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ACCOUNTS
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The Chemistry of Aromatic Osmacycles

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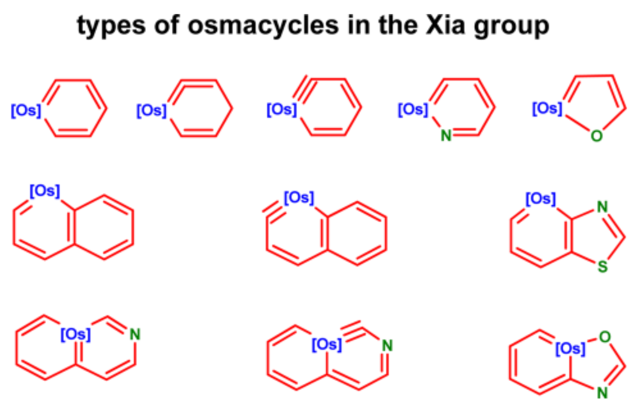
CONSPECTUS

Aromatic compounds, such as benzene and its derivatives, porphyrins, fullerenes, carbon nanotubes, and graphene, have numerous applications in biomedicine, materials science, energy science, and environmental science. Metalla-aromatics are analogues of conventional organic aromatic molecules in which one of the (hydro)carbon segments is formally replaced by an isolobal transition-metal fragment. Researchers have studied these transition-metal-containing aromatic molecules for the past three decades, particularly the synthesis and reactivity of metallabenzenes. Another focus has been the preparation and characterization of other metalla-aromatics such as metallafurans, metallapyridines, metallabenzynes, and more. Despite significant advances, remaining challenges in this field include the limited number of convenient and versatile synthetic methods to construct stable and fully characterized metalla-aromatics, and the relative shortage of new topologies.



To address these challenges, we have developed new methods for preparing metalla-aromatics, especially those possessing new topologies. Our synthetic efforts have led to a large family of closely related metalla-aromatics known as aromatic osmacycles. This Account summarizes the synthesis and reactivity of these compounds, with a focus on features that are different from those of compounds developed by other groups. These osmacycles can be synthesized from simple precursors under mild conditions. Using these efficient methods, we have synthesized aromatic osmacycles such as osmabenzene, osmabenzyne, isoosmabenzene, osmafuran, and osmanaphthalene. Furthermore, these methods have also created a series of new topologies, such as osmabenzothiazole and osmapyridyne. Our studies of the reactivity of these osma-aromatics revealed unprecedented reaction patterns, and we demonstrated the interconversion of several osmacycles.

Like other metalla-aromatics, osma-aromatics have spectroscopic features of aromaticity, such as ring planarity and the characteristic bond lengths between a single and double bond, but the osma-aromatics we have prepared also exhibit good stability towards air, water, and heat. Indeed, some seemingly unstable species proved stable, and their stability made it possible to study their optical, electrochemical, and magnetic properties. The stability of these compouds results from their aromaticity and the phosphonium substituents on the aromatic plane: most of our osma-aromatics carry at least one phosphonium group. The phosphonium group offers stability via both electronic and steric mechanisms. The phosphonium acts as an electron reservoir, allowing the circulation of electron pairs along metallacycles and lowering the electron density of the aromatic rings. Meanwhile, the bulky phosphonium groups surrounding the aromatic metallacycle prevent most reactions that could decompose the skeleton.

Introduction

Aromaticity is an important concept in organic chemistry. The fruitful interplay of theory and experiment facilitates the molecular engineering of aromatic compounds, thereby providing numerous new compounds and materials with interesting properties. Formal replacement of one CH group in benzene by a main group element provides aromatic analogues of benzene (for instance in pyridine one CH

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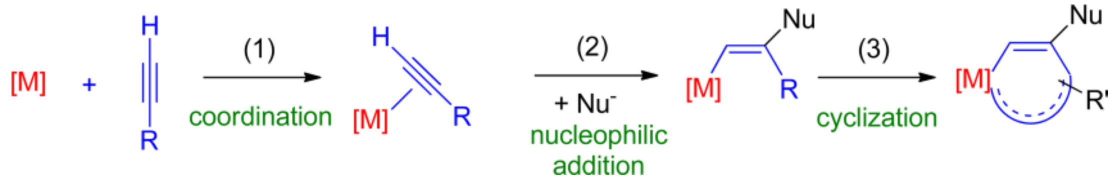
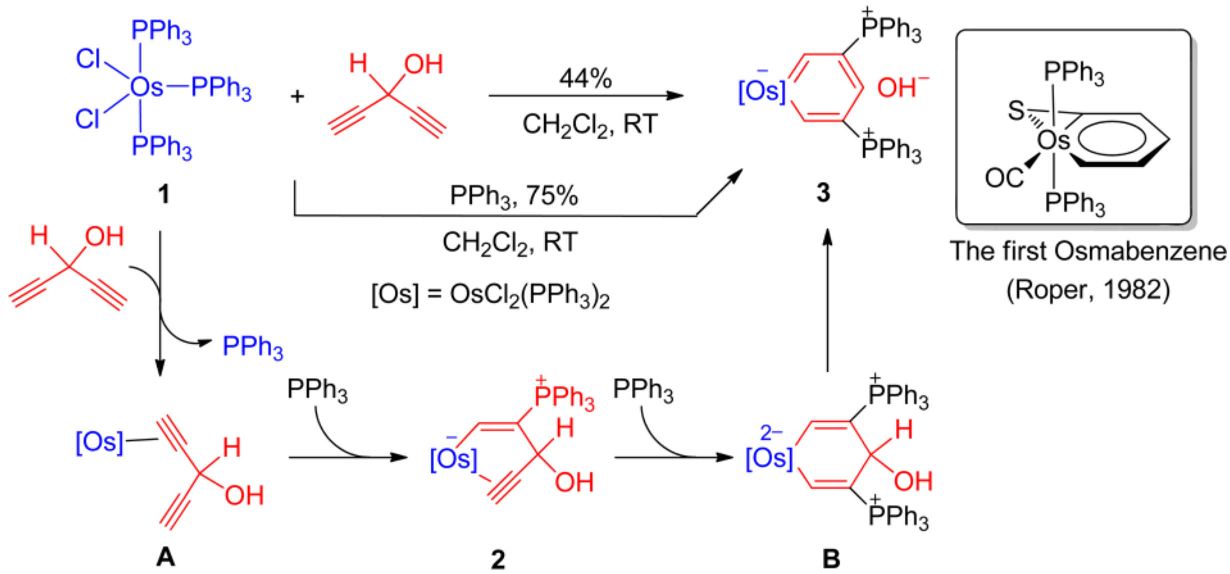
CHART 1



SCHEME 1



group is replaced by a N atom). Likewise, formal replacement of the CH group by an isolobal transition metal fragment yields "metallabenzenes".

In the past 30 years, significant progress has been made in the synthesis and reactivity of metallabenzenes.[1−5] Since the theoretical prediction by Thorn and Hoffmann in 1979[6] and the first preparation of an osmabenzene by Roper et al. in 1982,[7] stable metallabenzenes with different metals have been prepared.[1−5] The flurry of activity has also expanded to other topologies of aromatic metallacycles,[5,8,9] moving the field forward from metallabenzenes to metalla-aromatics.

Since 2004, we have concentrated on the development of synthetic strategies for metalla-aromatics, with a particular focus on their reactivity that would lead to new metalla-aromatic species.[10] Our key ring-forming reactions of metalla-aromatics were characterized by the initial coordination of the alkyne to the metal center, followed by subsequent attack of nucleophiles (mostly triphenylphosphines, or anions such as I^-, SCN^-, and Br^-) on the coordinated alkyne (Chart 1), and finally ring-closing through cycloaddition, C−H activation, or coordination. Our efforts over the past 8 years have expanded the library of closely related osma-aromatics. This Account seeks to highlight our contributions on osma-aromatics, focusing particularly on their synthesis, reactivity, and stability resulting from aromaticity and phosphonium substituents. The aromatic features of the osmacycles, be it theoretical (by different calculations)[11,12] or experimental (planar π-skeleton and negligible bond alternation in crystal structures for instance), will not be discussed here but could be found in greater detail in theoretical reviews[11,12] or corresponding articles for each osmacycle. Furthermore, we make no attempt to cover comprehensively the history of metalla-aromatics and seminal work from many other researchers in this field but rather refer the reader to some relevant literature.[1,2,4,8,9,13,14]

Osmabenzene

The first metallabenzene was prepared from the reaction of $Os(CS)(CO)(PPh_3)_3$ and ethyne (Scheme 1, right).[7] Thereafter, the field of metalla-aromtics flourished with significant development of synthetic methods to yield metallabenzenes with different metals. However, Roper's method remained the only pathway to osmabenzenes.[1] In close collaboration with Jia et al. from Hong Kong University of Science and

SCHEME 2

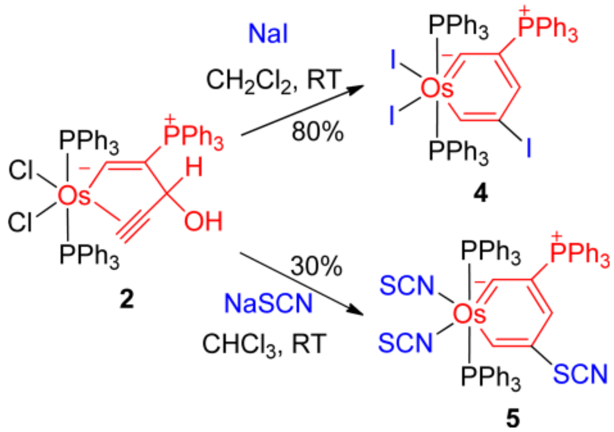


CHART 2

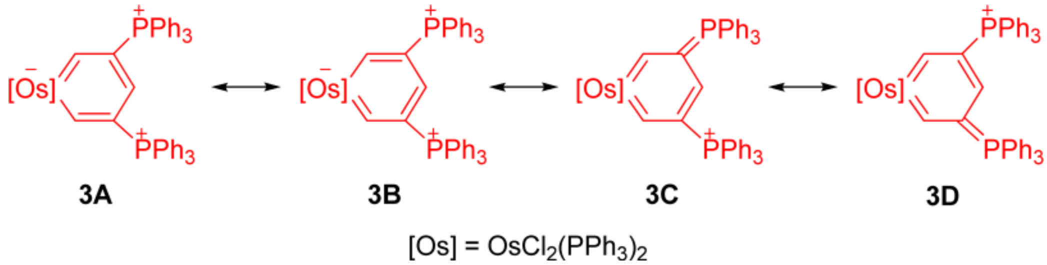
Technology, we developed the second route to stable osmabenzenes.[10] We found that the reaction of $OsCl_2(PPh_3)_3$ with readily accessible 1,4-pentadiyn-3-ol produced bisphosponium-substituted osmabenzene **3** at room temperature (Scheme 1). When PPh_3 was added to the reaction mixture, the isolated yield of **3** was increased from 44% to 75%. The proposed mechanism for this reaction involved initiation with the substitution of a coordinated phosphine ligand with an η^2-coordinated alkyne to form intermediate **A**, followed by nucleophilic attack of the PPh_3 at the coordinated alkyne to furnish intermediate **2**. Another PPh_3 attacked **2** to give intermediate **B**, which then lost OH^- from the sp^3-carbon on the γ position to yield osmabenzene **3**.

We then tried to isolate the intermediates of this reaction. In situ NMR spectroscopy indicated that several new species along with osmabenzene **3** were produced initially, and osmabenzene **3** dominated eventually (Scheme 1). It was difficult to isolate these species directly from dichloromethane solution. Fortunately, however, intermediate **2** was precipitated as a yellow solid and isolated in good yield when the reaction was carried out in THF. Intermediate **2** was stable for weeks as a solid under nitrogen but became unstable in solution, especially in the presence of acid or base. It was also susceptible to nucleophiles other than PPh_3 (Scheme 2).[15] The addition of NaI to the solution of **2** gave iodoosmabenzene **4**, representing a rare halogen-substituted metallabenzene. Accordingly, the addition of NaSCN yielded osmabenzene **5**. Iodoosmabenzene **4** was synthetically interesting because it may undergo a series of cross-coupling reactions. Intermediate **2** and osmabenzene **5** were important starting materials for a series of reactions described below.

Geometrically, the construction of a six-membered metallacycle from two components has three possible retrosyntheses: [5 + 1], [4 + 2], and [3 + 3] (Chart 2). The synthesis of osmabenzenes **3**–**5** represented the most straightforward [5 + 1] approach to metallabenzenes, starting from a metal complex and a commercially available C_5 segment under ambient conditions at room temperature. The reactions were completed in one pot and can easily be scaled up to gram quantities. This strategy is general and robust as reflected not only by the structural diversity of osmabenzene products (e.g., **3**, **4**, and **5**) or organic starting materials (e.g., the synthesis of osmabenzene **10**[16] and osmatoluene **14**,[17] see below) but also by the synthesis of stable ruthenabenzene.[18]

Osmabenzene **3**, the first member of the osma-aromatic family developed by us, exhibited several unique characteristics. The presence of bulky and electron-deficient phosphonium substituents on the metalla-aromatic plane distinguished our osma-aromatics from those developed by other groups (Scheme 1),[7,19−21] resulting in differences in spectroscopy, properties, and reactivity. For instance, the *ortho* proton of osmabenzene **3** resonated at 23.13 ppm, significantly farther downfield than that in Roper's first osmabenzene (13.95 ppm).[7] This downfield shift was mainly due to the electron-withdrawing effect of phosphonium substituents. When the electronic effect became less intense, as in osmabenzene **4**, which carried only one phosphonium group, the proton resonances of the metallacycle shifted back to upfield (20.1 ppm for OsC*H*Cl and 19.0 ppm for OsC*H*CPPh$_3$). The X-ray diffraction data revealed that the metallacycle of **3** was essentially a planar ring structure similar to Roper's osmabenzene, and the C–C bond distances of the metallacycle were longer than typical C═C double bonds and shorter than typical C–C single bonds.[7] Nonetheless, the Os–C bond lengths were shorter than those of Roper's osmabenzene.[7,22] Four resonance structures of osmabenzene **3** were proposed (Chart 3). The similarity in P–C(phenyl) and P–C(metallabenzene) bond lengths suggested that **3A** and **3B** were the dominant contributors to the overall structure in the solid state; however, cyclically unconjugated **3C** and **3D** may influence the reactivity of osmabenzene **3** in solution and contribute to the stability of **3**. Our osma-aromatics usually possessed good air and thermal stability. For instance, osmabenzene **3**

CHART 3



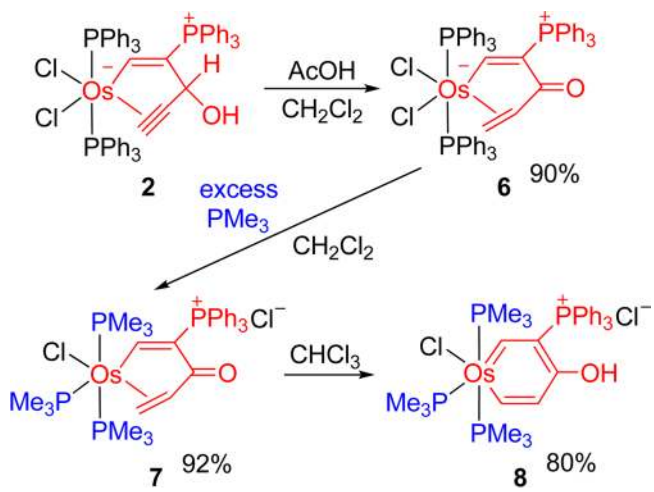
can be kept for months without appreciable decomposition in the solid state at room temperature; its solid sample remained unchanged after being heated at 120 °C for 24 h in air. Such stability greatly facilitated the synthesis, purification, characterization, and storage of our osma-aromatics.

The unique function of the phosphonium group can be understood in two ways: electronic and steric. Acting as an electron reservoir, the phosphonium allows the circulation of electron pairs along metallacycles and lowers the electron density of aromatic ring (Chart 3; **3C** and **3D**). The capability of phosphonium to accept electrons also makes the β-carbon of phosphonium group electrophilic. The bulky PPh_3 groups surrounding aromatic metallacycle prevent most possible reactions that may decompose the skeleton.

The reaction of intermediate **2** with acetic acid afforded highly insoluble α,β-unsaturated ketone complex **6** as a red solid, which precipitated from the solution (Scheme 3).[23] When **6** was treated with excess PMe_3, two PPh_3 ligands and a chloride ligand of **6** were substituted by PMe_3 ligands to yield **7** (Scheme 3). Interestingly, **7** was slowly isomerized to *p*-osmaphenol **8** in chloroform solution (Scheme 3). The difference in the stability of **6** and **7** was presumably related to the decreased electron density of the metal cycle in the latter due to the replacement of one Cl^- ligand with PMe_3 ligand, thus facilitating the deprotonation of the terminal α-H of the coordinated olefin. In comparison with previous metallaphenol[7] and the organic phenol derivatives, osmaphenol **8** was air-stable in both the solution and the solid state. The chloroform solution of **8** remained unchanged in air for over 1 week.

Motivated by the successful synthesis of our first osmabenzene, we extended the organic substrate to the alternatives of 1,4-pentadiyn-3-ol, with a lower degree of unsaturation, and found osmabenzenes could still be obtained. The reaction of $OsCl_2(PPh_3)_3$ with 1-pentyn-4-en-3-ol in THF produced the η^2-allyl alcohol complex **9** (Scheme 4).[16] Similar to **2**, this reaction was also initiated with the coordination of the alkyne to the metal center and nucleophilic

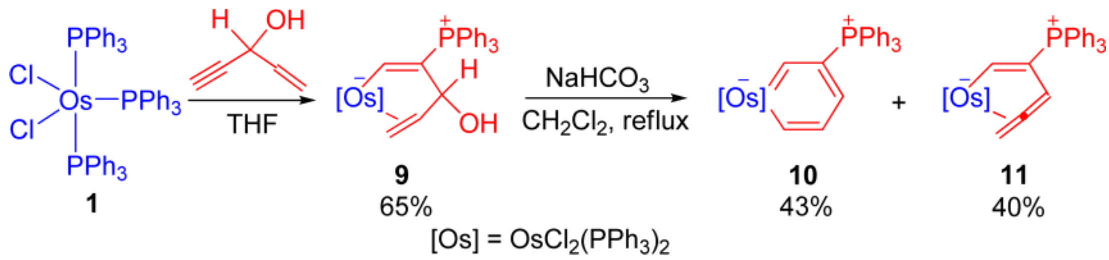
SCHEME 3



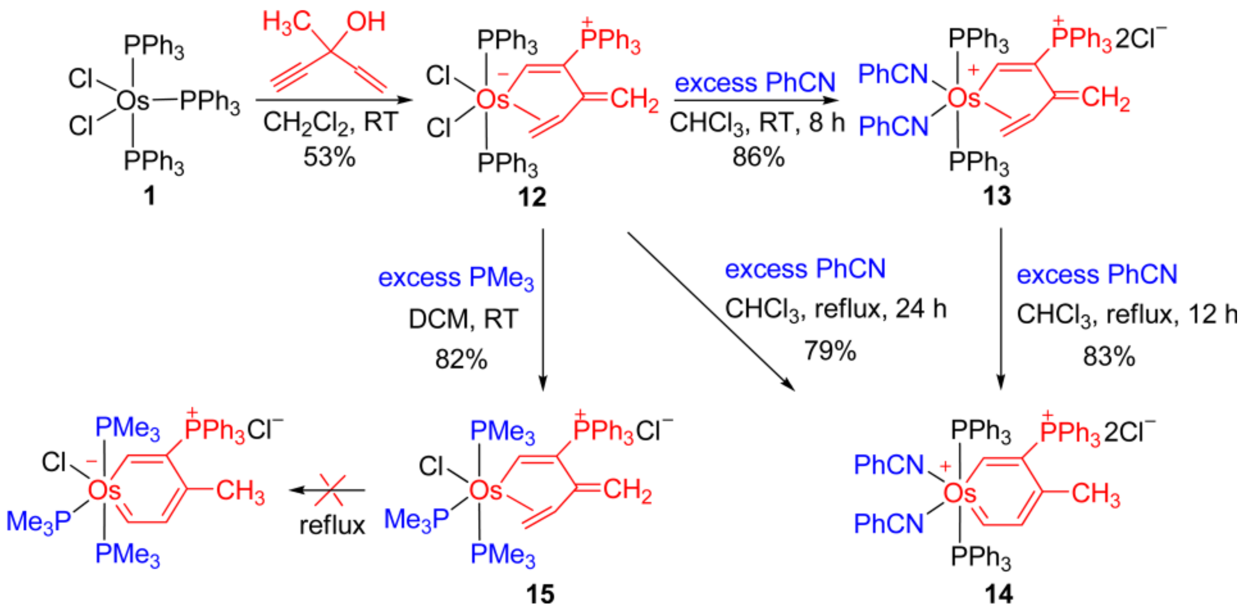
attack by phosphines on the coordinated alkyne. Heating **9** in dichloromethane with reflux led to the formation of monophosphonium substituted osmabenzene **10**, η^2-allene complex **11**, and other species (Scheme 4). Notably, **10** and **11** were isomers. The formation of osmabenzene **10** involved the dissociation of OH^- from **9** and subsequent α-H deprotonation; thus the addition of $NaHCO_3$ increased the yield of **10** from 28% to 43%.

Although the reaction of $OsCl_2(PPh_3)_3$ with commercially available 3-methyl-1-pentyn-4-en-3-ol proceeded well to give intermediate **12** (Scheme 5),[17] the pathway to osmabenzene was more problematic. The PMe_3 substitution of **12** led to complex **15**, but unlike **7**, which was gradually isomerized to osmaphenol **8**, no anticipated osmatoluene was observed under the same conditions. The contrasting outcomes of structurally similar **7** and **15** were probably due to the different electronic nature of the exocyclic group on the γ-carbon of the metallacycle of these two complexes because the ketone in **7** was more electron-withdrawing than the alkene in **12**. The replacement of two Cl^- in the neutral complex **12** by two benzonitriles led to dicationic complex **13** (Scheme 5). The electron density of the

SCHEME 4



SCHEME 5

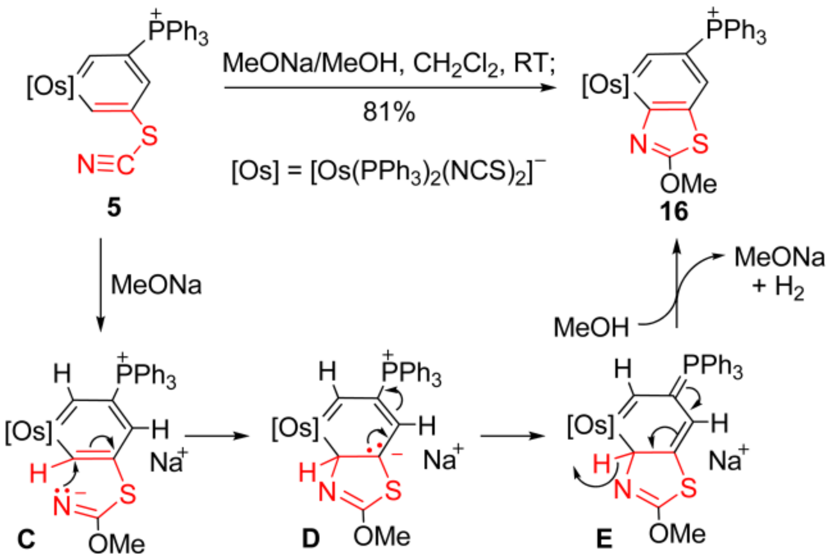


osmacycle was significantly decreased as a direct consequence of ligand exchange, thus facilitating the hydrogen-transfer process for the formation of osmatoluene **14** from **13** (Scheme 5). The allene complex **13** was then isomerized almost quantitatively to give osmatoluene **14**.

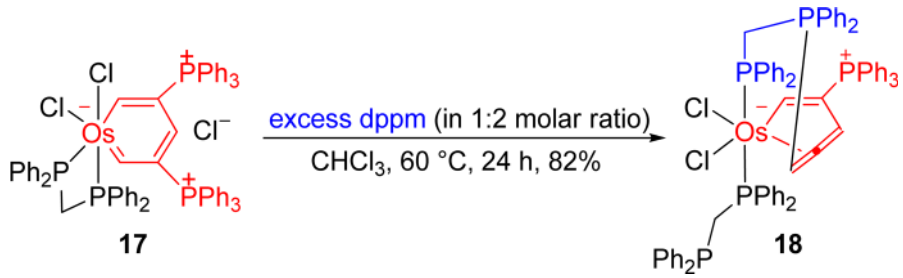
The reactivity of metallabenzenes is a result of the presence of an aromatic ring and a reactive metal center and was explored first by Roper, Wright and co-workers.[24] Although metallabenzenes tend to react in ways that are atypical of conventional aromatic molecules,[4] Roper, Wright and co-workers demonstrated the first electrophilic aromatic substitution of metallabenzene with an osmabenzene.[24] The directing effects in these reactions were in accordance with those of benzene.

Arenes, in particular heteroarenes, can undergo nucleophilic aromatic substitution (S_NAr) reactions if electron-withdrawing groups are *ortho* or *para* to the leaving group (typically a halogen) on the ring. Nonetheless, the conditions for S_NAr reactions are usually harsh. We reported the first S_NAr reaction of metallabenzene under ambient conditions.[25] Osmabenzene **5** reacted with MeONa/MeOH to generate osmabenzothiazole **16** (Scheme 6). The proposed mechanism revealed that the addition reaction of **5** with MeONa gave intermediate **C**, which then underwent intramolecular nucleophilic attack to afford intermediate **D**. The intermediate **D** can be regarded as a Jackson–Meisenheimer complex.[26] The phosphonium group acted as an electron reservoir, creating a more stable resonance form of **D** and the intermediate **E**. The electron was then pushed back from the phosphonium group, driving the loss of the hydride ion and furnishing osmabenzothiazole **16**. The mechanism involved a similar addition–elimination manner to the classic S_NAr reactions of arenes. But unlike the tough conditions required for the classic reactions, the presence of the phosphonium substituent and the osmium center effectively lowered the electron density of the aromatic metallacycle, thus rendering the S_NAr reaction and the leaving of H^- able to proceed under ambient conditions.

SCHEME 6



SCHEME 7



This reaction, using metallabenzene as a starting material, realized the annulation reaction of metallabenzenes, thus representing a novel pathway to construct fused metalla-aromatics. It also demonstrated the aromaticity of osmabenzene.

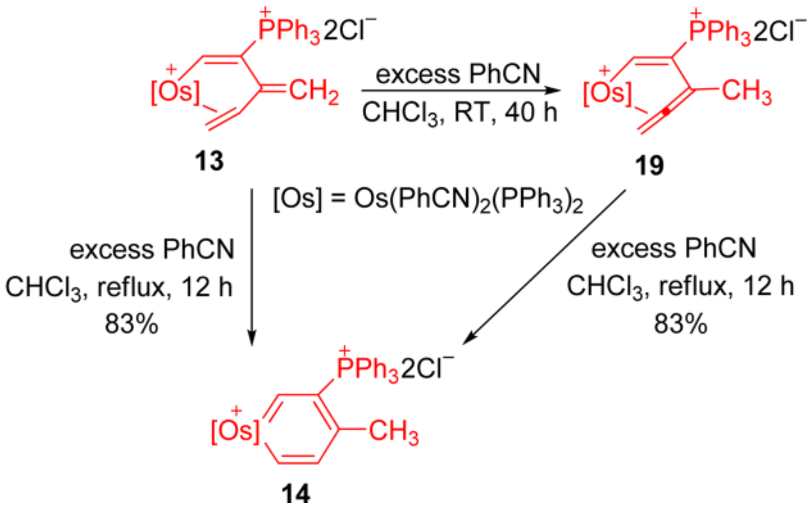
When osmabenzene **3** was treated with an excess of the nuceophile bis(diphenylphosphino)methane (dppm), bisphosphonium substituted osmabenzene **17** was first obtained, which then underwent intramolecular nucleophilic addition and subsequent cleavage of the P–C bond to give a cyclic osmium η^2 allene complex **18** (Scheme 7).[27] Similar reactions also took place in ruthenabenzene and osmapyridinium.

While Scheme 7 depicted that osmabenzene can be converted to an allene complex, Scheme 8 showed that the alternative was also possible.[17] Investigation of the conversion of **13** to osmabenzene **14** (Scheme 8) revealed that **13** underwent double bond shifting to generate the allene complex **19** at room temperature. Upon heating with reflux, complex **19** was transformed to osmabenzene **14** through an intermolecular proton-transfer process.

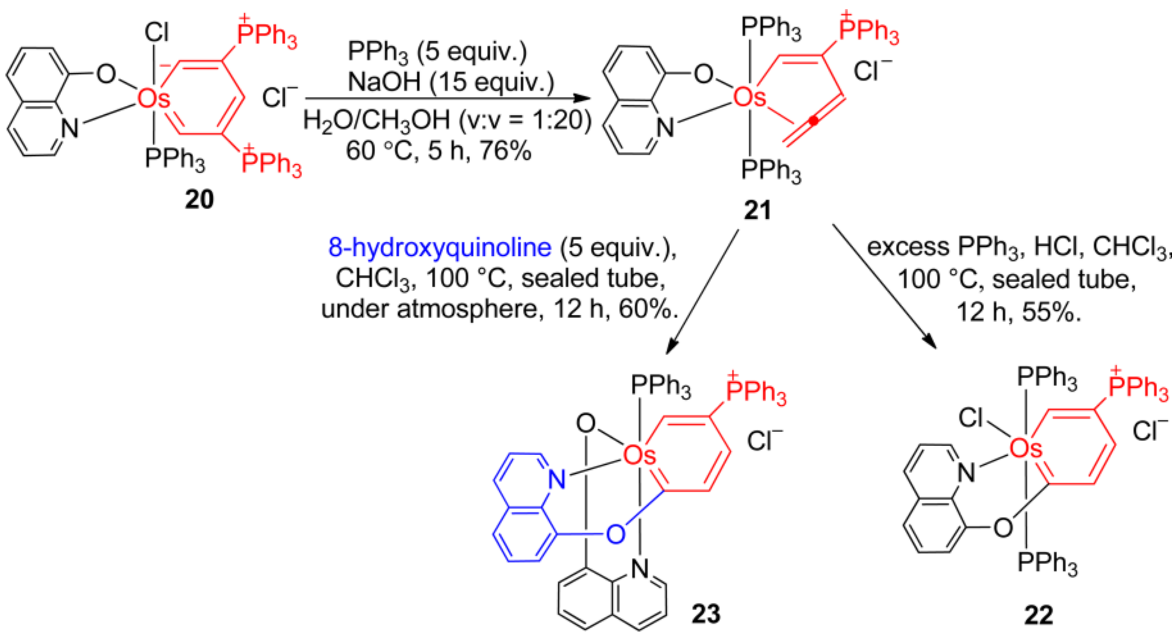
Recently, we achieved the interconversion of osmabenzenes and cyclic osmium η^2 allene complexes on the same system (Scheme 9).[28] In the presence of excess PPh_3 and NaOH, osmabenzene **20** evolved into η^2-allene-coordinated complex **21**, and NaOH presumably facilitated the P–C bond cleavage of the metallacycle. The treatment of complex **21** with excess PPh_3 in the presence of acid produced mono(8-hydroxyquinoline)-substituted osmabenzene **22**, and with the excess 8-hydroxyquinoline under air, di(8-hydroxyquinoline)-substituted osmabenzene **23** was obtained. Both reactions involved intramolecular nucleophilic substitutions.

The ligand substitution reactions of osmabenzene **3** led to a series of new osmabenzenes **25**–**27** (Scheme 10).[15] The electron density of aromatic metallacycles can be tuned through ligand exchange, thereby resulting in different reactivity and physical properties. The replacement of one Cl^- with a pyridine or a $^-N(CN)_2$ (coordinated through N in

SCHEME 8



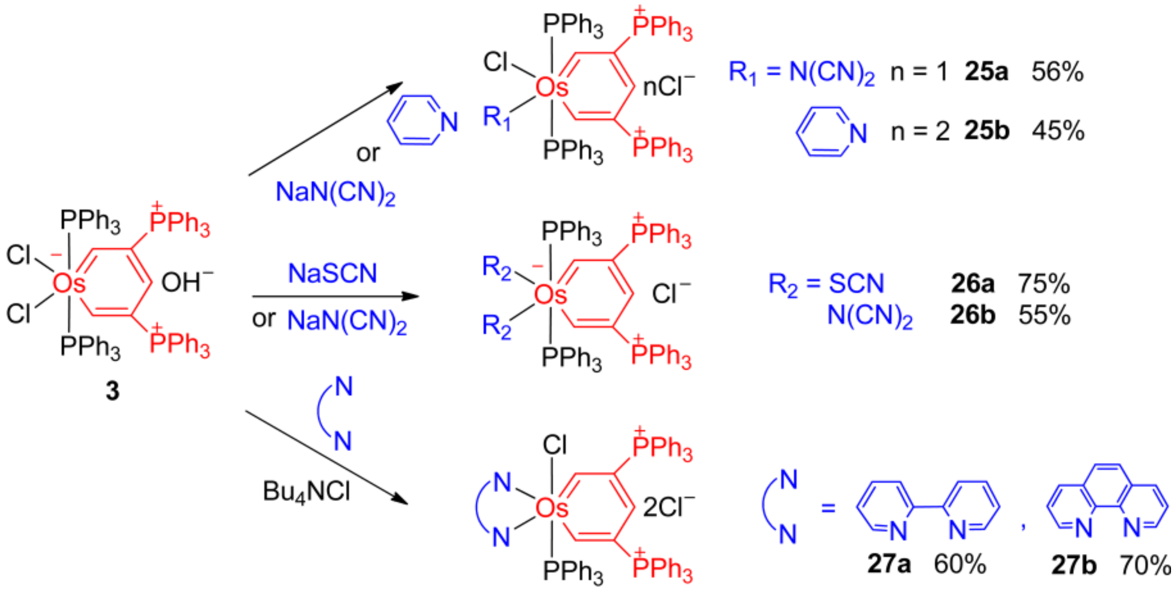
SCHEME 9



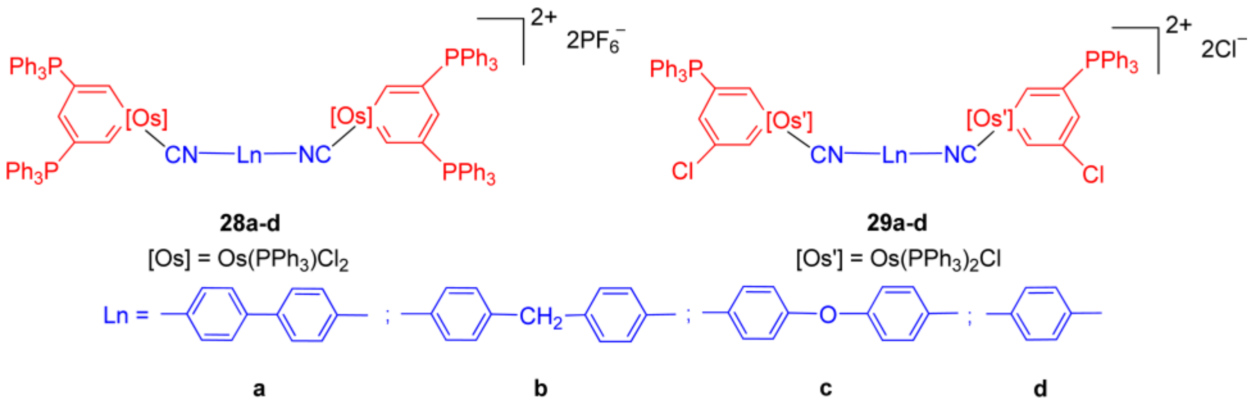
the CN) produced monosubstituted osmabenzenes **25a** and **25b**. The reaction of **3** with NaSCN or excess NaN(CN)$_2$, on the other hand, led to the replacement of two Cl$^-$, giving disubstituted osmabenzenes **26a** and **26b**. When the monodentate ligands were changed to bidentate ligands 2,2′-dipyridine or 1,10-phenanthroline, osmabenzenes **27a** and **27b** were formed. Note that the metallacycle of **27a** deviates significantly from planarity, the osmium center was 0.6748 Å out of the plane of the metallacyclic carbon atoms. The nonplanarity induced by bis-substitution was presumably due to both electronic and steric factors induced by the asymmetrical ligand environment above and below the six-membered metallacycle.[29]

The ligand substitution reaction of osmabenzene **3** with various diisocyanides afforded a series of diisocyanide-bridged bisosmabenzenes **28a**−**d** (Scheme 11).[30] Bisosmabenzenes containing a Cl$^-$ and a phosphonium substitutent on each metallacycle **29a**−**d** were obtained from the reactions of intermediate **2** with diisocyanides in the presence of NH_4PF_6 and NaCl through nucleophilic addition reactions. Cyclic voltammetry of osmabenzenes **29a**−**d** indicated that the two metal centers in osmabenzenes **29c** and **29d** could interact with each other through the diisocyanide bridge.

SCHEME 10



SCHEME 11



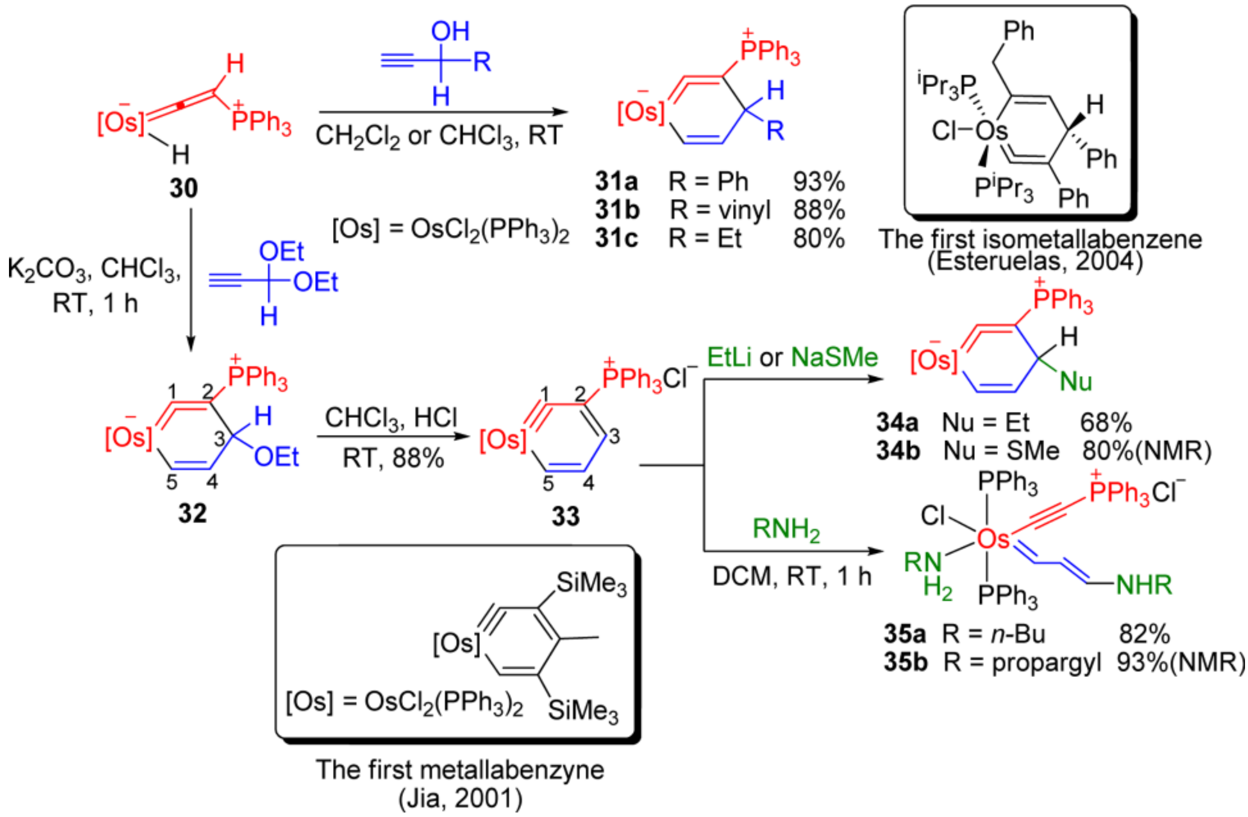
Osmabenzyne and Isoosmabenzene

Benzyne is a well-known yet transient intermediate involved in a wide variety of chemical transformations. Therefore, isolation and full characterization of metallabenzyne seems impossible at first glance. Nonetheless, Jia et al. isolated the first stable osmabenzyne in 2001 (Scheme 12, lower left).[31] Since then, the Jia group has developed a series of approaches toward metallabenzynes and explored their reactivity thoroughly.[5,8,9]

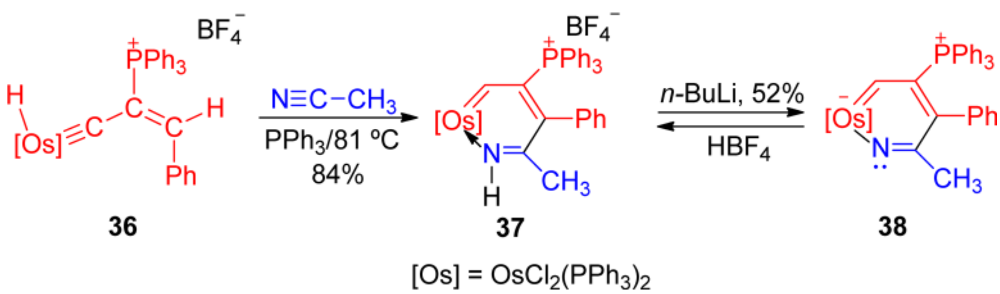
Esteruelas et al. prepared the first isometallabenzene (Scheme 12, right).[32] In 2011, we capitalized on an unprecedented formal [3 + 3] cycloaddition reaction between osmium hydride vinylidene **31** and alkynols to prepare stable isoosmabenzenes **31a**−**c** (Scheme 12).[33] We then further expanded the organic substrate to HC≡CCH(OEt)$_2$ and obtained an osmabenzyne **33** unexpectedly (Scheme 12).[34] The reaction started with a similar [3 + 3] cycloaddition process to an intermediate isoosmabenzene **32**, which then eliminated an ethoxyl group to give a stable osmabenzyne **33**. Isoosmabenzene **32** was stable in solution for several hours, thus allowing in situ NMR monitoring of the transformation from **32** to **33**.

Note that osmabenzyne **33** was remarkably stable. It can survive heating in air at 120 °C for 5 h in the solid state. It was also resistant to several acids, bases, terminal alkynes, and nucleophiles. Strong nucleophiles, nonetheless, could attack osmabenzyne **33** at C3 to restore isoosmabenzenes (**34a**[33] and **34b**, Scheme 12) or open the metallacycles (**35a** and **35b**, Scheme 12). Clearly, the formal interconversion of isometallabenzene and metallabenzyne (Scheme 12) was achieved.

SCHEME 12



SCHEME 13



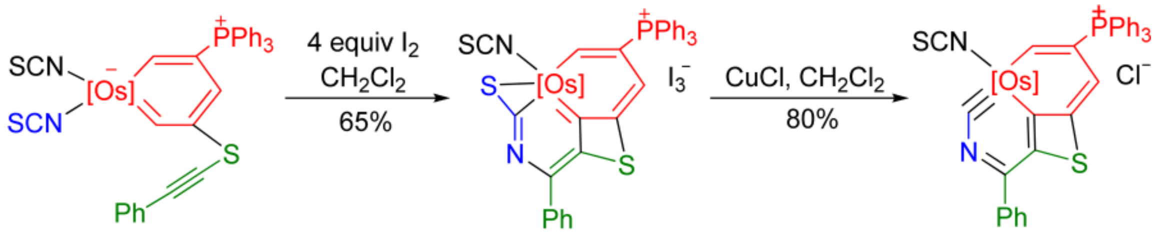
Osmapyridine and Osmapyridyne

Although considerable progress has been made in the synthesis of metallabenzenes, their aza-containing analogue metallapyridine[35,36] was significantly less developed. The first metallapyridine (tantalapyridine), which was not delocalized, was reported by Wigley et al. in 1998.[35] Note that our discovery in 2009 represented the second metallapyridine and the first metallapyridinium and osmapyridine.[36]

When complex **36** was mixed with PPh_3 in acetonitrile under reflux, osmapyridinium **37** was obtained (Scheme 13). The reaction may be regarded as a formal hetero-Diels–Alder reaction[37] in which osmium hydride alkenylcarbyne **36** acted as 1-metalla-1,3-diene with acetonitrile as a dienophile. The deprotonation of **37** by *n*-BuLi produced osmapyridine **38**, and the treatment of **38** with HBF_4 regenerated **37** (Scheme 13). The construction of **36** can be considered as a [4 + 2] approach toward the six-membered metallapyridinium. Hence, we realized all three possible retrosyntheses to construct a six-membered matallacycle from the two constituents mentioned in Chart 2: [5 + 1], [4 + 2], and [3 + 3].

Most notably, these osmapyridiniums are paramagnetic. Osmapyridinium **37** showed low-field chemical shifts for the ^{1}H NMR signals of Os*CH* ($\delta = 48.01$) and N*H* ($\delta = 25.38$). For osmapyridine **38**, the ^{31}P NMR signals cannot be observed at room temperature or even at lower temperatures

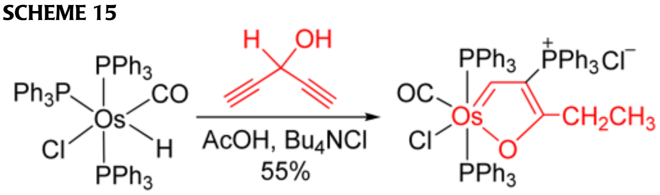
SCHEME 14



39 40 41

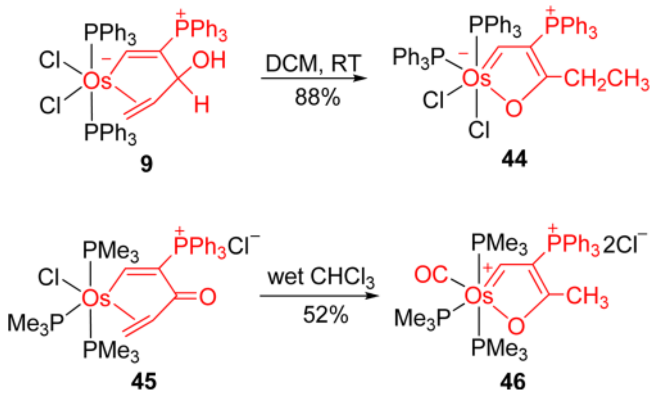
[Os] = Os(PPh$_3$)$_2$

SCHEME 15



42 43

SCHEME 16



(200−293 K), while the ^{1}H NMR spectrum displayed several irregular broad signals at these temperatures. In addition, magnetic measurement experiments confirmed the paramagnetism of **37** and **38**. The computational results indicated that the net spin populations primarily reside on the Os^{IV} (5d^4) center, and the Os-bonded C and N atoms also exhibited some paramagnetism. These paramagnetic centers could significantly modify the NMR behavior of the neighboring hydrogen atoms as observed in NMR spectroscopy. Note that **37** is the first metallapyridinium and **38** is the first late-transition-metal containing metallapyridine.

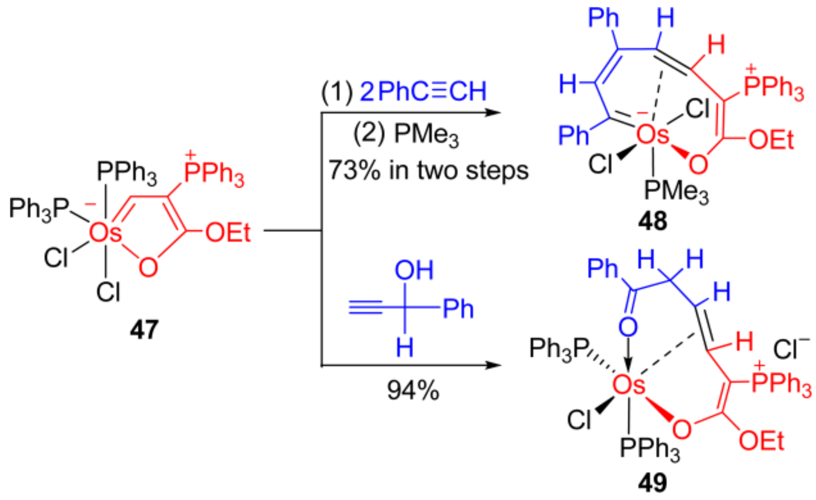
Recently, we synthesized the first *m*-metallapyridine (osmapyridine **40**, Scheme 14, which can also be defined as an osmaisoquinoline) and the first metallapyridyne (osmapyridyne **41**, Scheme 14).[38] In comparison to the two previously reported azametallabenzenes[35,36] (i.e., *o*-metallapyridines in which the nitrogen atom was directly connected to the metal atom), osmapyridine **40** had its nitrogen atom only connected with carbon atoms. The treatment of osmabenzene **39** with I$_2$ gave osmapyridine **40**. The main structure of **40** was an osmium-bridged polycycle containing an osmabenzene ring and an *m*-osmapyridine ring. Surprisingly, copper(I) chloride can reduce complex **40** to osmapyridyne **41**, the first metallapyridyne. The complexes **40** and **41** were metal-bridged polycyclic metallabenzenoid aromatics, in which the transition-metal center was shared by both six-membered rings. Interestingly, the synthetic method permitted the use of metallabenzene as a starting material to prepare polycyclic metallaaromatics.

Notably, complexes **40** and **41** were stable in air and elevated temperatures. Solid samples of **40** and **41** can be heated at 100 °C in air for more than 5 h without noticeable decomposition. We also found that **41** did not react with common nucleophiles (e.g., H_2O, MeOH, MeONa, KOH, and NaSH) or electrophiles (e.g., HCl, HBF_4, O_2, MeI, and MeOTf).

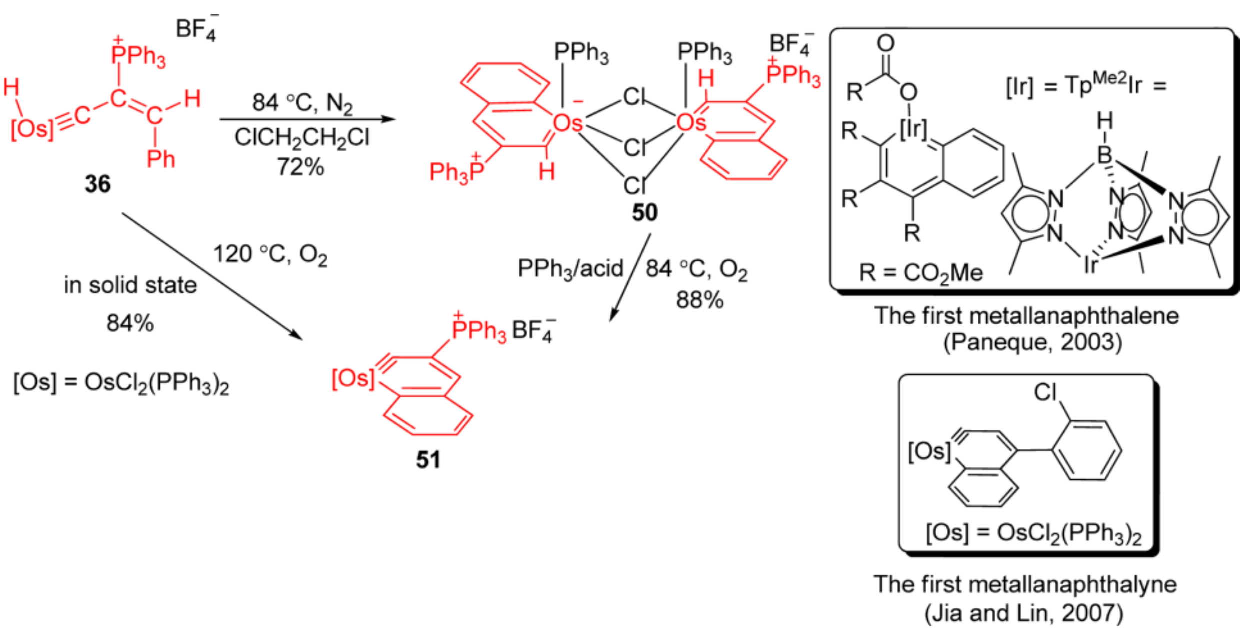
Osmafurans

Osmafurans are the most extensively investigated five-membered osma-aromatics.[39] We found that complex **42** reacted readily with 1,4-pentadiyn-3-ol to give osmafuran **43** (Scheme 15).[40] The η^2-allyl alcohol complex **9** yielded osmafuran **44** through a rearrangement in dichloromethane (Scheme 16).[16] Osmafuran **46** was formed from complex **45** through complicated transformations, including the hydrolyzation of the terminal carbon−carbon double bond and removal of the carbonyl group (Scheme 16).[41] Interestingly, because the osmium−carbon bond in complex osmafuran **47** showed obvious carbenic character, it underwent ring-expansion reactions through the alkyne insertion to produce nine-membered osmacycles **48** and

SCHEME 17



SCHEME 18

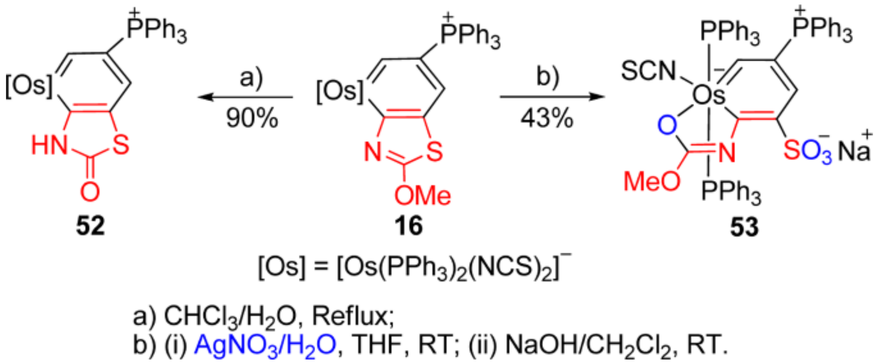


49 (Scheme 17).[42] The osmacycles **48** and **49** can be regarded as intermediates stabilized by an internal coordinated olefin, leading to the olefin metathesis or alkyne polymerization.

Osmanaphthalene and Osmanaphthalyne

Paneque et al. prepared the first metallanaphthalene in 2003 (Scheme 18, right).[26] Jia, Lin, and co-workers synthesized the first metallanaphthalyne in 2007 (Scheme 18, right).[43] We discovered the synthesis of osmanaphthalene and osmanaphthalyne unexpectedly in 2009, when we studied the thermal and air stability of osmium hydride alkenylcarbyne **36**.[44] Heating **36** in $ClCH_2CH_2Cl$ under a N_2 atmosphere afforded the (μ-Cl)$_3$-bridged bisosmanaphthalene **50**, while under an O_2 atmosphere osmanaphthalyne **51** was produced. Interestingly, **51** could even be obtained by directly heating the solid sample of **50** in air (Scheme 18).[44] The formation of **50** and **51** underwent a similar migration of the hydride ligand from the osmium center to the carbyne carbon atom. The subsequent *ortho* C−H bond activation of the phenyl ring led to the formation of a hydride osmanaphthalene intermediate. The reaction then began to diverge depending on the atmosphere. Under a N_2 atmosphere, the dimerization dominated, and an O_2

SCHEME 19



atmosphere led to the oxidation of the osmanaphthalene intermediate, yielding osmanaphthalyne **51**. Notably, bisosmanaphthalene **50** could also be converted to osmanaphthalyne **51** in the presence of acids (HCl and HBF_4), PPh_3, and O_2. Because osmanaphthalene **50** and osmanaphthalyne **51** contained a metallabenzene segment and a metallabenzyne segment, respectively, the transformation from **50** to **51** represented the first example of the conversion from metallabenzene to metallabenzyne. The Jia group has realized the conversion from metallabenzyne to metallabenzene;[45] hence we completed the formal interconversion of metallabenzene and metallabenzyne.

Osmabenzothiazolone and Osmabenzoxazole

As mentioned above, osmabenzothiazole **16** was formed through an intramolecular S_NAr reaction. Heating **16** in wet chloroform gave osmabenzothiazolone **52** (Scheme 19),[25] as a result of the hydrolysis of the methoxy group on the thiazole ring. When osmabenzothiazole **16** was treated with silver nitrate and then NaOH, another fused metalla-aromatic compound, osmabenzoxazole sulfonate **53**, was obtained (Scheme 19).[25] The formation of **53** involved the oxidation and ring-opening of the thiazole moiety. The subsequent coordination of the ester carbonyl oxygen atom to the osmium center formed the new oxazole ring. Our results represented the first metallathiazole, metallabenzothiazolone, and metallabenzoxazole.

Concluding Remarks

Over the past 8 years, we have developed a series of synthetic methods toward aromatic osmacycles. Our reactions are characterized by the alkyne coordination and subsequent nucleophilic attack by a triphenylphosphine, producing a great variety of osma-aromatics with phosphonium substituents. These substituents are critical because they stabilize both the intermediates and products, making it possible to isolate and use them as starting materials for the construction of osma-aromatics with new topologies. We have completed three possible retrosyntheses to six-membered metallacycles (i.e., [5 + 1], [4 + 2], and [3 + 3]). The concept of the interconversion of metallacycles, such as the interconversion of metallabenzene and metallabenzyne, as well as isometallabenzene and metallabenzyne, has also been proposed and realized. Our metalla-aromatics include both monocycles and polycycles, with the transition metal either in the bridge or not in the bridge. We have demonstrated that the formal replacement of a CH segment (or C atom) in a conjugated cyclic system by an Os fragment not only can maintain aromaticity (as in metallabenzene and metallafuran) but also can overcome extreme strain in aromatic organic analogues (as in metallabenzyne and metallapyridyne).

The extraordinarily rich chemistry and diversified structures of our osma-aromatics corroborate the importance of metalla-aromatics, which remain as an active area of exploration; this field should have a bright and rapidly evolving future. On the other hand, the good stability of our osmacycles in air, water, and heat may enable their potential applications as materials. We have investigated, for the first time, the optical,[25] electrochemical,[15,30] and magnetic[36] properties of these intriguing metalla-aromatics. Some of these properties are promising for use in materials science. We envision that the different substituents, metals, organic fragments, and ligands will further expand the family of metalla-aromatics, thus creating a multitude of candidates for various applications in the field of material science.

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FOOTNOTES

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