections. The structures were solved by direct methods (SIR97[17]) and refined by least-squares procedures on *F2* with the SHELXL-97 program[18] using the integrated system WINGX(1.63).[19] Hydrogen atoms attached to carbon atoms were introduced at calculated positions and treated as riding on their parent atoms [d(CH) = 0.96–0.98 Å] with a displacement parameter equal to 1.2 (C_6H_5, CH_2) or 1.5 (CH_3) times that of the parent atom. The hydride atom was located in difference Fourier syntheses and its coordinates were refined using a Ir-H restraint of 1.60(2) Å. The BF_4 anion was partially disordered by rotation around one B-F axis, this disorder was treated using the tools available in SHELX-97[17]. Some residual electron densities were difficult to modelise and therefore, the SQUEEZE function of PLATON[20] was used to eliminate the contribution of the electron density in the solvent region from the intensity data, and the solvent-free model was employed for the final refinement. There are two cavities of 127 Å^3 per unit cell. PLATON estimated that each cavity contains 62 electrons which may correspond to a mixture of dichloromethane and pentane solvent molecules. The molecular views were realised with the help of ORTEP-III.[21],[22]

CCDC 681170 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

Acknowledgements

We thank the Centre National de la Recherche Scientifique (C.N.R.S.) for support of this work, the Fonds Social Européen (F.S.E.) for a Ph.D. fellowship to Joffrey Wolf, and Yannick Coppel for N.M.R. analysis of the iridium complexes.

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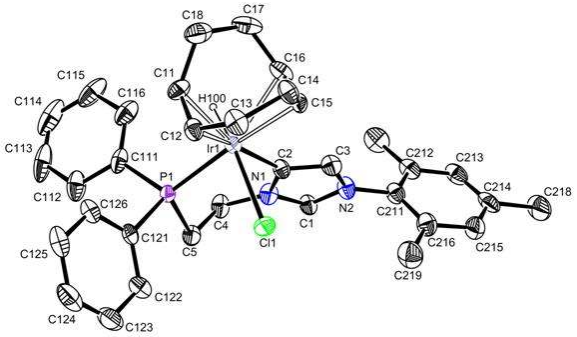
1 **Graphical abstract**



Phosphine-imidazolium salts add to iridium complex $[Ir(COD)(\mu\text{-}Cl)]_2$ without the need of a base and lead to iridium(III) hydride complexes containing "abnormal" carbene ligands, through C-H insertion at the C5 position of the imidazolium ring.

Keywords: Carbenes / Phosphane ligands / Iridium / Hydrides / C-H activation

Key Topic: Iridium complexes of abnormal carbenes

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