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Minireview

Organometallic Chemistry

Reactions of Metal–Carbon Bonds within Six-Membered Metallaaromatic Rings

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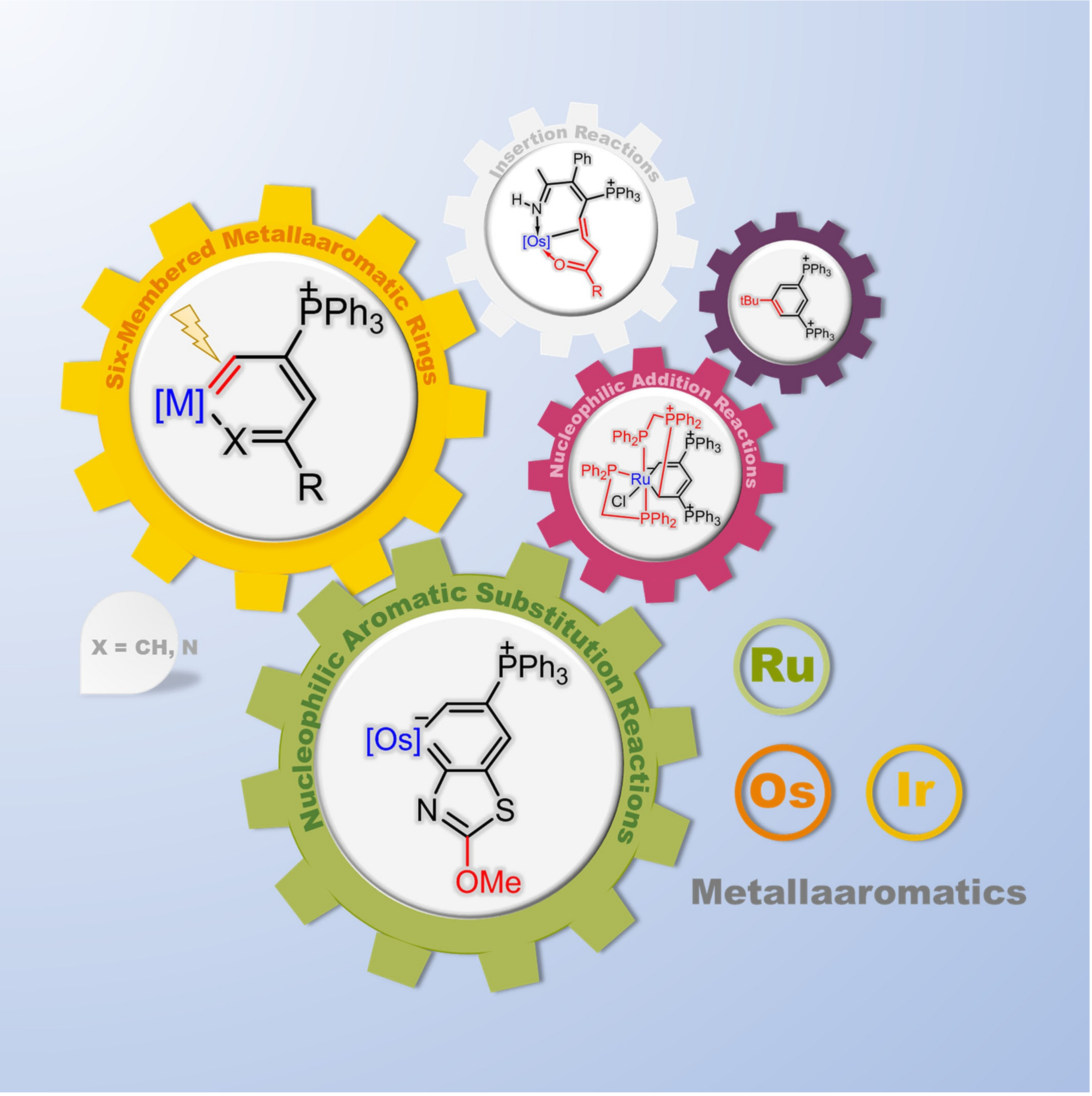

Abstract: Metallaaromatics represent a distinct and attractive class of heterocycles, which have greatly expanded the library of known aromatics. They have garnered extensive research interest on account of their unique properties, organometallic reactivity, and aromaticity. The metal–carbon bonds have been regarded as the most active reaction sites of metallaaromatics and a variety of related reactions have been demonstrated in the literature. This Minireview summarized recent findings on the reactivity of the metal–carbon bonds, mainly relevant to the representative metallaaromatics with six-membered ring scaffolds. A series of reactions occurred on the metal–carbon bonds, including the nucleophilic addition reactions, nucleophilic aromatic substitution reactions, electrophilic addition reactions, reactions with unsaturated compounds, and migratory insertion reactions, have been classified. These reactions demonstrate that the metal–carbon bonds of metallaaromatics can undergo typical reactions for both aromatic species and metal carbene/carbyne complexes. Meanwhile, the reactivity trends of the metal–carbon bonds are strongly affected by the metal centers and the effect of the corresponding substituents of metallacycles.

1. Introduction

Metallaaromatics are a distinctive species of aromatics, which have been broadly recognized as compounds structurally derived from formal replacement of a C(H) segment in conventional organic aromatic molecules by an isolobal transition metal fragment. In the past decades, metallaaromatics have been attracting widespread interest because of their unique structural features, aromatic, and organometallic nature.[1] Various synthetic methods for these species have been well developed, and their reactivity has also been extensively investigated. A number of interesting reactions have been demonstrated in the literature, which can be classified into two major types with comparison to conventional organic aromatics. For example, metallaaromatics can undergo characteristic reactions of aromatics, such as electrophilic aromatic substitution (S_EAr) reactions,[2] nucleophilic aromatic substitution (S_NAr) reactions,[3] and forming half-sandwich,[4] sandwich,[5] and triple-decker complexes as η^6 ligands.[6] Besides, they present typical reactivity of organometallics such as ligand substitution reactions,[1a,c,7] cycloaddition reactions,[8] nucleophilic addition reactions,[3,9] and C–C coupling to form cyclopentadienyl ligands.[10]

The chemistry of metallaaromatics originated from the pioneering work of Thorn and Hoffman in 1979,[11] and the early development of this enticing field has been summarized in excellent reviews by different groups over the past several decades. Synthetic chemistry of metallaaromatics involving the synthesis, characterization, and evaluation of aromaticity are depicted in these previous comprehensive reviews.[1] In this Minireview, we survey recent advances concerning reactivity of the metal–carbon bonds within six-membered metallaaromatic rings, which have been reported at a steadily increasing pace over the last few years. The metal–carbon bonds in metallaaromatics can act like metal carbenes/carbynes to undergo nucleophilic or electrophilic addition reactions, insertion reaction, cycloaddition reactions, and migratory insertion reactions. Meanwhile, aromaticity of the metallacycles exerted considerable influence on the reactivity of metal–carbon bonds. It is therefore not surprising that typical aromatic substitution reactions, such as S_NAr reactions, have been presented in some cases, yielding a number of unique derivatives with metallaaromatic features. In addition, the metal centers and the substituents of metallacycles play a pivotal role in the reactivity of the metal–carbon bonds towards nucleophiles or electrophiles. For instance, the metallabenzenes bearing triphenylphosphonium substituents easily undergo addition or substitution reactions with nucleophiles, but are not reactive to classical electrophiles. The scope of this review has been limited to examples within six-membered metallaaromatic species but seeks to provide a thorough picture of reactivity trends of the metal–carbon bonds.

2. Structural Features of the M–C Bonds within Six-Membered Metallaaromatic Rings

The metallaaromatics and their resonance structures discussed in all the sections are provided in Figure 1, organized according to the ring types. Most of the discussed six-membered

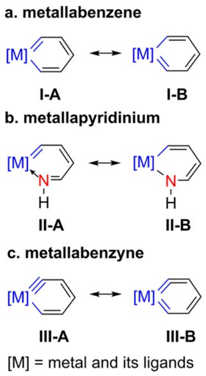

Figure 1. Main resonance structures of six-membered metallaaromatic species.

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metallaaromatic species have been fully characterized by single crystal X-ray diffraction analysis and nuclear magnetic resonance (NMR) spectroscopy. The structures of these six-membered metallacycles can be almost planar or deviate appreciably from planarity.[12] The metal–carbon bond lengths of metallabenzenoid and metallapyridinium rings are intermediate between standard metal–carbon single and double bond lengths due to the π-electron delocalization (typically ranging between 1.894–2.162 Å for Os, 1.881–2.110 Å for Ru, and 1.915–2.066 Å for Ir).[13] The significantly downfield ^1H and ^{13}C NMR chemical shifts of C_α-H (typically ranging between 12.6–23.1 ppm for Os, 13.7–18.1 ppm for Ru, and 10.4–14.7 ppm for Ir) and C_α (typically ranging between 143.1–262.0 ppm for Os, 244.8–294.1 ppm for Ru, and 176.9–302.1 ppm for Ir)[14] of metallabenzenes indicate the carbene character of the corresponding M–C bonds. However, the ^1H NMR signal of osmapyridinium (C_α–H: 48.0 ppm) is unusually downfield compared to typical metallaaromatic systems, which is attributed to its paramagnetism.[15]

Another illustrative example of six-membered metallaaromatic species is metallabenzyne, containing one *sp*-hybridized carbon atom adjacent to the metal center, for which two major resonance structures are proposed in the literature as shown in Figure 1 c. Accordingly, the $M–C_{sp}$ bond lengths of metallabenzynes (ranging between 1.726–1.815 Å for Os)[13] are slightly longer than those observed for typical $M\equiv C$ bonds and at the lower end of those found in $M{=}C{=}CRR'$ complexes.[16] In contrast, the $M–C_{sp2}$ bond lengths (ranging between 1.940–2.097 Å for Os)[13] are very close to those observed for typical Os–C(vinyl) bonds and within the range of Os–C(carbene) bonds. The peculiar downfield ^{13}C NMR signals of metallabenzynes are observed in the range of 288.7–316.4 ppm,[14] indicating the carbyne character of the $M–C_{sp}$ bonds.

The structural features of the metal–carbon bonds discussed above suggest that the metal–carbon bonds within six-membered metallaaromatics are not exactly identical with those of classical metal–carbene/carbyne complexes. The inherent aromatic character of metallacycles obviously affect the structural features and the reactivity of metal–carbon bonds.

3. Reactions with Nucleophiles

In 1979, Thorn and Hoffmann theoretically predicted that metallabenzenes with electron-donating groups *ortho* or *para* to the metal would be more stable.[11] Indeed, the isolated metallabenzene structures validated the prediction that most of the stable metallabenzenes are decorated with electron-donating groups.[1a,c–g] Subsequent research into the synthesis of metallabenzenes with a diversity of structures has resulted in some well-characterized metallabenzenes bearing electron-withdrawing groups. The iridabenzenes and iridanaphthalenes reported by Paneque et al. were the first examples of metallaromatics with electron-withdrawing groups, namely CO_2Me.[9a,b,17] Roper, Wright, and co-workers demonstrated a series of tethered metallabenzenes with ester groups.[18] The phosphonium-substituted metallabenzenes reported by our group, including osmabenzenes, ruthenabenzenes, and their derivatives, constitute an important addition to this special class of metallaaromatics with electron-withdrawing groups.[1l,10d,19] The metal–carbon bonds of these metallaaromatics exhibit high reactivity toward various nucleophiles, such as H^-, Me^-, OH^-, MeO^-, EtO^-, amines, 8-hydroxyquinoline, and DPPM (bis(diphenylphosphino)methane). In this section, we set the stage for discussion by briefly surveying various reactions with nucleophiles, which is organized by the reaction types.

3.1. Nucleophilic addition reactions

Typically, organic aromatic compounds tend to undergo substitution reactions, rather than addition reactions. However, as shown by a number of metallabenzenes, the incorporation of transition metal centers promotes the addition reactions of aromatic rings. In 2006, Paneque and co-workers reported the preparation of iridabenzene **1** through the coupling reaction of an alkene with an iridacyclopentadiene. Iridabenzene **1** could react with MeCN to give a 6:1 kinetic mixture of **2** and **3**, through the migration of the hydride ligand onto the two Ir–C bonds at room temperature (Scheme 1).[17a] By heating these mixtures, in C_6H_6 or C_6H_{12} at 90 °C with a drop of MeCN, **2** completely converted to the thermodynamically more favored **3**, possibly via **1**. These reactions can be regarded as intramolecular nucleophilic additions of hydride to the metal–carbon bonds. They also demonstrated the addition reactions of iridanaphthalenes and iridabenzenes with nucleophiles by attacking the *para* carbon atom of a metallacycle.[9a,b]

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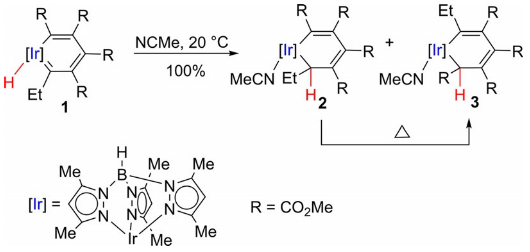
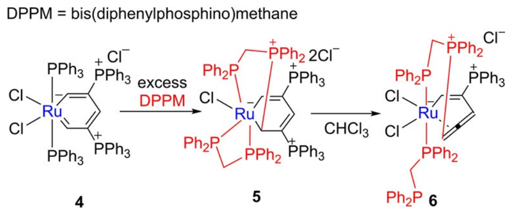
Hong Zhang received her Ph.D. in Prof. Haiping Xia's group at Xiamen University in 2007. She was appointed as Assistant Professor (2007–2011) and Associate Professor (2011-present) at Xiamen University. She was a postdoctoral researcher in Prof. Zhenyang Lin's group at the Hong Kong University of Science & Technology (2012–2013). Her research interests focus on the synthesis and reactivity of metallaaromatics and extending classical organic reactions to metallacycle chemistry.



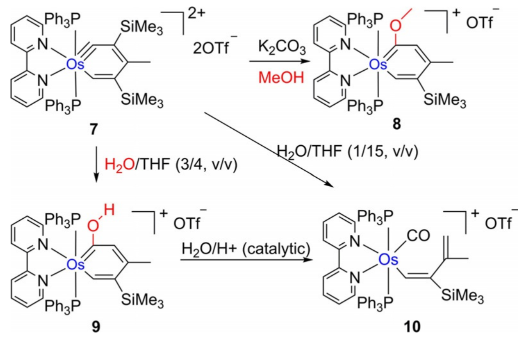
Scheme 1. Intramolecular nucleophilic addition reactions of iridabenzene **1** with hydride.

Phosphonium-substituted ruthenabenzene **4** can be readily prepared by the reaction of $RuCl_2(PPh_3)_3$ with 3-hydroxypenta-1,4-diyne (HC≡CCH(OH)C≡CH) in the presence of excess PPh_3 through a [5+1] cyclization process.[19] As shown in Scheme 2,[20] ruthenabenzene **4** is reactive toward nucleophiles. When ruthenabenzene **4** was subjected to DPPM in 1:3 molar ratio, the nucleophilic addition product, ruthenacyclohexadiene complex **5**, was isolated as a major product. Complex **5** can slowly convert in $CHCl_3$ to form the η^2-allene complex **6**. The analogous cyclic η^2-allene osmium complex could also be obtained when the phosphonium-substituted osmabenzene or osmapyridinium was treated with excess DPPM. However, the ligand substitution product rather than the nucleophilic addition product was isolated when the amount of DPPM was reduced.



Scheme 2. Nucleophilic addition reactions of ruthenabenzene 4 with DPPM.

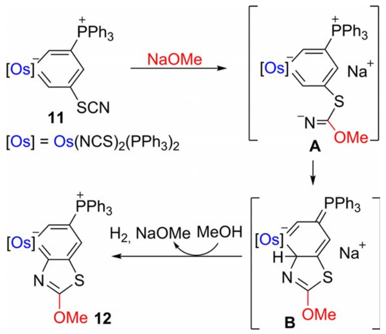
Metallabenzyne is derived from formal replacement of a *sp*-hybridized carbon atom in benzyne by an isolobal transition-metal fragment, which was first experimentally achieved by Jia and co-workers in 2001.[16] The neutral osmabenzyne $Os(\equiv CC(SiMe_3)=C(CH_3)C-(SiMe_3)=CH)Cl_2(PPh_3)_2$ was found to be unreactive toward nucleophiles such as $NaBH_4$, amines, and phosphines. By comparison, the dicationic osmabenzyne **7**, derived from a ligand substitution reaction of neutral osmabenzyne with bipyridyl, can readily react with nucleophiles.[10d] The reaction with methanol in the presence of K_2CO_3 leads to osmabenzene **8** via the nucleophilic addition on the metal–carbon triple bond (Scheme 3). **7** can also undergo nucleophilic addition reaction with $NaBH_4$ on the metal–carbon triple bond to generate a cyclopentadienyl complex, presumably via an osmabenzene intermediate. Even water can act as a nucleophile to react with **7**, which produces the OH-substituted osmabenzene, namely osmaphenol **9**. Osmaphenol **9** is not stable in water solution, which would undergo further reaction with water to form the osmium vinyl product **10**. As supported computationally, the regioselectivity of the nucleophilic addition reaction seems to be LUMO-controlled.[1j, 21]



Scheme 3. Nucleophilic addition reaction of osmabenzyne **7**.

3.2. Nucleophilic aromatic substitution reactions

Substitution reaction has been widely regarded as the characteristic reaction of classical aromatic species. Although aromatic substitution reactions usually occur by an electrophilic mechanism, electron-withdrawing substituents can activate the aromatic ring toward nucleophilic aromatic substitution (S_NAr). Similarly, some metallaaromatics that have electron-withdrawing substituents can also undergo a typical S_NAr reaction. In 2009, we reported the synthesis of osmabenzene **11** with a phosphonium group and a reactive thiocyano substituent.[7] It can undergo an intramolecular S_NAr reaction in the presence of MeONa/MeOH to give the osmabenzothiazole **12** in a yield of 81%.[22] The proposed mechanism is depicted in Scheme 4.

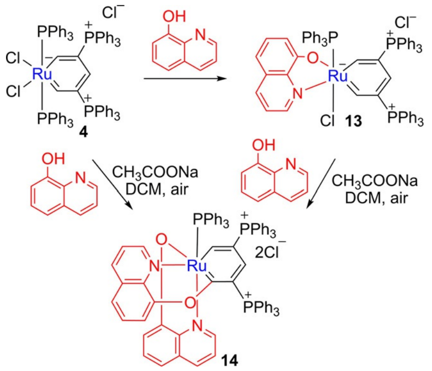


Scheme 4. Nucleophilic aromatic substitution reaction of osmabenzene **11** in the presence of NaOMe.

The addition reaction of **11** with MeONa initially gave intermediate **A**, which then underwent intramolecular nucleophilic attack to afford intermediate **B**. The intermediate **B** could be regarded as an analogue of a Jackson-Meisenheimer complex. Subsequent elimination of the hydride ion with the assistant of MeOH gave the annulation product osmabenzothiazole **12** and H_2. The release of H_2 has been confirmed by gas chromatography. The addition–elimination process involved in the S_NAr reaction of osmabenzene **11** is in accord with classic S_NAr reactions of aryl halides, which require strong electron-withdrawing substituents on the aromatic rings.

Hydroxyl group substituted osmabenzene, that is, *m*-osmaphenol can also perform similar S_NAr reactions. By treatment of different isocyanates with *m*-osmaphenol, a series of osmabenzenes with urethane linkages could be generated.[23] The following intramolecular S_NAr reaction by urethane linkages in the presence of bases afforded a series of annulation products.

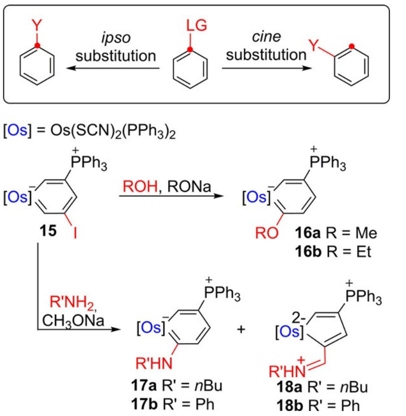
As shown in Scheme 5,[24] the reaction of ruthenabenzene **4** and 8-hydroxyquinoline has been investigated. In the reactions, 8-hydroxyquinoline molecules can be exploited as bidentate ligands as well as nucleophiles. The reaction initially formed the monosubstituted ruthenabenzene **13** through the displacement of one chloride and one triphenylphosphine ligand by a 8-hydroxyquinoline molecule. When complex **13** was further treated with excess 8-hydroxyquinoline in the presence of CH_3COONa under an air atmosphere, the fused-ring ruthenabenzene **14** was obtained in a yield of 76%. The mechanism for the formation of **14** has been suggested as a tandem coordination and intramolecular nucleophilic aromatic substitution of the ruthenacycle by 8-hydroxyquinoline.



Scheme 5. Reaction of ruthenabenzene **4** with 8-hydroxyquinoline.

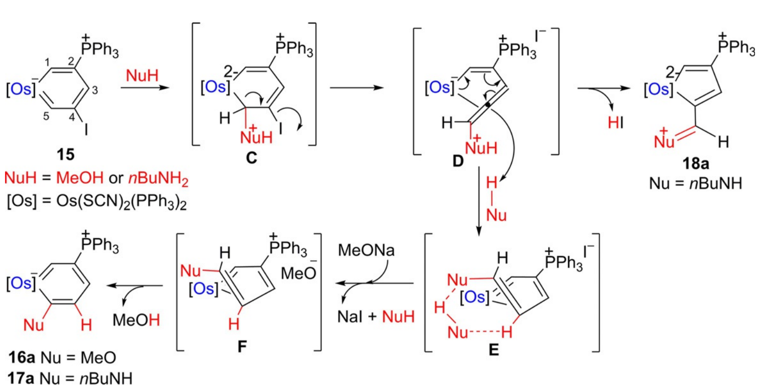
The nucleophilic addition/substitution reactions of metallabenzenes and osmabenzynes suggest that the electron-withdrawing substituents (such as triphenylphosphonium groups) and the metal centers facilitate the approach of nucleophiles to the carbons adjacent to metal centers. In fact, electron-withdrawing substituents might slow or stop the reactions of metal–carbon bonds with electrophiles. The metallabenzene ring bearing triphenylphosphonium groups are inert to typical electrophilic agents such as acids and halogens. It turns out however, that only nitric acid can react with ruthenabenzene **4**, resulting in the cleavage of the metal–carbon bonds (Section 4, Scheme 14).

Ipso-substitutions are the most common substitution patterns in aromatics, in which a new substituent is introduced to the same ring position as the departing leaving group. By contrast, *cine*-substitution, in which the newly entering group takes up a position adjacent to that previously occupied by the leaving group, is much rarer.[25] Most reported substitution reactions of metallabenzenes are *ipso*-substitutions, but the phosphonium-substituted metallabenzenes **15** shown in Scheme 6 is an exception.[26] In the presence of a strong alkali, osmabenzene **15** could react with nucleophiles such as methanol or ethanol to give the *cine*-substitution products **16a** or **16b**, respectively. For nucleophiles containing nitrogen, for example, *n*-butylamine or aniline, the desired *cine*-substitution products **17a**/**b** and the five-membered metallacyclopentadiene by-products **18a**/**b** could be formed in the presence of sodium methoxide. If the reactions of **15** with amines were performed without sodium methoxide, **15** could completely convert to the corresponding metallacyclopentadienes **18a**/**b** in five minutes.



Scheme 6. The *cine*-substitution reactions of osmabenzene **15**.

The mechanism for the formation of the *cine*-substitution products and metallacyclopentadiene species has been studied with the aid of in situ NMR experiments and isotopic labelling experiments. As shown in Scheme 7, the initial nucleophilic attack of MeOH (or *n*-butylamine) to the C5 atom leads to the formation of σ-H adduct **C**. Then, dissociation of the iodine anion afforded allene-coordinated intermediate **D**. The protonation of C4 atom by another nucleophile produced the alkene-coordinated intermediate **E**. In the presence of sodium methoxide, subsequent replacement of the counteranion and the dissociation of a molecule of nucleophile may generate in-



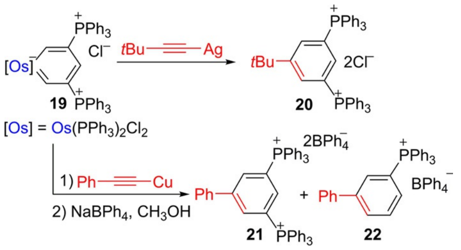
Scheme 7. Proposed mechanism for the *cine*-substitution reactions of osmabenzene **15**.

termediate **F**. Finally, deprotonation of the C5−H bond and the aromatization gave osmabenzenes **16 a** or **17 a**. The whole process resembles the classical addition of nucleophile, ring-opening, ring-closure (ANRORC) mechanism, which has been investigated in detail by van de Plas and co-workers.[27] In the absence of strong alkali, five-membered ring product **18 a** was exclusively formed by the elimination of HI from intermediate **D**.

The fact that only the *cine*-substitution product was observed in the reaction with alcohols has been elaborated by computational study. DFT calculations showed that the formation of metallacyclopentadiene species was both kinetically and thermodynamically less favourable in the reaction with alcohols. For the analogous reaction with amines, the pathway for the formation of the *cine*-substitution product was kinetically unfavourable but thermodynamically favourable compared with the pathway for the formation of the metallacyclopentadiene species. These calculation results were further supported by the experimental observations that metallacyclopentadiene **18** can convert to the *cine*-substitution product **17** in the presence of excess *n*-butylamine, hydriodic acid, and sodium methoxide.

3.3. Other reactions

The reactions depicted above concerned the nucleophiles containing heteroatoms, such as nitrogen, oxygen, and phosphorus atoms. As shown in Scheme 8, organometallic reagents can also act as nucleophiles to react with osmabenzene **19**.[28] The reaction of osmabenzene **19** with acetylide *t*BuC≡CAg at 0 °C led to formation of the dicationic phosphonium salt **20** in a yield of 96 %. Analogous reaction of osmabenzene **19** with organocuprate reagent PhC≡CCu produced a mixture of dicationic phosphonium salt **21** and cationic phosphonium salt **22**.



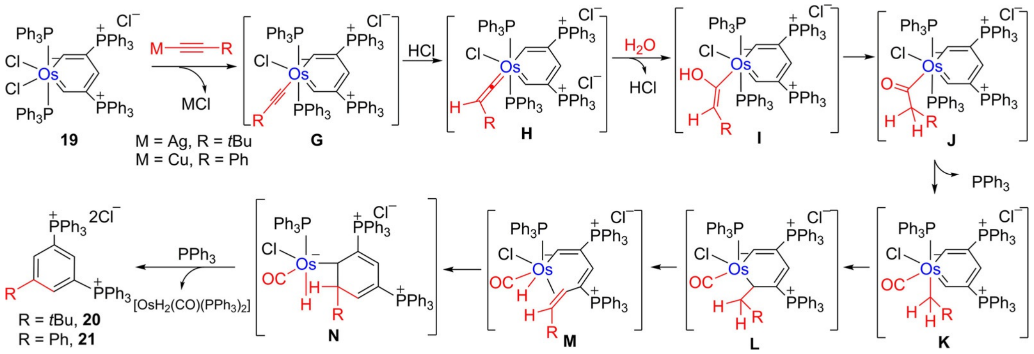
Scheme 8. Reactions of the osmabenzene **19** with transition-metal acetylides.

A possible mechanism for the transformations from triphenylphosphonium substituted osmabenzene **19** to the tetraphenylphosphonium salts **20** or **21** is depicted in Scheme 9. Initially, osmabenzene **19** reacted with a silver/copper acetylide to afford the alkynyl intermediate **G**. The protonation at C_β atom of the alkynyl ligand of **G** by traces of HCl (which may act as a catalyst) in the solvent chloroform can generate the vinylidene intermediate **H**. With the aid of water, vinylidene complex **H** could convert to the acyl **J**, via intermediate **I**. Acyl decarbonylation of **J** would generate alkyl-carbonyl **K**, which may undergo the 1,2-migration of the alkyl ligand from the metal center to the C_α atom to afford **L**. Subsequent β-H elimination of **L** may generate the η^2-alkenyl-coordinated osmium complex **M**. Finally, a 6-*endo-trig* cyclization produced the intermediate **N**, which could easily convert to the aromatic tetraphenylphosphonium salt, **20** or **21**, and an osmium dihydride complex. The P−C bond cleavage of **21** may give the tetraphenylphosphonium salt **22**. The proposed reaction mechanism was supported by further experimental observations. When the reaction was carried out in anhydrous dichloromethane (without water and acid), only a trace amount of tetraphenylphosphonium salt was observed within one week. In addition, the crude mixture of the reaction showed a strong band at 1916.87 cm^{-1} in the infrared (IR) spectrum, which could be assigned to an osmium carbonyl complex and demonstrates the presence of a carbonyl ligand.

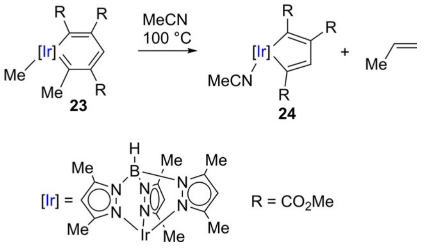
A somehow related reaction that involves initial migration of an alkyl ligand to the C_α of the metallaaromatic ring was reported by Paneque and co-workers in 2006. The 1,2-migration of Me⁻ from metal center of iridabenzene **23** to the α-carbon atom afforded the product iridacyclopentadiene **24** (Scheme 10).[17a] This reaction has been considered as the reverse reaction for the synthesis of iridabenzene from the coupling of an alkene with iridacyclopentadienes.

4. Reactions with Electrophiles

The reactions of metal–carbon bonds within six-membered metallaaromatics with electrophiles are less common than the reactions with nucleophiles. The exceptional examples are the

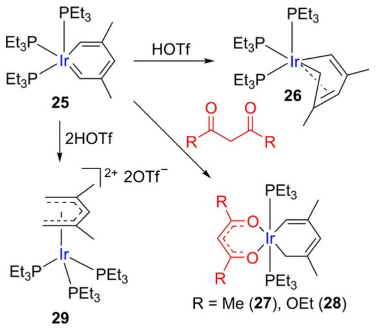


Scheme 9. Proposed mechanism for reactions of the osmabenzene **19** with transition-metal acetylides.



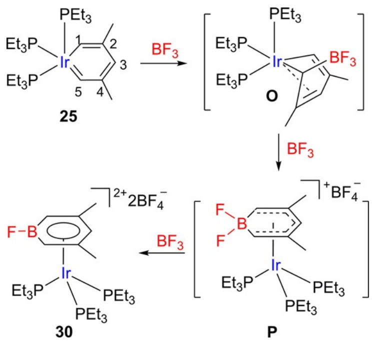
Scheme 10. Reaction of iridabenzene **23** with MeCN.

electrophilic addition reactions of an iridabenzene **25**. In 1989, Bleeke and coauthors reported a neutral iridabenzene **25**, which contains two electron-donating groups (methyl) *meta*- to the metal center and three phosphine ligands (PEt_3).[29] The electron-rich α-carbon atom of **25** show high reactivity toward a series of electrophiles.[8a,c] Treatment of **25** with acid, such as HO_3SCF_3 (HOTf), acetylacetone, or diethyl malonate, resulted in the protonation of α-carbon atom, generating the corresponding addition products **26**, **27**, or **28** (Scheme 11).[8c] When iridabenzene **25** was treated with 2 equivalent of HOTf, protonation occurs at two α-carbon atoms, leading to the formation of η^5-2,4-dimethylpentadienyl coordinated iridium complex **29**.



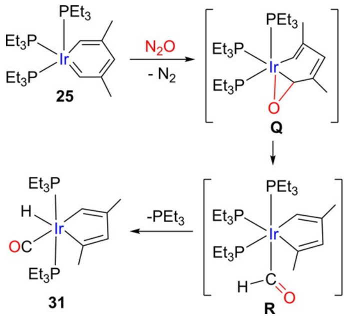
Scheme 11. Reactions of iridabenzene **25** with electrophiles.

Interestingly, reaction of **25** with excess boron trifluoride proceeded differently, giving a novel (η^6-borabenzene) metal complex **30**.[8c] The proposed mechanism (Scheme 12) including the electrophilic attack of BF_3 at α-carbon atom (C5) and migration of another α-carbon atom (C1) to boron along with the removal of fluoride as BF_4^- to form the boracyclohexadienyl ring coordinated intermediate **P**. The removal of another fluoride as BF_4^- by a third equivalent of BF_3 resulted in the aromatization of the borabenzene ring and lead to the final complex **30**. The iridium center of **25** can react with electrophiles, such as I_2, Br_2, and $AgBF_4$, which underwent ligand-dissociation, oxidative-addition, and electron-transfer processes to give the corresponding iridabenzenes with octahedral coordination geometry.[8c] In addition, reaction of iridabenzene **25** with excess H_2 gas generated 2,4-dimethyl-1,3-pentadiene, 2,4-dimethyl-1-pentene, and iridium polyhydrides. Although this reaction involved the cleavage of metal–carbon bonds, the mechanism for the formation of C–H bonds has been considered to generate from the hydride migration from metal center to an α-carbon.[8c]



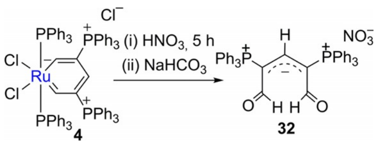
Scheme 12. Proposed mechanism for the reaction of iridabenzene **25** with BF_3.

Reaction of iridabenzene **25** with nitrous oxide N_2O or amine *N*-oxides, such as 4-methylmorpholine *N*-oxide and trimethylamine *N*-oxide, led to the ring contraction product **31**.[8c] The proposed mechanism shown in Scheme 13 involves the oxidation of metal–carbon bond, the following rearrangement of the metallacycle and the migration of the formyl hydrogen ("retroinsertion").



Scheme 13. Reaction of iridabenzene **25** with N_2O and the proposed mechanism.

Besides, some phosphonium-substituted metallaaromatics exhibit reactivity toward oxidant agents. The metal–carbon bond of osmanaphthalene could be oxidized in the presence of oxygen to generate an osmanaphthalyne with metal–carbon triple bond.[30] As shown in Scheme 14, treatment of ruthenabenzene **4** with nitric acid, followed by the addition of $NaHCO_3$, led to the cleavage of the two ruthenium–carbon bonds to produce an unusual dialdehyde containing two phosphonium groups (**32**).[31]

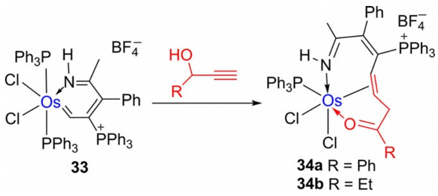


Scheme 14. Reaction of ruthenabenzene **4** with HNO_3.

5. Reactions with Unsaturated Compounds

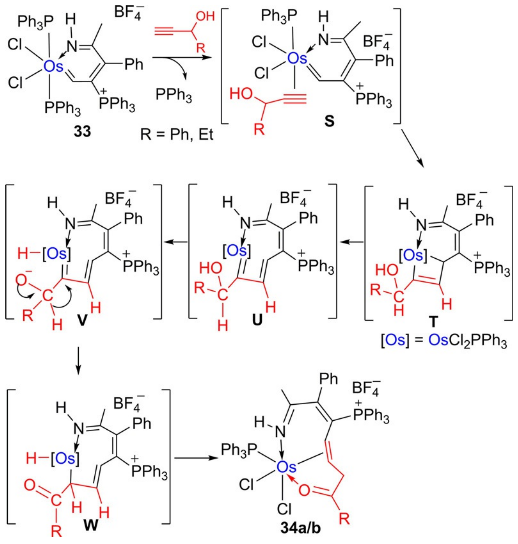
5.1. Insertion of alkynes into metal–carbon bonds

Metal carbene complexes readily react with unsaturated compounds to undergo the insertion reaction through [2+2] cycloaddition and cycloreversion process.[32] In some cases, the metal–carbon bonds of metallaaromatics possess carbene character, which are suitable to undergo insertion reaction with unsaturated molecules. In 2009, we reported an osmapydinium complex **33**, which was prepared by a formal [4+2] cycloaddition reaction of metalladiene complex with nitrile.[15] As shown in Scheme 15, the Os–C bond of **33** reacted with propargyl alcohols PhCH(OH)C≡CH or EtCH(OH)C≡CH, producing the corresponding insertion products **34a** or **34b** in high yield.[33]



Scheme 15. Reactions of osmapyridinium **33** with propargyl alcohols.

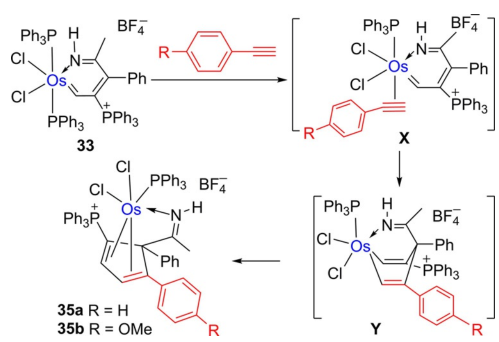
These reactions are thought to proceed via stepwise mechanism (Scheme 16). Dissociation of the PPh_3 ligand, along with the coordination of the terminal alkyne to the metal center in **33**, could lead to the formation of intermediate **S**. The following [2+2] cycloaddition and cycloreversion of the alkyne with Os=C in **S** may generate the nine-membered intermediate **U** via intermediate **T**. The hydroxyl in **U** could be activated by the osmium center to give the hydride intermediate **V**. Subsequent 1,2-hydrogen migration, reductive elimination, and coordination of the carbonyl group to osmium center could yield the final metallacycles **34a/b**. The intramolecular 1,2-hydrogen migration (from **V** to **W**) might be induced by the electrophilic carbon of the osmium carbene intermediate **V**. Experimentally, the hydrogen in **V** is more likely to migrate than the phenyl and ethyl group. Another pathway is also possible that the proton on the oxygen would transfer directly to the carbene carbon without the participation of metal center.



Scheme 16. Proposed mechanism for reactions of **33** with HC≡CCH(OH)R.

5.2. [4+2] Cycloaddition reactions with alkynes or allenes

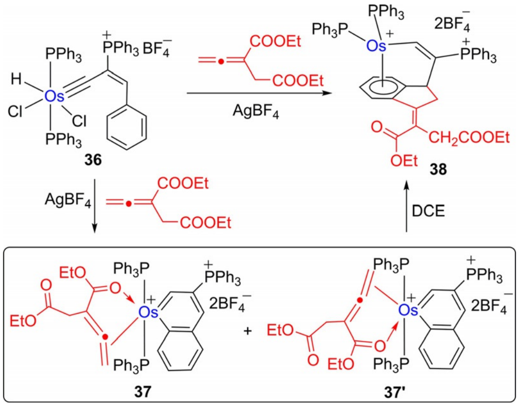
Unlike the insertion reactions with propargyl alcohols, osmapyridinium **33** reacted with substituted phenylacetylenes to generate [4+2] cycloaddition products, namely the η^4-coordinated cyclopentadiene complexes **35a** and **35b**.[33] On the basis of the characterized structures, the reasonable mechanism for the formation of [4+2] cycloaddition products outlined in Scheme 17. Initially, one of the PPh_3 ligand in **33** could be displaced by phenylacetylene to give the π-alkyne complex **X**. The following [4+2] cycloaddition of the osmadiene moiety with the coordinated alkyne in **X** may lead to the formation of the metallacyclohexadiene intermediate **Y**. A similar [4+2] cycloaddition process has been previously proposed in the reactions of alkenyl carbene complexes with alkynes or alkenes.[34] Finally, reductive elimination of the two, osmium bond carbon atoms in **Y** could form the cyclopentadiene ring and complete the transformation from **33** to **35a/b**.



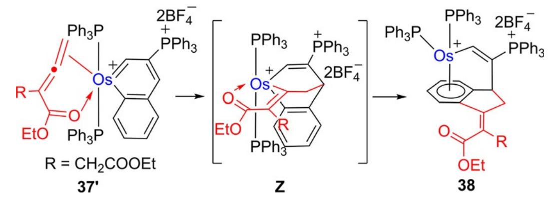
Scheme 17. [4+2] Cycloaddition reactions of **33** with phenylacetylenes.

Allene compounds can also adopt as unsaturated source to undergo analogous [4+2] cycloaddition reactions with metallaaromatics. As shown in Scheme 18, treatment of osmium hydrido alkenylcarbyne **36** with diethyl 2-vinylidenesuccinate in the presence of excess $AgBF_4$ in dichloroethane at 60 °C for 2 days results in the osmium vinyl complex **38**.[35] When the reaction was performed at room temperature or the reaction time was shorten to 1 h, two inseparable isomers, osmanaphthalene intermediates **37** and **37′**, were isolated as a red solid. Heating the mixture of **37** and **37′** could further convert to the annulation product **38**. The experimental results indicated that the osmanaphthalenes **37** and **37′** are the key intermediates of this conversion.

A plausible mechanism for the transformation from osmanaphthalene **37′** to osmium vinyl complex **38** is shown in Scheme 19. Again, intramolecular [4+2] cycloaddition was proposed as a key step for the formation of **38**. The cycloaddition



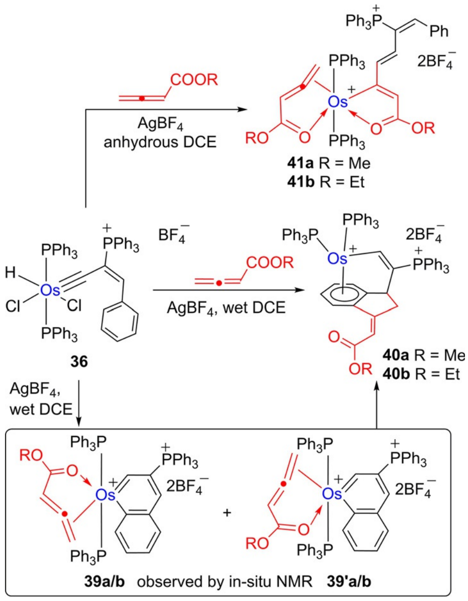
Scheme 18. Reactions of osmium hydrido alkenylcarbyne **36** with diethyl 2-vinylidenesuccinate.



Scheme 19. Proposed mechanism for the transformation from osmanaphthalene **37**′ to osmium vinyl complex **38**.

of allenoate with the osmanaphthalene would generate the metallacyclohexadiene intermediate **Z.** Subsequent reductive elimination and coordination would afford the racemic osmium vinyl complex **38**.

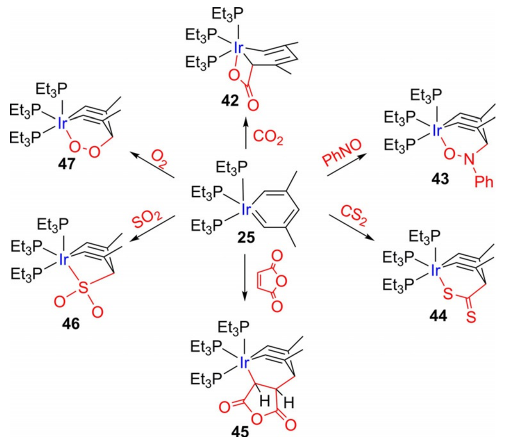
As shown in Scheme 20, the mono-substituted allene, that is, methyl/ethyl buta-2,3-dienoates, can react with osmium hydrido alkenylcarbyne **36** to generate the osmium vinyl complex **40 a** or **40 b**, respectively. Similarly, osmanaphthalene intermediates **39** and **39**′ were identified by in situ NMR in these reactions, which were thought to transform to the final products through [4+2] cycloaddition and reductive elimination steps. The trace amount of water in the solvent is vital for the formation of osmanaphthalene intermediates. Instead, clean insertion product **41 a/b** would be obtained when the reaction was performed in anhydrous solvent.



Scheme 20. Reactions of osmium hydrido alkenylcarbyne **36** with methyl/ethyl buta-2,3-dienoates.

5.3. Cycloaddition reactions with olefins, heteroolefins, and heterocumulenes

In 1994, Bleeke and co-workers described the [2+2] cycloaddition reaction of the Ir–C bond in iridabenzene **25** with CO_2 and the [4+2] cycloaddition reactions of it with maleic anhydride, CS_2, PhNO, SO_2, and O_2, producing a series of polycyclic products **42**–**47** (Scheme 21).[8a–c] Most of the reactions were proposed to occur in a concerted fashion, although some reactions might be proceed via stepwise mechanisms. It has been established that the square-pyramidal coordination geometry of iridabenzene **25** and the rigid geometry of the metalladiene moiety play an important role for the approach of substrate molecules, which would facilitate the cycloaddition reactions of metallacycle.

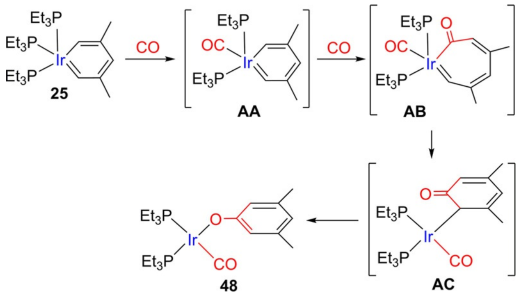


Scheme 21. Reactions of iridabenzene **25** with olefins, heteroolefins, and heterocumulenes.

In particular, treatment of **25** with excess CO produced the iridium phenoxide compound **48** (Scheme 22). The proposed mechanism involved the initial insertion of CO into the Ir–C bond, ring closure and metal migration to the oxygen center.[8c]

6. Migratory Insertion Reactions

The rearrangement to the corresponding cyclopentadienyl complexes has been regarded as the major decomposition pathway for metallabenzenes or metallabenzynes. This rearrangement involves the migratory insertion step, in which the two α-carbon atoms undergo the coupling reaction to form cyclopentadienyl moiety. Synergistic interplay of theoretical

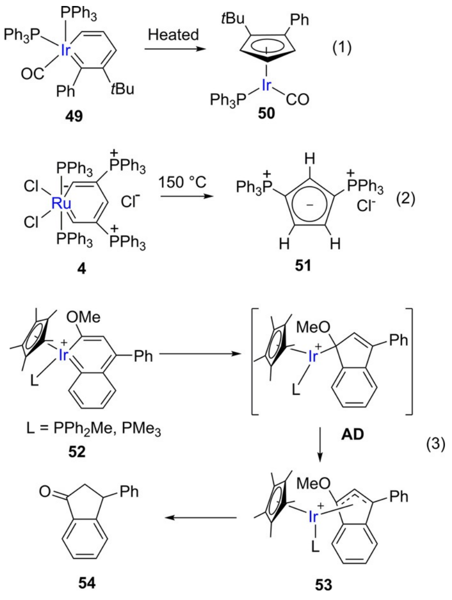


Scheme 22. Proposed mechanism for the reaction of iridabenzene **25** with CO.

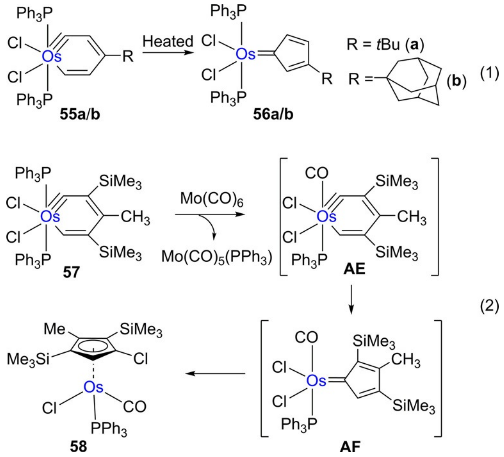
and experimental investigations demonstrated that this rearrangement originates from the different thermodynamic stability between the cyclopentadienyl complexes and the metallabenzenes/metallabenzynes, and this process is strongly influenced by the metal centers, the ligands, and the substituents of the metallacycles.[36]

As shown in Scheme 23, cyclopentadienyl complex **50** could be generated when iridabenzene **49** was heated in benzene at 50 °C for 15 h.[36d] In addition, we have shown that heating a solid sample of ruthenabenzene **4** at 150 °C gave a free cyclopentadienyl derivative **51**.[10c] In 2013, Bolaño and co-workers reported the formation of an indanone starting from an α-OMe substituted iridanaphthalene.[36h] It was proposed that the transformation involves the initial carbene migratory insertion to form the 16e intermediate **AD**. The following η^1 to η^3 hapticity switch could lead to the isolation of intermediate **53**. Heterolytic cleavage of the O–CH_3 bond of **53** and the hydrogenation of the remaining double bond would finally produce the indanone **54**.

Metallabenzynes could also undergo migratory insertion reactions to form carbene complexes or cyclopentadienyl complexes. As shown in Scheme 24, osmabenzynes bearing a *tert*-butyl or 1-adamantyl substituents *para* to the metal center (**55 a**/**b**) were thermally unstable in solution, which would convert to the corresponding osmium carbene complexes **56 a** and **56 b** at room temperature.[36f] Computational studies demonstrated that the steric repulsion between the *meta*-hydrogen atom of the metallacycle and the hydrogen atom of *tert*-butyl or 1-adamantyl group account for this conversion. The formation of the carbene structural form could release the steric congestion.



Scheme 23. Examples of migratory insertion reactions of metallabenzenes species.



Scheme 24. Examples of migratory insertion reactions of metallabenzyne species.

The ligand effect on the rearrangement of osmabenzynes to the corresponding cyclopentadienyl complexes has also been illustrated by Jia and co-workers.[36j] As shown in Scheme 24, treatment of the osmabenzyne complex **57** with $Mo(CO)_6$ in refluxing benzene produced the η^5-chlorocyclopentadienyl complex **58** and $Mo(CO)_5(PPh_3)$. The most likely reaction pathway has been proposed to proceed via the initial migratory insertion reaction of the osmabenzyne complex **57** to a carbene intermediate, a following migratory insertion of metal carbene to Os–Cl bonds, and final transformation to chlorocyclopentadienyl complex **58**. DFT calculations suggested that the π-accepting ligands, such as carbonyl group and acetonitrile, could facilitate the migratory insertion reactions of osmabenzynes to form the corresponding cyclopentadienyl complexes. The metal effect on this migratory insertion reactions has also been studied computationally.[37] The calculation results show that the metallabenzynes with lighter metal centers are easier to transform to the corresponding cyclopentadienyl complexes for both thermodynamic and kinetic rea.

7. Summary and Outlook

Since the first report of a metallabenzene in 1982,[38] significant advances have been made in understanding of the nature of these species relevant to classical aromatics, and offered new insights into the reactivity of a variety of metallaaromatics that may change the way we think about their role in classical reactions. In this review, we provide an overview of the reactivity of metal–carbon bonds within six-membered metallaaromatics. As illustrated by these reactions, the reactivity of metal–carbon bonds are strongly affected by the metal centers, ligands, and substituents of metallaaromatic rings. Metallaaromatics bearing strong electron-withdrawing substituents or cationic species have considerable tendency to react with a series of nucleophiles to undergo the nucleophilic addition, nucleophilic aromatic substitution or *cine*-substitution reactions. In contrast, neutral metallabenzenes containing electron-donating groups and ligands exhibit high reactivity toward electrophiles to undergo electrophilic addition or oxidation reactions. In addition, insertion reactions or cycloaddition reactions with unsaturated molecules have been observed in some metallaaromatics, which resemble the classical metal carbene complexes. These reactions demonstrate that the metal–carbon bonds of metallaaromatics are affected by the aromaticity of the metallacycles, and can present typical reactivity of organometallic complexes, especially the metal carbene/carbyne complexes. Recent advances of the reactivity of a variety of metallaaromatic species described herein promote our understanding of the nature of metal–carbon bonds of metallaaromatic complexes, and a number of novel monocyclic or polycyclic metallacycles or organic rings are obtained through these reactions of metal–carbon bonds. However, the understanding of the reactivity of metallaaromatics is still much more primitive compared with classical aromatics. Many important challenges remain, however, that continue to stimulate research. The need to investigate their unique reactivity and properties would provide ample impetus for further approaches that involve the clever use of reagents and the design of the metallaaromatics with different metal centers, ligands, and substituents to probe new reaction types. Future developments of metallaaromatics and exploitation of their potential applications would further enrich the fundamental organometallic chemistry.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: aromatic compounds · heterocycles · metal–carbon bonds · metallaaromatics · reactivity

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