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Review

Recent progress in the chemistry of osmium carbyne and metallabenzyne complexes

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Contents

Abstract

There has been much research activity in the chemistry of osmium complexes with an osmium–carbon triple bond. This paper summarizes recent progress in the synthesis, reactivities, and structural properties of osmium carbyne and osmabenzynes complexes.

Keywords: Osmium; Carbyne; Metallabenzyne; Metallabenzene; Metallacycle

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1. Introduction

Transition metal complexes with a metal–carbon triple bond, namely, carbyne (or alkylidyne) complexes, have attracted considerable attention because of their interesting properties and their significance as catalysts or reagents in the synthesis of organometallic and organic compounds [1]. Many transition metals, including osmium, can form stable carbyne complexes.

This work mainly concerns the chemistry of osmium complexes with an osmium–carbon triple bond. The first synthesis of osmium carbyne complexes was reported by Roper and coworkers [2]. The chemistry of osmium carbyne complexes, although it has not been developed as extensively as that of groups 5–7 metals, has advanced significantly. A number of osmium carbyne complexes have been obtained from various synthetic routes, especially in recent years. There are also many reports related to the chemical reactivities of osmium carbyne complexes. The chemistry of osmium carbyne complexes has been previously reviewed in articles dealing with metal carbyne complexes in general [1] and in reviews dealing more specifically with group 8 carbyne complexes [3,4].

Metallabenzynes can be regarded as compounds being formed by formal replacement of a carbon atom or CH group in benzyne by an isolobal metal fragment. These compounds are interesting because they may, like metallabenzenes [5], display properties of both aromatic organic compounds and organometallic compounds. In the past few years, stable metallabenzynes with a formal osmium–carbon triple bond have been isolated. Osmabenzynes can be regarded as a special class of osmium carbyne complexes. Reactivity studies of this interesting class of compounds have also been carried out. Some of the chemistry of osmabenzynes has been summarized in a short account in 2004 [6] and in recent review articles on the chemistry of metallabenzenes [5b,c].

In this work, we will summarize recent work on the synthesis and chemical reactions of osmium carbyne and osmabenzyne complexes from our own perspective. It is not our intention to include all the available literature related to the topic.

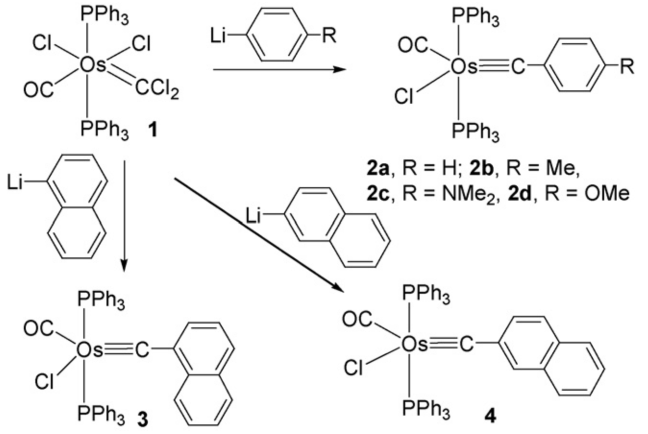
2. Osmium carbyne complexes

2.1. Syntheses

Osmium carbyne complexes can be obtained from different routes or starting materials. In this section, the main reactions leading to the formation of osmium carbyne complexes will be described.

2.1.1. Conversion of carbene complexes to carbyne complexes

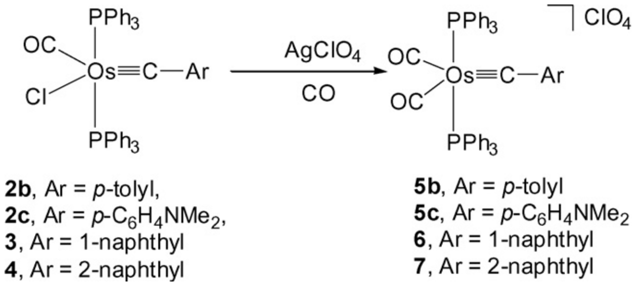
The first preparation of osmium carbyne complexes was reported by Roper and co-workers [2]. The osmium carbyne complexes **2** are obtained by reacting the dichlorocarbene complex **1** with two equivalents of lithium aryls (Scheme 1) [2,7]. The chemistry can be extended. Thus, similar reactions with 1-naphthyllithium or 2-naphthyllithium produce the corresponding carbyne complexes **3** and **4**, respectively [8].



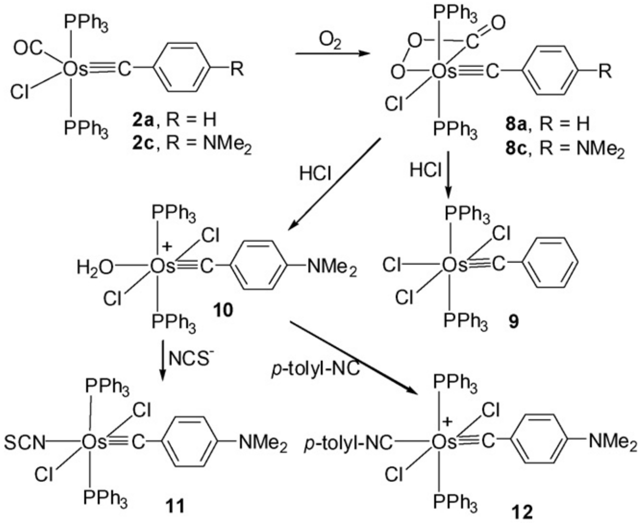
Scheme 1.

The carbyne complexes of type Os ($\equiv$CAr)Cl (CO) $(PPh_3)_2$ can undergo ligand substitution reactions with CO with the help of $AgClO_4$ to give cationic carbyne complexes as illustrated by the formation of **5** [9], **6** [8], and **7** [8] (Scheme 2). A related carbyne complex, $[Os(\equiv CTeMe)(CO)_2(PPh_3)_2]^+$, has been prepared from the reaction of Os (Te) $(CO)_2$ $(PPh_3)_2$ with MeI [7b].

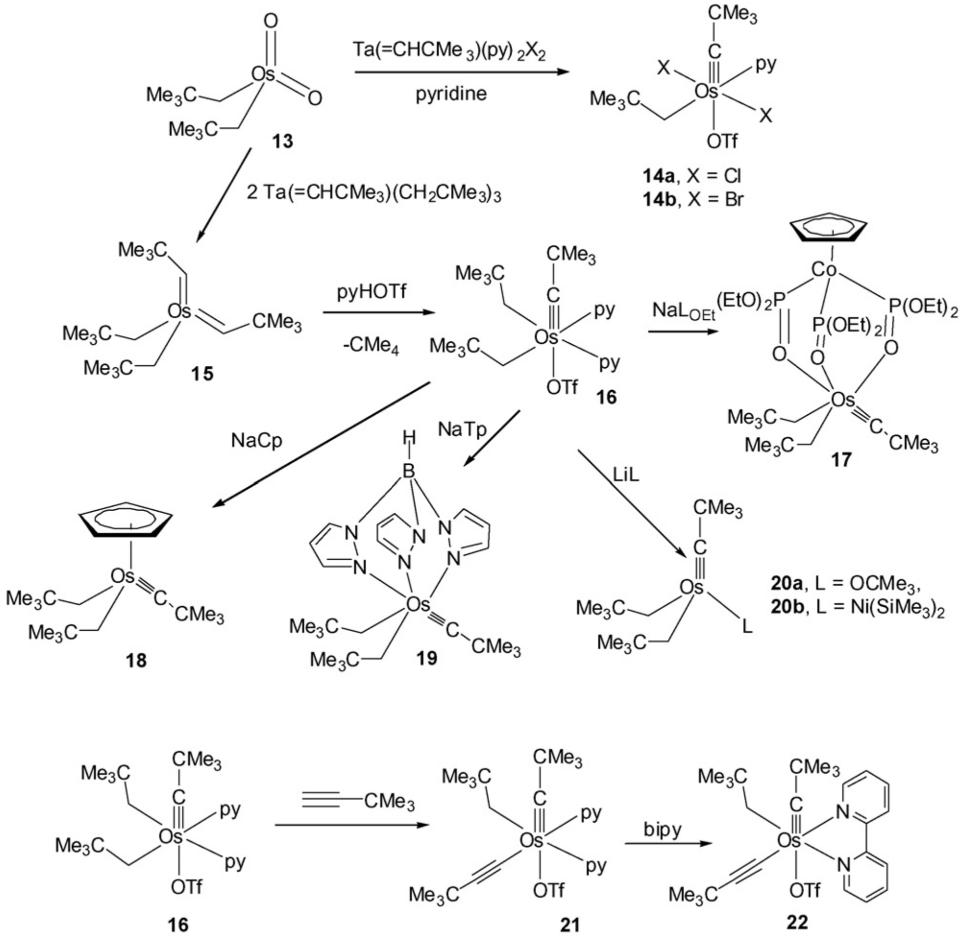
The carbyne complexes of type Os ($\equiv$CAr)Cl (CO) $(PPh_3)_2$ can also be used as starting materials to prepare osmium carbyne complexes of higher oxidation state. Thus, **2a** [3] and **2c** [10]



Scheme 2.



Scheme 3.



Scheme 4.

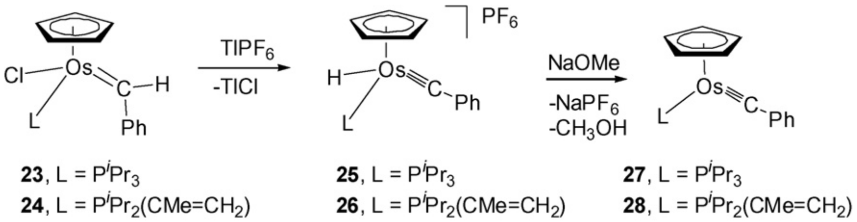
react with oxygen to give complexes **8a** and **8c**, respectively, which can be converted to the carbyne complexes **9** [3] and **10** [10], respectively on treatment with HCl (Scheme 3). The H_2O molecule in **10** can be displaced by NCS^- or isocyanide to give **11** and **12**, respectively [10].

A series of osmium carbyne complexes is obtained starting from the osmium carbene complex Os $(=CHCMe_3)_2(CH_2CMe_3)_2$ (**15**), which can be prepared from the reaction of $OsO_2(CH_2CMe_3)_2$ (**13**) with the carbene complex Ta $(=CHCMe_3)(CH_2CMe_3)_3$ (Scheme 4) [11]. The key compound in the series is complex **16**, which is formed by treating complex **15** with pyHOTf involving α-H elimination. Treatment of $OsO_2(CH_2CMe_3)_2$ (**13**) with the carbene complex Ta $(=CHCMe_3)(py)_2X_2$ (X = Cl, Br) produces carbyne complex **14** [11].

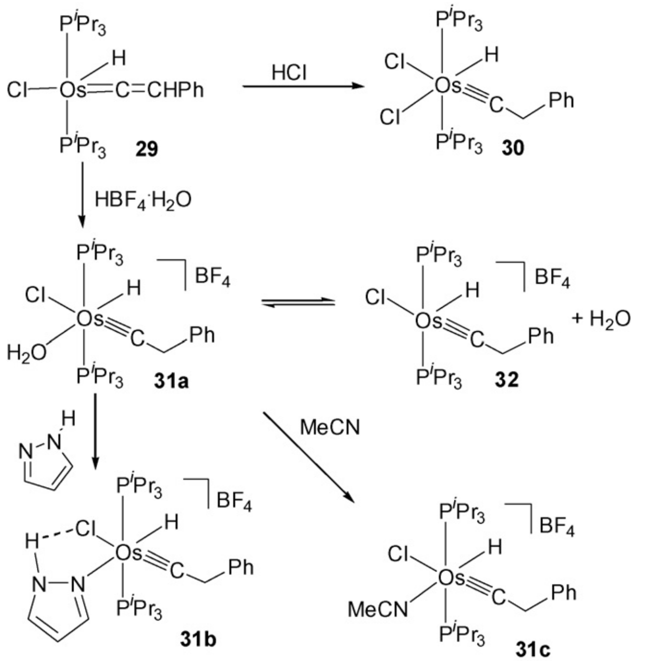
As additional examples of formation of osmium carbyne complexes from carbene complexes, complexes **23** [12] and **24** [13] react with $TlPF_6$ to give the hydrido-carbyne complexes **25** and **26**, respectively, presumably through α-H elimination of the carbene ligand in unsaturated intermediates generated in situ (Scheme 5). The latter cationic complexes can be deprotonated by NaOMe to give neutral carbyne complexes **27** and **28**.

2.1.2. *Protonation of vinylidene, allenylidene and related complexes*

Protonation of osmium vinylidene complexes can often lead to the formation of osmium carbyne complexes. For example, complex **29** reacts with HCl and $HBF_4 \cdot H_2O$ to produce carbyne complexes **30** and **31a**, respectively [14] (Scheme 6). In solution, the aqua-carbyne **31a** was found to be in equilibrium with com-



Scheme 5.

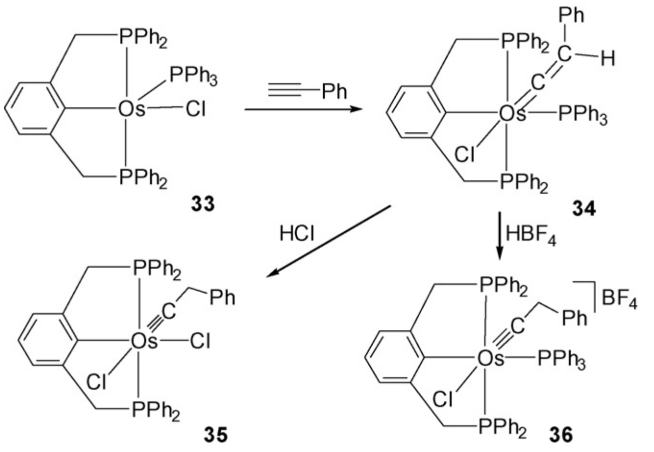


Scheme 6.

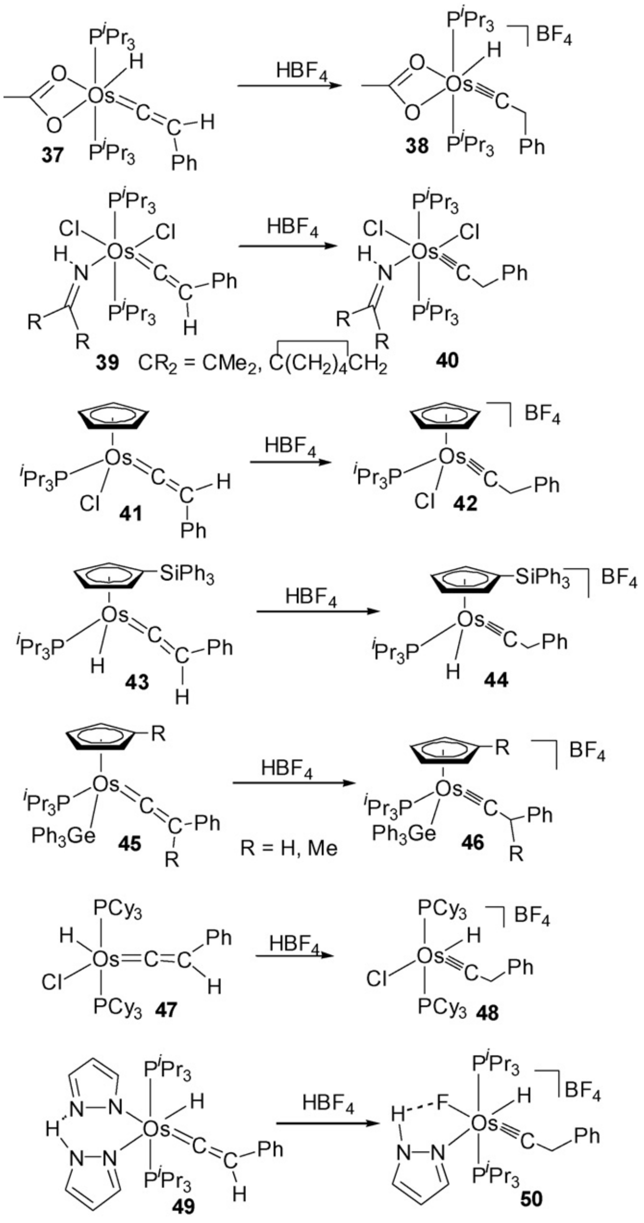
plex **32**. Indeed, the H_2O molecule is only weakly coordinated in **31a**, as it can be readily replaced by pyrazole and CH_3CN to give carbyne complexes **31b** and **31c**, respectively (Scheme 6) [15].

In our work, we have investigated the protonation reactions of the vinylidene complex **34** (Scheme 7), which can be readily prepared from the reactions of **33** with phenylacetylene [16]. Protonation of **34** with HBF_4 produces the expected carbyne complex **36**. Interestingly, protonation of **34** with HCl gives carbyne complex **35**. Thus, a PPh_3 ligand is also replaced by the chloride ligand in the process.

The protonation reactions of complexes **37** [17], **39** [18], **41** [19], **43** [20], **45** [20], **47** [21], and **49** [15] with HBF_4 are additional examples of formation of carbyne complexes from protonation of vinylidene complexes (Scheme 8).



Scheme 7.

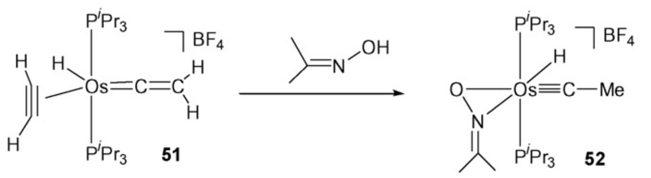


Scheme 8.

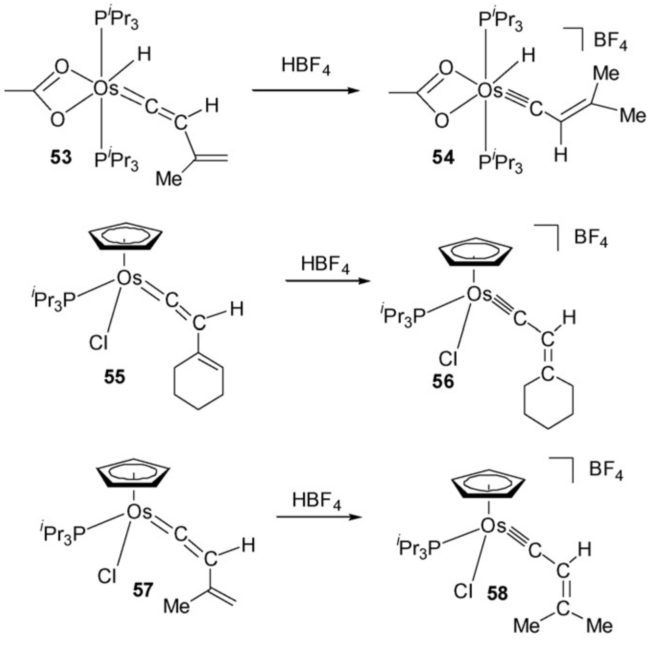
Acetone oxime can also protonate the vinylidene complex **51** to give the oximate-carbyne complex **52** (Scheme 9) [22].

Vinylvinylidene complexes can be protonated at the δ-carbon to give vinylcarbyne complexes, for example, by the protonation reactions of complexes **53** [23], **55** [19], and **57** [19] (Scheme 10).

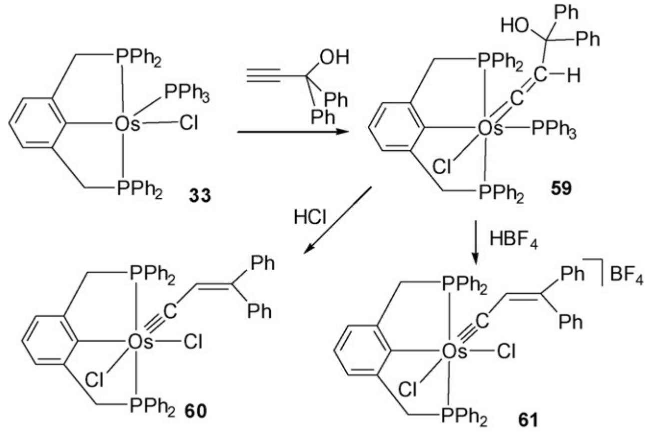
Protonation of hydroxy-vinylidene complexes can also lead to the formation of vinylcarbyne complexes. For example, the



Scheme 9.

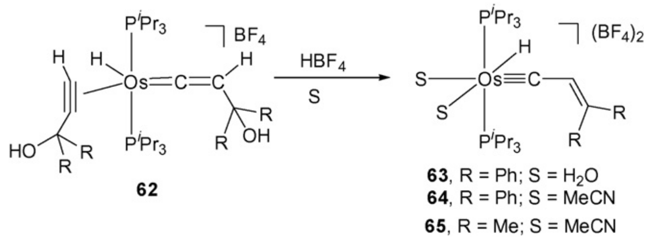


Scheme 10.



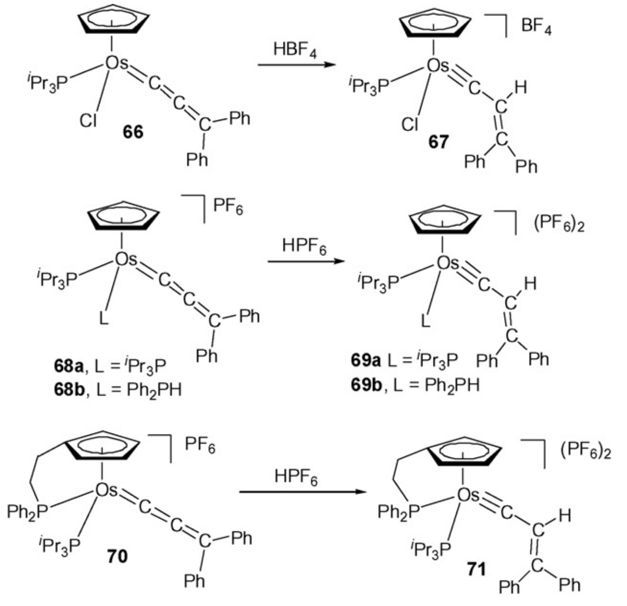
Scheme 11.

vinylidene complex **59**, which can be readily prepared from the reaction of **33** with HC≡CC(OH)Ph_2 [16], reacts with HBF_4 and HCl to give carbyne complexes **61** and **60**, respectively (Scheme 11). Esteruelas and co-workers found that complexes **62** can react with HBF_4 in the presence of H_2O or CH_3CN to give complexes **63–65** (Scheme 12) [24].



63, R = Ph; S = H_2O
64, R = Ph; S = MeCN
65, R = Me; S = MeCN

Scheme 12.

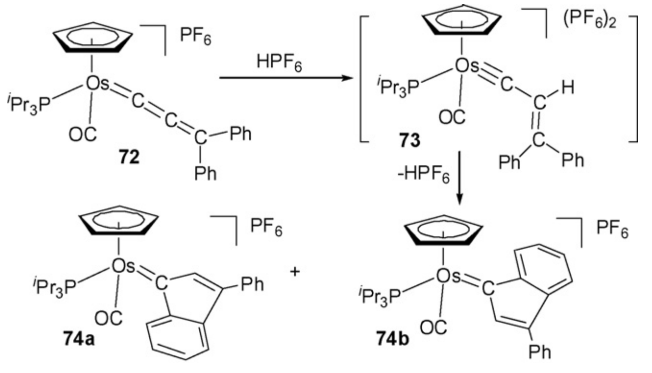


Scheme 13.

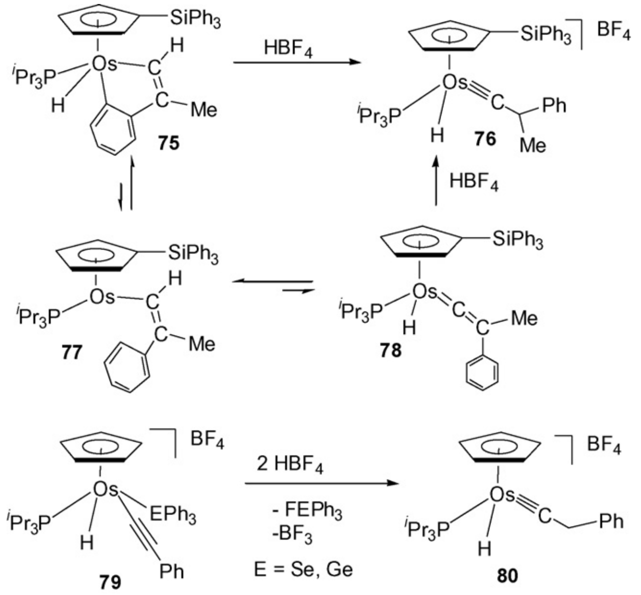
Protonation of allenylidene complexes may also give vinylcarbyne complexes as illustrated by the reactions of complexes **66** [25], **68a** [26], **68b** [27], and **70** [28] with HBF_4 (Scheme 13).

Protonation of the CO-containing complex **72** apparently also produces the vinylcarbyne complex **73** (Scheme 14) [27]. However, the complex is unstable and rearranges to a 1:1 mixture of the rotamers of the indenylidene complex **74**. Formation of **74** was proposed to involve electrophilic substitution of an *ortho* proton of one of the phenyl groups by the C_α atom of the vinylcarbyne unit.

Protonation of vinyl and acetylide complexes to give osmium carbyne complexes is also known. The carbyne complex **76** was produced when the vinyl complex **75** was protonated with HBF_4 [20]. Complex **76** may be formed through protonation of the non-detectable hydrido-vinylidene intermediate **78**, which is in equilibrium with **75** in solution (Scheme 15). Treatment of complex **79** with two equivalents of $HBF_4 \cdot Et_2O$ produced the carbyne complex **80** [29]. The reaction may also involve a vinylidene intermediate.



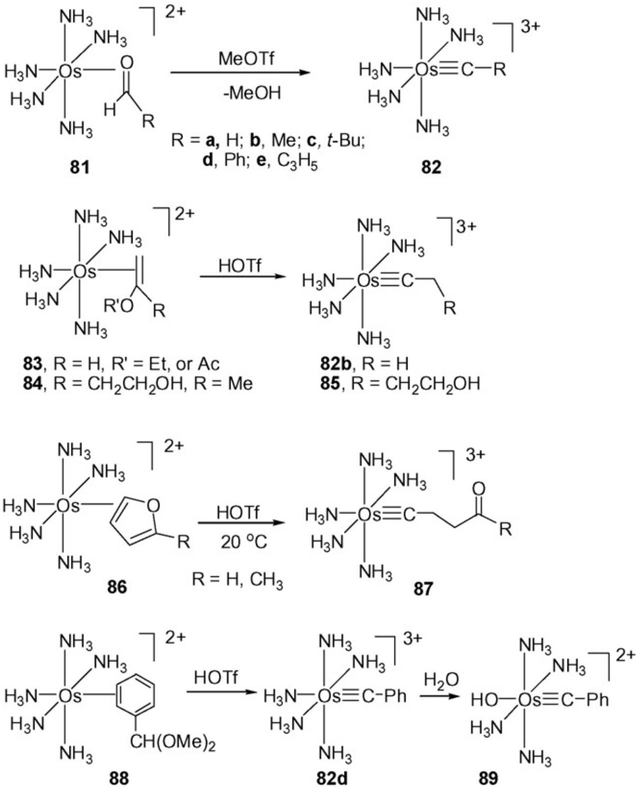
Scheme 14.



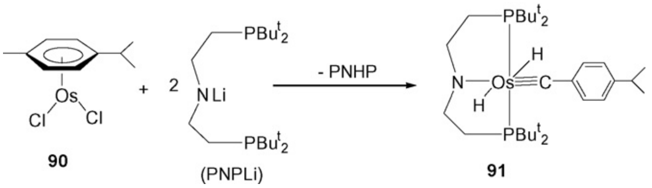
Scheme 15.

2.1.3. Conversion of π-coordinated ligands to carbyne ligands

Harman et al. have shown that osmium π-complexes of aldehydes and vinylethers can be converted to osmium carbyne complexes (Scheme 16). For example, the aldehyde complexes **81** react with MeOTf to give complexes **82** [30]; complexes **83** and **84** react with HOTf to produce **82b** and **85**, respectively [31]. The furan and alkylated furan complexes **86** can be converted to the carbyne complexes **87** on treatment with HOTf [32]. The phenyl-substituted carbyne complex **82d** could also be obtained from the protonation reaction of the acetal complex **88** [33]. Reaction of **82d** with H_2O gives carbyne complex **89** [33].



Scheme 16.



Scheme 17.

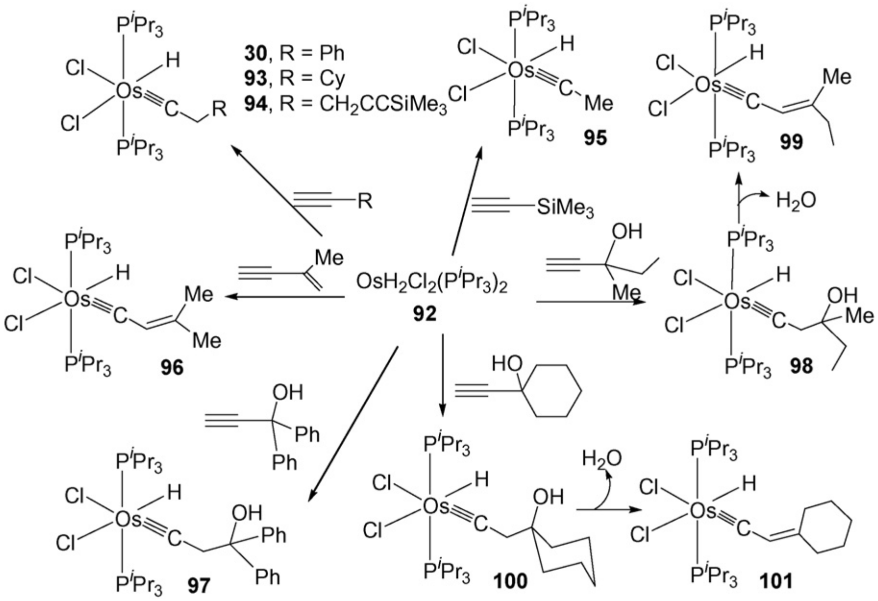
Caulton et al. discovered an unusual triple benzylic dehydrogenation reaction leading to the formation of an osmium carbyne complex. Thus, the cymene complex **90** reacts with two equivalents of LiPNP ligand to give the carbyne complex **91** (Scheme 17) [34].

2.1.4. Reactions of osmium hydride and alkyl complexes with terminal alkynes

A number of osmium carbyne complexes have been obtained from the reactions of osmium hydride complexes with terminal alkynes. In 1993, Esteruelas et al. reported the syntheses of a series of osmium carbyne complexes (**30**, **93–101**) from the reactions of $OsH_2Cl_2(P^iPr_3)_2$ (**92**) with various terminal alkynes (Scheme 18) [35]. The reactions presumably proceed through the intermediates Os (=C=CHR)$Cl_2(H_2)(P^iPr_3)_2$, followed by electrophilic attack of the acidic hydrogen of the dihydrogen ligand on the β-C atom of the vinylidene ligands. When 3-alkynols such as 3-methyl-l-pentyn-3-ol or 1-ethynyl-l-cyclohexanol are used, the initially formed carbyne complexes (e.g. **98**, **100**) can undergo dehydration to give vinylcarbyne complexes (e.g. **99**, **101**).

The related dihydride complex $OsH_2Cl_2(PCy_3)_2$ (**102**) behaves similarly (Scheme 19) [21]. It reacts with alkynes such as phenylacetylene and trimethylsilylacetylene to give complexes **103a** and **103b**, respectively. Related neutral six-coordinated hydridocarbyne complexes could also be obtained by the reaction of propargylic chlorides with the osmium trihydride complex OsH_3Cl $(PCy_3)_2$ (**105**). Thus, **105** reacts with 3-chloro-3-methylbut-l-yne at −40 °C to produce a mixture of complexes **106** and **107**. On warming, the carbene complex **107** is converted to the carbyne complex **106**.

The dihydride complex with an aminophosphine ligand **108** reacts with HC≡CC(OH)Ph_2 to give a similar hydridocarbyne complex **109** (Scheme 20) [36]. In contrast, the dihydride complex with a phosphinoester ligand **110** reacts with HC≡CC(OH)PhMe and HC≡CC(OH)Ph_2 to give the dichlorocarbyne complexes **111** and **112**, respectively. In the reactions, ester cleavage also occurs for one of the phosphinoester ligands to give a phosphinoacetate moiety. The dichlorocarbyne complexes **111** and **112** were also produced when $OsCl_2(^iPr_2PCH_2CO_2Me)_2$ was treated with HC≡CC(OH)PhMe and HC≡CC(OH)Ph_2, respectively.



Scheme 18.

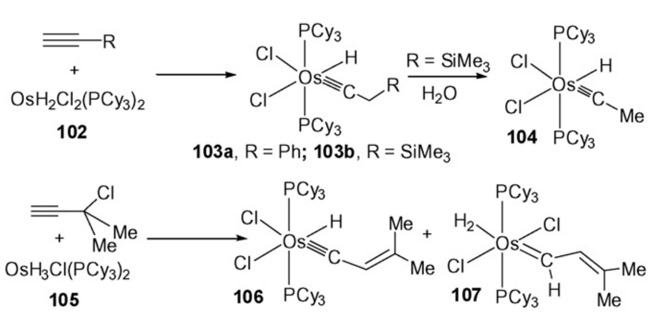
Cationic hydride complexes can also react with terminal alkynes to give carbyne complexes. Thus, complex **113** reacts with HC≡CH [37] or HC≡CSiMe$_3$ [17] to give the hydrido-carbyne complex **114** (Scheme 21), which undergoes an insertion reaction with HC≡CH to give the vinyl-carbyne complex **115** [37]. Similarly, reaction of complex **113** with HC≡CCMe$_3$ produces the analogous hydrido-carbyne complex **116** [17]. When HC≡CC(OH)MeR were used, the reactions produced a mixture of the expected hydrido-carbyne complexes **117** as the major products along with hydroxyosmacyclopropene complexes **118** [38]. In chloroform, complexes **117** slowly undergo dehydration reactions to give vinylcarbyne complexes [Os(≡CCH=CMeR)H(OAc)(P^{i}Pr$_3$)$_2$]BF$_4$. Al$_2$O$_3$ can accelerate the dehydration reactions.

The cationic hydride complex generated from the reaction of AgOTf with complex **119** can also react with alkylalkynes to give carbyne complexes **120** (Scheme 22). When HC≡CCMe=CH$_2$ was used, the reaction produced the vinylcarbyne complex **121** [39].

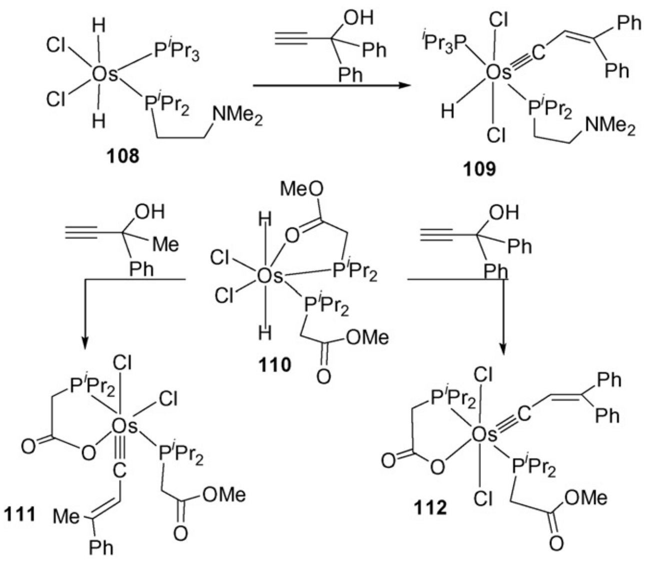
Some aryl complexes can also react with terminal alkynes to give carbyne complexes. For example, complex **122** reacts with aryl- and alkylalkynes to give carbyne complexes **123**, which can be converted to the fluorocarbyne complexes **124** on treatment with HBF$_4$ (Scheme 23) [40]. Complex **125** reacts with 4.5 equiv. of phenylacetylene in the presence of 2.0 equiv. of HBF$_4$·Et$_2$O to produce the interesting carbyne complex **126** [41].

2.1.5. Reactions of osmium halide complexes with terminal alkynes

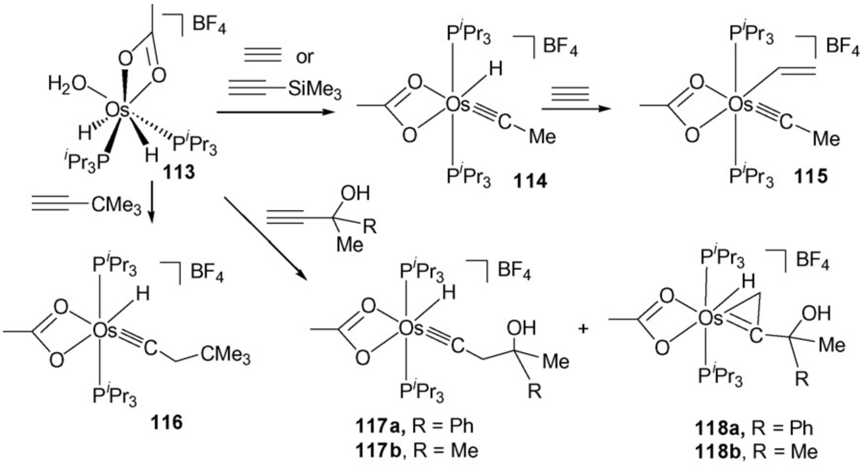
Osmium carbyne complexes are also produced in the reactions of OsCl$_2$(PPh$_3$)$_3$ (**127**) with terminal alkynes (Scheme 24). Thus, treatment of **127** with HC≡CCMe$_3$ produced a mixture of the carbyne complex **128** and the vinylidene complex **129** [42]. Treatment of **127** with HC≡CC(OH)Ph$_2$ produced a mixture of the vinylidene complex **130**, the allenylidene complex **131**, and *fac*- and *mer*-Os (≡CCH=CPh$_2$)Cl$_3$(PPh$_3$)$_2$ (**132** and **133**) [43].



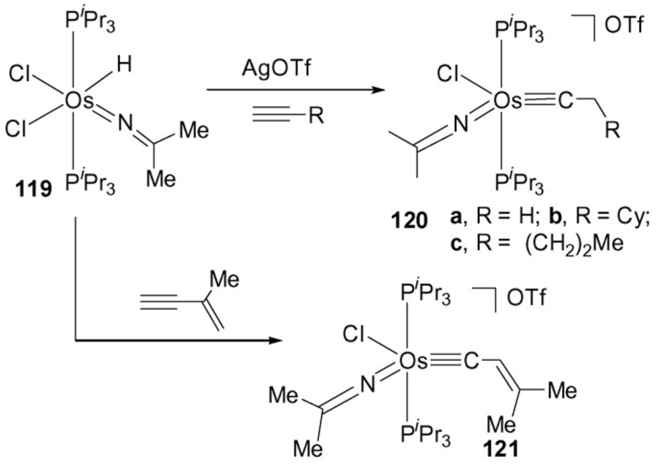
Scheme 19.



Scheme 20.



Scheme 21.



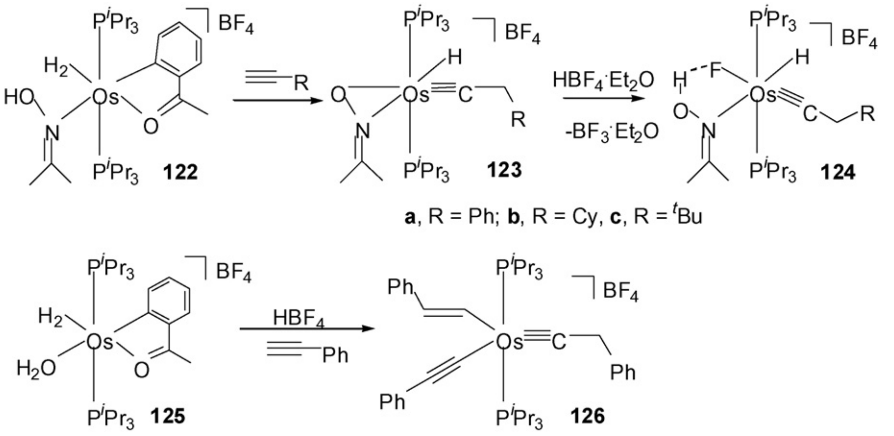
Scheme 22.

In the presence of acid, the reactions of **127** with terminal alkynes produce carbyne complexes selectively (Scheme 25). Thus, **127** reacts with $HC{\equiv}CC(OH)Ph_2$ in the presence of HCl cleanly to give complexes **132** and **133**, and in the presence of HBF_4 to produce the cationic carbyne complex **135** [43]. The reactions appear to be general. Treatment of **127** with aryl- and alkylalkynes in the presence of HCl produces carbine complexes **136**, **137**, and **128**. [44]. When $HC{\equiv}CSiMe_3$ was used, desilylation also occurs and the reaction produces complex **134**.

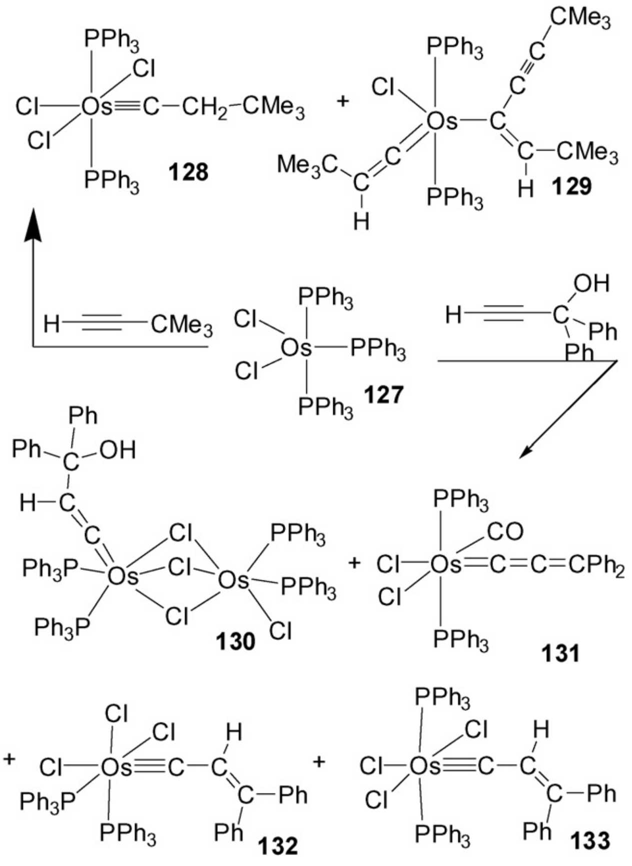
2.1.6. Reactions of osmium hydride complexes with olefins

Reactions of osmium hydride complexes with olefins can also lead to the formation of osmium carbyne complexes. Caulton and co-workers found that the dihydride complex $OsH_2Cl_2(P^iPr_3)_2$ (**92**) reacts with 2–3 equiv. of terminal olefins $RCH{=}CH_2$ ($R{=}CH_3$, Ph) at 85 °C to produce hydrido-carbyne complexes such as **30** and **138** together with equimolar amounts of alkanes (Scheme 26) [45]. The carbyne complex **95** was produced when **92** was treated with excess of $CH_2{=}CHOR$ (R=Et or ^{t}Bu) [46].

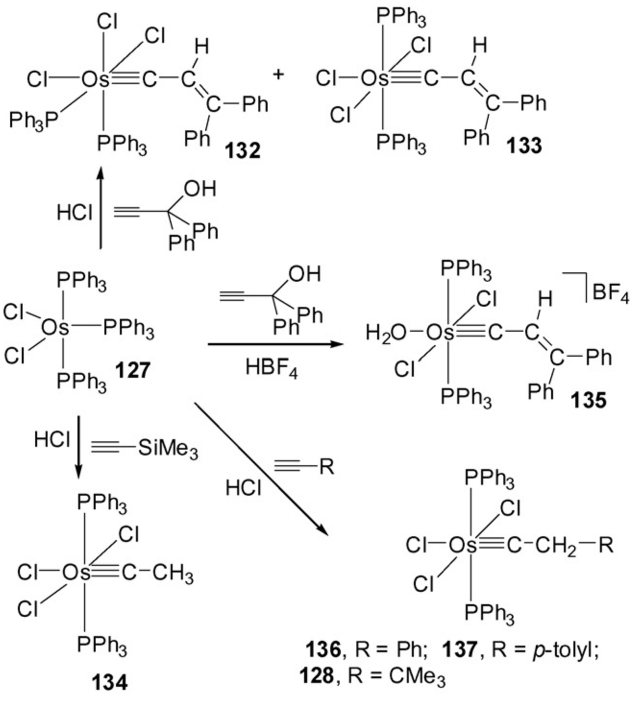
The trihydrido osmium complex $OsH_3Cl\ (P^iPr_3)_2$ (**139**) reacts with $PhOCH{=}CH_2$ to give the carbyne complex **141** (Scheme 27) [46]. Mechanistically, **141** is formed via the carbene intermediate **140**, which has been detected spectroscopically. When $CH_2{=}CHOEt$ was used, the reaction under similar reaction conditions produced the vinylidene complex $Os\ ({=}C{=}CH_2)HCl\ (P^iPr_3)_2$. When $OsH_3Cl(P^tBu_2Me)_2$ was used instead of **139**, the carbene com-



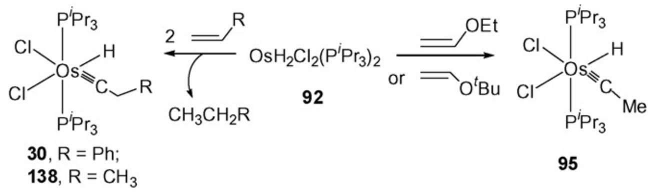
Scheme 23.



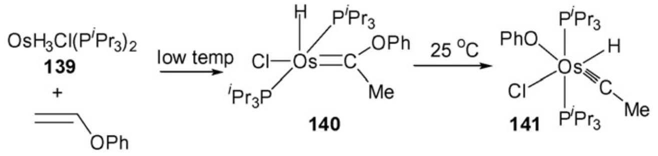
Scheme 24.



Scheme 25.



Scheme 26.

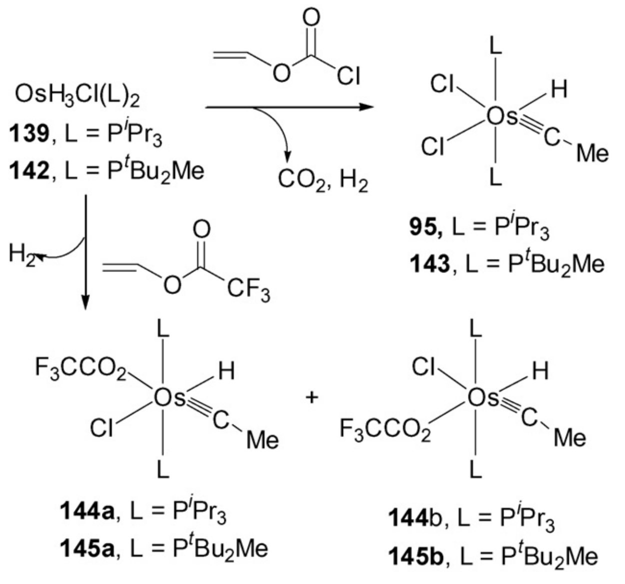


Scheme 27.

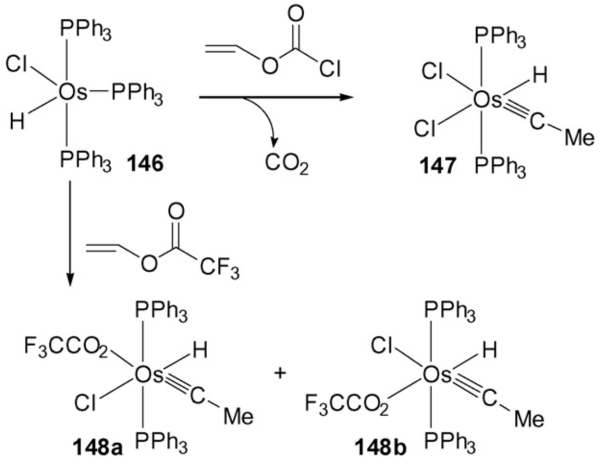
plex Os(=C(OPh)Me)HCl(P^{t}Bu$_2$Me)$_2$ can be isolated, although it does not rearrange to an analogous carbyne complex.

Osmium hydride complexes OsH$_3$Cl(L$_2$) (L = P^{i}Pr$_3$ (**139**), P^{t}Bu$_2$Me (**142**)) react with vinyl chloroformate to give hydrido-carbyne complexes **95** and **143**, respectively (Scheme 28) [47]. These hydride complexes also react with vinyl trifluoacetate to give carbyne complexes **144** and **145**, which exist as a mixture of two isomers. Analogous reactions with OsHCl(PPh$_3$)$_3$ (**146**) give carbyne complexes **147** and **148** (Scheme 29) [47].

Carbyne complexes are also produced from the reactions of hydride complex OsH$_3$Cl(P^{i}Pr$_3$)$_2$ (**139**) with fluoro-olefins (Scheme 30) [48]. Complex **139** reacts with vinylfluoride to produce the carbyne complex **149** and H$_2$. The liberated H$_2$ reacts with vinylfluoride to give C$_2$H$_4$ and HF. Complexes OsHCl(H$_2$)(CH$_2$=CHF)(P^{i}Pr$_3$)$_2$ and OsClF(=CHMe))(P^{i}Pr$_3$)$_2$, which have been detected spectroscopically, are the reaction intermediates for the formation of **149**. In the presence of NEt$_3$, complex **139** reacts with vinylfluoride to give exclusively the dihydrido-carbyne complex **150** and HF, which is trapped by



Scheme 28.



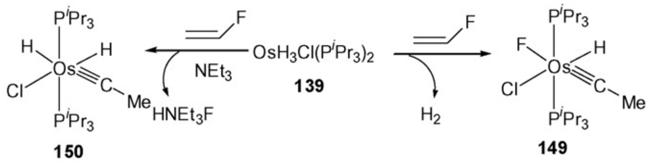
Scheme 29.

NEt_3 as $HNEt_3F$. Complex **149** can also be produced from the reaction of **139** with $CH_2{=}CF_2$.

2.2. *Chemical properties*

2.2.1. *Reactions with electrophiles*

As shown in Scheme 31, the carbyne carbon of $Os(\equiv CR)Cl(CO)(PPh_3)_2$ is nucleophilic and can be attacked by a variety of electrophiles, including X_n (X = S, Se, Te) [2,7], Cl_2 [2,7,8], CuI [49], AgCl [7,49], $AgClO_4$ [49], $AuCl(PPh_3)$ [49], HCl [7,8], $HClO_4$ [7a,8], HO Ac [7b], and HF [8].



Scheme 30.

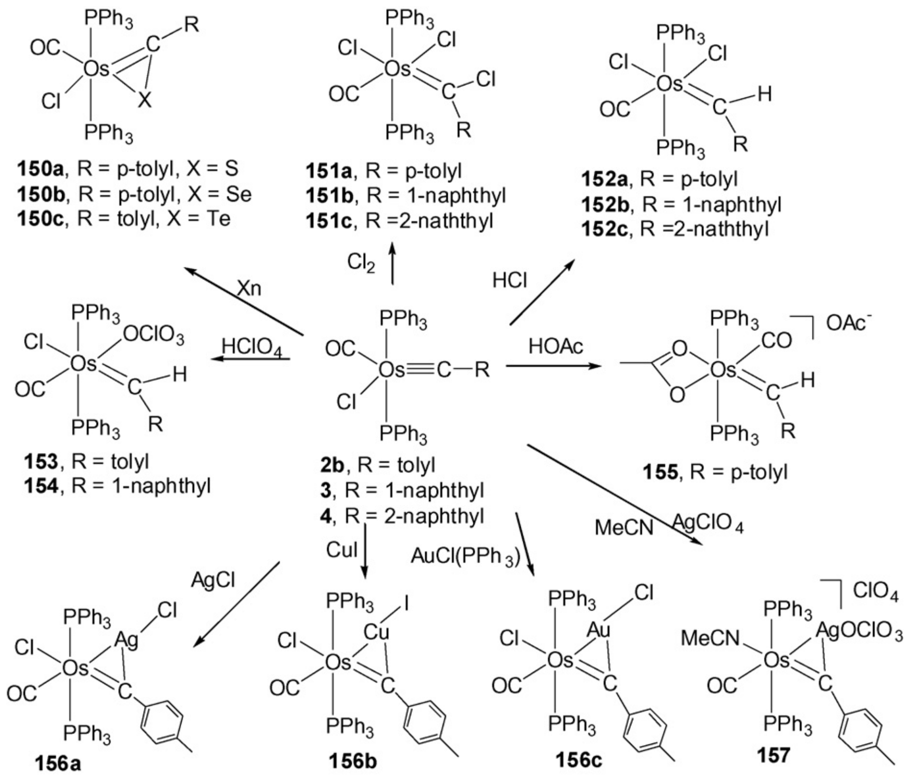
2.2.2. *Nucleophilic addition reactions*

In contrast, the carbyne carbon in the cationic carbyne complexes **12** and **159** is electrophilic (Scheme 32). Complex **12** reacts with SH^- to give complex **158** after elimination of HCl. Complex **159** reacts with water to give initially intermediate **160**, which loses a molecule of HI to give the aryl complex **161** [3].

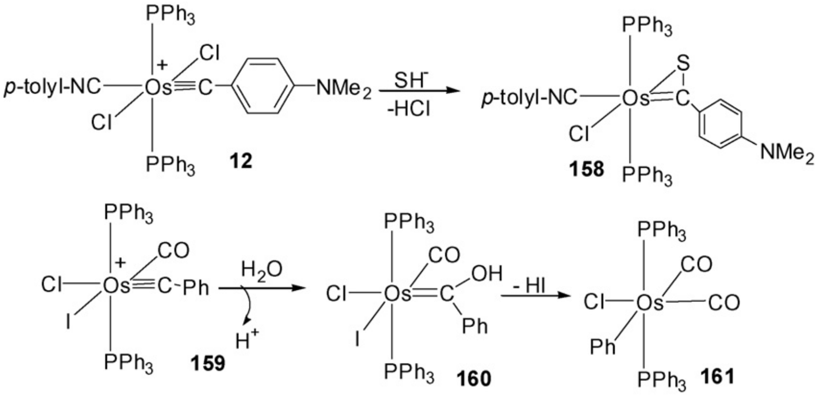
The tricationic complexes **82d** and **87** are also highly electrophilic (Scheme 33). Complex **82d** reacts with methanol to give carbene complex **162** [33], while complex **87** reacts with methanol in the presence of diisopropylethylamine to give the carbene complex **163** [32].

The neutral carbyne complexes **27** and **28** are also reactive towards ROH (Scheme 34). Complexes **27** and **28** react with methanol to give hydrido-carbene complexes **165** [12] and **164** [13], respectively. When phenol reacts with complex **27**, the reaction produces a metallacyclic hydrido-carbene complex **166** due to cyclometallation [12].

Nucleophiles may not always attack the carbyne carbons of carbyne complexes. Thus, Roper et al. found that complex **2b** reacts with $LiBEt_3H$ at the *para* position of the aromatic ring to give the vinylidene complex **167** (Scheme 35) [9]. Similarly, H^-



Scheme 31.

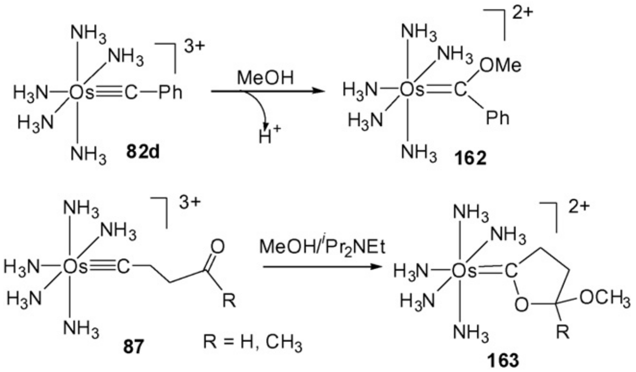


Scheme 32.

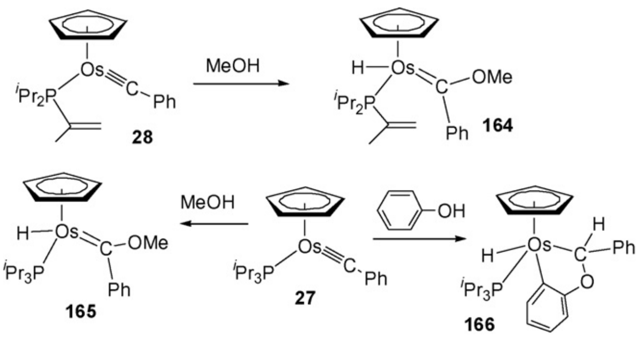
attacks on the naphthyl ring of complex **3** at the position *para* to the carbyne carbon to give complex **168**. Interestingly, H^- attacks on the naphthyl ring of complex **4** at the position *ortho* to the carbyne carbon to give complex **169** [50].

2.2.3. Deprotonation reactions

The proton on the carbon α to the carbyne carbon in complexes $L_nOs{\equiv}CCH_2R$ can be quite acidic and could often be deprotonated when treated with nucleophiles or bases to give vinylidene complexes. For such carbyne complexes, nucleophilic additions at the carbon usually do not occur. Scheme 36 shows examples of carbyne complexes that can be deprotonated by KOH to give vinylidene complexes. Treatment of **80** in methanol with KOH produced a mixture of the vinylidene complex **170** and its metalated isomer **171**. The two isomers are in equilibrium though the vinyl intermediate $CpOs(CH{=}CHPh)(P^iPr_3)$ [29]. The corresponding vinylidene complexes are also produced when complexes **114** [17], **115** [37], **116** [17], and **123** [40] are treated with KOH.



Scheme 33.

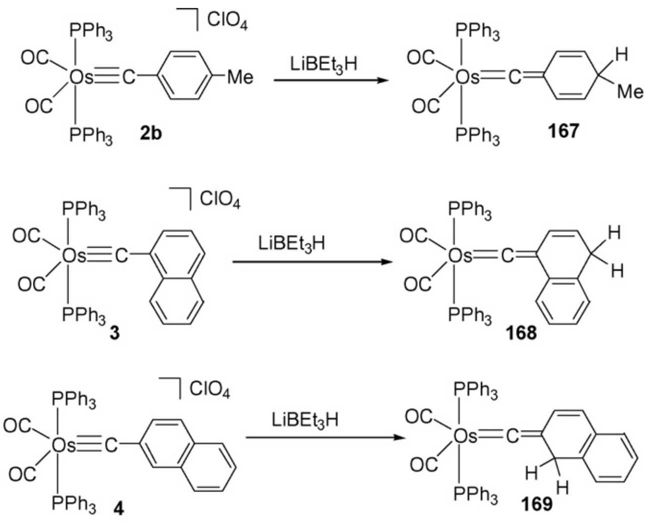


Scheme 34.

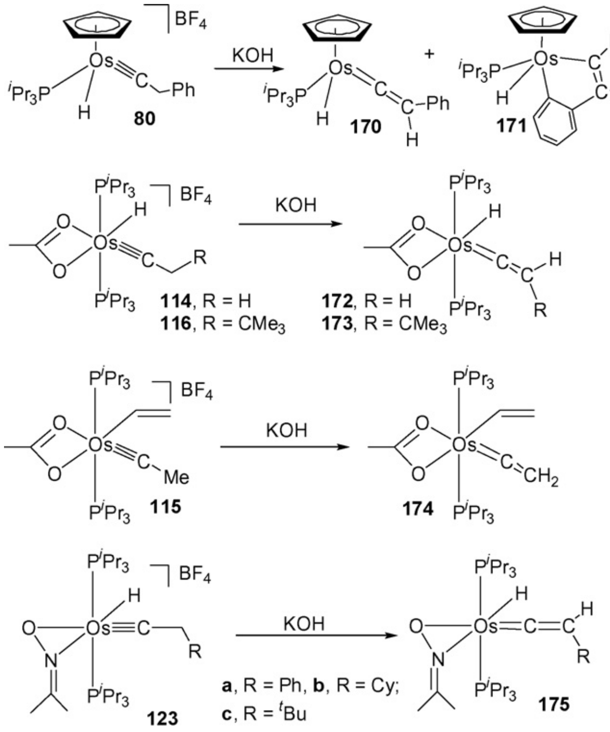
The neutral carbyne complexes **30** [14] and **103a** [21] can be deprotonated by the strong base NaOMe to give the five-coordinate 16e vinylidene complexes **29** and **47**, respectively (Scheme 37). MeLi functions as a base to deprotonate complexes **120** to give the vinylidene complexes **176** [39].

The trichlorocarbyne complexes **136**, **137**, and **128** can be deprotonated by NEt_3 to give five-coordinate vinylidene complexes **177–179**, respectively (Scheme 38) [44].

Additional examples of deprotonation reactions of osmium carbyne complexes are shown in Scheme 39. Treatment of complex **117a** with NaOMe produced hydrido-alkenylvinylidene complex **180**, as a result of deprotonation and dehydration of **117a** [38]. Methyl lithium deprotonates complex **121** to give alkenylvinylidene complex **181** [39]. The complex **69a** is so acidic that it can be deprotonated by ether to give the allenylidene complex **68a** [26]. Complex **64** is deprotonated



Scheme 35.



Scheme 36.

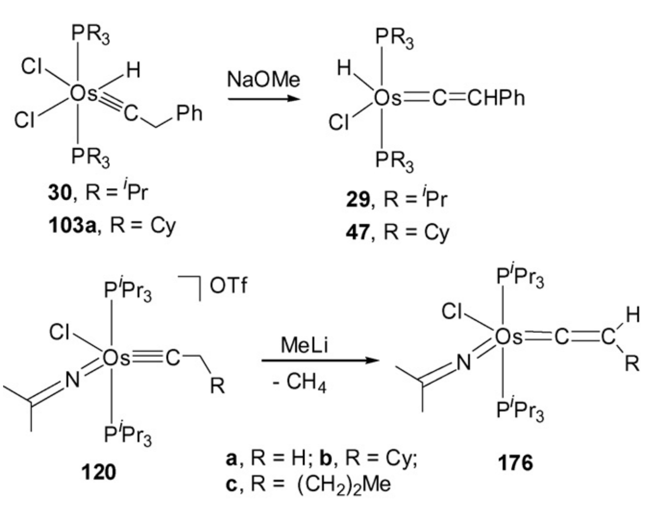
by ^{t}BuOK in acetonitrile at −30 °C to give the allenylidene complex **182**. In dichloromethane at room temperature, the deprotonation reaction gives the carbyne complex [Os(≡CCH=CPh$_2$)H(F)(MeCN)(P^{i}Pr$_3$)$_2$]BF$_4$ [51].

2.2.4. *Intramolecular coupling reactions of carbyne with a cis σ-bonded group*

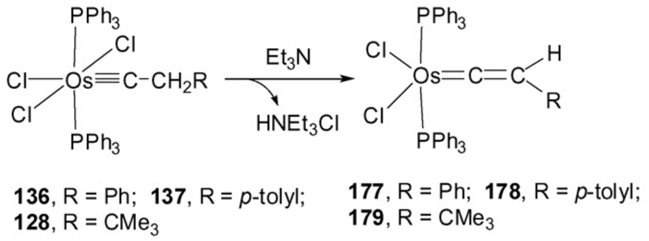
Coupling of carbyne ligand with a *cis* σ bonded ligand to give a carbene complex is another common reaction exhibited by osmium carbyne complexes. The factors governing the equilibrium between carbene and carbyne complexes have been discussed in detail by Caulton [52]. Caulton and co-workers shown that CO promotes the coupling of the H and the carbyne ligands in complexes **30** [53] and **138** [45,53] to give the carbene complexes **183a** and **183b**, respectively (Scheme 40). The chloride ligand in complexes **30** [53] and **138** [45,53] could be abstracted when treated with NaBAr$_4$ (Ar = 3,5-C$_6$H$_3$(CF$_3$)$_2$) to give the cationic carbyne complexes **184**. Complex **184** can react with CO to give carbene complexes **185d** and **185e**. The complex **184a** reacts with terminal alkynes to give carbene complexes **185a–c**. Interestingly, when HC≡CMe or HC≡CCMe$_3$ are used, the carbene complexes transform to the vinyl complexes **186**.

Coupling of hydride and carbyne ligand was also observed in the reaction of **91** with CO and H$_2$ (Scheme 41) [34]. Thus, **91** was converted to the carbene complex **187** when treated with 1 atm of CO within 10 min at 22 °C in benzene. Complex **91** can be completely hydrogenated to give the trihydride complex **188**.

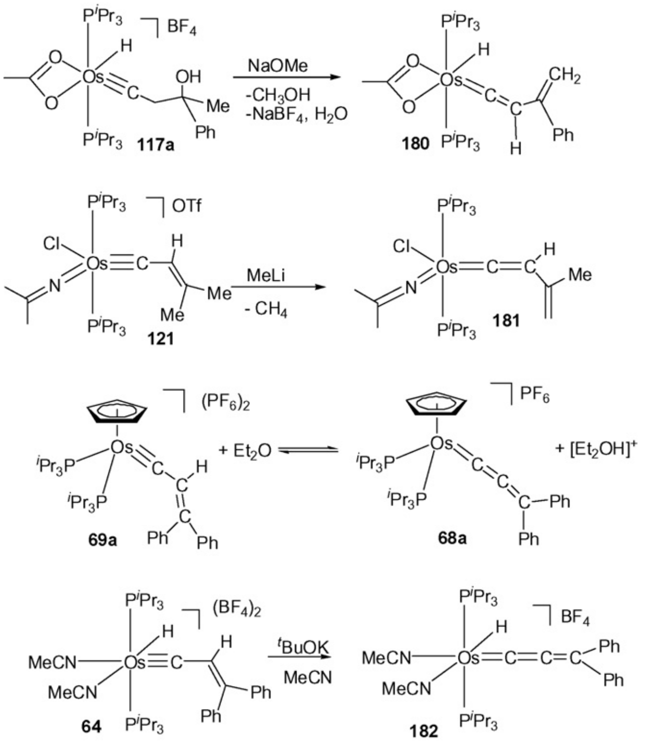
Ligands can have a drastic influence on the coupling of carbyne and hydride, as demonstrated in a study carried out by Esteruelas and co-workers [24] who found that complexes **64** and **65**, when refluxed in MeCN, can be converted to the carbene complexes **189** and **190**, respectively (Scheme 42). Complex **64**



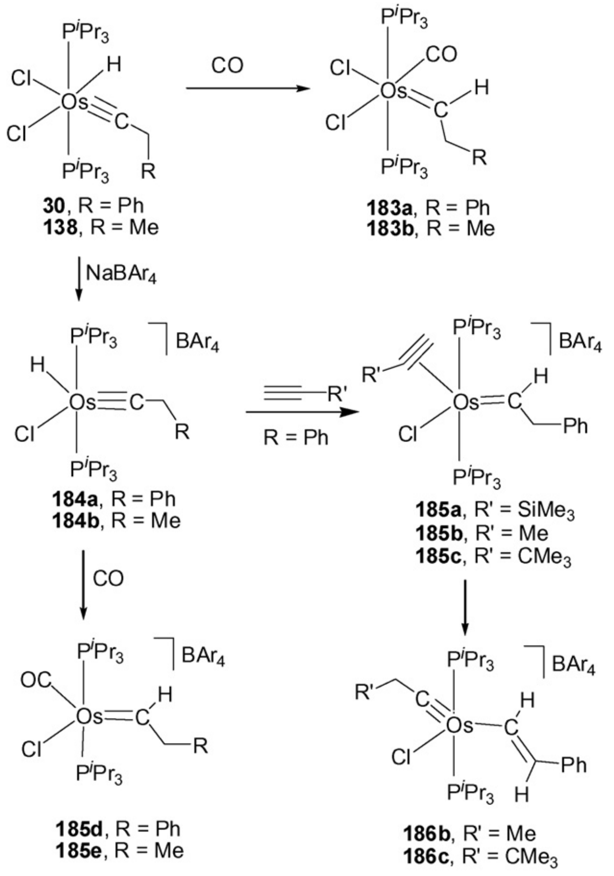
Scheme 37.



Scheme 38.



Scheme 39.

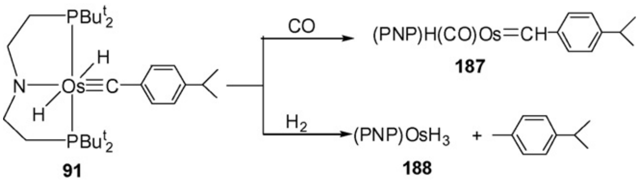


Scheme 40.

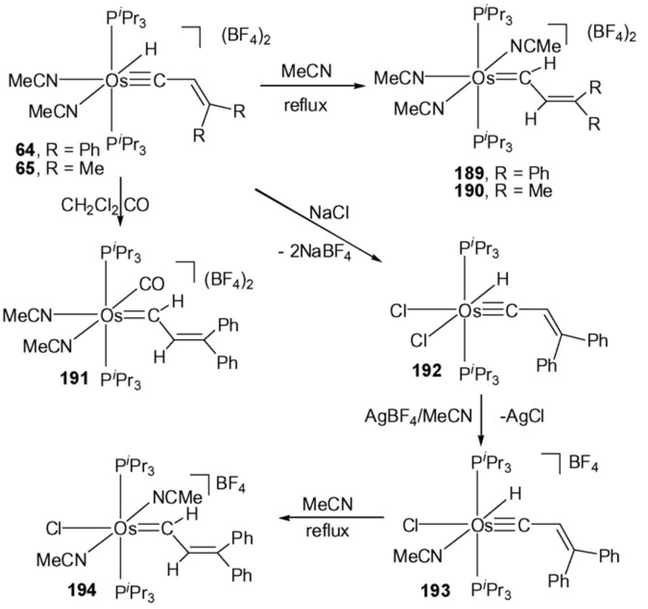
reacts with CO at room temperature in dichloromethane to give the carbene complex **191**.

The mono cationic monochloro complex **193** can also undergo hydride-carbyne coupling to give carbene complex **194** when refluxed in MeCN [24]. In contrast, the neutral dichloro complex **192** is reluctant to undergo the hydride-carbyne coupling. A computational study shows that the different reactivity is of kinetic origin. The hydride-carbyne coupling is kinetically favored by the presence of a CO ligand, but is disfavored by the presence of a chloride ligand. The transition states are calculated to be 10.2, 22.8, and 26.3 kcal/mol higher than the staring model carbyne complexes $[Os(\equiv CCH{=}CH_2)H(CO)(MeCN)(PH_3)_2]^{2+}$, $[Os(\equiv CCH{=}CH_2)HCl(MeCN)(PH_3)_2]^{+}$, and $Os(\equiv CCH{=}CH_2)HCl_2(PH_3)_2$, respectively [24]. A similar activation barrier (27.2 kcal/mol) was found for the coupling of hydride and carbyne ligands in $Os(\equiv CMe)HCl_2(PH_3)_2$ [54].

Scheme 43 shows two reactions involving carbyne and hydride ligands. When complex **80** is treated with $P(OMe)_3$ and KBr, complexes **195** and **196** were produced, respectively [20]. However, a deuterium labelling study shows that these reactions do not involve direct transfer of hydride to the carbyne carbon in **80**. Instead, the carbyne ligand initially dissociates a proton to give the vinylidene species $CpOsH({=}C{=}CHPh)(P^iPr_3)$, which evolves into the vinyl species $CpOs(CH{=}CHPh)(P^iPr_3)$. The vinyl species can react with $P(OMe)_3$ and Br^-, followed by protonation to give the observed products. Complex **44** slowly isomerizes to complex **197** when heated [55]. A mechanistic study shows that the reaction involves initial isomerization of the carbyne ligand to hydrido-vinylidene species.

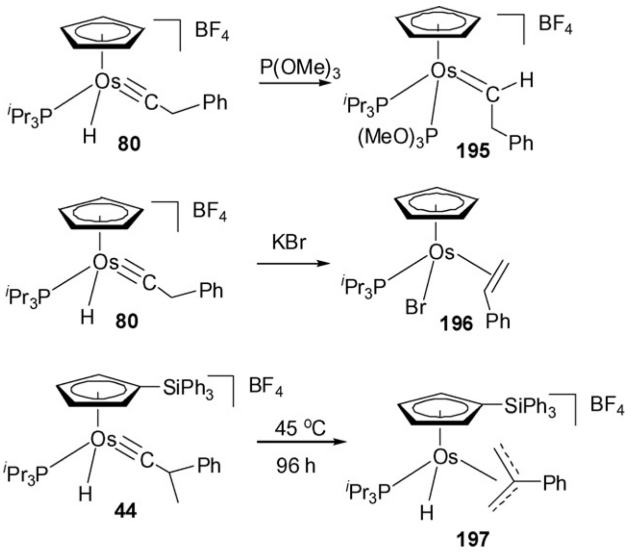


Scheme 41.

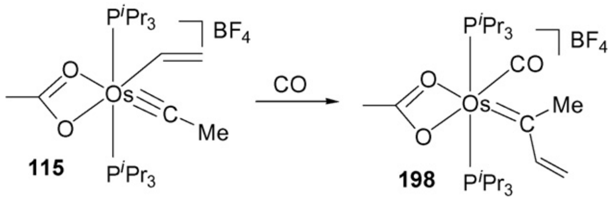


Scheme 42.

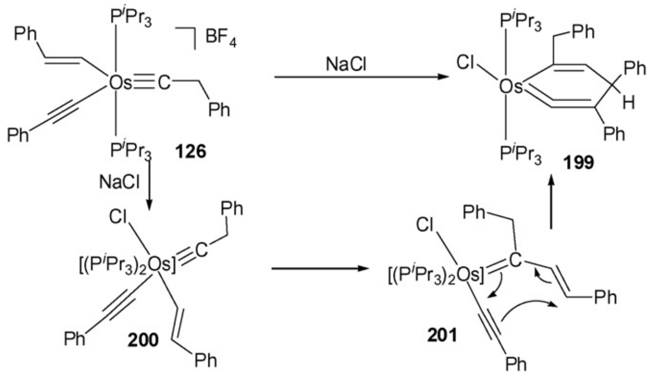
As a rare example in osmium chemistry, the coupling of vinyl and carbyne groups has been observed in the reaction of complex **115** with CO to give the carbene complex **198** (Scheme 44) [39].



Scheme 43.

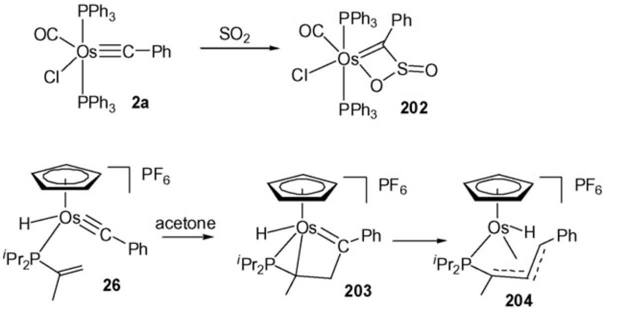


Scheme 44.



Scheme 45.

Coupling of vinyl and carbyne ligand has also been proposed in the reaction of complex **126** with NaCl to give the novel isometallabenzene complex **199** via intermediates **200** and **201** (Scheme 45) [41].



Scheme 46.

2.2.5. *Reactions with unsaturated substrates*

While there are many examples of cycloaddition reactions of unsaturated substrates to M≡C bond of high-valent group 6 metals, such reactions have rarely been observed for osmium carbyne complexes. Roper et al. found that the carbyne complex **2a** can react with SO$_2$ to give complex **202** [3a] (Scheme 46). Esteruelas et al. found that complex **26** can isomerize to the allyl complex **204**, through intermediate **203** generated from [2 + 2] cycloaddition reaction of the alkene with Os≡C bond [13].

2.3. *Structural properties*

A number of osmium carbyne complexes have been characterized by X-ray diffraction studies. Table 1 shows the OsC bond distances and the bond angles around carbyne carbon in selected osmium carbyne complexes. The OsC bond distances

Table 1
Structural parameters of selected osmium carbyne complexes

Complex	Os–C (Å)	Os–C–X (°)	Ref.
Os (≡CC$_6$H$_4$-*p*-Me)Cl (CO) (PPh$_3$)$_2$ (**2b**)	1.77 (2)	164 (2)	[2,7a]
Os (≡CC$_6$H$_4$-*p*-NMe$_2$)Cl$_2$ (NCS) (PPh$_3$)$_2$ (**11**)	1.75 (1)	169.5 (9)	[10]
[Os (≡CC$_6$H$_4$-*p*-NMe$_2$)Cl$_2$ (CN-*p*-tolyl)-(PPh$_3$)$_2$]ClO$_4$ (**12**)	1.78 (1)	174 (1)	[10]
[Os (≡C-1-naphthyl) (CO)$_2$ (PPh$_3$)$_2$]ClO$_4$ (**6**)	1.792 (10)	173.6 (10)	[8]
[Os (≡CPh) (NH$_3$)$_5$] (OTf)$_3$ (**82d**)	1.73 (1)	175.3 (8)	[33]
Os (≡CC$_6$H$_4$-*p*-^{i}Pr)H$_2$ (PNP) (**91**)	1.746 (3)		[34]
[Os (≡CTeMe) (CO)$_2$ (PPh$_3$)$_2$]$^+$	1.841 (16)		[7b]
[Os (≡CCH$_3$)Cl (═N═CMe$_2$) (P^{i}Pr$_3$)$_2$]OTf (**120a**)	1.720 (13)	169.4 (12)	[39]
Os (≡CCH$_2$CMe$_3$)Cl$_3$ (PPh$_3$)$_2$ (**128**)	1.728 (3)	176.8 (2)	[42]
Os (≡CCH$_3$)Cl$_3$ (PPh$_3$)$_2$ (**134**)	1.724 (5)	174.8 (3)	[44]
Os (≡CCH$_2$Ph)Cl$_3$ (PPh$_3$)$_2$ (**136**)	1.734 (3)	173.84 (10)	[44]
[Os (≡CCH$_2$Ph)H (ON═CMe$_2$) (P^{i}Pr$_3$)$_2$]BF$_4$ (**123a**)	1.708 (8)	178.3 (6)	[40]
[Os (≡CCH$_2$Cy) (F· · ·HON═CMe$_2$)H-(P^{i}Pr$_3$)$_2$]BF$_4$ (**124b**)	1.694 (4)	176.4 (4)	[40]
[Os (≡CCH$_2$Ph) (CαCPh) (CH═CHPh)-(P^{i}Pr$_3$)$_2$]BF$_4$ (**126**)	1.699 (7)		[41]
[Os (≡CCH$_2$Ph)H (F) (HPz) (P^{i}Pr$_3$)$_2$]BF$_4$ (**50**)	1.724 (4)	176.7 (4)	[15]
Os (≡CCH$_3$)HCl$_2$ (P^{i}Pr$_3$)$_2$ (**95**)	1.711 (4)	174.5 (4)	[46]
Os (≡CCH$_2$Ph)HCl$_2$ (P^{i}Pr$_3$)$_2$ (**30**)	1.711 (4)	172.4 (4)	[35]
[Os (≡CCH═CPh$_2$)H (H$_2$O)$_2$ (P^{i}Pr$_3$)$_2$]BF$_4$ (**63**)	1.733 (6)	168.0 (5)	[24]
Os (≡CCH═CMe$_2$)HCl$_2$ (PCy3)$_2$ (**106**)	1.715 (4)	174.4 (3)	[21]
[Os (≡CCH═CMe$_2$)H (O2CMe) (P^{i}Pr$_3$)$_2$]BF$_4$ (**54**)	1.734	177.4 (5)	[23]
Os (≡C-CH═CPH$_2$)Cl$_2$ (P^{i}Pr2CH$_2$CO2Me)-(P^{i}Pr$_2$CH$_2$CO$_2$) (**111**)	1.72 (1)	172.0 (7)	[36]
fac-Os (≡CCH═CPH$_2$)Cl$_3$ (PPh$_3$)$_2$ (**132**)	1.750 (4)	168.6 (3)	[43]
mer-Os (αCCH═CPH$_2$)Cl$_3$ (PPh$_3$)$_2$ (**133**)	1.750 (3)	168.4 (3)	[43]
[Os (≡CCH═CPH$_2$) (H$_2$O)Cl$_2$ (PPh$_3$)$_2$]BF$_4$ (**135**)	1.735 (6)	172.4 (6)	[43]
[CpOs (≡CPh)H (P^{i}Pr$_3$)]PF$_6$ (**25**)	1.733 (9)	176.9 (7)	[12]
[CpOs (≡CCH═C$_6$H$_{10}$)Cl (P^{i}Pr$_3$)]BF$_4$ (**56**)	1.756 (8)	167.8 (6)	[19]
[CpOs (≡CCH═CPH$_2$) (P^{i}Pr$_3$)$_2$] (PF$_6$)$_2$ (**69a**)	1.764 (8)	176.5 (7)	[26]
TpOs (≡C-^{t}Bu) (CH$_2$-^{t}Bu)$_2$ (**19**)	1.73 (2)	161 (2)	[11]

fall in a small range of 1.694(4)–1.841(16) Å. As expected, the geometry about the carbyne carbon is approximately linear in most of the compounds. However, several complexes with OsCC angles smaller than 170° were noted. For example, in complex TpOs(≡C-^{t}Bu)(CH_2-^{t}Bu)$_2$, the angle is 161 (2)°; in complex Os(≡CC_6H_4-*p*-Me)(CO)(PPh_3)$_2$, the angle is 164(2)°.

3. Osmabenzynes

The chemistry of transition metal-containing metallabenzenes has attracted considerable attention both experimentally and theoretically especially in recent years [5]. Transition metal-containing metallabenzenes can be regarded as compounds being formed by formal replacement of a CH group in benzene by an isolobal transition metal fragment. These compounds are interesting, because they could display properties of both aromatic organic compounds and organometallic compounds.

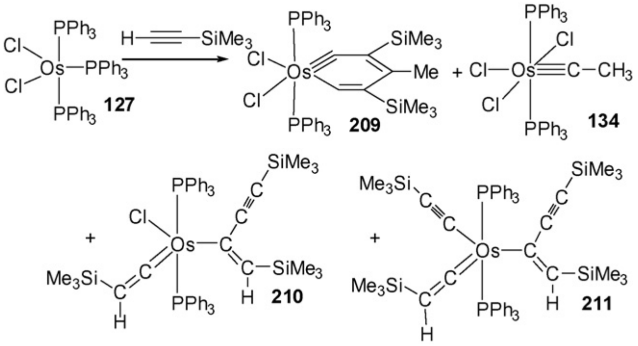
Remarkable progress has been made in the chemistry of metallabenzenes [5], since the first report of stable metallabenzenes in 1982 [56]. Previous studies have led to the isolation and characterization of an impressive number of stable metallabenzenes, especially those of osmium [56,57,58], iridium [59], platinum [60], and ruthenium [61,62]. Rich chemical properties of metallabenzenes have also been demonstrated [5].

Metallabenzynes [63] are compounds closely related to metallabenzenes. These compounds can be thought as compounds being formed by formal replacement of a carbon atom or CH group in benzyne (**205**) with a isolobal metal fragment. There are three possible classes of metallabenzynes, depending on the position of the triple bond in the six-membered ring, as illustrated by structures **206**–**208** in Scheme 47.

Class I (**206**) contains a formal M≡C bond, while class II (**207**) and class III (**208**) contain a formal C≡C bond. Organic compounds with a C≡C triple bond in the six-membered ring, for example, benzyne and cyclohexyne are thermally unstable due to the presence of ring strain [64]. Thus, at first sight, one might expect that metallabenzynes may also be thermally unstable. Nevertheless, several stable osmabenzynes of class I have been isolated in recent years. Some reactivity studies were also carried out with osmabenzynes. In this section, the work in this area will be summarized.

3.1. Syntheses

The first stable metallabenzyne **209** was obtained unexpectly from the reaction of $OsCl_2(PPh_3)_3$ (**127**) with HC≡$CSiMe_3$ in wet benzene [65]. The reaction produces a mixture of species, including the osmabenzyne complex **209**, the trichlorocarbyne complex **134** and the vinyl-vinylidene complexes **210** and **211** (Scheme 48). Although the detailed mechanism for the formation of **209** is not well defined yet, a vinylidene intermediate was suggested.

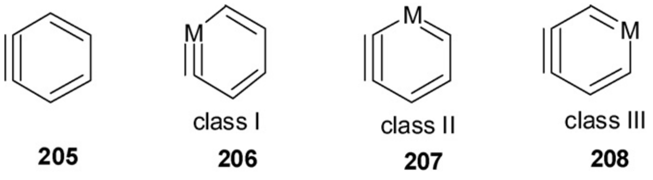


Scheme 48.

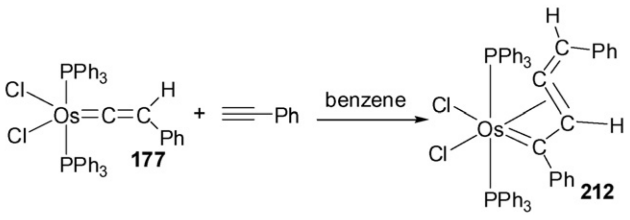
Extension of the chemistry involving $OsCl_2(PPh_3)_3$ as the starting material to prepare metallabenzynes, apparently, failed when other alkynes were used. Reactions of $OsCl_2(PPh_3)_3$ (**127**) with HC≡$CCMe_3$ was found to give the trichlorocarbyne complex **128** and the vinyl-vinylidene complex **129** (see Scheme 24) [42]. Reaction of $OsCl_2(PPh_3)_3$ (**127**) with HC≡CC(OH)Ph_2 was found to produce a mixture of species, including a dinuclear vinylidene complex **130**, an allenylidene complex **131**, and the carbyne complexes **132** (see Scheme 24) [43]. When PhC≡CH was used, the major product is the allenylcarbene complex $OsCl_2$(=CPh-η^2-CH=C=CHPh)(PPh_3)$_2$ (**212**), which can also be obtained by treatment of the vinylidene complex $OsCl_2$(=C=CHPh)(PPh_3)$_2$ (**177**) with HC≡CPh in benzene (Scheme 49) [66].

The possibility of using the allenylcarbene complex **212** as a starting material for the preparation of metallabenzynes has been investigated [66]. When **212** was treated with HC≡CPh in CH_2Cl_2, most of the HC≡CPh was polymerized and a mixture of phosphorus-containing species were produced. The expected osmabenzyne was only produced in trace amount, if any. In the presence of NEt_3, osmabenzyne **213** (see Scheme 50 for its structure) was slowly produced as the major species. Attempts to obtain osmabenzynes from the reactions of **212** with other alkynes such as HC≡$CSiMe_3$ or aliphatic terminal alkynes under similar conditions were unsuccessful.

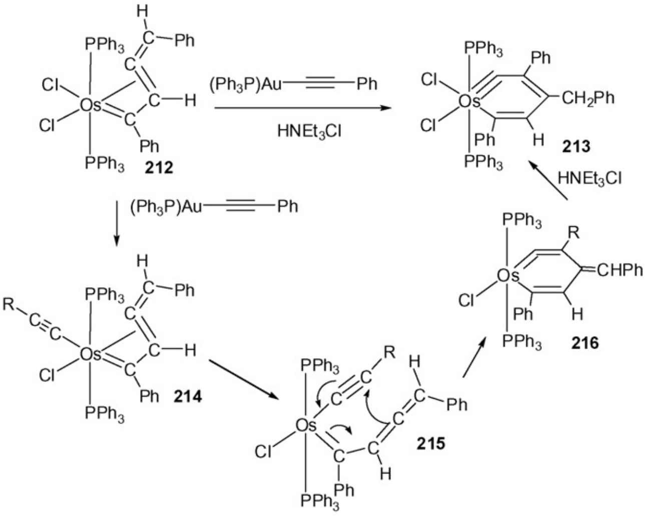
A better way to prepare complex **213** is to treat **212** with (PPh_3)AuC≡CPh in the presence of $HNEt_3Cl$ (Scheme 50) [66]. A plausible mechanism for the formation of **213** in the reactions of **212** with (PPh_3)AuC≡CR in the presence of $HNEt_3Cl$ is shown in Scheme 50. Metathesis reaction of



Scheme 47.



Scheme 49.

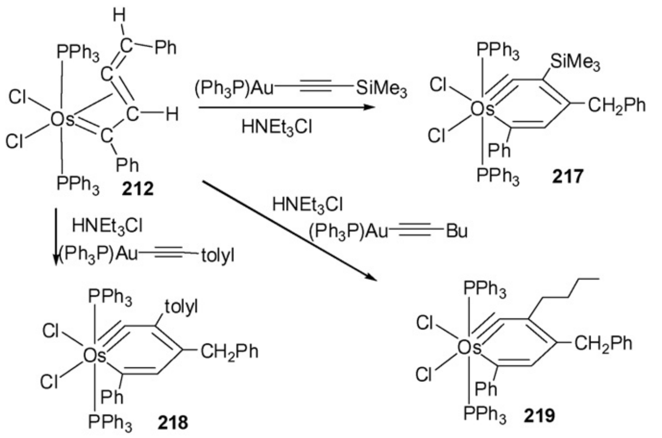


Scheme 50.

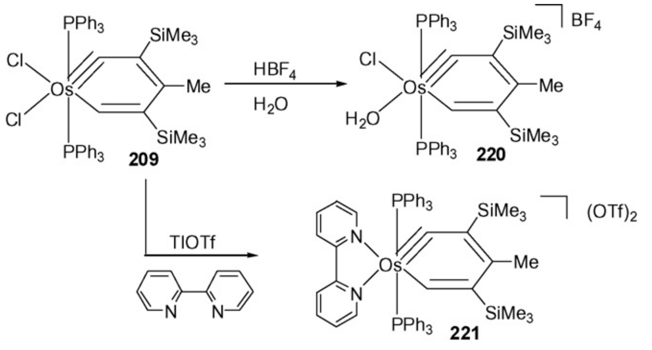
212 with $(PPh_3)AuC{\equiv}CR$ may initially produce the acetylide intermediate **214** or **215** which may undergo an intramolecular cycloaddition reaction to give **216**. A similar cyclization reaction was proposed for the formation of a novel osmium isometallabenzene complex by intramolecular coupling of alkenylcarbene and acetylide ligands [41]. Protonation of **216** with $HNEt_3Cl$ would then lead to the formation of **213**.

The chemistry can be extended to prepare other osmabenzynes using other gold (I) acetylide derivatives [66]. For example, treatment of **212** with $(PPh_3)AuC{\equiv}C$tolyl produced the tolyl-containing osmabenzyne **218**, with $(PPh_3)AuC{\equiv}C$-*n*-Bu produced the *n*-Bu-containing osmabenzyne **219**, and with $(PPh_3)AuC{\equiv}CSiMe_3$ produced the $SiMe_3$-containing osmabenzyne **217** (Scheme 51).

Osmabenzynes could also be obtained from **209** by ligand substitution reactions (Scheme 52). For example, treatment of **209** with 2,2′-bipyridine in the presence of TlOTf produced osmabenzyne **221** [67]. When a mixture of **209** and two equivalents of HBF_4 in wet dichloromethane was stirred for 8 h, the cationic osmabenzyne **220** was produced (Scheme 52) [68].



Scheme 51.



Scheme 52.

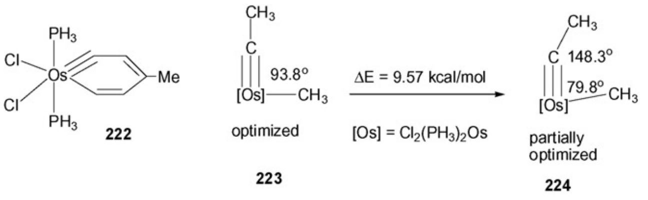
3.2. Reactivity

3.2.1. Thermal stability

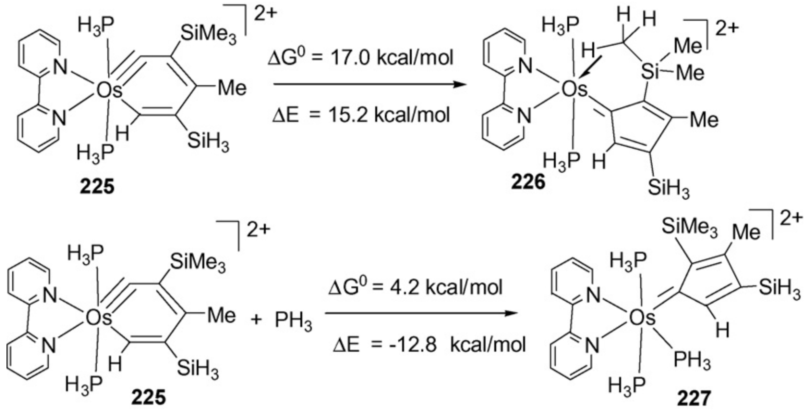
Benzyne has low thermal stability due to the large ring strain caused by bending of the formal C≡C triple bond. However, isolated osmabenzynes are thermally much more stable than benzyne. The difference in the thermal stabilities of osmabenzynes and benzyne has been studied by computational chemistry and was found to be related to the difference in ring strain and conjugation energies [69].

The ring strain of model osmabenzyne **222** 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 $[Os({\equiv}CCH_3)(CH_3)Cl_2(PH_3)_2]$ (**223**) to a geometry (**224**) similar to that of osmabenzyne **209** (Scheme 53) [69]. In contrast, the ring strain of benzyne is much large and was estimated to be 53.60 kcal/mol based on the calculated energy needed for the angle bending of optimized $CH_2{=}CHCH{=}CHC{\equiv}CCH{=}CHCH{=}CH_2$ to a geometry similar to that of benzyne [64b]. The significant difference of the two strain energies can be related to the fact that in the osmabenzyne system a relatively small angle bending (from 180° to 148.3°) occurs at the carbyne carbon while in the benzyne ring system, significant angle bending (from the ideal value 180° to 127°) occurs at two carbons. The smaller angle bending at the carbyne atom for an osmabenzyne can be traced back to the small ring angle at the metal center.

One of the common reactions of metallabenzenes is that they can undergo reductive elimination reactions to give cyclopentadienyl (Cp) complexes. In principle, a metallabenzyne could also undergo a similar transformation to give a carbene complex containing a five-membered ring. However, such reaction has rarely been observed. A DFT calculation shows that the reductive elimination reaction of **225** to give **226** is thermodynamically unfavorable (Scheme 54) [67].



Scheme 53.



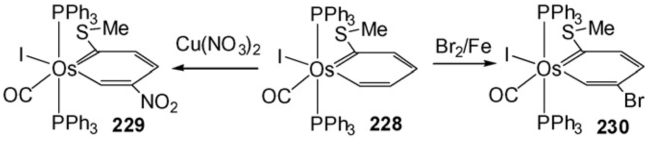
Scheme 54.

Reactions of osmium carbyne complexes $L_nOs(\equiv CR)$ (R′) with a two-electron donor ligand L′ are known to give carbene complexes $L_nL'Os$ (=CRR′) (see discussion in previous section). Indeed, the calculation shows that the reaction (electronic) energy for the reaction of **225** + PH_3 → **227** (Scheme 54) has a favorable value of −12.8 kcal/mol. However, when the entropy effect is considered, the reaction has a reaction free energy of 4.2 kcal/mol, indicating that the reaction is still thermodynamically unfavorable [67].

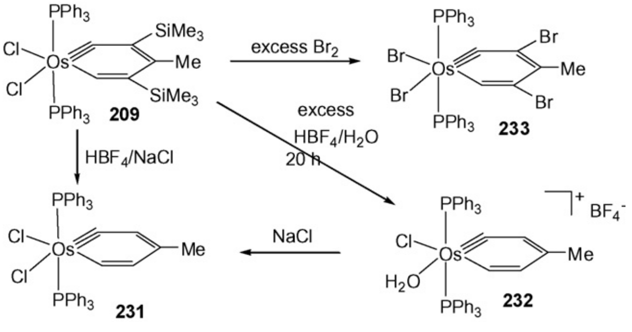
3.2.2. *Electrophilic substitution reactions*

Metallabenzenes can undergo typical aromatic electrophilic substitution reactions, as illustrated by the reactions of **228** with $Cu(NO_3)_2$ and Br_2 to give **229** and **230**, respectively (Scheme 55) [57c].

Osmabenzynes can also undergo electrophilic substitution reactions [68]. Thus, in the presence of NaCl, complex **209** reacts with $HBF_4{\cdot}Et_2O$ to give the neutral desilylated osmabenzyne **231** (Scheme 56). When aqueous HBF_4 was used, the cationic complex **232** was also slowly obtained. The cationic osmabenzyne complex **220** (see Scheme 52 for its structure) could also be desilylated to give **232** when treated with excess of HBF_4, although the reaction is slow and takes a few days to go completion. The electrophilic nature of the desilylation reactions is consistent with the observation that desilylation of the cationic complex **220** with HBF_4 to give **232** occurs at a much slower rate than the desilylation of **209** with HBF_4 in the presence of NaCl to give **231**, as it is more favorable for proton to attack on the neutral complex than the less electron-rich cationic complex. Complex **209** also reacts with excess Br_2 to give the osmabenzyne **233** as the predominant species (Scheme 56).



Scheme 55.



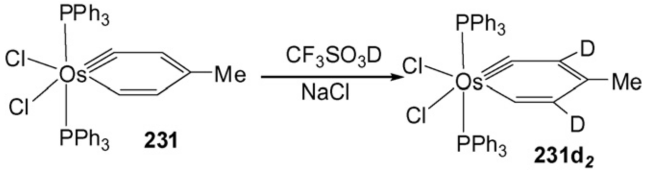
Scheme 56.

As an additional example of electrophilic substitution reactions, complex **231**, in the presence of NaCl, was found to undergo H/D exchange reaction with CF_3SO_3D to give partially deuterated osmabenzyne **231d₂** in which deuterium is only introduced at the 3,5 positions of the metallacycle (Scheme 57) [68]. The deuterated osmabenzyne **231d₂** is also produced from the reaction of **209** with CF_3SO_3D in the presence of NaCl. It appears that the carbons of Os*C* and Os*C*H are not attacked by the acids in the protonation reactions.

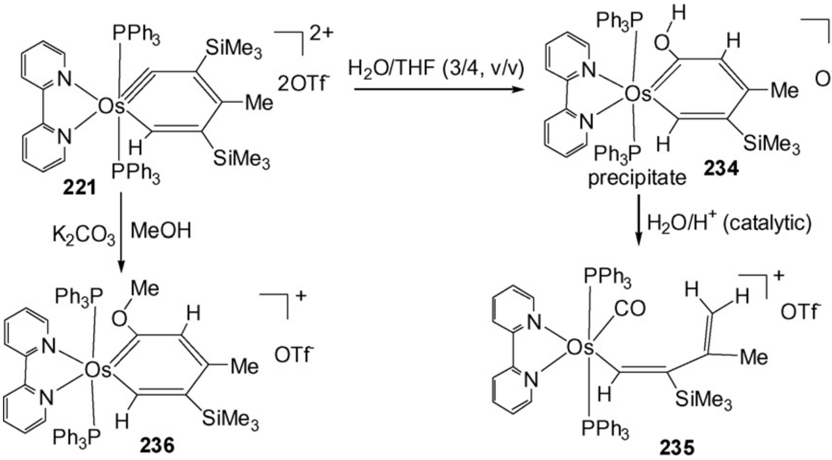
The electrophilic substitution reactions of osmabenzynes with acids and Br_2 at the 3,5-position of the metallacycles are interesting especially when the reactivity of benzynes is considered. Benzynes readily react at the C≡C bond with reagents such as RCO_2H [70], ROH [70], Br_2 [71] and I_2 [71] to give benzene derivatives, rather than electrophilic substitution reactions. Computational studies show that the regio chemistry of the electrophilic substitution reactions of osmabenzynes is related to the electron density distribution of the HOMO of the metallacycles [68].

3.2.3. *Nucleophilic addition reactions*

Complex **221** was found to be quite electrophilic and readily reacts with nucleophiles [67]. Even water can function as



Scheme 57.

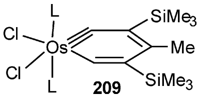
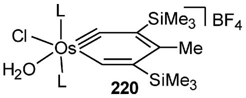
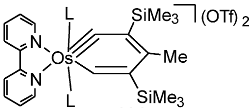
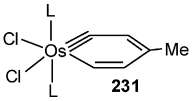
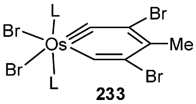
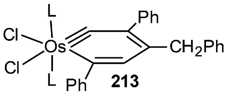
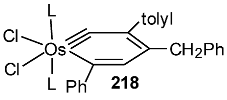
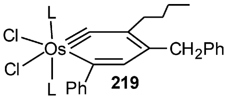


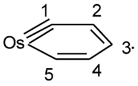
Scheme 58.

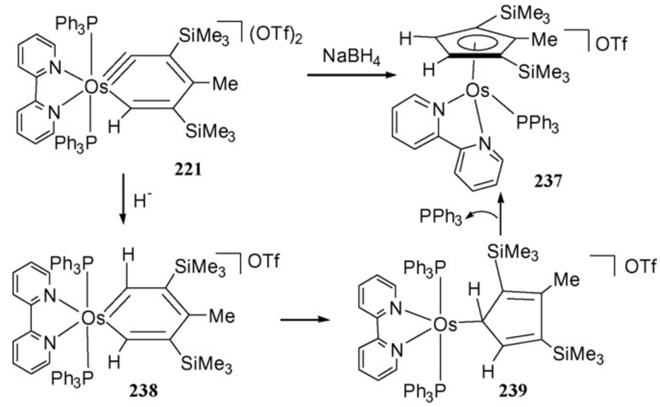
a nucleophile to react with **221** to give the osmabenzene **234** (Scheme 58). The reaction can also produce the vinyl complex **235**, due to acid-catalyzed isomerization of **234**. Complex **221** is also reactive towards methanol. In the presence of K_2CO_3, complex **221** in dichloromethane readily reacts with MeOH to give the osmabenzene **236**. In the absence of K_2CO_3, formation of complex **236** also occurred, although the reaction is much slower and also produces other uncharacterized products.

Treatment of **221** with $NaBH_4$ in THF produced the cyclopentadienyl complex **237** (Scheme 59), rather than an expected

Table 2
Selected bond distances (Å) for osmabenzynes (L = PPh_3)

Compound	Os–C1	Os–C5	C1–C2	C2–C3	C3–C4	C4–C5	Ref.
 **209**	1.815 (4)	1.939 (5)	1.376 (5)	1.420 (5)	1.416 (6)	1.378 (6)	[65]
 **220**	1.756 (5)	2.016 (5)	1.378 (7)	1.424 (8)	1.433 (8)	1.388 (7)	[68]
 **221**	1.780 (3)	2.015 (3)	1.370 (5)	1.419 (5)	1.436 (5)	1.379 (5)	[67]
 **231**	1.805 (7)	2.008 (7)	1.363 (9)	1.413 (9)	1.405 (9)	1.372 (8)	[68]
 **233**	1.766 (3)	2.048 (3)	1.368 (5)	1.391 (5)	1.432 (5)	1.352 (5)	[68]
 **213**	1.726 (10)	2.052 (12)	1.403 (14)	1.366 (15)	1.428 (14)	1.410 (13)	[66]
 **218**	1.766 (5)	2.056 (5)	1.380 (6)	1.393 (7)	1.429 (6)	1.393 (6)	[66]
 **219**	1.757 (4)	2.070 (4)	1.384 (6)	1.388 (6)	1.431 (6)	1.289 (6)	[66]

Labeling scheme: .



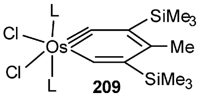
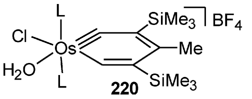
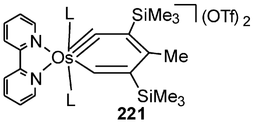
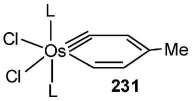
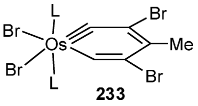
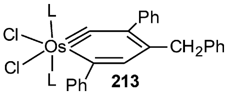
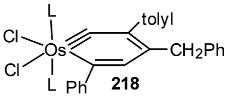
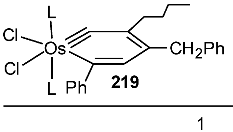
Scheme 59.

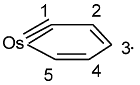
metallabenzene. Mechanistically, complex **237** can be formed by initial attacking of the carbyne carbon of the osmabenzyne **221** by H$^-$ to give intermediate **238**. Intermediate **238** can undergo a reductive elimination reaction to give the η^1-cyclopentadienyl complex **239**, which then rearranges to give **237**. The higher tendency of **239** relative to **234** and **236** in the formation of cyclopentadienyl complexes has been investigated by computational chemistry [67].

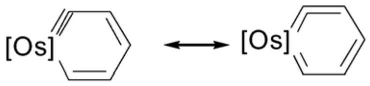
3.3. Structural properties

The structures of eight osmabenzynes have been determined by X-ray diffraction studies. The relevant bond distances and angles of the metallacycles are listed in Tables 2 and 3, respectively. All the complexes contain an essentially planar six-membered metallacycle, as reflected by the sums of internal angles in the six-membered ring (see Table 3), which are very close to the ideal value of 720° required for a planar hexagon. The Os–Cl–C2 angles are in the range of 148.3(6)–154.9(4)°, which are significantly smaller than 180° expected for carbyne complexes. The Os–C5–C4 angles are in the range of 125.3(3)–138.6(5)°, which are slightly larger than the expected angle (120°) around an sp^2-hybridized carbon. The Cl–Os–C5 angles are in the range of 78.1(1)–80.5(2)° The C–C bond distances of the metallacycles are typical of aromatic systems. The Os–Cl bond distances (1.726(5)–1.815 Å) are similar or at the high end of those observed for typical [L$_n$Os≡CR] complexes (see Table 1) and are close or at the low end of those observed for

Table 3
Selected bond angles (°) for osmabenzynes (L = PPh$_3$)

Compound	C5–Os–C1	Os–C1–C2	C1–C2–C3	C2–C3–C4	C3–C4–C5	C4–C5–Os	Sum	Ref.
 209	78.1 (2)	148.7 (3)	112.4 (4)	124.0 (4)	117.7 (4)	138.6 (5)	719.5	[65]
 220	78.2 (2)	153.8 (4)	110.0 (5)	123.5 (5)	120.3 (5)	132.8 (4)	718.6	[68]
 221	76.32 (14)	153.8 (3)	111.1 (3)	122.2 (3)	120.0 (3)	134.7 (3)	718.1	[67]
 231	79.8 (3)	148.3 (6)	114.9 (6)	121.3 (6)	123.5 (6)	132.1 (5)	719.9	[68]
 233	78.95 (14)	150.8 (3)	116.4 (3)	116.8 (3)	128.1 (3)	128.9 (3)	720.0	[68]
 213	79.0 (4)	154.9 (9)	111.4 (10)	120.9 (10)	126.4 (10)	125.8 (8)	718.4	[66]
 218	80.5 (2)	153.4 (4)	111.1 (4)	122.0 (4)	127.1 (5)	125.6 (3)	719.7	[66]
 219	79.78 (7)	154.7 (3)	110.3 (4)	122.3 (4)	127.1 (4)	125.3 (3)	719.5	[66]

Labeling scheme: 



240A **240B**

Scheme 60.

[L_nOs=C=CRR′] complexes (1.786–1.892 Å) [72]. The Os–C5 bond distances (1.939(5)–2.070(4) Å) are within the range of Os–C (vinyl) bonds (1.897–2.195 Å) [72].

The structural data of the six-membered rings together with their planar nature indicate that the osmabenzynes have a delocalized structure. Resonance structures **240A** and **240B** (Scheme 60) can be used to describe the delocalization of the π-electrons in an osmabenzyne ring.

4. Conclusion

The chemistry of osmium carbyne complexes has advanced significantly. Osmium carbyne complexes can be produced in many different ways. For example, carbyne ligands can be generated from ligands such as carbene, vinylidene, allenylidene, and coordinated unsaturated aldehydes, vinylethers; carbyne complexes can also be obtained from the reactions of osmium complexes with alkynes and olefins. Osmium carbyne complexes can be reactive toward nucleophiles and electrophiles, and to a lesser extent, unsaturated substrates. In our opinion, there are still many opportunities to further develop the chemistry of osmium carbyne complexes, especially in the area of reactivity and catalytic properties of osmium carbyne complexes.

Progress in the chemistry of osmabenzynes has been made over the past few years, especially in their synthesis, and their reactions with electrophiles and nucleophiles. The area is relatively new and much remains to be done in the chemistry of metallabenzynes in general. Development of general methods to synthesize metallabenzynes is of critical importance.

Acknowledgements

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