Acetylenic carbon-containing stable five-membered metallacycles

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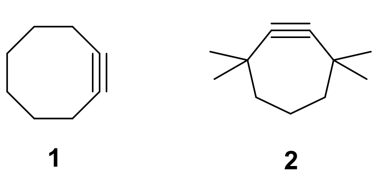
Abstract: Due to the linear property around an acetylenic carbon, the introduction of such an atom to a small cycle would result in high ring strain. Currently, the smallest isolated rings are five-membered, including metallacycloalkynes and metallapentalynes. Both types contain at least one unusual small bond angle around the acetylenic carbon, thus exhibiting abnormal reactivities. This feature article gives a comprehensive overview on these two kind complexes. The synthesis and reactivities are extensively described, the source of stability is presented, and the future prospect is discussed. The article aims to provide a better development for the chemical diversity of five-membered metallacycloalkynes and metallapentalynes.

Keywords: metallacycloalkynes; metallapentalynes; synthesis, reactivities

1. Introduction

Due to the sp hybridization of acetylenic carbon, the X≡C-Y moiety is normally linear. If such a moiety is introduced into a small cycle, large angle strain would be caused, which increases with decreasing ring size.[1,2] To date, the smallest purified unsubstituted carbocyclic alkyne is cyclooctyne with an eight-membered ring (**1**, Fig. 1).[3] One of the methods to stabilize such small cyclic compounds is by the introduction of bulky substituent(s) into the α-position(s) of the X≡C bond. The bulky group(s) can prevent the dimerization of the unsaturated bond(s), and also the attack from other molecules.[2] For example, cycloheptyne is highly unstable and has a half-life of 1 h at -78 °C,[4] however, after the introduction of four methyl groups into the α-positions, the resulting compound 3,3,7,7,-tetramethylcycloheptyne could be purified and is stable at room temperature (**2**, Fig. 1).[5]



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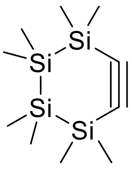

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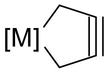
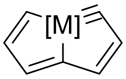
Fig. 1 Representative examples of isolable cyclic alkynes.

The substitution of carbon atoms in the ring by heteroatoms sometimes also stabilizes the strained carbocyclic cycles. Cyclohexyne is not stable above -100 °C, and could only be characterized by IR spectroscopy at low temperature.[6] In comparison, the six-membered tetrasilacyclohexyne is isolated and stable in boiling toluene even after 1 day (**3**, Fig. 1).[7,8] The stability of tetrasilacyclohexyne is due to the reduction of the angle strain by the longer Si-C bonds, which make the C≡C-Si angles closer to linear.

The incorporation of a metal center is another elegant method to stabilize the strained acetylenic carbon-containing compounds. For example, cyclopentyne is too unstable to be trapped,[9] in contrast, two types of five-membered metallacycles containing at least one acetylenic carbon atom have been developed (metallacycloalkyne **A** and metallapentalyne **B**, Fig. 2)[10-15] These five-membered metallacycles are interesting not only due to their abnormal structures and unusual reactivities, but also because five-membered metallacycles are intermediates in many transition-metal catalyzed organic reactions.[10-18] Surprisingly, there is no review paper covering both types. Considering the similarity of **A** and **B**, and the emergence of more and more novel chemistry, this review will discuss them together for the first time. Through the summarization and comparison on the synthesis and reactivities of **A** and **B**, it is favorable for the development of their chemical diversity, which is the aim of this account.



A



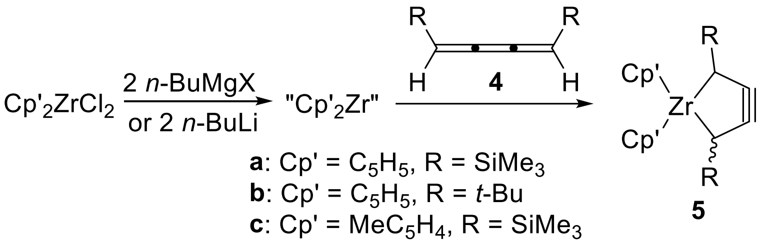
B

Fig. 2 Strained five-membered metallacycles with triple bond.

2. Five-membered metallacycloalkynes

2.1 Synthesis of five-membered metallacycloalkynes

The first five-membered metallacycloalkynes with the structure of **A** shown in Fig. 2 were reported by Suzuki *et al.* in 2002.[19] Treatment of $CpZrCl_2$ with 2 equivalents of *n*-BuMgX at low temperature generated a low-valent zirconocene, which further reacted with (*Z*)-1,4-disubstituted-1,2,3-butatriene (**4a**: R = $SiMe_3$, **4b**: R = *t*-Bu) for 1 hour at room temperature to provide two 1-zirconacyclopent-3-ynes **5a** and **5b**, existing as *cis*- and *trans*-isomers (Scheme 1). *n*-BuMgX can be replaced by *n*-BuLi or EtMgBr, while in the latter case, a seven-membered metalacyclic alkyne would be afforded as the by-product.[20,21] Initially, *cis*-configurations were dominant for both **5a** and **5b**. However, after 48 hours at room temperature in solution, the ratios of *cis*/*trans* isomers of **5a** and **5b** changed to 36/64 and 12/88, respectively. The isomerization from *cis* to *trans* resulted in the isolation of *trans*-isomers as good single crystals only. Later on, complex **5c** with a *cis*/*trans* ratio of 50/50 was prepared in a similar procedure (Scheme 1).[22] This strategy could also be extended for the preparation of titanium and hafnium analogues.[22,23]



Scheme 1 Synthesis of metallacyclopentynes **5a**-**5c**.

Complex *trans*-**5a** is selected as the example to illustrate the structures of these metallacyclopentynes. The five atoms in the cyclopentyne ring are almost coplanar, with an interior angle sum of the five-membered zirconacycle as 539.5°, close to an ideal planar pentagon (Fig. 3). The bond length of C2≡C3 is 1.195(7) Å, slightly shorter than that of cyclonoyne (1.21 Å) determined by gas phase electron diffraction,[24] and at the longer end of those in normal acyclic alkynes (1.167-1.197 Å).[25] The Zr-C2 and Zr-C3 distances are 2.291(5) and 2.286(6) Å, respectively, comparable to the Zr-CH_3 lengths in $Cp_2Zr(CH_3)_2$ (2.280(5) and 2.273(5) Å),[26] and even shorter than those of Zr-C1 (2.469(5) Å) and Zr-C4 (2.456(7) Å) in *trans*-**5a**. Therefore, one may think the C2≡C3 bond is coordinated with the metal and it is actually a metallacyclopentene complex. However, in normal zirconocene-alkyne complexes, the lengths of coordinated triple bonds are in the range for double bonds,[27] which is contradictory to the C2≡C3 distance in *trans*-**5a**. Besides, the IR absorption band for C2≡C3 bond at 2014 cm^{-1}, which is in a sharp contrast to those in Zr-alkyne complexes (i.e., 1611 cm^{-1}),[28] further supports its triple bond property. Notably, the authors also stated that a weak interaction between C2≡C3 and the Zr atom could not be excluded.

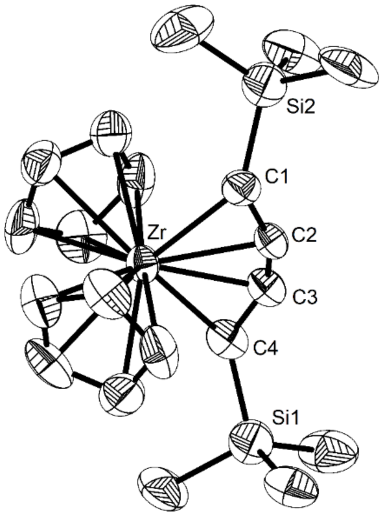
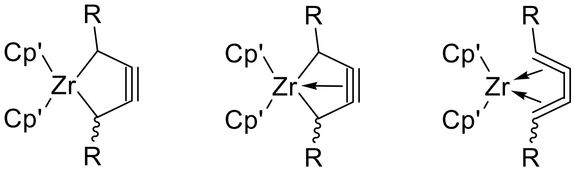


Fig. 3 X-ray single crystal structure of *trans*-**5a**. The thermal ellipsoids are displayed at 50% probability. Hydrogen atoms are omitted for clarity.

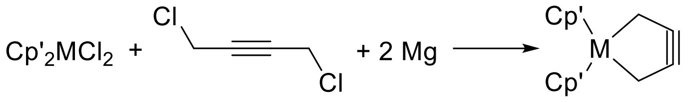
The C1-C2≡C3 and C2≡C3-C4 angles are 154.2(6)° and 154.4(7)°, respectively, which largely deviate from the standard angle around sp-hybridized carbon. Thus, there must be a high ring strain, and how can this kind of complexes be stable? Jemmis and coworkers proposed that the stability of **5** is due to the Lewis structure of **5B** (η^2-σ,σ + η^2-π coordination mode), in which the C≡C triple bond is coordinated by the Zr atom (Fig. 4).[29-31] Lin *et al.*, on the other hand, proposed that the cumulene coordinated resonance form **5C** is the major contribution for their stability (Fig. 4, η^4-π,π mode).[32] Through an electron density analysis based on X-ray diffraction data, Hashizume, Suzuki and Chihara, however, stated that the mode is a resonance hybrid, with the major contributor as the η^2-σ,σ form (**5A**, Fig. 4), and the minor one as **5C**.[33] The existence of **5C** explains the interconversion of *cis*/*trans* isomers.



5A **5B** **5C**

Fig. 4 The proposed bonding modes of 1-zirconacyclopent-3-ynes **5**.

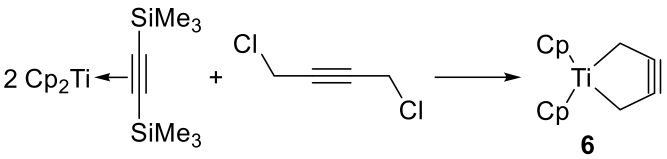
In 2004, the Suzuki group developed a more convenient route, in which butatriene derivatives are not necessary, for the construction of 1-metallacyclopent-3-ynes. Reduction of $Cp'ZrCl_2$ and 1,4-dichlorobut-2-yne by Mg in THF resulted in the formation of **5d** and **5e**,[34] and 1-titanacyclopent-3-yne **6** was generated similarly (Scheme 2).[22,23] The synthetic route was also applicable for the synthesis of 1-hafnacyclopent-3-yne **7**, although it could not be purified and was only characterized by NMR spectroscopy (Scheme 2).[22] Note that a variety of strain five-membered metallacyclocumulene complexes have been reported by the group of Rosenthal, while all of them contain substitutuents at the metallacycle.[35,36] The "non-substituted" metallacyclocumulenes might be too instable to be isolated, because as described in the introduction, bulky substituent(s) at the adjacent carbon(s) of C≡C bond can make strain cyclic alkynes more stable. Therefore, it is surprising that the "non-substituted" **5d**, **6** and **7** can be isolated successfully.



5d: M = Zr, Cp' = C_5H_5
5e: M = Zr, Cp' = *t*-BuC_5H_4
6: M = Ti, Cp' = C_5H_5
7: M = Hf, Cp' = C_5H_5

Scheme 2 Synthesis of "non-substituted" metallacyclopentynes **5d**, **5e**, **6** and **7**.

In fact, an alternative synthetic route to target the titanium complex **6** was developed by Rosenthal and coworkers in prior to that shown in Scheme 2. When $ClCH_2C\equiv CCH_2Cl$ was added into two equivalents of $Cp_2Ti(\eta^2\text{-}Me_3SiC\equiv CSiMe_3)$ in hexane, complex **6** was formed rapidly, accompanied by the generation of $Me_3SiC\equiv CSiMe_3$ and Cp_2TiCl_2 (Scheme 3).[37]



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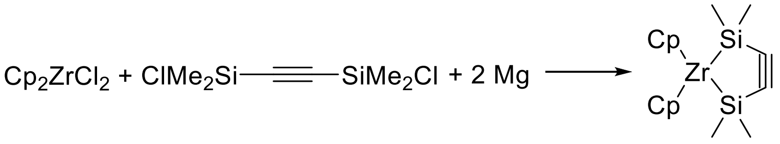
Scheme 3 An alternative route for the synthesis of **6**.

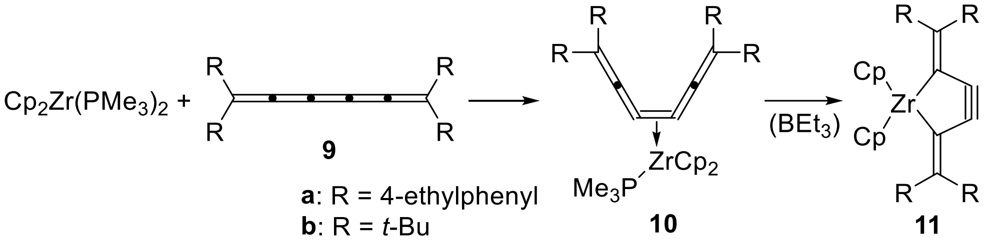
The same group later synthesized 1-zircona-2,5-disilacyclopent-3-yne **8**, through reduction of Cp_2ZrCl_2 and $ClMe_2SiC\equiv CSiMe_2Cl$ by Mg (Scheme 4). The structural and spectral parameters, together with DFT calculations, suggest **8** is a Si-substituted metallacyclopentyne with a weak interaction between the triple bond and the metal center, rather than a metallocene-stabilized 1,4-disilabutatriene complex.[38] The results are consistent with Suzuki's all-C metallacycloalkynes **5**.[19,33]



8

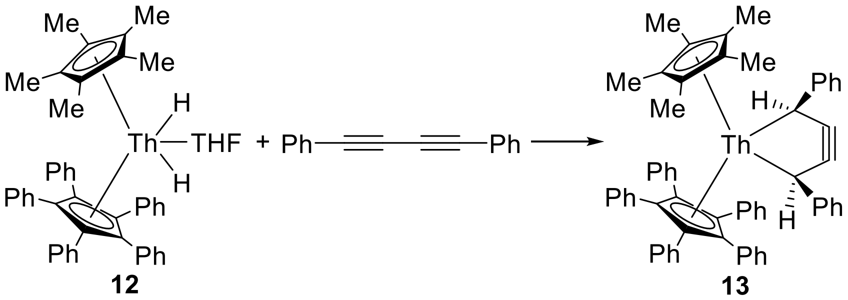
Scheme 4 Synthesis of 1-zircona-2,5-disilacyclopent-3-yne **8**.

The other type of metallacyclopentynes, with an alkylidene at each α-carbon of the C≡C bond, was designed by the group of Suzuki, either. Treatment of the low-valent zirconocene-bisphosphine complex $Cp_2Zr(PMe_3)_2$ with hexapentaene **9a** in THF at room temperature gave 2,5-bisalkylidene-1-zirconacyclopent-3-yne **11a**. If the reaction was carried out at -40 °C, the η^2-π-complex **10a** could be detected (Scheme 5).[39,40] When **9a** was switched to **9b**, complex **10b** was formed selectively in high yield. Only when BEt_3 was added to abstract the coordinated PMe_3, **10b** was converted to **11b**. Interestingly, this transformation is reversible: **11b** was changed back to **10b** upon the addition of excess PMe_3 (Scheme 5).[40] Several other analogues of **11** were prepared as well, and if the starting four substituents in hexapentaene are not the same, the resulted zirconacyclopentynes would exist as several isomers.[21,41,42]



Scheme 5 Synthesis of 2,5-bisalkylidene-1-zirconacyclopent-3-ynes **11**.

Recently, a *cis* thorium cyclopentyne **13**, was afforded *via* hydride insertion by treatment of **12** with 1,4-diphenyl-1,3-butadiyne (Scheme 6).[43] This new route breaks the limitation that the metallacyclopentyne chemistry is restricted to group 4 metals.

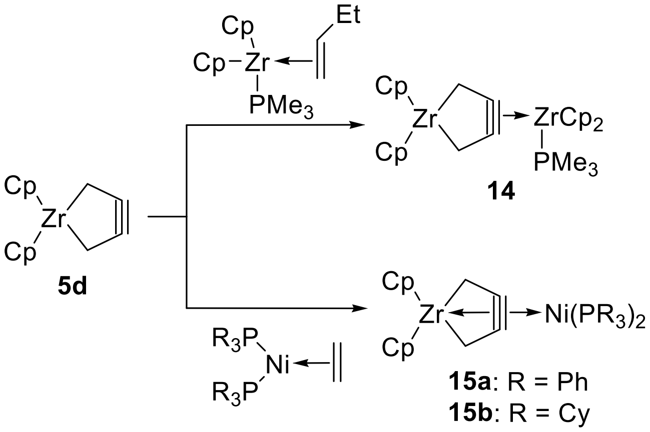


Scheme 6 Synthesis of thorium cyclopentyne **13**.

2.2 Reactivities of five-membered metallacycloalkynes

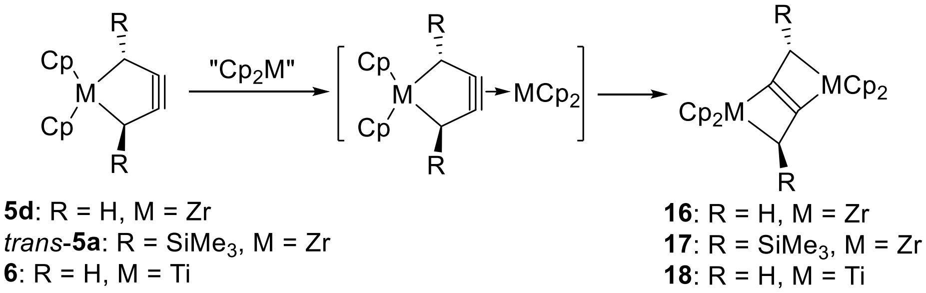
2.2.1 Formation of alkyne-coordinated complexes

As mentioned previously, Suzuki and coworkers regarded the major contributor of metallacycloalkynes **5** as the η^2-σ,σ form **5A** (Fig. 4).[33] **5A** contains a free C≡C bond, which might act as a 2e$^-$ ligand to be coordinated with other metals. Thus, the reactions of **5d** with $Cp_2Zr(\eta^2\text{-}CH_2{=}CHEt)(PMe_3)$ or $(PR_3)_2Ni(\eta^2\text{-}CH_2{=}CH_2)$ (R = Ph or Cy) were carried out, and as expected, the alkyne-coordinated products **14**, **15a** and **15b** were obtained respectively (Scheme 7).[34,44] Noteworthily, after comparing the structural data between **15a** and **15b** with **5d**, **14** and the Ni(0) zirconacyclocumulene complex $Cp_2Zr[\mu\text{-}(\eta^4\text{-}PhC_4Ph)]Ni(PPh_3)_2$, the authors pointed out that in both of **15a** and **15b**, the interactions of the C≡C bond with Zr center are stronger than those in **5d** and **14**.[44]



Scheme 7 Reactions of **5d** with phosphine-containing metal complexes.

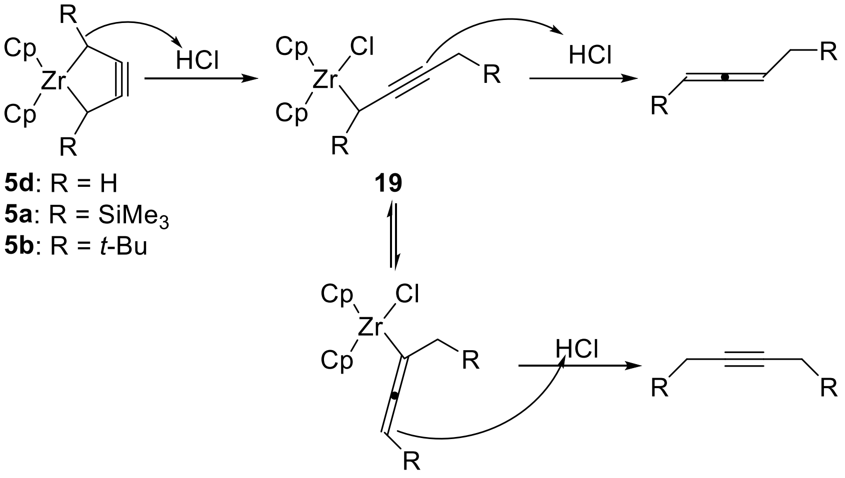
On the other hand, if the starting metal precursors do not contain phosphine ligand, symmetric bimetallic complexes would be produced. For example, upon treatment of **5d** with Cp_2ZrCl_2 and Mg, or $Cp_2Zr(n\text{-}Bu)_2$, complex **16** was afforded, and the alkyne-coordinated intermediate was not detected (Scheme 8).[45] **16** can be regarded as a μ-*trans*-butatriene complex, with a "zig-zag" C4 ligand connecting the two zirconocenes. Alternatively, **16** could be synthesized directly from $ClCH_2C{\equiv}CCH_2Cl$ with 2 equivalents of Cp_2ZrCl_2 and 3 equivalents of Mg, or from **14** with BEt_3.[45] Two analogues **17** and **18** were produced similarly (Scheme 8).[37,46]



Scheme 8 Synthesis of bimetallic complexes **16-18**.

2.2.2 Reactions with electrophiles

Organic alkynes can react with electrophiles to give alkenes, in contrast, the reactions between five-membered metallacycloalkynes and electrophiles normally result in ring-opening, due to their high ring strain. For example, treatment of **5d** in THF with excess HCl in diethyl ether (1.0 M) gave a mixture of 1,2-butadiene and 2-butyne in NMR yields of 83% and 3%, respectively (Scheme 9).[47] To investigate the reaction mechanism, the amount of HCl in ether was decreased to 0.3 equivalent, and the protonated intermediate **19** (R = H) was observed. Together with a deuterium labeling experiment, it was proposed that **19** is in equilibrium with **19A**, which is the originality of 2-butyne (Scheme 9).[47] When **5d** was replaced by **5a** or **5b**, the major products would be the corresponding alkynes rather than allene derivatives, probably because the equilibrium favors **19A** under the effect of the bulky R group.[47]



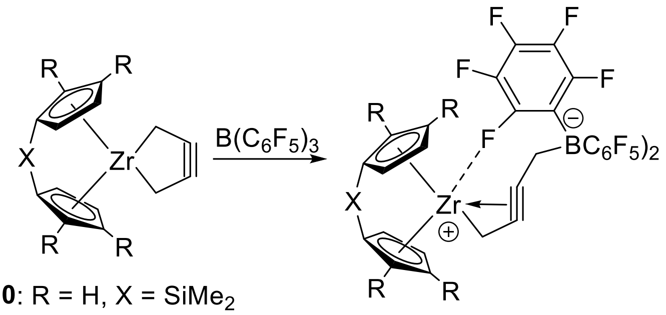
5d: R = H
5a: R = SiMe$_3$
5b: R = *t*-Bu

19

19A

Scheme 9 Protonation of **5d**.

Similar to the formation of **19**, the group of Rosenthal found that B(C$_6$F$_5$)$_3$ could activate one of the α-C-Zr bonds in their five-membered zirconacycloalkynes as well. When **20** and **21** were treated with B(C$_6$F$_5$)$_3$, two zwitterionic boranate complexes **22** and **23** were generated, respectively (Scheme 10).[48,49] In each of complexes **22** and **23**, one of the *ortho*-F atoms has certain interactions with the Zr center. These two complexes are analogous with the products of metallacyclocumulenes with B(C$_6$F$_5$)$_3$.[50] 1-Titanacyclopent-3-yne **6** displayed a similar reactivity, except that no F-Ti interaction is found in the final product.[48]

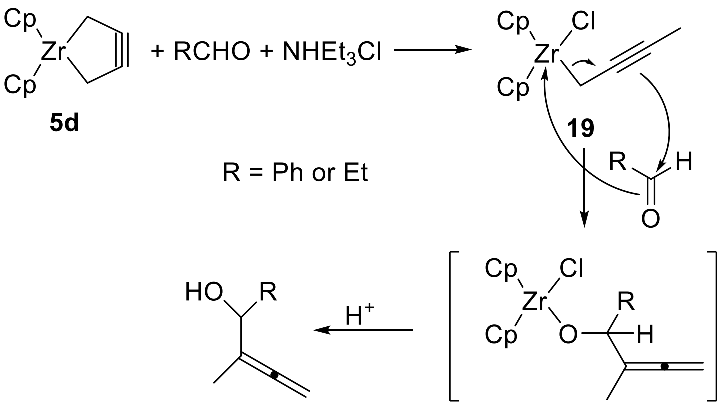


20: R = H, X = $SiMe_2$
21: R = CH=CH-CH=CH, X = CH_2CH_2

22: R = H, X = $SiMe_2$
23: R = CH=CH-CH=CH, X = CH_2CH_2

Scheme 10 Reactions of **20** and **21** with $B(C_6F_5)_3$.

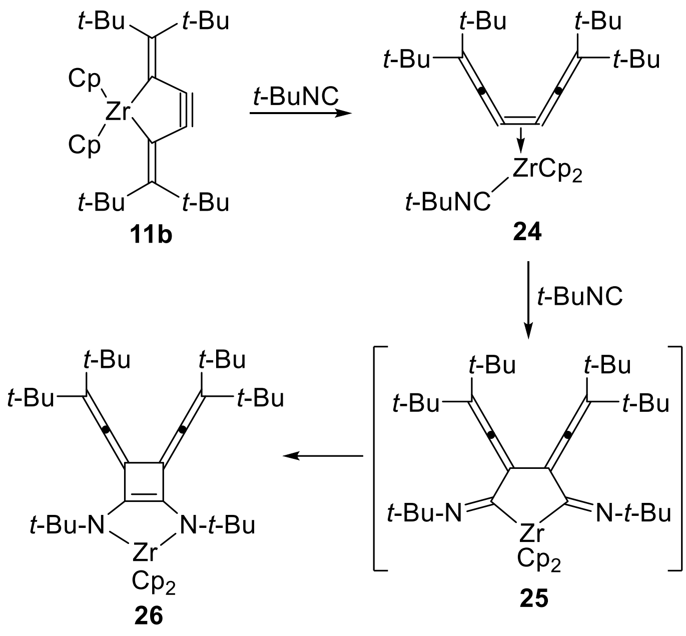
In the presence of a proton source, metallacycloalkynes could further react with aldehydes. For example, treatment of **5d** and triethylamine hydrochloride with benzaldehyde or propylaldehyde gave 2-methyl-1-phenyl-2,3-butadien-1-ol and 1-ethyl-2-methyl-2,3-butadien-1-ol, respectively. The intermediate was also supposed as **19** (R = H), which further attacks the carbonyl group of aldehyde, accompanied by the formation of O-Zr bond and the cleavage of Zr-C bond, to form an allene moiety. After the quenching by H^+, the final products are generated (Scheme 11).[47]



Scheme 11 Reactions of **5d** with aldehydes in the presence of $NHEt_3Cl$.

2.2.3 Isocyanide insertion reactions

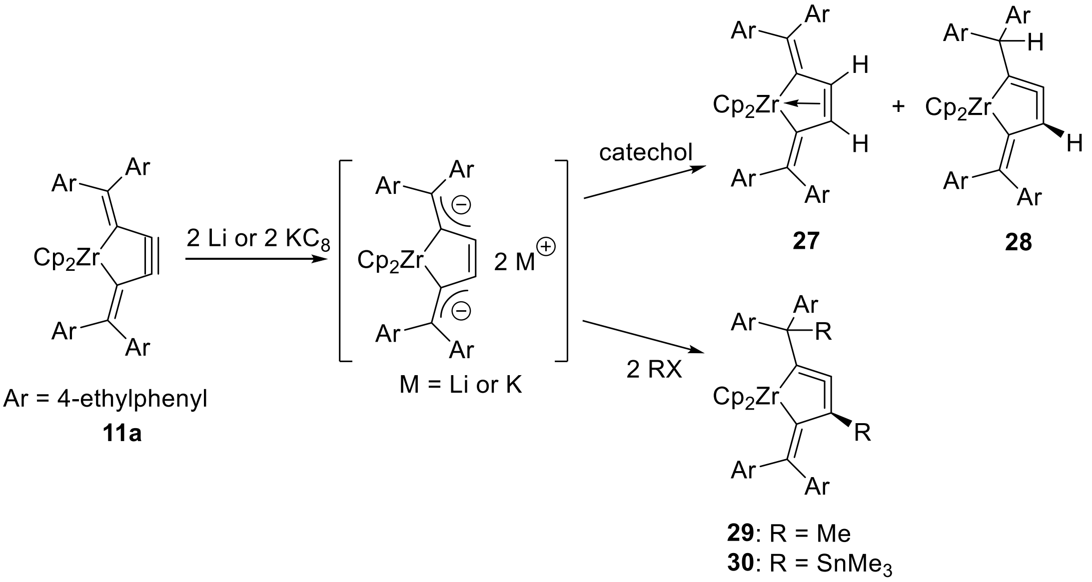
As discussed in Scheme 5, **10b** can be converted back from **11b** with PMe_3.[40] *Tert*-butylisocyanide has a strong coordination ability, either, thus it might behave similarly as PMe_3. Indeed, the formation of **24** was achieved expectedly upon treatment of **11b** with 1 equivalent of *t*-BuNC. Interestingly, excess of *t*-BuNC would result in the carbon insertion into the three-membered zirconacycle to form intermediate **25**, which could further rearrange into **26** with a cyclobutene structure (Scheme 12).[40,42] Actually, similar reactivities of the "non-substituted" zirconacyclocumulenes **5d** and **20** with *t*-BuNC had been reported earlier.[51]



Scheme 12 Reaction of **11b** with *t*-BuNC.

2.2.4 Formation of 1-metallacyclopenta-2,3-dienes

By the treatment of the five-membered zirconacycloalkyne **11a** with 2 equivalents of Li (or KC_8), a two-electron reduction occurred, generating a dianionic complex. Addition of catechol produced the major product **27**, and a minor zirconacycloallene **28**. However, the addition of catechol is not a good method for the synthesis of zirconacycloallene, because the yield of **28** was very low (18%). Delightedly, when catechol was replaced by MeI or Me_3SnI, products **29** and **30** could be isolated in high yields (83% and 92%, respectively) (Scheme 13).[39] 1-Zirconacyclopenta-2,3-dienes **28-30** are another type of five-membered strain metallacycles.[35,52]

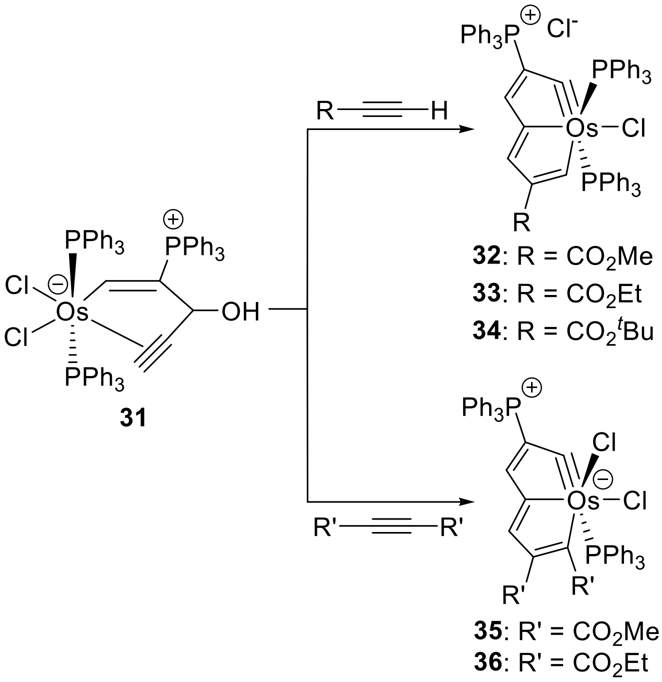


Scheme 13 Synthesis of 1-metallacyclopenta-2,3-dienes **28-30**.

3. Metallapentalynes

3.1 Synthesis of metallapentalynes

The first metallapentalynes with the structure of **B** shown in Fig. 2 were reported by Xia group in 2013. Treatment of **31** with terminal alkynes, including methyl propiolate, ethyl propiolate and *tert*-butyl propiolate, produced the cationic osmapentalynes **32-34**, respectively (Scheme 14).[53] On the other hand, when internal alkynes dimethyl but-2-ynedioate or dimethyl but-2-ynedioate were used, the neutral products **35** and **36** were afforded (Scheme 14).[54]



Scheme 14 Synthesis of osmapentalynes **32-36**.

The X-ray single crystal structure of complex **32** is shown in Fig. 5. The Os center is in an octahedral geometry. The nearly coplanar metallabicycle is composed of seven carbon atoms and one osmium atom, with the mean deviation from the least-squares plane as 0.0415 Å. Besides the three carbon atoms, there are one Cl and two PPh_3 groups linking directly with the Os center. The C-C bond lengths in the two fused rings are with small alternation (between 1.377 and 1.402 Å). The Os-C1 triple bond distance is 1.845 Å, slightly longer than those in acyclic osmium carbynes (1.671-1.841 Å). The most remarkable feature is the Os≡C1-C2 angle (129.5°), which is much smaller than those around the sp-carbons in *trans*-**5a** as discussed previously (154.2(6)° and 154.4(7)°),[19] and represents the smallest one around a carbyne carbon at that time (the smallest angle now is 127.9(5)° in complex **35**).[54] How can such a small angle exist in a stable organometallic complex?

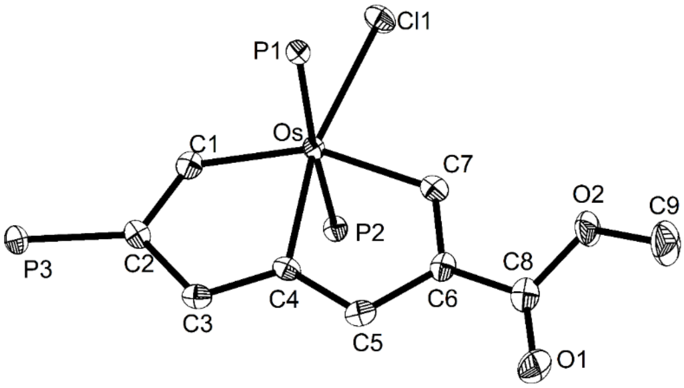
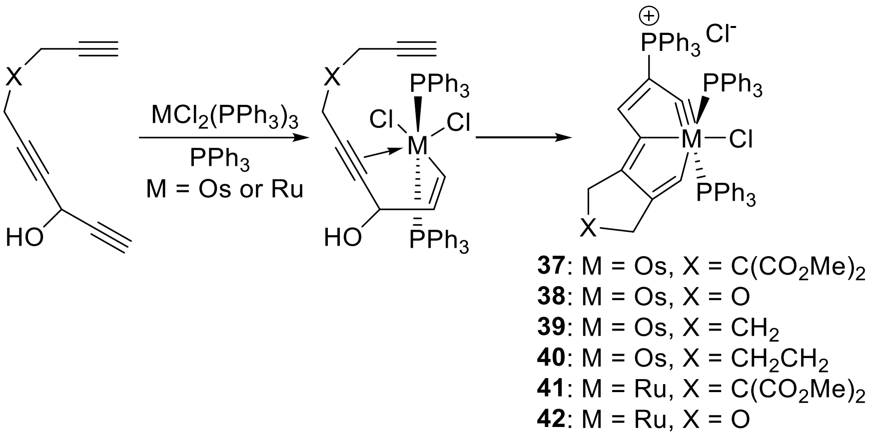


Fig. 5 X-ray single crystal structure of **32**. The thermal ellipsoids are displayed at 50% probability. Hydrogen atoms and the phenyl groups of PPh_3 are omitted for clarity.

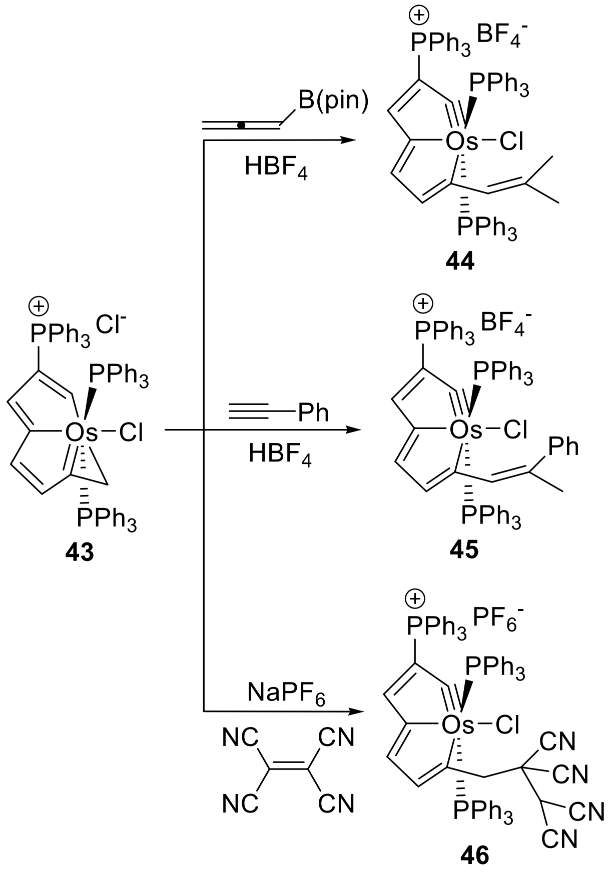
To answer that question, DFT calculations were performed. Compared to the estimated angles around acetylenic carbons in organic cyclopentyne (116.0°), the 129.5° in **32** indicates the great release of angle strain. In fact, due to the bridgehead Os atom, the computed strain energy (24.3 kcal mol^{-1}) on the basis of a chain model molecule is much smaller than that of cyclopentyne (71.9 kcal mol^{-1}). Besides, according to a model in which the PPh_3 ligands are simplified to PH_3, the authors stated that complex **32** is a cyclic eight-center eight-electron Craig-type Möbius aromatic complex, which is supported by the calculated values of $NICS(0)_{zz}$ (-11.1 and -10.8 ppm in each ring) and isomerization stabilization energies (ISE). Moreover, the down-fielded proton chemical shifts (H3, 8.32; H5, 9.27; H7, 14.25 ppm), and delocalized C-C bonds in the osmapentalyne cycle as described in the previous paragraph, further confirm its aromaticity. Thus, the stability of metallapentalynes is attributed to both of the reduced ring strain and the aromaticity. Notably, organic pentalyne is *anti*-aromatic, hence, the incorporation of a metal into organics might change their aromaticity.[53]

Alternatively, metallapentalynes can be synthesized directly from organics with metal precursors. Xia and coworkers found that triynes with a hydroxyl group reacted with $MCl_2(PPh_3)_3$ (M = Os or Ru) in the presence of PPh_3 to give a series of metallapentalynes **37-42** (Scheme 15).[55,56] When X = CH_2CH_2, the alkyne-coordinated intermediate was isolable.[55] It is worth pointing out that complexes **41** and **42** are the first metallapentalynes based on a second-row transition metal.[56]



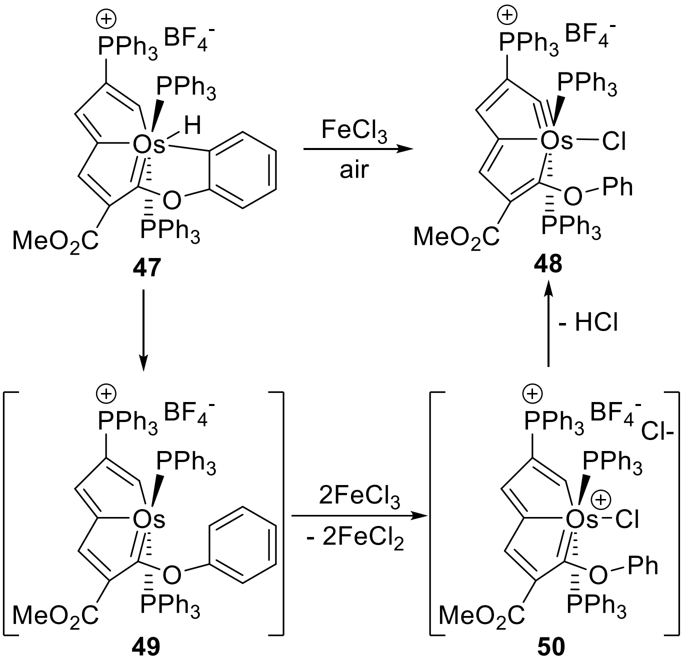
Scheme 15 Synthesis of metallapentalynes **37-42**.

Sometimes metallapentalenes,[57,58] which is another kind of metallaaromatics, could act as the starting materials for the preparation of metallapentalynes. For example, in the presence of HBF_4, osmapentalene **43** reacted with allenylboronic acid pinacol ester to afford osmapentalyne **44**. Similarly, treatment of **43** with phenylacetylene and HBF_4 led to the formation of osmapentalyne **45**. Tetracyanoethylene (TCNE) was active, too, and under the existence of $NaBF_4$, osmapentalyne **46** was generated (Scheme 16).[59]



Scheme 16 Synthesis of osmapentalynes **44-46**.

When osmapentalenofuran **47** was treated with $FeCl_3$ under air, osmapentalyne **48** was afforded. Mechanistically, it was proposed that **47** is initially converted to intermediate **49** *via* reductive elimination; subsequently, **49** is oxidized by $FeCl_3$ to be transformed into **50**; after the elimination of HCl, **48** is produced ultimately (Scheme 17).[60]

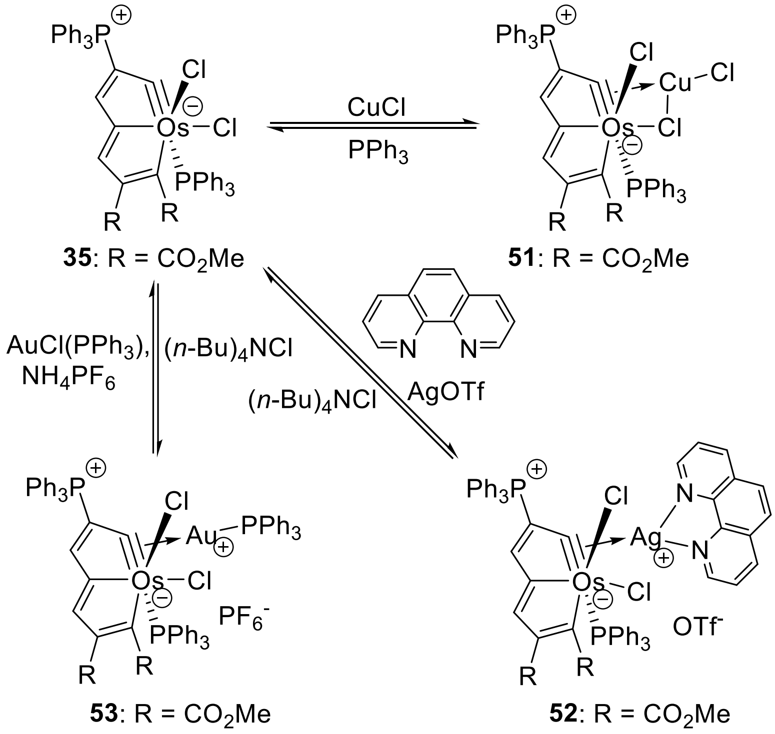


Scheme 17 Synthesis of osmapentalyne **48**.

3.2 Reactivities of metallapentalynes

3.2.1 Formation of metal carbyne-coordinated complexes

Similar to five-membered metallacycloalkynes, in which the alkyne can act as a $2e^-$ donor to be coordinated with other metals, the metal carbyne moiety in metallapentalynes is somehow “alkyne-like”, thus can also react with an external metal precursor to form metal carbyne-coordinated complexes.[56,61] For example, Xia *et al.* treated complex **35** with CuCl to provide the hetero dinuclear complex **51** in 96% yield. In **51**, the Cl atom linking with Os is also coordinated with the Cu atom. Similarly, **35** could be transformed into the hetero dinuclear complexes **52** and **53** when CuCl was replaced by silver or gold precursors. The interactions between the osmacarbyne and coinage metals are not strong, which can be reflected by the fact that **51-53** were easily converted back to **35** upon the addition of PPh_3 (for **51**) or $(n\text{-Bu})_4NCl$ (for **52** and **53**) (Scheme 18).[61]

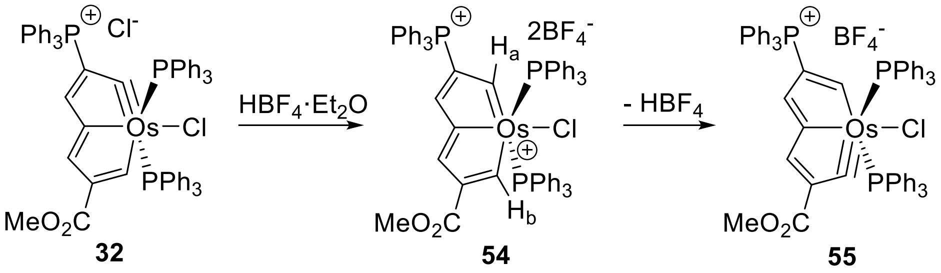


Scheme 18 Reactions of **35** with different metal precursors.

3.2.2 Reactions with electrophiles

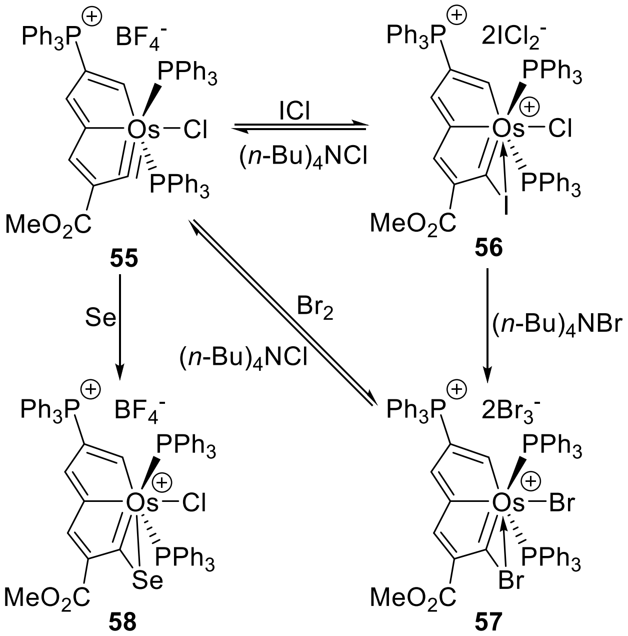
As mentioned in Section 2.2.2, acids are active and can easily break the metallacycle of five-membered metallacycloalkynes. Metallapentalynes are also sensitive to acids, however, the fused rings are always reserved, indicating their higher stability owing to the aromaticity.

Treatment of osmapentalyne **32** with $HBF_4 \cdot Et_2O$ at room temperature for 30 min resulted in the formation of osmapentalene **54**.[53,62] Complex **54** is not stable in solution due to its $16e^-$ character, and is easily converted to the new $18e^-$ osmapentalyne **55** (Scheme 19). During the process from **54** to **55**, there are two possibilities: elimination of H_a or H_b. DFT calculations suggest that the deprotonation of H_b is more favorable both kinetically and dynamically, thus forming **55** primarily.[62] In comparison the structures between **32** and **55**, we can see clearly that the addition of $HBF_4 \cdot Et_2O$ resulted in the shift of Os≡C from one cycle to the other. Some other metallapentalynes, such as osmapentalynes **33** and **34**, and ruthenapentalyne **42**, display similar metal carbyne bond shift reactivity.[53,56]



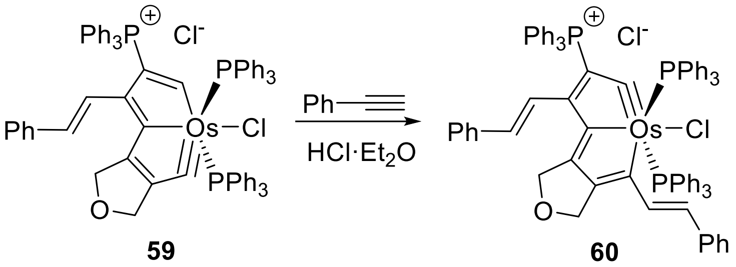
Scheme 19 Reaction of **32** with $HBF_4{\cdot}Et_2O$.

Complex **55** could further react with other electrophiles. Upon the addition of ICl or Br_2, **55** was converted to iodocarbene **56** and bromocarbene **57**, respectively (Scheme 20).[63] **56** and **57** are the first metallaiodirenium ion and metallabromirenium ion, which have similar structures as the proposed intermediates in the halogenation of alkynes. The results further support the “alkyne-like” properties of M≡C in metallapentalynes. Interestingly, nucleophilic substitution of **56** by $(n\text{-Bu})_4NBr$ was observed, and **57** was produced. However, when $(n\text{-Bu})_4NCl$ was used, the regeneration of **55** rather than the formation of an analogous metallachlorirenium ion was discovered. This is probably because of the smaller atomic size of the Cl atom compared to Br and I, which makes the three-membered metallachlorirenium ring unstable. In addition, Se was another electrophile to be active with **55**, and osmapentaloselenirene **58** was given (Scheme 20).[64] **58** was regarded as the first complex that contains an unsaturated Se-containing ring, in which the aromaticity is dominated by σ-type.



Scheme 20 Electrophilic reactions of osmapentalyne **55**.

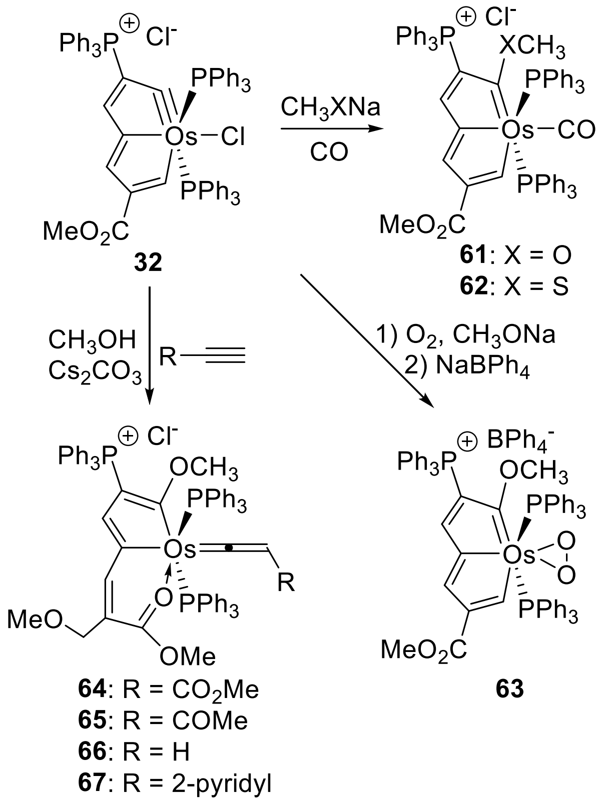
Alkynes could act as electrophiles to react with metallapentalynes, either. Treatment of osmapentalyne **59** with phenylacetylene in the presence of HCl·Et₂O resulted in the formation of **60**, in which a *trans*-alkenyl is positioned in the α-position, accompanied by the C≡C bond shift (Scheme 21). This reaction is highly efficient, and a series of other alkynes are also applicable.[65]



Scheme 21 Electrophilic addition reaction of osmapentalyne **59** with phenylacetylene.

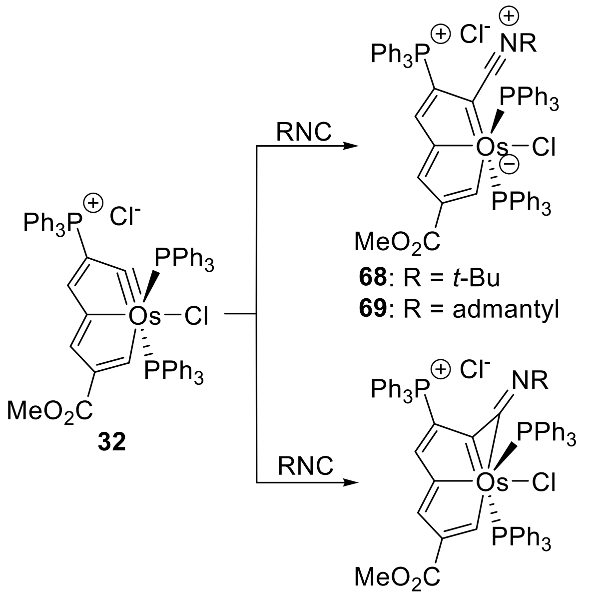
3.2.3 Reactions with nucleophiles

Although there is no report on five-membered metallacycloalkynes with nucleophiles, such reactivities have been discovered for metallapentalynes. For example, under CO atmosphere, complex **32** reacted with CH_3ONa or CH_3SNa to give osmapentalenes **61** and **62**, respectively (Scheme 22).[62] On the other hand, when CO was replaced by O_2, in the presence of CH_3OH, **32** was transformed to the osmium-peroxo complex **63**, which is active for alcohol dehydrogenation reactions (Scheme 22).[66] Given that alkynes sometimes can act as 2e⁻ donor analogous to CO, Xia *et al.* further treated **32** with CH_3OH and Cs_2CO_3 in the presence of different alkynes, and several osmafulvenallenes **64-67** were afforded (Scheme 22).[67] It was proposed that the first step is the nucleophilic attack of methoxide to the Os≡C bond, the same as that from **32** to **61**. After the coordination of alkyne to Os center, an isomerization occurs to form a vinylidene intermediate, which can be further attacked by CH_3OH. In the end, the ring opening followed by the ester coordination provides the final product. Noteworthily, complexes **64-67** are the first metallafulvenallenes.



Scheme 22 Nucleophilic reactions of osmapentalyne **32** to form **61-67**.

Isocyanides are another kind of reactive nucleophiles. Treatment of **32** with *t*-BuNC or 1-adamantanyl isocyanide resulted in the formation of the C-C coupling complexes **68** and **69**, where the isocyanides only connect with the α-carbon of the resulting osmapentalene ring. On the other hand, the η^2-iminoketenyl products **70-74** were isolated, respectively, when tosylmethyl isocyanide, *p*-nitrophenyl isocyanide, cyclohexyl isocyanide, 2-naphthyl isocyanide or *p*-anisyl isocyanide was used (Scheme 23).[68] For **68** and **69**, they do not adopt the η^2-iminoketenyl coordination mode, probably because the bulky *tert*-butyl and 1-adamantyl groups inhibit bending at their isocyanide nitrogen atoms. It is worthy to mention that η^2-iminoketenyl species were often proposed as the intermediates in nucleophile-induced carbyne-isocyanide coupling processes, while they had never been isolated before this publication reported by Xia and coworkers. Later on, the η^2-iminoketenyl complexes were extended to ruthenium, reported by the same group.[69]

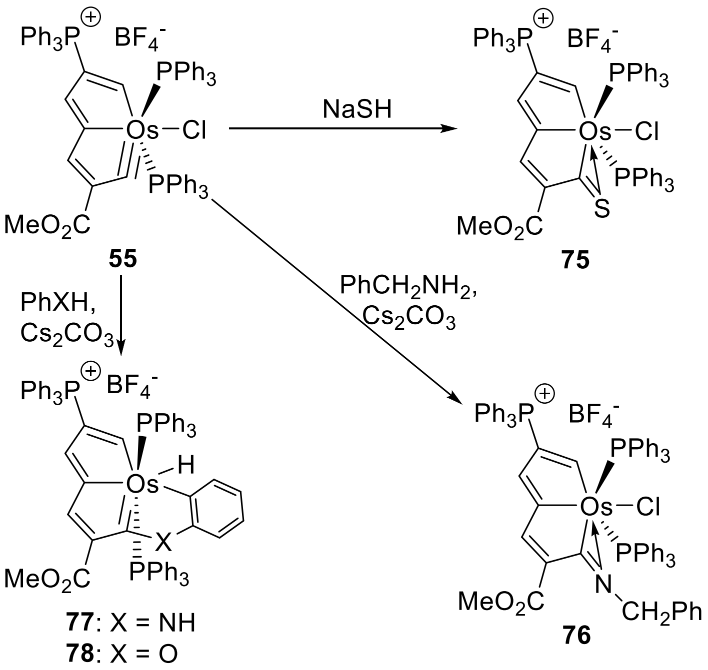


68: R = *t*-Bu
69: R = admantyl

70: R = tosylmethyl
71: R = *p*-nitrophenyl
72: R = 2-naphthyl
73: R = 2-naphthyl
74: R = *p*-anisyl

Scheme 23 Nucleophilic reactions of **32** with isocyanides.

The metal carbyne bond shifted complex **55** is also active to nucleophiles. For example, the addition of NaSH produced **75**, and the reaction with PhCH$_2$NH$_2$ in the presence of Cs$_2$CO$_3$ led to the formation of **76** (Scheme 24).[53] Interestingly, when PhNH$_2$ was selected as the nucleophile, under basic conditions, the product was a polycyclic aromatic complex **77**, formed involving C-H activation. PhOH exhibited a similar reactivity as PhNH$_2$ and **78** was afforded (Scheme 24).[70] Complexes **77** and **78** are the first metal-bridged tricyclic aromatic complexes, in which the three five-membered rings are all aromatic. By using the same strategy, a series of polycyclic aromatics,[70-72] including one with six and one with seven fused aromatic rings, derived from 1-aminopyrene and 9-phenanthrenol respectively, had been developed.[70] Noteworthily, when a lactone-fused osmapentalyne[73] was mixed with 3-(methylsulfanyl)-benzenol in the presence of K$_2$CO$_3$, the resulting polycyclic osmaaromatic complex possesses high charge transport ability.[74] These results indicate that metallapentalynes and their derivatives have a very broad application prospect in the field of material chemistry.

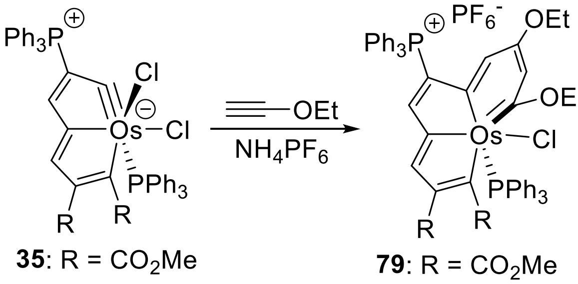


Scheme 24 Nucleophilic reactions of osmapentalyne **55** to form **75-78**.

3.2.4 Cycloaddition Reactions

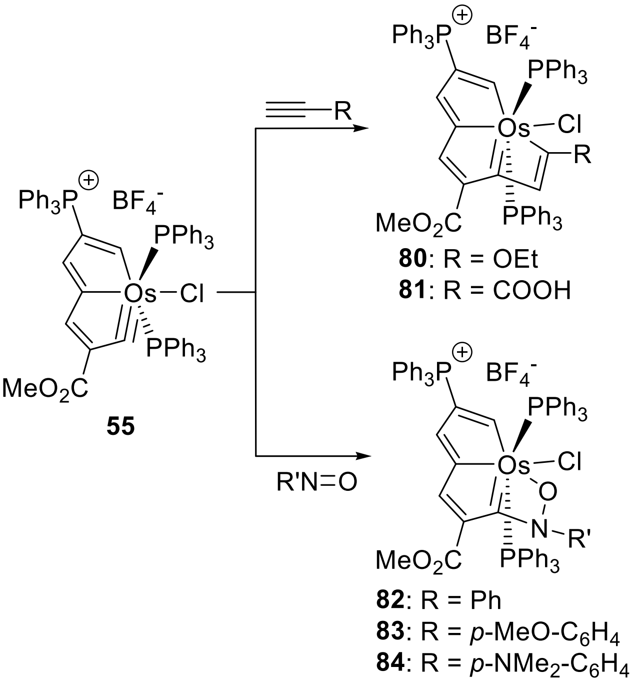
In principle, cycloaddition of the C≡C bond in five-membered metallacycloalkynes would greatly reduce their ring strain, while surprisingly, such reactions have not been reported up to date. In contrast, many cycloaddition reactions involving the M≡C bond in metallapentalynes have been discovered.

The first [2+2+2] cycloaddition reaction of an alkyne with a late transition metal carbyne occurred between the neutral osmapentalyne **35** and HC≡COEt, generating complex **79** (Scheme 25).[54] The three fused rings in **79** are not planar, with the carbene carbon of Os=C(OEt) almost perpendicular to the two five-membered rings. It was proposed that the reaction underwent a [2+2] intermediate, which could not be detected.



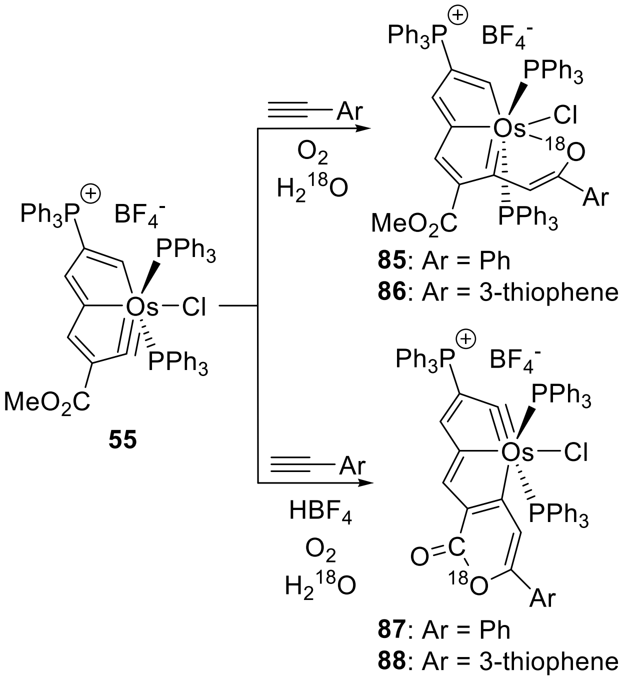
Scheme 25 [2+2+2] cycloaddition of **35** with HC≡COEt.

Interestingly, when **35** was replaced by the cationic osmapentalyne **55**, the [2+2] product **80** could be isolated, and NH_4PF_6 is not necessary (Scheme 26).[75] Different from **79**, the four-membered ring and the osmapentalene cycle in **80** are almost planar. Notably, pentalene and cyclobutadiene are both antiaromatic, therefore, the incorporation of a transition metal can stabilize two antiaromatic systems. The other alkyne, HC≡CCOOH, was also active to give **81** (Scheme 26).[75] Complexes **80** and **81** are the first [2+2] cycloaddition products formed between a late transition metal carbyne with alkynes. Unlike **35**, even excess alkynes did not result in further insertion to give 5,5,6-fused complexes. The reaction of nitrosobenzene with **55** is similar, giving **82**, and the introduction of an electron-donating group at the *para*-position of nitrosobenzene is beneficial for the reactivity, due to the enhanced nucleophilicity of the N atom. For instance, the generation of **83** and **84** are faster than that of **82** (Scheme 26).[76] **82-84** are the first metallapentalenoxazetes.



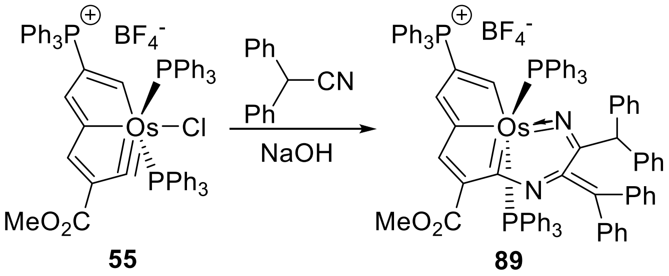
Scheme 26 [2+2] cycloaddition reactions of **55** with alkynes and nitrosoarenes.

As just mentioned, [2+2] cycloaddition is found between **55** and alkynes, such as HC≡COEt and HC≡CCOOH. Unexpectedly, when aryl alkynes were treated to **55** in the presence of O_2 and H_2O, the products were totally different. For example, complexes **85** and **86** were afforded respectively, when phenylacetylene or 3-ethynylthiophene was selected (Scheme 27).[73,77] **85** and **86** are the first α-metallapentalenofurans, and DFT calculations suggest that their Möbius aromaticity is derived from d_π-p_π π-conjugation. Deuterium labeling experiments indicate the oxygen in the furan ring comes from H_2O. Interestingly, upon the existence of HBF_4, two lactone-fused metallapentalynes **87** and **88** were constructed, accompanied by the shift of Os≡C bond (Scheme 27).[73] It is worthy to compare the formation of **87** and **88** with that of **60** shown in Scheme 21: during the formation of **60**, H_2O and O_2 are absent, and the reactant **59** does not contain a methyl ester substituent.



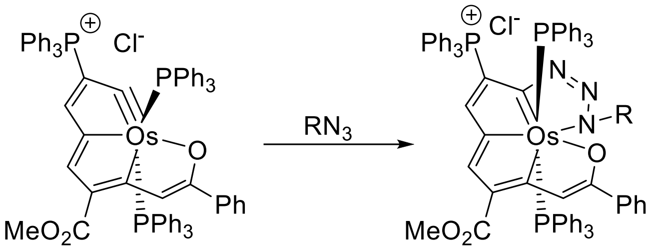
Scheme 27 Synthesis of complexes **85-88**.

Although [2+2+2] cycloaddition has not been reported between **55** and alkynes, it has been found between **55** and two molecules of 2,2-diphenylacetonitrile. The product is metallapentalenopyrazine **89**, which contains three fused aromatic rings. **89** is the first aromatic complex with a metallapyrazine fragment (Scheme 28).[78]



Scheme 28 Reaction of **55** with 2,2-diphenylacetonitrile.

Recently, Xia group found a new type of "alkyne-like" reactivity. The authors used the osmapentalyne derivative **90**, which already contains three fused aromatic rings, as the starting material to react with azides, and several polycyclic products **91-95** were produced (Scheme 29).[79] They are "metalla-click" type reactions, and the products consist of four fused five-membered rings. Moreover, these rings are all aromatic. Before this publication, the maximum number of fused aromatic rings sharing with one bridgehead metal was three, thus, these results broke through the record.

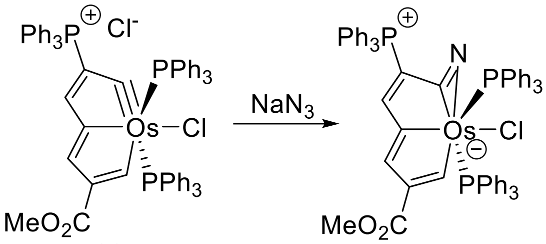


90

91: R = Ph
92: R = $PhCH_2$
93: R = MeO-*p*-C_6H_4
94: R = CF_3-*p*-C_6H_4
95: R = $MeOC_2H_4OC_2H_4$

Scheme 29 Reactions of **90** with azides.

NaN_3 is also active for some metallapentalynes. For example, when NaN_3 was added, **32** was converted to the [3+1] cycloaddition product **96** (Scheme 30).[80]



32 **96**

Scheme 30 Reaction of **32** with NaN_3.

4. Conclusions and perspectives

Challenging the limits is the driving force of social progress. Chemists have devoted to the isolation of small cyclic compounds with acetylenic carbon(s), for more than half a century. After continuous efforts, the number of atoms in the ring has been decreased to as small as five. Such complexes can be divided into two types: metallacycloalkynes and metallapentalynes. For the former type, the angles around the acetylenic carbons are around 155°, representing the smallest ones before the discovery of the latter type (around 130°). These angles are far away from 180°, thus leading to extremely high ring strain and unusual reactivities.

For metallacycloalkynes, four main classes of reactions have been investigated, including the reactions with external metal precursors to form alkyne-coordinated complexes, the reactions with electrophiles, isocyanide insertion reactions and the formation of 1-metallacyclopenta-2,3-dienes. The first two classes of reactions have been discovered for metallapentalynes as well, although for the reactions with electrophiles, the products were totally different. The addition of an electrophile, such as H^+ or $B(C_6F_5)_3$, into metallacycloalkynes normally resulted in the broken of the metallacycles. In contrast, when H^+, ICl, Br_2 or Se was added into metallapentalynes, the metallacycles could be preserved. The results might be attributed to the higher stability of metallapentalynes resulted by their aromaticity, although the angles around the carbyne carbons are much smaller than those in metallacycloalkynes. On the other hand, the last two classes of reactions for metallacycloalkynes have not been discovered for metallapentalynes, whereas two other "alkyne-like" reactivities, namely nucleophilic addition and cycloaddition reactions, had been explored.

Compared to the abundant chemistry of alkynes, the research on five-membered metallacycloalkynes and metallapentalynes is still limited. Except one example based on thorium (complex **13**), five-membered metallacyclopentynes are restricted on group 4 metals; metallapentalynes have only been discovered for ruthenium and osmium complexes. Especially, in consideration that five-membered metallacycles are regarded as intermediates in many transition-metal catalyzed reactions, and the reactivity studies of metallapentalynes have given a variety of novel metallapentalene derivatives, which showed a great application prospect in various areas, such as near-infrared dyes,[53] photothermal therapy,[81-83] phototherapy,[84] and self-healing materials,[85] the chemistry on these two kinds of five-membered metallacycles is still far more anticipated.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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