

Progress in the Chemistry of Metallabenzynes

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ABSTRACT

The synthesis and chemical and structural properties of metallabenzynes are reviewed. Reaction of $[\text{OsCl}_2(\text{PPh}_3)_3]$ with $\text{HC}\equiv\text{CSiMe}_3$ produces the osmabenzynes $[\text{Os}(\equiv\text{CC}(\text{SiMe}_3)=\text{C}(\text{CH}_3)\text{C}(\text{SiMe}_3)=\text{CH})\text{Cl}_2(\text{PPh}_3)_2]$, which undergoes electrophilic substitution reactions with HBF_4 and Br_2 to give new osmabenzynes. The reactivities and the X-ray diffraction data of osmabenzynes indicate that these metallacycles have aromatic properties. Unlike benzyne, which is thermally unstable, osmabenzynes are thermally much more stable and can be stored for months at room temperature without decomposition. The higher thermal stability of osmabenzynes compared to benzyne can be related to the relatively smaller ring strain and larger conjugation energy.

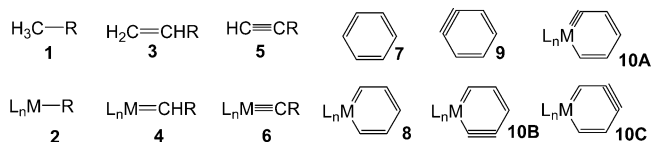
Introduction

Many organometallic compounds can be regarded as being formed by formal replacement of carbon groups of organic compounds with isolobal transition metal fragments.¹ For example, replacement of the CH_3 group in $\text{CH}_3\text{-R}$ (**1**) by 17-electron transition metal fragments would give alkyl complexes $[\text{L}_n\text{M-R}]$ (**2**), replacement of the CH_2 group in $\text{CH}_2=\text{CHR}$ (**3**) by 16-electron transition metal fragments would give carbene complexes $[\text{L}_n\text{M}=\text{CHR}]$ (**4**), and replacement of the CH group in $\text{HC}\equiv\text{CR}$ (**5**) by 15-electron transition metal fragments would give carbyne complexes $[\text{L}_n\text{M}\equiv\text{CR}]$ (**6**) (Scheme 1). Transition metal alkyl, carbene, and carbyne complexes are very important organometallic compounds and have found wide applications in organic synthesis and catalysis. These organometallic compounds also have chemical properties different from those of the organic compounds they formally resemble.

Benzene and benzyne are important organic molecules. Formal replacement of a CH group in benzene (**7**) by 15-electron transition metal fragments would give metallabenzenes (**8**); formal replacement of a CH group or a C atom in benzyne (**9**) by 15-electron or 14-electron transition metal fragments would give metallabenzynes (**10**).

Guochen Jia was born in China in 1962. He received his B.Sc. degree in chemistry from Wuhan University in 1983 and his Ph.D. degree from The Ohio State University in 1989 under the guidance of Professors Devon W. Meek and Andrew Wojcicki. After his postdoctoral stays with Professor Robert H. Morris at University of Toronto and Professor Richard J. Puddephatt at The University of Western Ontario, he joined Hong Kong University of Science and Technology as an assistant professor in 1992, and he is now an associate professor. His research interests include transition-metal hydrides, vinylidenes, carbynes, metallabenzynes, carbon-rich organometallics, and homogeneous catalysis.

Scheme 1



Metallabenzenes and metallabenzynes are interesting because they may have aromatic properties and they can mediate organometallic reactions. Compounds with aromatic properties have fascinated chemists for over a century and are still attracting considerable current attention as evidenced by the publication of a special issue of *Chemical Reviews* on the topic in 2001.²

In the past 20 years, the synthesis and properties of transition-metal containing metallabenzenes have attracted considerable attention both experimentally and theoretically.^{3–5} Metallabenzenes were first studied theoretically by Hoffmann et al. as early as 1979.⁶ The first isolated metallabenzene was reported by Roper et al. in 1982.⁷ Over the past 20 years, impressive progress has been made in the chemistry of this interesting class of compounds. A number of stable metallabenzenes have now been isolated and characterized, especially those of Os, Ir, and Pt. Metallabenzenes have also been found as intermediates in organometallic transformations. Interesting properties, including aromatic electrophilic substitution reactions,⁸ have been revealed in recent years.

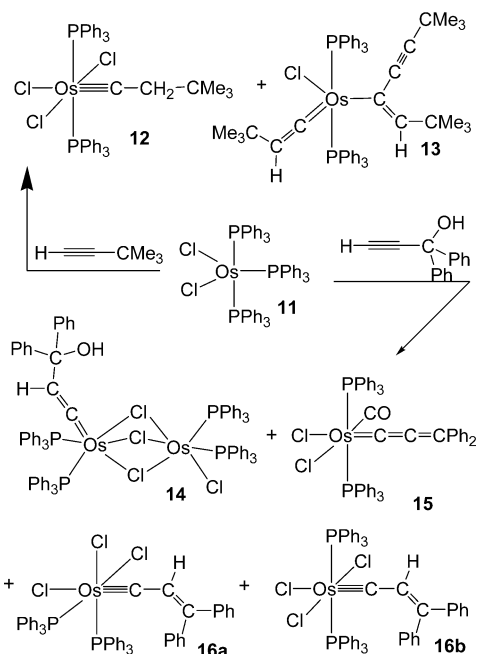
Compared to metallabenzenes, the chemistry of metallabenzynes is much less developed. At first sight, one might expect that metallabenzynes may be too unstable to be isolated because six-membered organic compounds with a $\text{C}\equiv\text{C}$ triple bond in the ring (for example, cyclohexynes and benzynes) are usually unstable at room temperature. However, the synthesis and characterization of a stable metallabenzynes was reported in 2001.^{9,10} In this Account, the progress in the synthesis, chemical properties, and stability of metallabenzynes will be summarized.

Discovery of the First Metallabenzynes

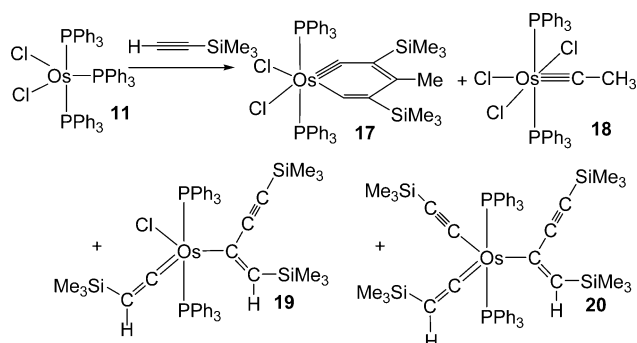
The first stable metallabenzynes $[\text{Os}(\equiv\text{CC}(\text{SiMe}_3)=\text{C}(\text{CH}_3)\text{C}(\text{SiMe}_3)=\text{CH})\text{Cl}_2(\text{PPh}_3)_2]$ was obtained unexpectedly during our attempt to prepare osmium vinylidene complexes of the type $[\text{OsCl}_2(=\text{C}=\text{CHR})(\text{PR}'_3)_2]$. Ruthenium vinylidene complexes of the type $[\text{RuCl}_2(=\text{C}=\text{CHR})(\text{PR}'_3)_2]$ have attracted attention because they are related to Grubbs catalysts $[\text{RuCl}_2(=\text{CHR})(\text{PR}'_3)_2]$ ¹¹ and they can be used as catalysts or catalytic precursors for olefin metathesis,^{12a,b} dimerization, and carboxylation of terminal alkynes.^{12c} These ruthenium vinylidene complexes can be easily prepared from the reactions of $\text{HC}\equiv\text{CR}$ with dichlororuthenium complexes¹³ such as $[\text{RuCl}_2(\text{PPh}_3)_3]$,^{13a} $[\text{RuCl}_2\text{H}_2(\text{PR}'_3)_2]$ ($\text{R}' = \text{Cy}, i\text{-Pr}$),^{13b,c} $[\text{RuCl}_2(\text{P}(i\text{-Pr})_3)_2]_n$,^{13d} $[\text{RuCl}_2(\text{MeCN})_2(\text{P}(i\text{-Pr})_3)_2]$,^{13d} and $[\text{RuCl}_2(p\text{-cymene})_2]/\text{PR}'_3$.^{13d}

Being prompted by the facile preparation of the ruthenium vinylidene complex $[\text{RuCl}_2(=\text{C}=\text{CHCMe}_3)(\text{PPh}_3)_2]$ from the reaction of $\text{HC}\equiv\text{CCMe}_3$ with $[\text{RuCl}_2-$

Scheme 2



Scheme 3

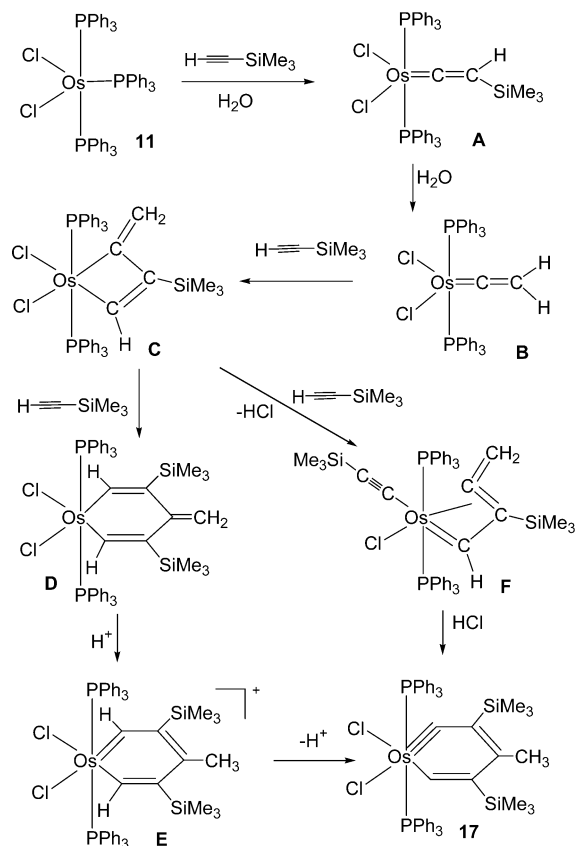


$(\text{PPh}_3)_3$],^{13a} we have tried to prepare analogous osmium vinylidene complexes $[\text{OsCl}_2(=\text{C}=\text{CHR})(\text{PPh}_3)_2]$ from the reactions of $[\text{OsCl}_2(\text{PPh}_3)_3]$ with $\text{HC}\equiv\text{CR}$. It was found that the isolable products of the reactions are strongly dependent on the $\text{RC}\equiv\text{CH}$ used. Reactions of $[\text{OsCl}_2(\text{PPh}_3)_3]$ (**11**) with $\text{HC}\equiv\text{CCMe}_3$ was found to give the trichlorocarbene complex **12** and the vinyl-vinylidene complex **13** (Scheme 2).¹⁴ Reaction of $[\text{OsCl}_2(\text{PPh}_3)_3]$ (**11**) with $\text{HC}\equiv\text{C}(\text{OH})\text{Ph}_2$ was found to produce the dinuclear vinylidene complex **14**, the allenylidene complex **15**, and the trichlorocarbene complexes **16a** and **16b** (Scheme 2).¹⁵

Under similar conditions, reaction of $[\text{OsCl}_2(\text{PPh}_3)_3]$ (**11**) with $\text{HC}\equiv\text{CSiMe}_3$ produces the osmabenzynes **17** along with other complexes such as trichlorocarbene complex **18** and vinyl-vinylidene complexes **19** and **20** (Scheme 3).⁹

The detailed mechanism for the formation of **17** is not clear yet. However, the reaction sequence shown in Scheme 4 is plausible.⁹ Reaction of **11** with $\text{HC}\equiv\text{CSiMe}_3$ could initially give the vinylidene intermediate $[\text{OsCl}_2(=\text{C}=\text{CHSiMe}_3)(\text{PPh}_3)_2]$ (**A**), although attempts to isolate the vinylidene intermediate from the reaction failed. The closely related vinylidene complex $[\text{OsCl}_2(=\text{C}=\text{CHPh})(\text{P}-$

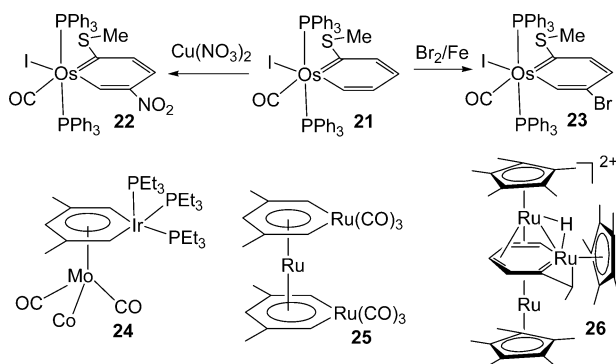
Scheme 4



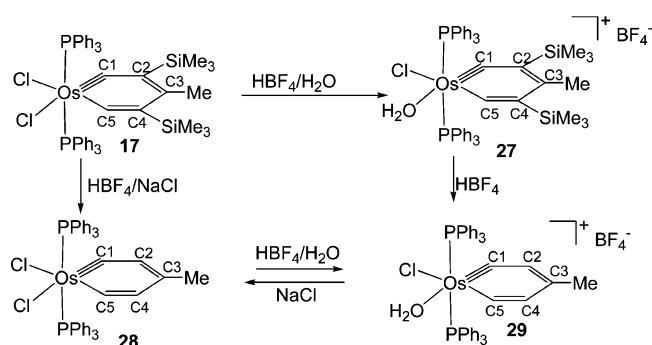
$(i\text{-Pr})_2$], which was produced by elimination of the imine ligands from the imine-vinylidene complexes $[\text{OsCl}_2(=\text{C}=\text{CHPh})(\text{NH}=\text{CR}_2)(\text{P}(i\text{-Pr})_3)_2]$ ($\text{CR}_2 = \text{CMe}_2, \text{C}(\text{CH}_2)_5$) in refluxing toluene, was recently reported by Esteruelas and co-workers.¹⁶ Intermediate **A** can undergo hydrolysis to give the coordinatively unsaturated vinylidene complex $\text{Os}(=\text{C}=\text{CH}_2)\text{Cl}_2(\text{PPh}_3)_2$ (**B**), which undergoes cycloaddition reactions with additional $\text{HC}\equiv\text{CSiMe}_3$ to give first an osmacyclobutene (**C**) and then an osmacyclohexadiene (**D**) intermediate. Protonation at the methylene of the osmacyclohexadiene complex **D** can lead to the cationic osmabenzynes **E**, which undergoes deprotonation from a metal-bound carbon atom to then give the metallabenzynes **17**. Alternatively, **17** could also be formed by an acid-promoted intramolecular cycloaddition reaction of the acetylide intermediate **F** formed from the reaction of intermediate **C** with $\text{HC}\equiv\text{CSiMe}_3$.

Complex **17** is structurally closely related to benzyne in that both of them contain a formal triple bond in a six-membered ring. However, they have marked difference in their thermal stability. Complex **17** is thermally quite stable and can be stored for months at room temperature without decomposition. In contrast, benzyne and its derivatives have low thermal stability and could not be isolated in pure form at room temperature. They can only be characterized spectroscopically in matrix¹⁷ or stabilized by complexation with transition metals.¹⁸ The low thermal stability of benzyne is related to the presence of a large ring strain caused by bending the formal C–C triple bond in the six-membered ring. For similar reason, cyclohex-

Scheme 5



Scheme 6



ynes also have very low thermal stability.¹⁹ Octaalkyl-tetrasilacyclohexynes are rare reported examples of six-membered cyclic alkynes that are stable at room temperature, due to the steric shielding and the long C–Si and Si–Si bonds.^{20,21}

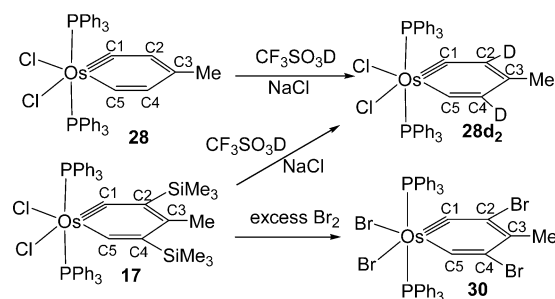
Reactivity of Metallabenzynes

Previous studies have revealed that metallabenzynes have chemical properties similar to that of benzene. For example, metallabenzene **21** can undergo typical aromatic electrophilic substitution reactions with $\text{Cu}(\text{NO}_3)_2$ and Br_2 to give **22** and **23**, respectively (Scheme 5).⁸ Like benzene, metallabenzynes can also function as η^6 -ligands to form half-sandwich (e.g., **24**²²), sandwich (e.g., **25**²³), or triple-decker (e.g., **26**²⁴) complexes.

The question whether metallabenzynes could also show chemical properties similar to those of benzene or metallabenzynes has been addressed by studying the reactivity of osmabenzynes.²⁵ Complex **17** was found to react with 2 equiv of HBF_4 in wet dichloromethane to give the cationic osmabenzynes **27**, which is presumably formed by protonation of one of the chloride ligands followed by trapping the intermediate with water present in the reaction medium (Scheme 6). In the presence of NaCl , the dissociation of the chloride is suppressed and the protonation reaction gives the neutral desilylated osmabenzynes **28**. Isolated **27** could also be desilylated to give **29** when treated with excess of HBF_4 , although the reaction is slow and takes a few days to go to completion. Like **17**, the chloride in **28** can also be easily replaced with water to give **29** when treated with $\text{HBF}_4/\text{H}_2\text{O}$.

The reactions of **17** and **27** with HBF_4 to give **28** and **29** are similar to the reactions of $\text{C}_6\text{H}_5\text{SiMe}_3$ with acids²⁶

Scheme 7



in that the Me_3Si groups of the six-membered rings are replaced with hydrogens. Replacement of the Me_3Si groups in the osmabenzynes with hydrogens in the protonation reactions was thought to proceed by initial protonation of the C2 and C4 carbons of the metallacycles, just like the reactions of $\text{C}_6\text{H}_5\text{SiMe}_3$ with acids. The electrophilic nature of the desilylation reactions is consistent with the observation that desilylation of the cationic complex **27** with HBF_4 to give **29** occurs at a much slower rate than the desilylation of **17** with HBF_4 in the presence of NaCl to give **28**, because it is more favorable for proton to attack on the neutral complex than the less electron-rich cationic complex.

Benzene can undergo H/D exchange reactions with deuterated acids through carbon cation intermediates.²⁷ It was found that complex **28**, in the presence of NaCl , can also undergo H/D exchange reaction with $\text{CF}_3\text{SO}_3\text{D}$ to give partially deuterated osmabenzynes **28d₂** in which deuterium is only on the C2 and C4 carbons of the metallacycle (Scheme 7).²⁵ The deuterated osmabenzynes **28d₂** is also produced from the reaction of **17** with $\text{CF}_3\text{SO}_3\text{D}$ in the presence of NaCl . It appears that the carbons of OsC and OsCH are not attacked by the acids in the protonation reactions.

Reactions of ArSiMe_3 with bromine are known to give $\text{Ar}-\text{Br}$.²⁸ Like ArSiMe_3 , complex **17** also reacts with excess Br_2 to give the osmabenzynes **30** as the predominant species (Scheme 7).²⁵ When a limiting amount of Br_2 is used, a complicated mixture is produced, probably due to partial displacements of the Me_3Si and Cl groups.

The reactions of osmabenzynes with Br_2 and acids described above clearly show that osmabenzynes can undergo typical aromatic electrophilic substitution reactions. The electrophilic substitution reactions of osmabenzynes with acids and Br_2 at the C2 and C4 carbons of the metallacycles are interesting especially when the reactivities of carbyne complexes and benzynes are considered. The reactivities of carbyne complexes and benzynes are usually associated with the $\text{M}\equiv\text{C}$ and $\text{C}\equiv\text{C}$ triple bonds. Electrophilic substitution reactions of benzynes, to our knowledge, have not been demonstrated. In fact, benzynes readily react at the $\text{C}\equiv\text{C}$ bond with reagents such as RCO_2H ,²⁹ ROH ,²⁹ Br_2 ,³⁰ and I_2 ³⁰ to give benzene derivatives.

One may ask why only the C2 and C4 carbons of the metallacycles and the chloride ligands are attacked by electrophiles in the reactions of osmabenzynes with acids

Scheme 8

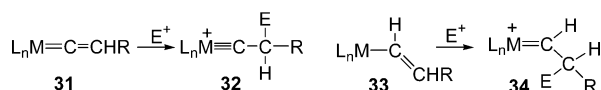


Table 1. Structural Data for Metallabenzynes

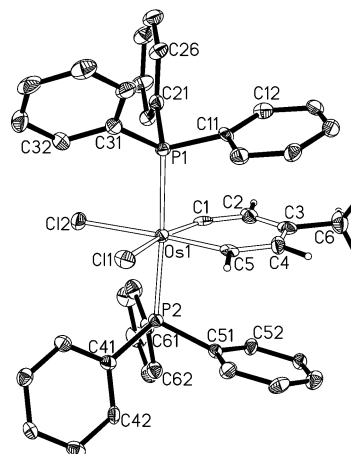
	compound no.			
	17	27	28	30
Bond Distances (Å)				
Os–C1	1.815(4)	1.756(5)	1.805(7)	1.766(3)
Os–C5	1.939(5)	2.016(5)	2.008(7)	2.048(3)
C1–C2	1.376(5)	1.378(7)	1.363(9)	1.368(5)
C2–C3	1.420(5)	1.424(8)	1.413(9)	1.391(5)
C3–C4	1.416(6)	1.433(8)	1.405(9)	1.432(5)
C4–C5	1.378(6)	1.388(7)	1.372(8)	1.352(5)
Bond Angles (deg)				
C1–Os–C5	78.1(2)	78.2(2)	79.8(3)	78.95(14)
Os–C1–C2	148.7(3)	153.8(4)	148.3(6)	150.8(3)
C1–C2–C3	112.4(4)	110.0(5)	114.9(6)	116.4(3)
C2–C3–C4	124.0(4)	123.5(5)	121.3(6)	116.8(3)
C3–C4–C5	117.7(4)	120.3(5)	123.5(6)	128.1(3)
C4–C5–Os	138.6(5)	132.8(4)	132.1(5)	128.9(3)
sum	719.5	718.6	719.9	719.95

and bromine. Computational studies shows that the regio chemistry is related to the electron density distribution of the HOMO of the metallacycles (see below). Apparently, the metal centers have significant effect on the electron density distribution of the HOMO and direct the electrophiles to attack on the carbons β to the metal centers. Similar directing effect of metals is also observed in the reactions of vinylidene and vinyl complexes with electrophiles. Vinylidene (**31**)³¹ and vinyl (**33**)³² complexes usually react with electrophiles (E^+) at β -carbons to give carbyne (**32**) and carbene (**34**) complexes, respectively (Scheme 8). Interestingly, the electrophilic substitution reactions of metallabenzene **21** with $\text{Cu}(\text{NO}_3)_2$ and Br_2 occur at the carbon atom that is also *meta* (β) to the osmium and *para* to the SME group (see Scheme 5).⁸ The regio chemistry probably results from the directing effects of both SME and osmium.

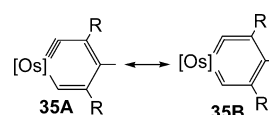
Structural Properties of Metallabenzynes

The structures of osmabenzynes **17**,⁹ **27**,²⁵ **28**,²⁵ and **30**²⁵ have been determined by X-ray diffraction studies, and the relevant bond distances and angles of the metallacycles are listed in Table 1 for comparison. All the complexes contain an essentially planar six-membered metallacycle, as illustrated by the molecular structure of **28** shown in Figure 1. The coplanarity of the metallacycles is reflected by the sums of internal angles in the six-membered ring (see Table 1), which are very close to the ideal value of 720° required for a planar hexagon. The Os–C1–C2 angles are in the range of $148.3(6)^\circ$ – $153.8(4)^\circ$, which are significantly smaller than 180° expected for carbyne or vinylidene complexes. The Os–C5–C4 angles are in the range of $128.9(3)^\circ$ – $138.6(5)^\circ$, which are slightly larger than the expected angle (120°) around an sp^2 -hybridized carbon. The C1–Os–C5 angles are in the range of $78.1(1)^\circ$ – $79.8(3)^\circ$.

The C–C bond distances of the metallacycles are typical of aromatic systems, and no obvious short–long

FIGURE 1. Molecular structure of **28**.

Scheme 9



alternations in the C–C bond distances are observed. The Os–C1 bond distances (1.756(5)–1.815 Å) are at the high end of those observed for typical $[\text{L}_n\text{Os}\equiv\text{CR}]$ complexes³³ and are at the low end of those observed for $[\text{L}_n\text{Os}=\text{C}=\text{CRR}']$ complexes.³⁴ The Os–C5 bond distances (1.939(5)–2.048(3) Å) are close or comparable to the Os–CH bond distances in Roper's osmabenzynes **22** (2.011(7) Å) and **23** (2.039(9) Å) (see Scheme 5 for the structures of **22** and **23**).⁸ These distances are within the range of those reported for Os–C(vinyl) bonds³⁵ and are at the low end of those reported for Os=CHR bonds.³⁶

The Os–C and C–C bond distances of the six-membered rings together with their planar nature indicate that the osmabenzynes have a delocalized structure. Resonance structures **35A** and **35B** (Scheme 9) can be used to describe the delocalization of the π -electrons in an osmabenzynone ring. The structural data suggest that the most dominant resonance structure is the one (**35A**) having one triple bond and two double bonds in the six-membered ring. The solution NMR data of osmabenzynes are in agreement with the structural assignment. For example, the ^1H NMR spectrum of **28** shows three CH signals at 12.65 (OsCH), 6.33 (OsCH=CH), and 4.26 ppm (Os=CCH). The relatively high chemical shift for Os=CCH is probably due to the effect of the adjacent Os=C group. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **28** displayed the Os=C signal at 309.3 ppm, the OsCH signal at 210.3 ppm, the other two CH signals at 125.2 and 107.7 ppm, and the CCH₃ signal at 176.6 ppm. The ^1H and ^{13}C chemical shifts of the OsCH signals are between those of typical Os=CHR and Os–CH=CR₂ signals.

The structural parameters of benzyne have been optimized at the B3LYP level of density functional theory.^{37,38} For the purpose of comparison, the calculated bond distances and angles of benzyne³⁸ and those of **28** determined by X-ray diffraction²⁵ are shown in Figure 2. It is clear that some of structural parameters, especially

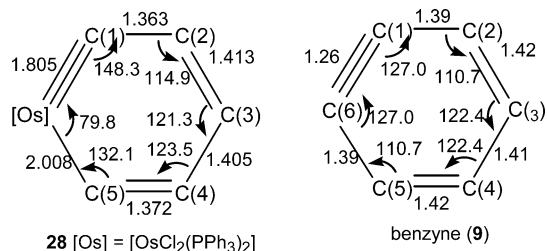
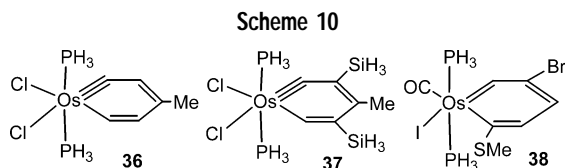


FIGURE 2. Comparison of the bond distances (Å) and angles (deg) of osmabenzene **28** and benzyne.



the bond distances of C1–C2, C2–C3, and C3–C4 and the bond angles of C1–C2–C3, C2–C3–C4, and C3–C4–C5, in the two compounds are quite similar.

Electronic Structures of Metallabenzynes

The electronic structures of model metallabenzene complexes including **36** and **37** (Scheme 10) have been studied by Yang et al.³⁹ and us.³⁸ These theoretical studies reproduced the structural features of the metallacycles obtained from X-ray diffraction studies.

In terms of bonding, osmabenzene complexes [Os(C₅R₄)Cl₂(PH₃)₂] can be thought of as being formed by combinations of the d⁶ metal fragment [OsCl₂(PH₃)₂] and a carbon fragment consisting of five ring-carbon atoms (C₅R₄). Figure 3 shows a schematic orbital interaction diagram between the “t_{2g}” orbitals (left column) of metal fragment [OsCl₂(PH₃)₂] and the π orbitals (right column) of carbon fragment (C₅H₄).³⁸ The metal–carbon σ bonding MOs are not shown in the figure for the purpose of clarity. The π orbitals of the C₅H₄ unit are the π_{in-plane} atomic orbital from the triply bonded carbon and the linear combinations of the five p_π atomic orbitals, perpendicular to the six-membered planar ring, from the five carbons in the ring. The central column in the figure gives the resulting molecular orbitals derived from the orbital interactions. MO1, MO4, and MO6 (LUMO) are orbitals derived from the orbital interactions among 1π, 3π, and 5π* of C₅H₄ and d_{xz} from the “t_{2g}” orbitals. MO2 and MO5 (HOMO) are derived from the interactions among 2π, 4π*, and d_{yz}. The MO3 is derived from the interaction of π_{in-plane} and d_{x²-y²} and corresponds to the in-plane bonding orbital in the Os≡C triple bond. There are 10 π electrons, which are housed in MO1, MO2, MO3, MO4, and MO5. Except the interaction between π_{in-plane} and d_{x²-y²}, the bonding between [Os(PH₃)₂Cl₂] and C₅R₄ fragment is very similar to that of metallabenzynes.³

Figure 4 shows the spatial plots of HOMO (MO5) and LUMO (MO6) molecular orbitals calculated for the model complex [Os(≡CCH=C(CH₃)CH=CH)Cl₂(PH₃)₂] (**36**).³⁸ As shown in Figure 4, the HOMO has significant contribution from the p_π orbitals at C2 and C4 carbons, Os(d) orbital, and p_π orbitals from the chloride ligands; the LUMO has

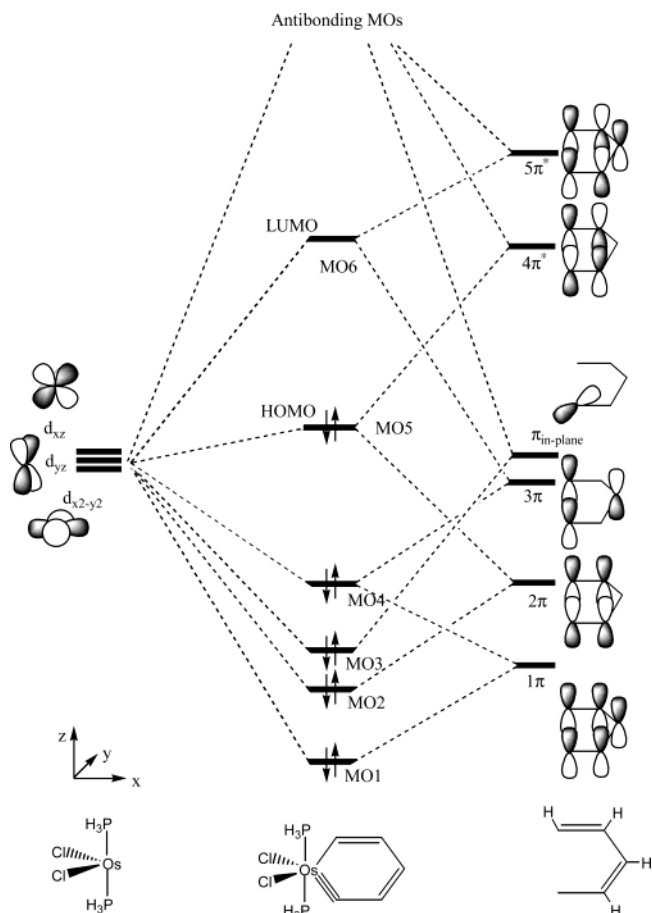


FIGURE 3. Schematic orbital correlation diagram showing the π-interaction for the all-H complex.

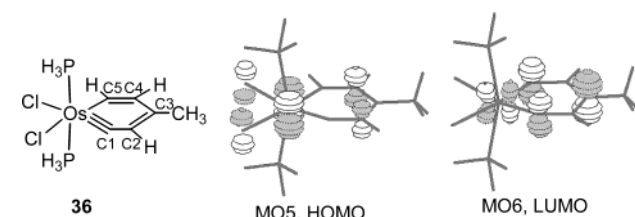


FIGURE 4. The spatial plots of the HOMO and LUMO of [Os(≡C–CH=C(CH₃)CH=CH)Cl₂(PH₃)₂] (**36**). The molecular orbitals were obtained from the B3LYP calculations.

significant contribution from the p_π orbitals at C1, C3, and C5 carbons and Os(d) orbital. The electron density distribution of the HOMO correlates well with the regio chemistry in the electrophilic substitution reactions of osmabenzynes with Br₂ and acids, as discussed above.

Stability of Metallabenzynes

Organic compounds with a C≡C triple bond in the six-membered ring, such as benzyne and cyclohexyne, have low thermal stability due to the large ring strain caused by bending the formal C≡C triple bond. In osmabenzynes, the angles at the carbyne atoms are in the range of 148.3–(6)°–153.8(4)°, which are deviated significantly from the ideal value of 180° expected for metal–carbyne complexes. The Os–C5–C4 angles (in the range of 128.9(3)°–138.6(5)°) are also slightly larger than the expected angle

around an sp^2 -hybridized carbon. The angle bendings in the complexes are also expected to cause a ring strain. However, isolated osmabenzynes are thermally much more stable than benzyne. The difference in the stabilities of osmabenzynes and benzyne has been studied by computational chemistry and was found to be related to the difference in ring strain and conjugation energies.³⁸

The ring strain of osmabenzynes **36** caused by angle bending at the carbyne carbon was estimated to be only 9.57 kcal/mol based on the calculated energy needed for the angle bending of optimized $[\text{Os}(\equiv\text{CCH}_3)(\text{CH}_3)\text{Cl}_2(\text{PH}_3)_2]$ to a geometry similar to that of osmabenzynes **36**.³⁸ The strain caused by angle bending at the Os–CH carbon was found to be insignificant and is less than 2.5 kcal/mol. In contrast, the ring strain of benzyne is much larger and was estimated to be 53.60 kcal/mol based on the calculated energy needed for the angle bending of optimized $\text{CH}_2=\text{CHCH}=\text{CHC}\equiv\text{CCH}=\text{CHCH}=\text{CH}_2$ to a geometry similar to that of benzyne.³⁷ The significant difference of the two strain energies can be related to the different magnitudes of the angle bending at the sp -hybridized carbons in the two ring systems. In the benzyne ring system, significant angle bending (from the ideal value 180° to 127°) occurs at two carbons, while in the osmabenzynes system, a relatively small angle bending (from 180° to 148.3°) occurs at the carbyne carbon. The smaller angle bending at the carbyne atom while maintaining a ring structure for an osmabenzynes can be traced back to the small ring angle at the metal center. In metal complexes, ligand–metal–ligand angles having ca. 80° are quite common. In benzyne, one has to reduce the angles at the two sp -hybridized carbons significantly to have a ring structure.

The conjugation energies of osmabenzynes **36**, benzyne, benzene, and $[\text{Os}(\text{C}(\text{SMe})\text{CHCHC}(\text{Br})\text{CH})\text{I}(\text{CO})(\text{PH}_3)_2]$ (**38**) (a model complex of Roper's osmabenzene $[\text{Os}(\text{C}(\text{SMe})\text{CHCHC}(\text{Br})\text{CH})\text{I}(\text{CO})(\text{PPh}_3)_2]$, see Scheme 10 for its structure) have been evaluated from the reaction energies of isodesmic reactions.^{38,40} The study reveals that the conjugation energy of osmabenzynes **36** (44.35 kcal/mol) is similar to those of benzene (46.66 kcal/mol) and osmabenzene **38** (43.52 kcal/mol) but is larger than that of benzyne (37.47 kcal/mol) by ca. 7 kcal/mol. Thus the higher thermal stability of osmabenzynes compared to benzyne can be related to the relatively smaller ring strain and larger conjugation energy.

The effect of substituents (BH_2 , SiH_3 , H, Me, Cl, NH_2) at C2 and C4 carbons of the ring of osmabenzynes on the stability of osmabenzynes has also been investigated by calculating the reaction energies of related isodesmic reactions of various substituted model osmabenzynes.³⁸ The results show that π -accepting substituents (e.g., silyl and boryl groups) have stabilizing effect while π -donating substituents (e.g., Cl, NH_2) have destabilizing effect. Examination on the structural parameters of the six-membered rings reveals that changing in the substituents causes only small variations in the bond distances (within 0.05 Å) and angles (within 6°). Therefore no significant change in the strain energy is expected when substituents

are varied. On the other hand, π -accepting substituents on C2 and C4 carbons can stabilize the HOMO (MO5 in Figure 3) leading to greater stabilities for the corresponding complexes, while π -donating substituents on C2 and C4 carbons destabilize the HOMO leading to lower stabilities for the corresponding complexes. The stabilization and destabilization apparently affects the conjugation energy and therefore the stability of the ring.

The effect of ligands trans to C1 and C5 carbons on the stability of osmabenzynes has been studied by Yang et al.³⁹ It was found that the ligands trans to C5 have no significant impact on the Os–C5 bond strength. The Os–C1 bond strength was found to increase when the ligands trans to C1 are changed from π acceptors to π donors.

Concluding Remarks

Several stable osmabenzynes have been successfully isolated in recent years. X-ray diffraction studies show that the metallacycles have a delocalized structure. Reactivity study shows that osmabenzynes can undergo electrophilic substitution reactions with acids and Br_2 . The X-ray diffraction data, as well as the chemical properties, indicate that osmabenzynes are aromatic. Osmabenzynes are thermally much more stable than benzyne because the ring strain is significantly smaller and the conjugation energy is larger. There exist many opportunities to further develop the chemistry of metallabenzynes. For example, it might be possible to make new types of metallabenzynes, especially those with different substituents, metals, and ligand environments and those with a $\text{C}\equiv\text{C}$ bond. It is also expected that new reactivities of metallabenzynes will be found in the future, for example, electrophilic substitution reactions with other reagents, reactions with nucleophiles, and formation of η^6 -metallabenzynes complexes.

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