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Metallaaromatics Containing Main-group Heteroatoms

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What is the most favorite and original chemistry developed in your research group?
The Carbolong Chemistry.

How do you get into this specific field? Could you please share some experiences with our readers?
My interests in organometallic chemistry and polymer sciences lead to this field. You will eventually reach your own chemistry, if you concentrate on a specific field and investigate with passion, perseverance and persistence.

What is the most important personality for scientific research?
Innovative spirit and persistence.

What's your hobbies?
I love growing plants, after retirement, I will engage in gardening work.

How do you keep balance between research and family?
Deal with everything properly in their order of urgency and know when to hold and when to go. Thus, you can keep balance between your research and family with skill and ease.

What is your favorite journal(s)?
Journals with fantastic pictures and witty remarks.

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Synthesis, reactivity, and applications of metallaaromatics.

ABSTRACT Metallaaromatics are metallacycles that are derived from the formal replacement of a carbon atom in the framework of organic aromatics with a metal fragment. As an important subclass of metallaaromatics, metallaaromatics that contain main-group heteroatoms have attracted considerable attention. In the past ten years, we have developed several new methods to construct metallaaromatics as well as those containing main-group heteroatoms, such as metallapyridine, metallapyridinium, metallapyridyne, metallafuran, metallabenzothiazole, metallabenzoxazole, metallabenzthiophene, aza-metallapentalene and some novel tricyclic/tetracyclic metallaaromatics. In addition, interesting reactions such as the first hetero-Diels Alder reaction between 1-metalla-1,3-dienes and nitriles, the first intramolecular nucleophilic aromatic substitution ($S_{N}Ar$) reaction of metallabenzene, and the first iodine-mediated electrophilic cyclizations of a metallabenzene complex were demonstrated. In this account, recent and novel approaches for their synthesis and property analyses are summarized. The structural diversity and unique properties of metallaaromatics containing main-group heteroatoms will strongly inspire further investigation of these species and provide a wide range of potential applications.

KEYWORDS metallacycles, aromatic, heteroatom, fused ring, synthesis

Contents

1. Introduction

The development of aromatic architectures continues to fascinate both experimentalists and theoreticians. The incorporation of heteroatoms or related groups into aromatic hydrocarbons can result in various heteroaromatic compounds. It is now well established that the introduced heteroatoms are not limited to main-group atoms or related groups. Since their first computational proposal by Thorn and Hoffman[1] in 1979 and the first experimental access in 1982,[2] metallaaromatic complexes have attracted increasing interest as novel heteroaromatic compounds derived from the replacement of a (hydro)carbon unit in conventional aromatic hydrocarbons with a transition-metal fragment. Because of the synergistic interplay of theoretical and experimental investigations, numerous metallaaromatic molecules with interesting structural features and properties have been demonstrated over the past several decades.[3-9] According to the category of classical organic aromatics, metallaaromatics can be classified as those in which a metal fragment replaces the carbon atom in the framework of aromatic hydrocarbons and those that contain main-group heteroatoms. Representative examples of the former type are well known, such as metallabenzene,[10-18] metallabenzyne,[19-23] metallanaphthalene,[24-26] and metallaanthra-

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cene.[27] Examples of the later type are also well evidenced by the discovery of metallapyridine,[28-32] metallafuran,[33] metallapyrole,[34-36] metallathiophene,[37-39] metallabenzothiazole[40-42] and other related compounds. The variety of the metallaaromatic family could be further increased by changing the ring size, composition of the framework, types of main-group atoms, or location of the heteroatoms.[43]

The incorporation of main-group heteroatoms such as B-N moieties into polycyclic aromatic hydrocarbons (PAHs) can afford conjugate compounds with versatile, structure-dependent properties that are distinctly different from those of their all-carbon counterparts.[44,45] Similarly, the introduction of main-group atoms into metallaaromatics can produce compounds with new and desirable chemical and physical properties. Based on the broad space to develop new aromatic frameworks and novel properties, metallaaromatics containing main-group heteroatoms have attracted a wide range of continuous interest.

This account summarizes our recent studies on the chemistry of aromatic osmacycles, ruthenacycles, and iridacycles that contain main-group heteroatoms (*e.g.,* N, O, S, Br, I). Most of these heteroatom-containing metallaaromatics have typical features of aromaticity, such as downfield chemical shifts, ring planarity and the delocalization of bond lengths between a single and double bond. In addition, most of them exhibit good stability towards air, water, and heat. Aromaticity is a key factor for their stability, and in particular, most of our metallaaromatics carry at least one phosphonium group on the equatorial plane and one phosphine ligand on the axial position, which also provide stability via both electronic and steric mechanisms. The phosphonium serves as an electron reservoir, which allows the circulation of electron pairs along metallacycles and lowers the electron density of the aromatic rings. Meanwhile, the surrounding bulky phosphonium groups and phosphine ligands offer steric protections for the metallacyles, preventing most possible reactions that may decompose the skeleton. In this account, we focus on the synthesis, related novel reactions, and some theoretical aromaticity evaluations of these main-group heteroatom-containing metallaaromatics. The detailed spectroscopic and structural parameters including chemical shifts, bond lengths, bond angles, and planarity of these metallacycles, unless some special cases, will not be discussed here but could be found in corresponding articles.

Hongjian Wang was born in 1994 in Hebei province (P. R. China). He received his B.S. degree in 2016 from Xiamen University, and continued his Ph.D. study at the same institution under the direction of Prof. Haiping Xia. He is currently working on the synthesis and reactivity of heteroatom-containing carbolong complexes.

Xiaoxi Zhou was born in 1988 in Henan province. She obtained her B.S. degree in 2010 at Henan Normal University. In 2015, she obtained her Ph.D. at Xiamen University under the supervision of Prof. Haiping Xia, and continued her post-doctoral research in the same group (2015 to present). Her present research topics include the synthesis, reactivity, and applications of novel heteroatom-containing metallaaromatics derived from metallapentalynes and metallapentalenes.

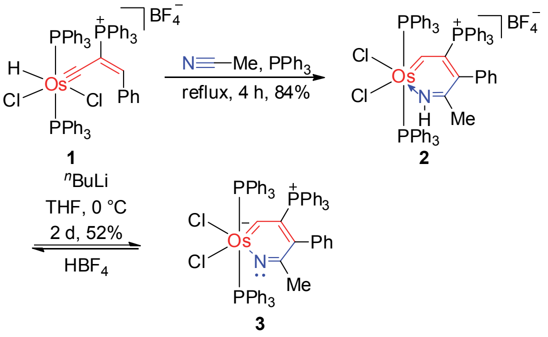
2. Monocyclic Metallaaromatics Containing Main-group Heteroatoms

2.1. Metallapyridine and metallapyridinium

In comparison to the well-established approaches to metallabenzenes,[10-18] the synthesis of azaheterocyclic analogues of metallabenzene, metallapyridine, has limited success.[28-32,46] In 2009, we reported the syntheses of metallapyridine and metallapyridinium through the first hetero-Diels Alder reaction between 1-metalla-1,3-dienes and nitriles.[30] As shown in Scheme 1, when complex **1** was treated with PPh_3 in acetonitrile under reflux, osmapyridinium **2** was obtained, in which osmium hydride alkenylcarbyne **1** could be considered 1-metalla-1,3-diene and acetonitrile could be considered a dienophile. In the presence of *n*-BuLi, the deprotonation reaction of **2** forms osmapyridine **3**, and in presence of HBF_4, **3** can regenerate **2**. In this regard, the transformation between **3** and **2** is similar to that between the organic pyridine and pyridinium. Before our delocalized osmapyridinium, Wigley and co-workers reported the preparation of a localized tantalapyridine.[28] Notably, **2** is the first metallapyridinium, and **3** is the first late-transition metal containing metallapyridine.

Density functional theory (DFT) calculations show that the nucleus-independent chemical shifts (NICS values)[47-49] of complexes **2** and **3** are –7.7 and –4.6, respectively. In general, negative values indicate aromaticity and positive values anti-aromaticity. The NICS values of complexes **2** and **3** are comparable to the value of organic pyridine (δ –8.0) and suggest their aromaticity.

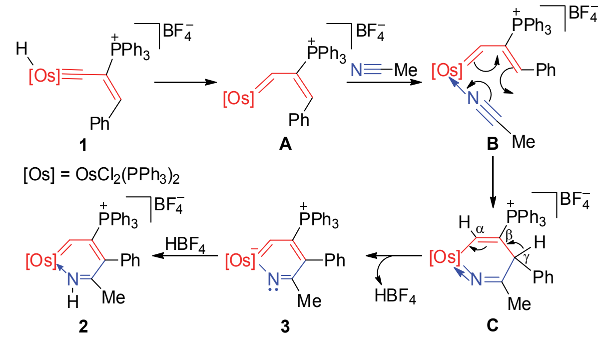
Scheme 1 Synthesis of osmapyridinium **2** and osmapyridine **3**



An important character of metallaaromatics is their relatively downfield ^{1}H NMR signals. For example, the signals of α-C*H* of the first phosphonium-substituted osmabenzene exhibit a chemical shift at 23.13, which is attributed to the effects of the metal and phosphonium substituents. Its chemical shift of γ-C*H* was observed at 8.57, which is comparable with those of typical arenes.[12] The incorporation of nitrogen atom also leads to unique properties. Osmapyridinium **2** exhibits unusual downfield chemical shifts in the ^{1}H NMR signals of OsC*H* (δ=48.01) and N*H* (δ=25.38). The ^{1}H NMR spectrum of osmapyridine **3** shows only several broad signals at room temperature or lower temperatures (200—293 K). Further magnetic measurement experiments demonstrate the paramagnetism of **2** and **3**. The irregular ^{1}H NMR signals of **2** and **3** are attributed to their paramagnetism. The DFT calculations show that the net spin populations primarily reside at the Os^{IV} (5d^4) center, and the Os-bonded C and N atoms exhibit some paramagnetism. These paramagnetic centers can signifincantly modify the NMR behavior of the neighboring hydrogen atoms, as observed in the NMR spectroscopy.

A plausible mechanism for the formation of **2** and **3** is shown in Scheme 2. The 1,2-migration of the hydride ligand to the carbyne carbon atom may produce the alkenylcarbene intermediate **A**. The coordination of acetonitrile can afford **B**, followed by the [4+2] cycloaddition of acetonitrile with the alkenylcarbene unit

Scheme 2 Proposed formation mechanism of osmapyridinium **2** and osmapyridine **3**

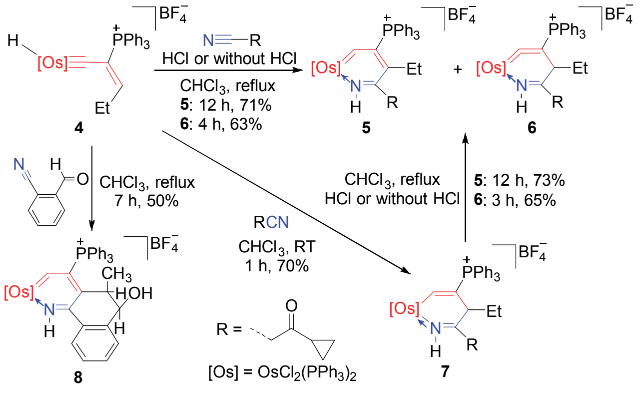


to generate **C**. The deprotonation of H^+ from the γ-carbon center and the counterion BF_4^- afford osmapyridine **3**. The nitrogen atom of osmapyridine can be easily protonated by the initially formed H^+ to produce the final product **2**.

This article has been highlighted by RSC "Chemistry World". Professor Michael Haley, an expert on metallaaromatic chemistry at the University of Oregon sang high praise for the work, "This is really a great result, the chemistry is well executed and the products are beautifully characterised." He also put forward the expectation towards this work, "But the million dollar question is whether or not it can be extended to other systems, if so, it could be an easy way to make new compounds with interesting properties".

Fortunately, the answer is yes. The formal [4+2] synthetic strategy to form metallapyridinium can be extended to other types of osmacarbynes and nitriles.[31] In 2016, we reported the reaction of hydrido-butenylcarbyne complex $[OsHCl_2(\equiv CC(PPh_3){=}CHEt)(PPh_3)_2]BF_4$ **4** with several nitriles, which forms a series of nitrogen-containing metallacycles. As shown in Scheme 3, the reaction of complex **4** with 3-cyclopropyl-3-oxopropanenitrile (2 equiv.) in $CHCl_3$ at reflux temperature primarily yielded osmapyridinium **5** with a small amount of iso-metallapyridinium **6** (Scheme 3). When excess HCl was added to the reaction mixture, complex **6** can be obtained as the major product in 63% yield. The reaction mechanism was revealed by the isolation of an intermediate **7** when the reaction was performed at room temperature. Experimentally, **7** can further convert to **5** or **6**. When a $CHCl_3$ solution of **7** was stirred for 12 h under reflux, complex **5** was obtained in 73% yield. When a $CHCl_3$ solution of **7** and HCl were heated at reflux temperature, **6** was produced as the major product within 3 h (Scheme 3). These reactions confirm that **7** is the key reaction intermediate to form **5** and **6**. Similarly, the reaction of **4** with 2-formylbenzonitrile in $CHCl_3$ under reflux can afford a fused osmapyridinium **8**.

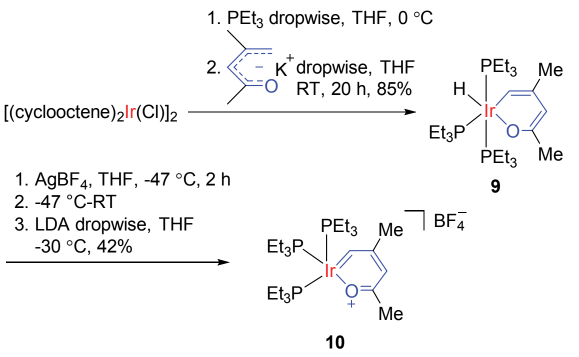
Scheme 3 Syntheses of osmapyridinium **5** and **8**



2.2. Metallapyrylium

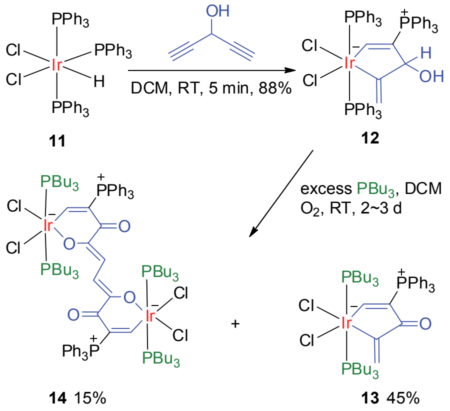
Metallapyrylium is a compound that is derived from the formal replacement of a carbon atom in the framework of pyran with a metal fragment. In 1993, Bleeke and co-workers achieved the first stable metallapyrylium complex **10**. As shown in Scheme 4, $[(cyclooctene)_2Ir(Cl)]_2$ was initially treated with triethylphosphine, which formed $(Cl)Ir(PEt_3)_3$. Then, potassium 2,4-dimethyloxapentadienide was added dropwise to the mixture and afforded iridacycle **9** in good yield. The reaction of **9** with $AgBF_4$ at –47 °C in THF afforded a mixture. When the mixture was re-dissolved in THF and treated with LDA at –30 °C, iridapyrylium **10** was obtained.[50]

Scheme 4 Synthesis of iridapyrylium **10**



In 2007, we reported the synthesis of a sp^2-carbon chain bridged bimetallic iridapyrylium derivative **14**. As shown in Scheme 5, the reaction of *cis*-$IrHCl_2(PPh_3)_3$ with $HC\equiv CCH(OH)$-$C\equiv CH$ in dichloromethane produces the dark yellow compound **12** in high yield. The treatment of **12** with PBu_3 in dichloromethane in air produces ligand substitution product **13** and iridapyrylium derivative **14**. We suppose that an oxidative coupling process and several unknown reactions may occur in the transformation. Although there are numerous experimental and theoretical studies on dinuclear organometallic compounds with two metal centers linked by a conjugated organic bridge, conjugated bimetallic iridium complexes are uncommon.[51]

Scheme 5 Synthesis of iridapyrylium derivative **14**

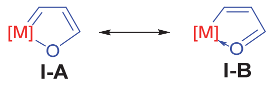


Six-membered metallaaromatics containing sulfur, *i.e.*, metallathiabenzene, were synthesized by Bleeke,[50,52] Angelici,[53,54] Jones[55] and co-workers. In addition, six-membered metallaaromatics containing two nitrogen atoms, *i.e.*, metallapyrimidine, were reported by Winter and co-workers.[56]

2.3. Metallafuran

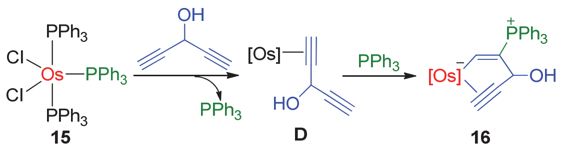
Metallafuran, which is derived from the formally replacement of one of the CH groups in furan by an isolobal metal fragment ML_n (M = metal; L = ligand), is the most widely investigated five-membered metallaaromatics. According to the position of the metal fragment, metallafuran can be classified into α-metallafuran[57] and β-metallafuran.[33] However, few examples of β-metallafuran have been reported. As shown in Scheme 6, two main resonance structures of α-metallafuran should account for the structure of α-metallafuran: a carbonyl coordinated vinyl metal complex **I-B** and alkoxymetal carbene **I-A**.

Scheme 6 Resonance structures of α-metallafuran



Synthesis of metallafuran starting from HC≡CCH(OH)C≡CH. We have developed an efficient ring-forming strategy that involves the following key steps: initial coordination of alkyne to the metal center, subsequent attack of nucleophiles on the coordinated alkyne,[6,12] and final ring-closing through cycloaddition, C—H activation, or coordination. This ring-forming strategy is also effective for the synthesis of metallafuran. As shown in Scheme 7, the reaction of $OsCl_2(PPh_3)_3$ with 1,4-pentadiyn-3-ol in THF produces η^2-alkynol-coordinated osmacycle **16** through the nucleophilic addition of PPh_3 to the coordinated alkyne. **16** can be used as a precursor to synthesize metallafuran.

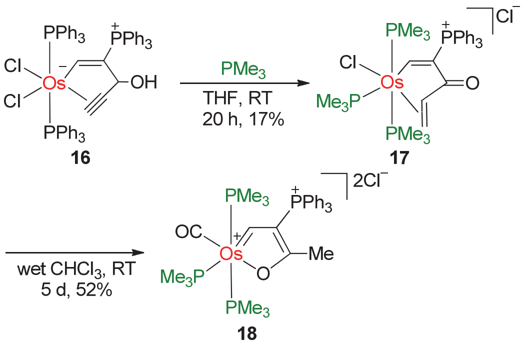
Scheme 7 Proposed mechanism for the formation of compound **16**



[Os] = $OsCl_2(PPh_3)_2$

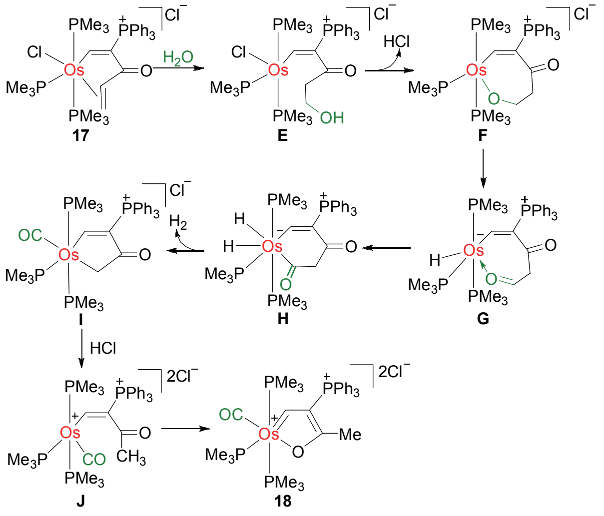
As shown in Scheme 8,[58] when η^2-alkynol-coordinated osmacycle **16** is treated with PMe_3 in THF, the ligand substitution and conversion from alkyne alcohol to α,β-unsaturated ketone occurs, which forms complex **17**. Complex **17** can convert to osmafuran **18** in wet chloroform in 5 d, with a yield of 52%.

Scheme 8 Synthesis of osmafuran **18**



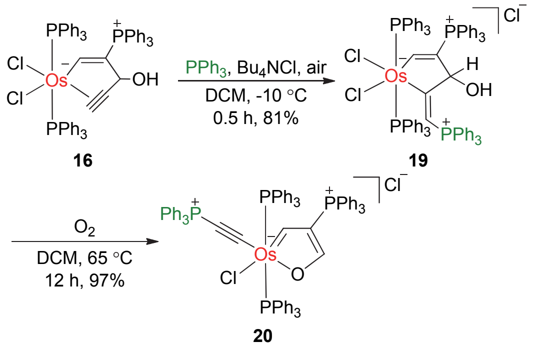
A plausible mechanism for the formation of **18** is shown in Scheme 9. Initially, the addition reaction of water to the coordinated terminal double bond of **17** produces **E**. The following elimination of HCl may produce **F**, which may undergo β-H elimination to generate the metal hydride **G**. The oxidative addition of the terminal aldehyde to the osmium center produces the dihydrideacyl intermediate **H**. The subsequent loss of H_2 and deinsertion of the carbonyl group produces **I**. The protonation of **I** by HCl and coordination of the carbonyl group to the osmium center produces the final product osmafuran **18**.

Scheme 9 Proposed mechanism for the formation of osmafuran **18**



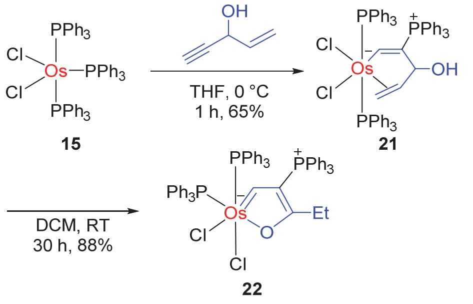
Another osmafuran **20** can also be prepared from η^2-alkynol-coordinated osmacycle **16**.[59] As shown in Scheme 10, the reaction of **16** with PPh_3 and Bu_4NCl in CH_2Cl_2 generates an osmacyclopentene **19**, probably through the nucleophilic addition of PPh_3 to the coordinated alkyne and an oxidation process. With the break of a C—C single bond and the oxidation of the hydroxyl group, osmacyclopentene **19** can further convert to osmafuran **20** in the presence of oxygen.

Scheme 10 Synthesis of osmafuran **20**



Synthesis of metallafuran starting from HC≡CCH(OH)C=CH. A propynol with a lower degree of unsaturation, *e.g.*, 1,4-pentadiyn-3-ol (HC≡CCH(OH)C=CH), is another effective organic substrate to form metallacycles (Scheme 11).[60] It can react with $OsCl_2(PPh_3)_3$ to produce an η^2-allylic alcohol coordinated osmacy-

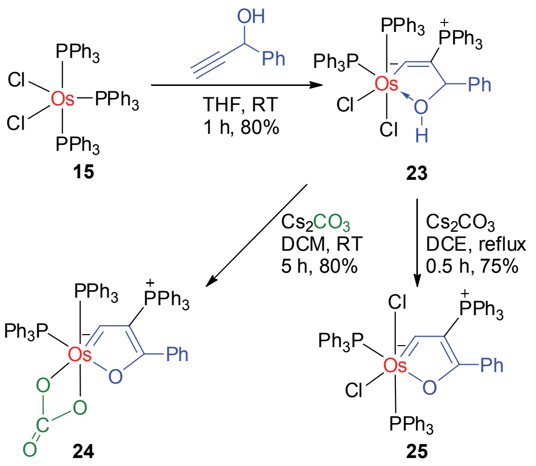
Scheme 11 Synthesis of osmafuran **22** from HC≡CCH(OH)C=CH



cle **21**. In the solution of CH_2Cl_2, **21** can transform into the ethyl-substituted osmafuran **22** with the yield of 88%. A possible mechanism for the formation of **22** may include multiple hydrogen migration steps. Formally, the alcohol is dehydrogenated with the hydrogenation of the coordinated alkene to the ethyl group.

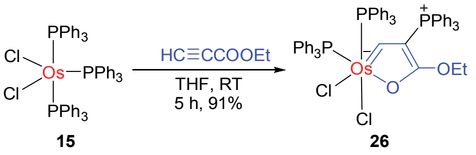
Synthesis of metallafuran starting from HC≡CCH(OH)Ph. The substituents of propynol is not limited to alkenyl or alkynyl; phenyl-substituted propynol has also been used to construct metallacycle (Scheme 12).[61] The reaction of $OsCl_2(PPh_3)_3$ with HC≡CCH(OH)Ph produces a hydroxyl-coordinated osmacycle **23**. The treatment of osmacycle **23** with Cs_2CO_3 in CH_2Cl_2 at room temperature deprotonates the hydroxyl group to produce osmafuran **24** in high yield. When the reaction is performed in $ClCH_2CH_2Cl$ under reflux, osmafuran **25** with different ligands is obtained.

Scheme 12 Synthesis of osmafuran **24** and **25** from alkynol HC≡CCH(OH)Ph



Synthesis of metallafuran starting from HC≡CCOOEt. In 2009, we demonstrated the synthesis of an osmafuran **26** via the reaction of HC≡CCOOEt with $OsCl_2(PPh_3)_3$ (Scheme 13).[62] The coordination of the alkyne to the metal center and the nucleophilic addition of PPh_3 to the alkyne carbon were proposed for the formation of osmafuran **26**. The Os—C bond distance (1.918(5) Å) in complex **26** shows obvious carbenic character, which facilitates a further ring expansion reaction with alkynes.

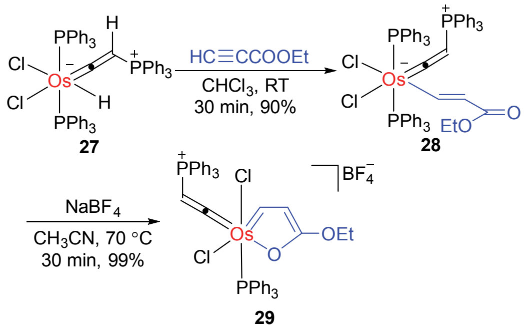
Scheme 13 Synthesis of osmafuran **26** from HC≡COOEt



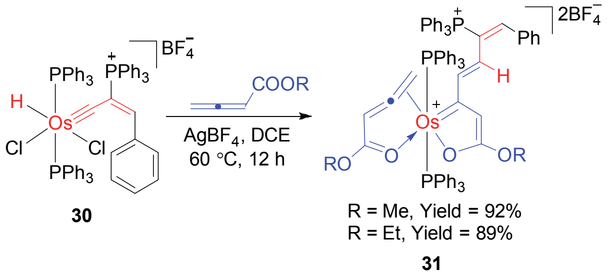
In 2013, we reported the synthesis of an osmafuran from HC≡CCOOEt using another method. As shown in Scheme 14,[63] the reaction of hydrido osmium vinylidene complex **27** with HC≡CCOOEt affords osmafuran **29** via the insertion of terminal alkyne into the metallic hydrogen bond followed by a ring-closing reaction.

Synthesis of metallafuran starting from allene. Allene is a unique class of unsaturated compound with the same degree of unsaturation as alkynes. Allene can also be used as an efficient organic substrate in our synthetic methodology for metallafuran. In 2015, we demonstrated the reactions of metal carbynes with allenes.[26] As shown in Scheme 15, the insertion of allenoate to osmium hydrido alkenylcarbyne complex **30** in the presence of $AgBF_4$ can produce osmafuran **31**. A possible mechanism of the formation of osmafuran **31** is shown in Scheme 16. In the presence of excess $AgBF_4$, the reaction of complex **30** with an equivalent of allenoate may initially generate the allenoate-coordinated intermediate **K**. The 1,2-hydrogen shift from the metal center to the carbyne carbon atom of **K** affords alkenylcarbene intermediate **L**. Several experimental and computational studies have been performed on the transformations from hydride carbyne to car-

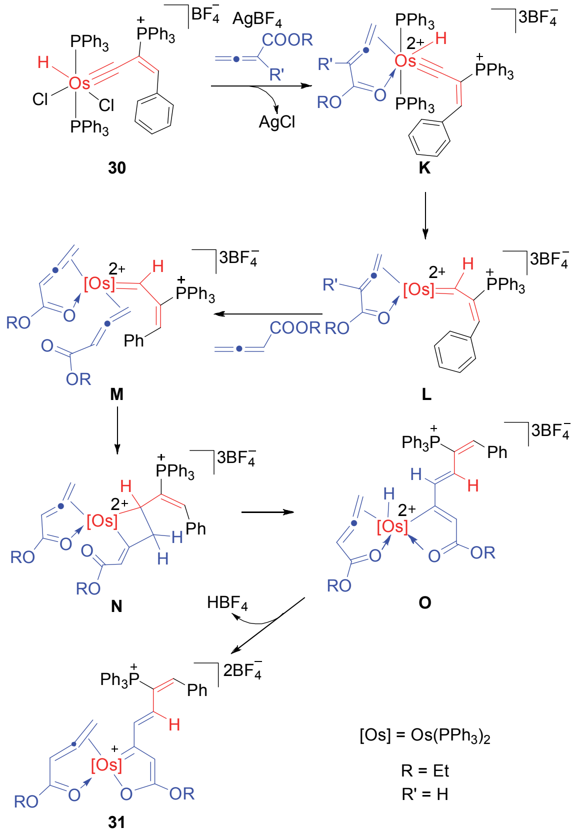
Scheme 14 Synthesis of osmafuran **29**



Scheme 15 Synthesis of osmafuran **31**



Scheme 16 Proposed mechanism for the formation of osmafuran **31**



bene species. The coordination of another ethyl buta-2,3-dienoate ($CH_2{=}C{=}CHCOOEt$) by its terminal double bond may produce the intermediate **M**. Subsequent [2+2] cycloaddition of the carbene unit and coordinated double bond may produce intermediate **O**. The β-H elimination, which is accompanied by the release of HBF_4, produces osmafuran **31**.

Other five-membered metallaaromatics that contain main-group heteroatoms, such as metallapyrrole and metallathiophene, were synthesized by Carmona,[35,36] Esterulas,[34] Bleeke[38,39] and Wright[37] and are not summarized in this account.

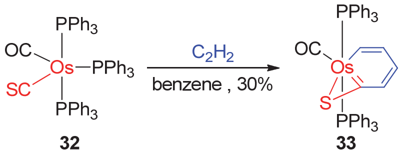
3. Bicyclic metallaaromatics Containing Main-group Heteroatoms

Several fused bicyclic metallaaromatics that contain main-group heteroatoms have been reported by our group in recent years.[6,64] Most of them are metallabenzenoid complexes such as metallabenzene fused with three-membered and five-membered rings. The only exception is aza-metallapentalene with a fused five-membered framework.[65]

3.1. Metallabenzenes with fused three-membered rings

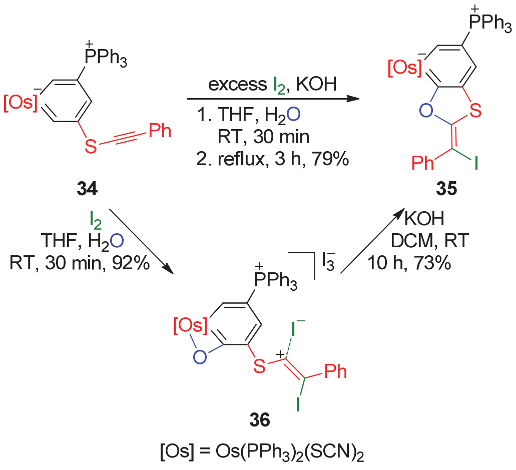
The first metallabenzene **33** reported by Roper group in 1982 was a metallabenzene with a fused three-membered ring containing sulfur.[2] As shown in Scheme 17, it was prepared via the [1+2+2] cyclization reaction of two acetylene molecules with the thiocarbonyl ligand in the osmium compound $Os(CO)(CS)(PPh_3)_3$.

Scheme 17 Synthesis of the first stable metallabenzene



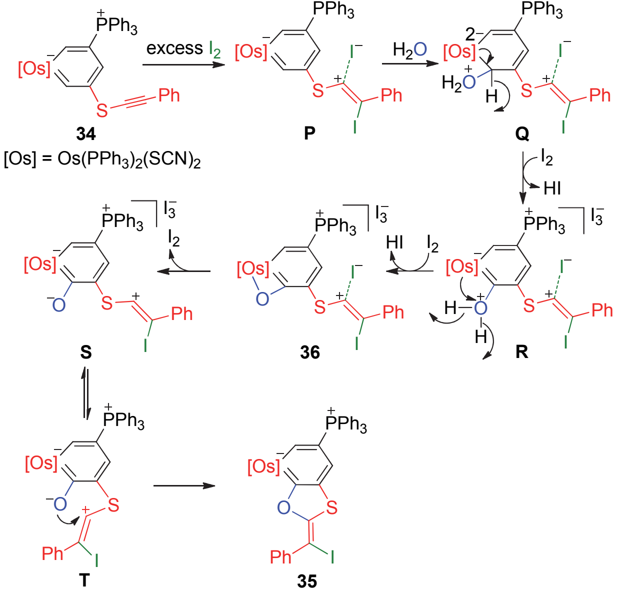
In 2013, we investigated the iodine-mediated electrophilic cyclizations of a metallabenzene complex bearing a phenylethynylthio substituent, from which several metallaaromatics that contained main-group heteroatoms were isolated (Scheme 18).[41] The reaction of metallabenzene **34** with I_2 and KOH produces the iodocyclization product **35**. In the absence of KOH, the reaction of **34** and I_2 produces osmabenzoxirene **36** in a yield of 92%. **36** can further convert to the final electrophilic cyclization product **35** when it is treated with KOH, which indicates that **36** is the key intermediate for the reaction. The most important character of **36** is its iodo-substituted phenylethenylthio substituent, which can be considered an intimate ion pair form, which is different from the generally accepted iodonium form.

Scheme 18 Syntheses of fused osmabenzene **35** and **36**



A plausible mechanism for the electrophilic cyclizations of metallabenzene via the key intermediate **36** is proposed in Scheme 19. The electrophilic addition of the electrophile I_2 to phenylethynylthio substituent may afford intermediate **P**, which facilitates the nucleophilic addition of H_2O at the C5 position to form intermediate **Q**. With the aid of excess I_2, the elimination of a hydride generates intermediate **R** with the restored aromatic ring. The following oxidative deprotonation and coordination of oxygen to the metal center affords intermediate **36**. Then, with the aid of KOH, I^- can be released from the triiodide anion in **36**. With I^- of the intimate ion pair, they reduce the metal center and disassociate the acyl oxygen to produce intermediate **S** and I_2. The conformational isomerization of **S** forms intermediate **T**. The final intramolecular electrophilic cyclization generates metallabenzene **35**. The oxygen atom in complexes **36** and **35** comes from water, as demonstrated in isotopic labeling experiments.

Scheme 19 Proposed mechanism for the formation of fused osmabenzene **35** and **36**



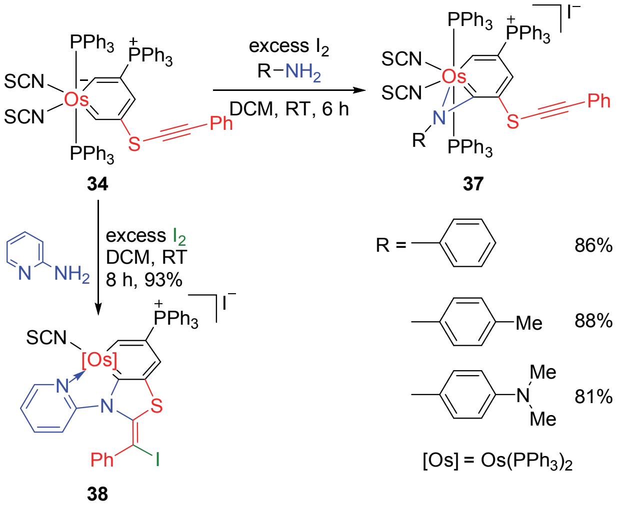
Under similar reaction conditions, the reaction of **34** with excess I_2 and RNH_2 at room temperature for 6 h produces osmabenzene fused with a three-membered nitrogen-containing ring **37** (R=Ph, *p*-tolyl, *p*-(dimethylamino)-phenyl)[41] (Scheme 20) instead of the expected iodocyclization products. The stronger bonding of Os—N in these compounds is assumed to impede further iodocyclization reaction of **37**. Interestingly, when 2-aminopyridine is subjected to the reaction as the nucleophile, the desired iodocyclization product **38** is obtained in a yield of 93%.

3.2. Metallabenzenes with fused five-membered rings

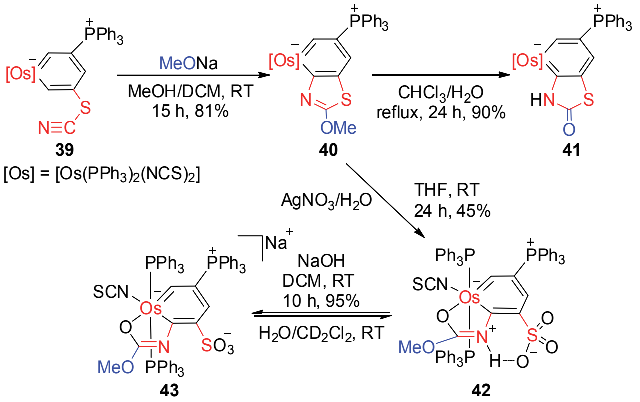
The derivation of metallabenzene is a facile method to construct higher π-electron metallaaromatics and those containing main-group heteroatoms. In 2009, we synthesized the first metallabenzothiazole via a new annulation reaction based on the intramolecular nucleophilic aromatic substitution (S_NAr) reaction of metallabenzene **39**.[40] As shown in Scheme 21, the treatment of osmabenzene **39** with MeONa/MeOH in CH_2Cl_2 forms osmabenzothiazole **40**.

A proposed mechanism for the formation of **40** is shown in Scheme 22. Initially, the addition of MeONa to **39** may produces

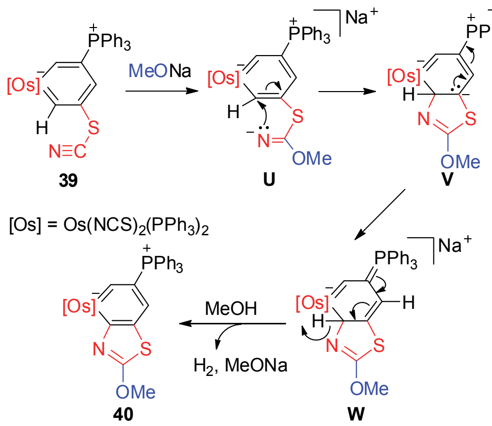
Scheme 20 Syntheses of fused osmabenzene **37** and **38**



Scheme 21 Synthesis of osmabenzothiazole **40** and metallabenzoxazoles **42** and **43**



Scheme 22 Proposed mechanism for the formation of metallabenzothiazole **40**

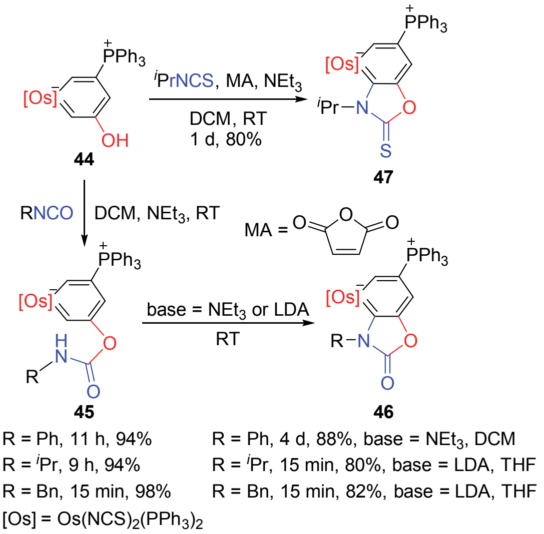


intermediate **U**. The intramolecular nucleophilic attack of the nitrogen atom to C5 may afford Jackson-Meisenheimer intermediate **V**. The following abstraction of the hydride ion by the combination with MeOH may release H$_2$ and produce the aromatic osmabenzothiazole **40**. The production of H$_2$ is further demonstrated by the GC chromatograms. The addition-elimination pathway in the mechanism is similar to the classical S$_N$Ar reaction of arenes.

By heating osmabenzothiazole **40** in moisture-bearing chloroform under refluxing for approximately 24 h, osmabenzothiazolone **41** is isolated via the hydrolysis of the methoxy group on the thiazole ring (Scheme 21). The reaction of **40** with silver nitrate in THF/H$_2$O produces the osmabenzoxazole sulfonic acid **42**. In the presence of NaOH, **42** experiences a basification to produce the metallabenzoxazole sulfonate **43**. As suggested by in situ NMR, **43** can quantitatively regenerate **42** with the addition of water (Scheme 21).

In 2014, we reported the synthesis of the first *m*-metallaphenol complex.[66] The *m*-metallaphenol readily reacts with nucleophiles and affords the metallabenzene with a fused five-membered ring. As shown in Scheme 23, the reaction of *m*-metallaphenol **44** with different isocyanates produces the carbamate intermediates **45**.[66] It can further convert to annulation reaction products (osmabenzoxazolone **46**) via an intramolecular S$_N$Ar reaction. The annulation reactions can be extended to isothiocyanates to produce the corresponding fused osmabenzene complexes **47**.

Scheme 23 Synthesis of fused osmabenzenes **46** and **47** from *m*-metallaphenol **44**

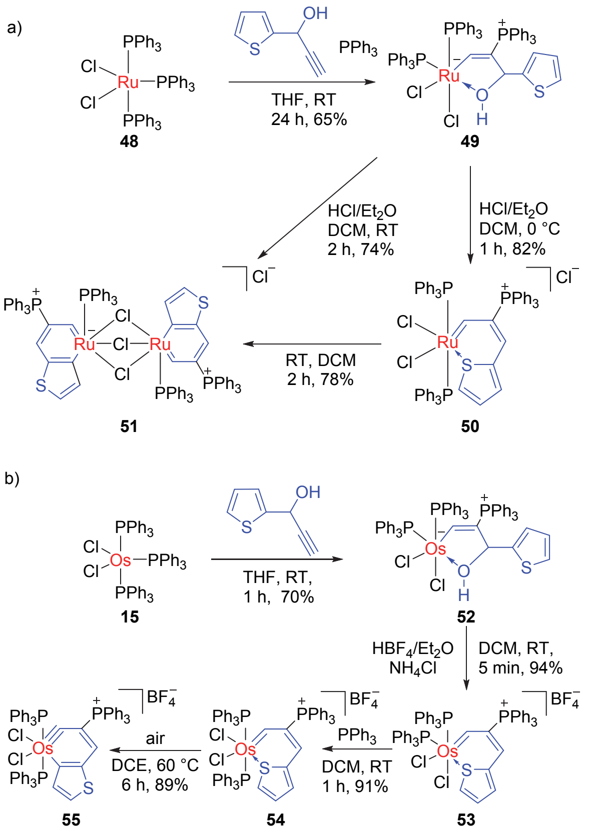


In addition to the annulation of metallabenzene, we recently reported a new synthetic route to form fused metallaaromatics via the intramolecular C—H activation of thiophenes. Remarkably, the synthetic route is effective for both ruthena-aromatics and osma-aromatics.[67,68] As shown in Scheme 24, when the mixture of RuCl$_2$(PPh$_3$)$_3$, PPh$_3$, and 1-(thiophen-2-yl)prop-2-yn-1-ol is stirred in THF for 24 h, ruthenacyclic complex **49** is formed as a yellow precipitate. The reaction of compound **49** with excess HCl for 2 h generates the bis-(ruthenabenzothiophene) **51**. It is a rare example of fused metallaaromatics with the second-row transition-metal center. When the reaction is performed at 0 °C, an active and air-sensitive intermediate thienyl-coordinated ruthenium alkenylcarbene complex **50** is detected by in situ NMR.

As shown in Scheme 24, when OsCl$_2$(PPh$_3$)$_3$ is treated with 1-(thiophen-2-yl)prop-2-yn-1-ol and PPh$_3$, a similar osmacycle **52** was obtained. The reaction of **52** with acid produces a related osmium alkenylcarbene complex **53**, which is sufficiently stable to be fully characterized. **53** can slowly transform to the *trans* isomer **54** in CH$_2$Cl$_2$ in an N$_2$ atmosphere at room temperature in several days. The addition of excess PPh$_3$ can facilitate this transformation, from which complex **54** is obtained in 1 h at 91% yield. Indeed, complex **54** is more stable than its ruthenium counterpart **50**. In a dichloroethane solution, it can persist for several days at room temperature in an N$_2$ atmosphere. When it is heated to

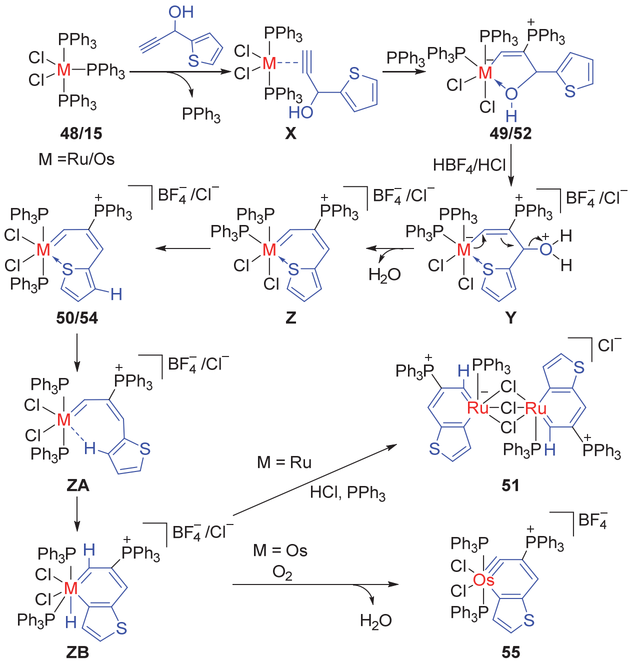
60 °C, it slowly transforms to several unidentified decomposed species. Heating a solution of complex **54** in air at 60 °C for 6 h causes the formation of the fused osmabenzyne **55** through the intramolecular C—H activation of thiophene. Notably, as the first metallabenzyne with a fused five-membered ring (thiophene ring), the synthesis of **55** provides a valuable addition to the rare examples of fused metallabenzynes.

Scheme 24 Syntheses of complexes **51** and **55** via the C—H activation



A plausible formation mechanism of **51** and **55** is shown in Scheme 25. The initial dissociation of PPh_3 ligand and coordination of HC≡CCH(OH)R (R=2-thienyl) to the metal center can produce the π-alkyne intermediate **X**. The nucleophilic addition of the dissociated PPh_3 to the coordinated alkyne may form the hydroxyl-coordinated metal vinyl compounds **49**/**52**. In the presence of acid, the hydroxyl group can be removed to give the metal alkenylcarbene complex **Z**. The isomerization of **Z** may form complexes **50**/**54**. Because of the dissociation of the thienyl group, **50**/**54** may convert to the agostic-form intermediate **ZA**. The hydrido metallabenzothiophene intermediate **ZB** can be formed by the C—H activation of thiophene. For the ruthenium center, with the loss of PPh_3 and HCl, the bis(ruthenabenzothiophene) **51** can be obtained in an N_2 atmosphere. For the osmium center, the oxidized product **55** can be obtained in the presence of O_2 by removing the hydride ligand and α-proton to generate H_2O.

Scheme 25 Proposed mechanism for the formation of complexes **51** and **55**



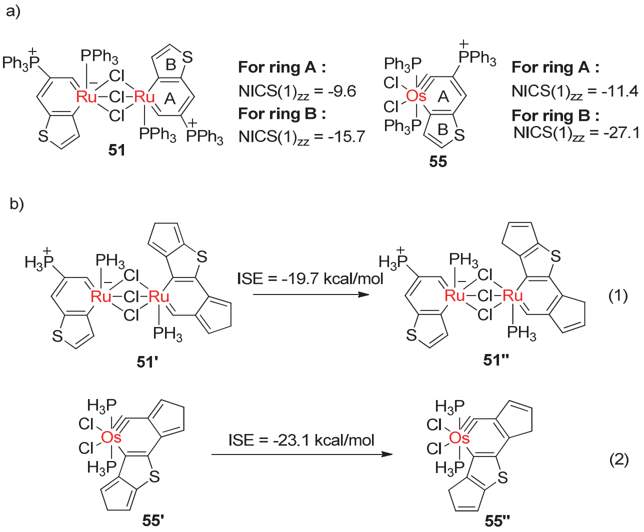


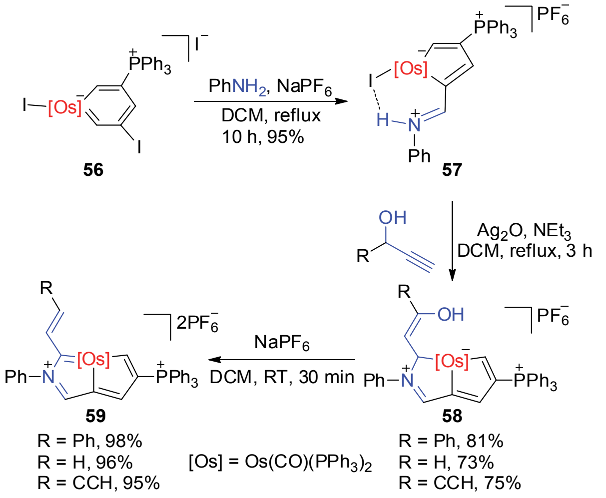
Figure 1 Evaluation of the aromaticity of complexes **51** and **55** using DFT calculations. (a) NICS(1)$_{zz}$ values of complexes **51** and **55**. (b) Isomerization stabilization energy (ISE) evaluations of the model complexes **51′** and **55′**.

Complexes **51** and **55** display typical aromatic characters such as downfield chemical shifts, delocalized planar structures and high thermal stability. Density functional theory (DFT) calculations were performed to further evaluate the aromaticity of **51** and **55**. As shown in Figure 1, all of the NICS(1)$_{zz}$ values of the fused thienyl rings and the six-membered metallacycle units in **51** and **55** are negative. The values of the metallacycle unit are comparable to those of other metallaaromatics.[67] In addition, the isomerization stabilization energy (ISE)[68] of the simplified model complexes **51′** (−19.7 kcal·mol^{-1}) and **55′** (−23.1 kcal·mol^{-1}), where the PPh_3 ligands are replaced by PH_3 ligands, was also evaluated. The isomerization stabilization energy (ISE) method was introduced by Schleyer and Pühlhofer, which is particularly effective for probing the magnitude of aromatic π conjugation systems.[47,69] The ISE values of **51′** (−19.7 kcal·mol^{-1})and **55′** (−23.1 kcal·mol^{-1}) are approximately two-thirds of the −33.2 kcal·mol^{-1} benzene ISE value,[70] which also suggests their aromaticity.

3.3. Aza-metallapentalenes and metallasilapentalynes

Azapentalenes are the nitrogen-atom-containing counterpart of pentalene. Our successful synthesis of metallapentalene prompted us to investigate the synthetic ability to get an aza-metallapentalene. In 2014, we reported the first synthesis of aza-metallapentalene via the cascade ring contraction/annulation reactions of osmabenzenes via osmapentafulvenes (Scheme 26).[65]

Scheme 26 Synthesis of aza-metallapentalene **59**



The treatment of **56** with aniline and sodium hexafluorophosphate under reflux affords the expected osmacyclopentadiene **57** in 95% yield. Its resonance structure can be described as a metallapentafulvene. Heating osmacyclopentadienes **57** in CH_2Cl_2 under reflux with a mixture of RCH(OH)C≡CH, Ag_2O, NEt_3 causes the formation of aza-metallapentalene **58** via the involvement of a terminal carbon atom of alkyne in the cyclization. The aza-metallapentalene **59** can be readily prepared by removing the hydroxyl group.

Unlike other common metallaaromatics with an aromatic organic counterpart, the organic counterpart of aza-metallapentalene **59** and our previously reported metallapentalyne[71] and metallapentalene[72], *i.e.*, aza-pentalene, pentalyne, and pentalene, respectively, are antiaromatic compounds. As indicated by comparing the NICS and aromatic stabilization energy (ASE)[47] of aza-metallapentalene and aza-pentalene (Figure 2), the metallacycle is aromatic, and the organic counterpart is antiaromatic. The incorporation of the osmium center converts its anti-aromaticity into aromaticity in the aza-metallapentalene. This phenomenon is very interesting and exceptional in metallaaromatic chemistry.

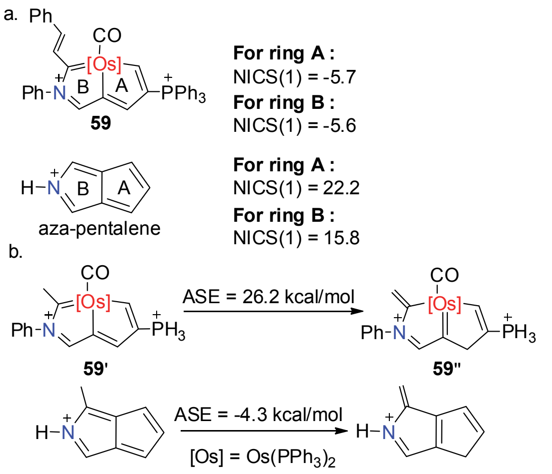


Figure 2 Evaluation of aromaticity of aza-osmapentalyne **59** using DFT calculations. (a) Calculated NICS values of the rings in aza-osmapentalyne **59**. (b) Calculated ASE values of the model complexes aza-osmapentalyne **59'**.

A theoretical study was performed to investigate the stability and aromaticity of metallasilapentalynes. Although the silicon atom is reluctant to participate in the π bonding, the computed negative ISE and NICS(1)$_{zz}$ values reveal the aromatic character of metallasilapentalyne (Figures 3 and 4). However, the aromaticity in metallasilapentalyne is less than that of osmapentalyne. This work can provide some theoretical foundation for the experimental realization of the first metallasilapentalyne.[73]

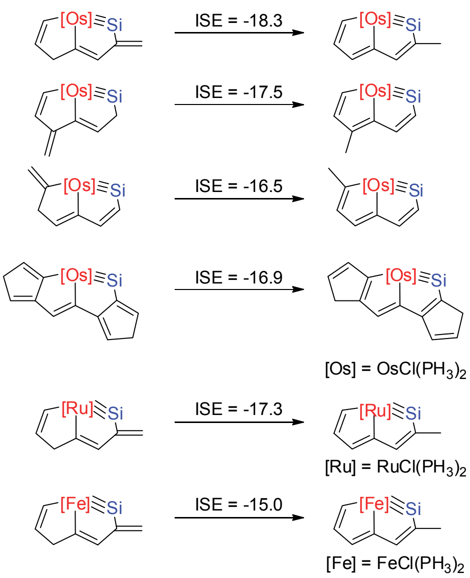


Figure 3 ISEs of metallapentalyne. The values are given in kcal•mol^{-1} including the zero-point energy corrections.


[M] = MCl(PH$_3$)$_2$

NICS(1)$_{zz}$	Os	Ru	Fe
Ring **A**	-19.8	-15.3	-14.2
Ring **B**	-16.2	-13.4	-10.2

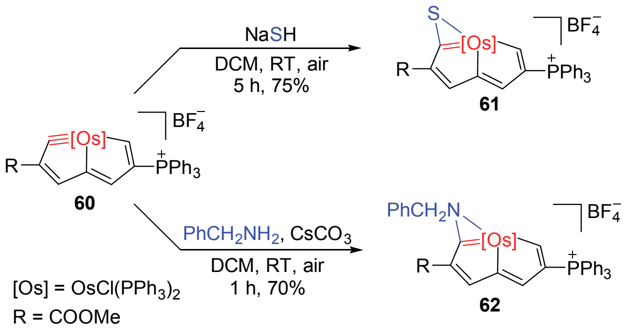
Figure 4 NICS(1)$_{zz}$ values of rings A and B in metallasilapentalynes.

4. Polycyclic Metallaaromatics Containing Main-group Heteroatoms

In 2013, we reported the first metallapentalyne, which has the smallest observed carbyne carbon bond angle (129.5°).[71] Such distortion results in considerable strain and high reactivity. The Os≡C triple bond can be attacked by both nucleophiles and electrophiles. Many metallapolycycles are prepared by using metallapentalynes as precursors.

As shown in Scheme 27, the nucleophilic reaction of osmapentalyne **60** with sodium hydrosulfide or benzylamine affords the sulfur- or nitrogen-containing tricyclic metallacycles **61** and

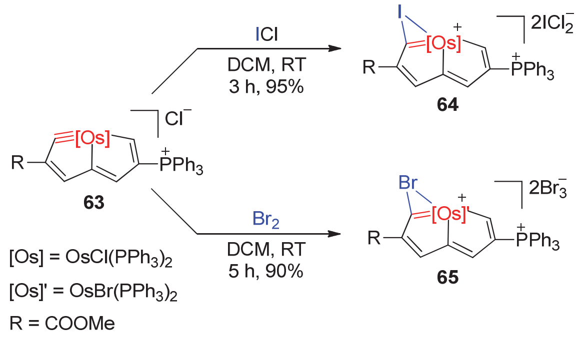
Scheme 27 Syntheses of polycyclic metallaaromatics **61** and **62**



62, respectively.[71]

The electrophilic addition of halogens is one of the most typical reactions for alkynes. As “alkyne-like” compounds, metal carbynes should provide new insights into the mechanism of halogenation. In 2016, we reported the halogenation of osmapentalyne, which produced the halogen-containing tricyclic metallapolycycles **64** and **65** (Scheme 28).[74] The experimental and computational studies demonstrate that one of the resonance structures of these halogen-containing tricyclic metallapolycycles can be considered the first examples of metallaiodirenium and metallabromirenium ions.

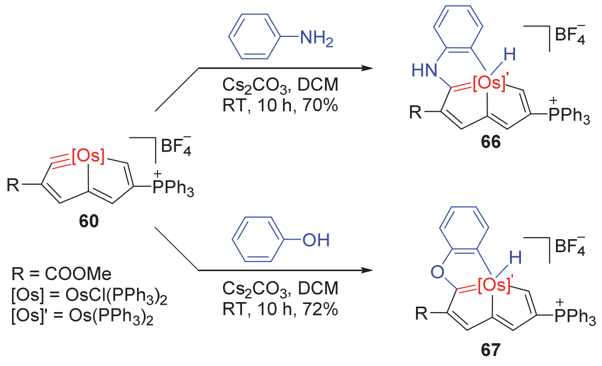
Scheme 28 Syntheses of polycyclic metallaaromatics **64** and **65**



In addition, DFT calculations were performed on the simplified unsubstituted model complex **64’** and **65’**, where the PH_3 ligands replace the PPh_3 ligands, to evaluate the aromaticity. The NICS values were computed for the rings of **64’** and **65’**. The calculated NICS$(1)_{zz}$ values for the two five-membered rings of **64’** and **65’** are negative (−17.8 and −19.5 for **64’**; −17.8 and −19.0 for **65’**). In addition, the NICS$(1)_{zz}$ values for the three-membered rings of **64’** and **65’** are −9.6 and −8.8, which illustrates the electron delocalization in the aromatic three-membered ring.

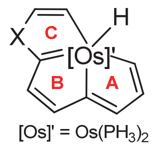
The cascade nucleophilic additions and C—H activation reactions of osmapentalyne with aniline or phenol in the presence of Cs_2CO_3 cause the formation of tetracyclic metallacycles **66** and **67** (Scheme 29), which are rare examples of β-metallapyrrole and β-metallafuran, respectively.[75]

Scheme 29 Syntheses of polycyclic metallaaromatics **66** and **67**



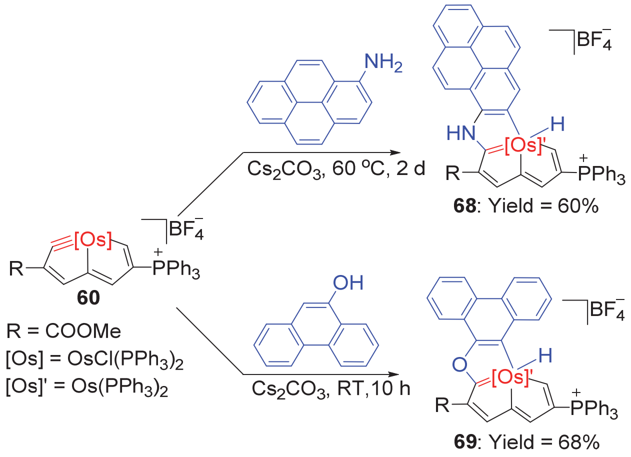
Experimental evidence for the aromaticity of complexes **66** and **67** is the planarity, high stability, and characteristic downfield ^1H chemical shifts. Their aromaticity was further verified by the isomerization stabilization energy values (ISE) based on simplified unsubstituted models **66’** and **67’** (by replacement of the PPh_3 ligands with PH_3 groups) and the NICS value. The ISE values of **66’** and **67’** are –31.5 and –35.1 kcal·mol^{-1}, which are close to those of aromatic osmapentalenes (–25.7 and –30.7 kcal·mol^{-1}) evaluated using the same method. The calculated NICS(1) and NICS$(1)_{zz}$ values for the three five-membered rings of model **66’** and **67’** are shown in Table 1. The ISE and negative NICS values demonstrate that complexes **66** and **67** have a unique metal-bridged tricyclic aromatic core. They are the first metal-bridged tricyclic aromatic system in which a metal center is shared by three aromatic five-membered rings.

Table 1 NICS(1) and NICS$(1)_{zz}$ values at rings A, B, and C of **66'** and **67’**

 [Os]' = Os(PH$_3$)$_2$		A	B	C
66’	NICS(1)	−11.2	−7.5	−6.3
X=NH	NICS$(1)_{zz}$	−23.9	−14.1	−10.7
67’	NICS(1)	−11.8	−8.4	−6.5
X=O	NICS$(1)_{zz}$	−25.5	−16.8	−9.1

Extended metallaaromatic systems can be constructed in the reaction of metallapentalyne with other nucleophiles that contain polycyclic aromatic rings. When osmapentalyne **60** is treated with commercially available 1-aminopyrene and Cs_2CO_3 under reflux for 2 d, metal-bridged polycyclic complex **68** is obtained in 60% yield (Scheme 30). Similarly, complex **69** is obtained from the reaction of osmapentalyne **60** with 9-phenanthrenol at room temperature.

Scheme 30 Syntheses of polycyclic metallaaromatics **68** and **69**



These unusual metal-bridged polycyclic aromatics **66—69** exhibit a broad absorption band from the ultraviolet region to the visible region (Figure 5). With the increase in size of the aromatic frameworks, red-shifts of the absorption maximum were observed, which suggests the extension of the effective conjugation lengths. These remarkable properties and their high stability will significantly facilitate the follow-up application study.

Osmapentalynes are also reactive towards alkynes. The reaction of osmapentalyne **60** with phenylacetylene and water in air affords an osmafuran fused osmapentalene **70** through the [2+2+1] cycloaddition (Scheme 31).[76] As suggested by the isotopic labeling experiments with ^{18}O-labeled water, the oxygen atom in the framework of **70** is assumed to be derived from water. Interestingly, when the reaction of osampentalyne **60** with phenylacetylene is performed in the presence of HBF_4 in air, a lactone-fused osmapentalyne **71** is obtained. A shift of the Os≡C triple

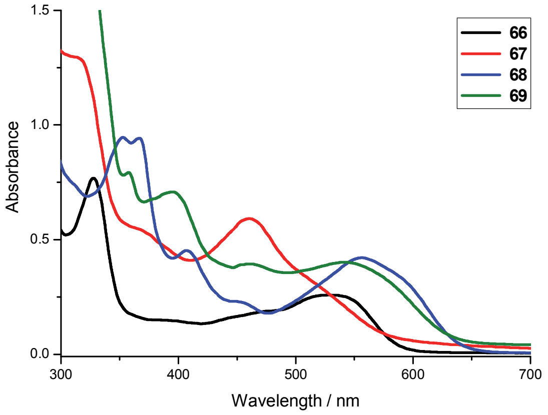
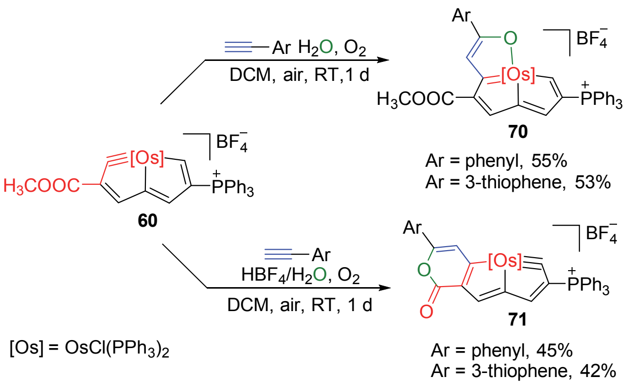


Figure 5 Measured UV/Vis absorption spectra of **66—69** in CH_2Cl_2 at room temperature.

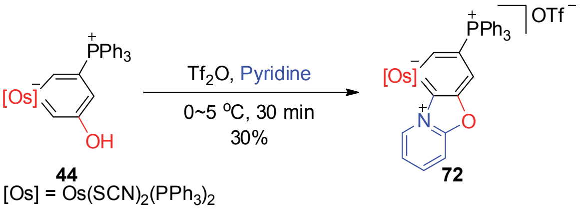
Scheme 31 Syntheses of polycyclic metallaaromatics **70** and **71**



bond from the left five-membered ring to the right is observed in the formation of the lactone unit. Further DFT calculations were performed to elucidate their aromaticity and electronic structure. The aromaticity of metallacycles is supported by the ISE evaluation and anisotropy of the induced current density (AICD) analysis.[77,78] The electronic structure analysis shows that the metallapentalenofuran **70** has a rare planar Craig-type Möbius aromaticity because of the 11-center-12-electron dπ-pπ π-conjugation. The osmapentalyne unit in complex **71** is essentially an 8-center-8-electron Möbius aromatic system.

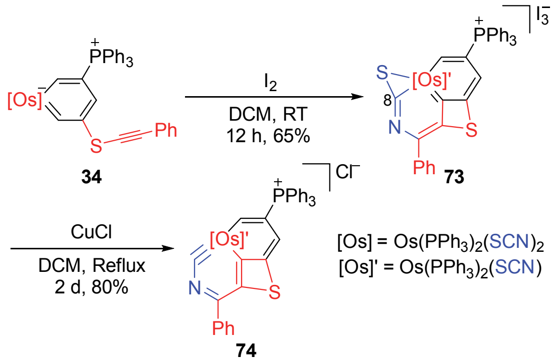
As mentioned, *m*-metallaphenol can be used as a good precursor to construct bicyclic metallaaromatics (Scheme 23). It can also be used to construct tricyclic metallacycles.[66] As shown in Scheme 32, the reaction of osmaphenol **44** with trifluoromethanesulfonic anhydride and pyridine at 0 °C produces tricyclic complex **72**. A plausible mechanism for the formation of complex **72** is proposed as the nucleophilic addition reaction of phenolic hydroxyl group to pyridine and a subsequent intermolecular S_NAr reaction of N atom to the metallabenzene ring.

Scheme 32 Synthesis of the polycyclic metallaaromatic **72**



The increase in variety of the metallaaromatic family is further evidenced by the discovery of metallapyridynes, which are azaheterocyclic analogues of metallabenzynes. In 2012, we reported the first metallapyridyne,[29] which is a metal-bridged polycyclic aromatic. As shown in Scheme 33, the metallapyridyne is synthesized from osmabenzene **34**. When **34** is treated with iodine, the first *m*-metallapyridine **73** is obtained. Complex **73** is a tetracyclic metallacycle containing a sulfur-tethered metallapyridine ring, which is similar to the sulfur-tethered metallabenzene ring.[2] The reaction of complex **73** with CuCl produces the metallapyridyne **74** with a yield of 80%. In this reaction, copper(I) chloride acts as a reductant for the abstraction of the tethered sulfur atom in **73**, which suggests that the bonding interaction with either C8 or the metal with S atom is not very strong. This synthetic example also indicates that metallabenzene is an excellent starting material for accessing higher π-electron metallaaromatics.

Scheme 33 Synthesis of the first metallapyridyne **74**



The aromaticity of the metallapyridyne ring of **74** was evaluated by DFT calculations. The calculated NICS values for the model **74'**, where the PPh_3 groups are replaced by PH_3, are $\delta = -4.5$ (NICS(0)) and −4.2 (NICS(1)). These values are comparable to those reported for other metallaaromatics.[29] The calculated ASE (11.3 kcal·mol^{-1}) is at the lower end of the values obtained for other metallaaromatics.[79-81] The negative NICS values and calculated ASE indicate that the aromaticity is associated with the metallapyridyne ring in complex **74**.

5. Conclusions and Outlook

The concept of aromaticity has long played an important role in chemistry and continues to motivate both experimentalists and theoreticians to search for unprecedented and exciting aromatic systems. Among the archetypal aromatic compounds, heteroaromatics are particularly attractive and have significantly broadened the scope of aromaticity. Metallaaromatics containing main-group heteroatoms clearly have important and enticing reactivities, which can explain their popularity and ever-increasing attention. In this account, we provide an overview of different procedures to access metallaaromatics that contain main-group heteroatoms, including the direct construction of aromatic rings starting from facile organic and metal substrates (the synthesis of metallapyridine, metallafuran, and thiophene-fused metallabenzene and metallabenyne) and annulation reactions of metallabenzene or metallapentalynes (the synthesis of most bicyclic and polycyclic examples). The efficient synthetic strategies result in the structural complexity with different metal centers (osmium, ruthenium, and iridium), main-group heteroatoms (nitrogen, oxygen, sulfur, bromine, and iodine), frameworks (monocyclic, bicyclic and polycyclic) and fused ring scaffolds (metal-bridged and non-metal-bridged metallacycles).

The ability to incorporate main-group heteroatoms into metallacyclic building blocks has been used to great effect in the design of new aromatic species with new topologies, interesting reactivity and unique properties. Given the available synthetic methods and an understanding of their aromaticity, metallaaromatics that contain main-group heteroatoms will continue to emerge and, more importantly, will result in a breakthrough or modification of the theories associated with aromaticity. Furthermore, their abundant reactivities and remarkable thermal stabilities offer aromatic models to extend classical organic reactions. Isolated intermediates in the reactions and DFT studies will provide much mechanistic insight, and further in-depth investigation in this direction is anticipated.

Acknowledgement

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