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Coordination Chemistry Reviews 251 (2007) 795–840
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Review

Osmium–carbon double bonds: Formation and reactions

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Received 23 June 2006; accepted 24 July 2006
Available online 27 September 2006

Contents

Abstract

The present review reports on the chemistry of the osmium–carbon double bond, including alkylidene or carbene, vinylidene, and allenylidene derivatives. Within the first type of compounds, we show the synthetic methods and reactivity of half-sandwich derivatives, including cyclopentadienyl and arene complexes, carbene compounds derived from alkynes, α,β-unsaturated carbene species, and osmacyclopropene, hydride–carbene, osmafurane, and osmapyrrole complexes. The vinylidene compounds include: half-sandwich, PCP "pincer", hydride–vinylidene, azavinylidene–vinylidene, and metallaarene derivatives. For their study the allenylidene complexes have been divided into half-sandwich and non-half-sandwich compounds. In addition, the transformation from hydride–carbyne to carbene is analyzed, the preparation of butadienyl compounds via vinylidene intermediates is shown, and the assembly of organic molecules on allenylidene species to form osmacyclopentapyrrole derivatives is described.

Keywords: Osmium; Alkylidene; Carbene; Vinylidene; Allenylidene; Osmacyclopropene; Osmafurane; Osmapyrrole; Azavinylidene; Metallabenzene; Metallabenzyne

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doi:10.1016/j.ccr.2006.07.008

1. Introduction

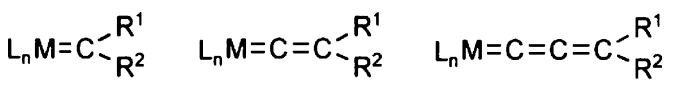
Transition metal complexes containing a metal–carbon double bond are tools of utmost importance in organic chemistry and organometallics, as they represent real catalysts or reaction intermediates for a number of highly valuable processes including carbon–carbon and carbon–heteroatom coupling reactions [1]. Thus, they have attracted much attention from both experimental and theoretical points of view, in particular alkylidene [2], vinylidene [3], and allenylidene [4] (A, B, and C, respectively, in Plate 1) derivatives.

Complexes $L_nM{=}CR^1R^2$ have been traditionally divided into electrophiles and nucleophiles depending upon the nature of the C(sp^2) atom [5]. The first of them are viewed as a singlet-state carbene donating to the metal from its sp^2-hybrid orbital, with a corresponding amount of back-donation from the metal to the empty π-orbital, while the second ones are viewed as a triplet-state carbene spin-coupled to two electrons on the metal center [6]. This classification is in contrast with the fact that there is an increasing number of compounds showing amphiphilic reactivity [7], which includes osmium derivatives.

The reactivity of vinylidene-metal moieties is dominated by the electrophilicity and nucleophilicity of the $M{=}C_\alpha$ and $=C_\beta R^1R^2$ carbon atoms, respectively [8]. As a result, nucleophiles add to C_α. The process may be considered as a counterpart to the coupling of a hydrocarbyl unit with an electrophilic alkylidene. The addition of electrophiles to C_β leads to carbyne derivatives [9].

Allenylidene complexes are generally prepared by following Selegue's protocol involving propargyl alcohols, which are converted into $C{=}C{=}CR^1R^2$ units in the coordination sphere of a transition metal center by elimination of water [10]. Recent studies indicate that these C_3-unsaturated species are an option with a promising future, in both stoichiometric and catalytic processes. Their potentiality can become greater than those of alkylidene and vinylidene derivatives. It stems from the presence in the carbon chain of both electrophilic (C_α and C_γ) and nucleophilic (C_β) sites, which provide unusually versatile reactivities [11].

Osmium, in addition to providing catalysts for carbon–carbon and carbon–heteroatom bond formation [12], affords stable models of reactive intermediates proposed in catalytic transformations with their ruthenium counterparts [13]. Our interest in developing new types of carbon–carbon and carbon–heteroatom coupling reactions [14] has prompted us during the last 10 years to investigate the chemistry of the osmium–carbon double bond. In the following pages, we review the most relevant aspects of this chemistry from our point of view.



(A) (B) (C)

Plate 1.

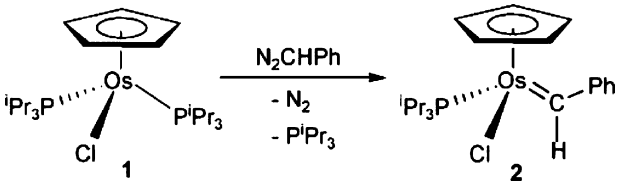
2. Os=CR_2 complexes

2.1. Half-sandwich derivatives

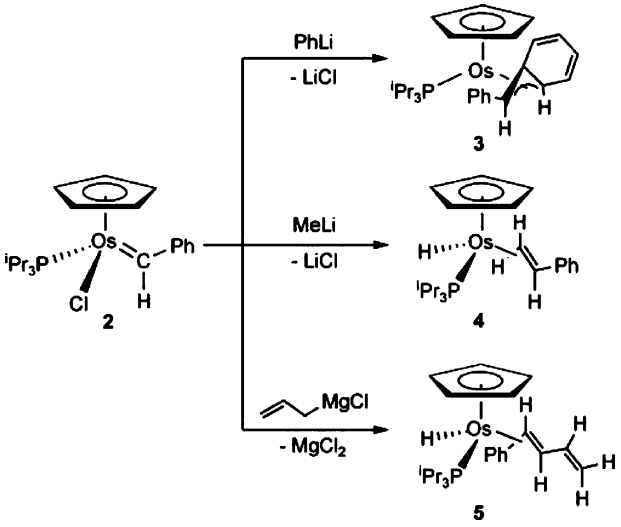
In spite of the inertness of the octahedral osmium(II) complexes, one of the phosphine ligands of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (**1**) can be easily replaced by carbene ligands. Treatment of a toluene solution of **1** with a toluene solution of phenyldiazomethane, at room temperature, results in the formation of the carbene derivative $Os(\eta^5\text{-}C_5H_5)Cl(=CHPh)(P^iPr_3)$ (**2**), according to Scheme 1 [15].

The carbene carbon atom of **2** shows a marked electrophilicity. Thus, it reacts with main-group organometallic compounds to afford carbene plus organic fragment coupling processes (Scheme 2). The addition at 0 °C of a cyclohexane/diethyl ether solution of phenyllithium to a stoichiometric amount of **2** in tetrahydrofuran gives the α-phenyl-η^3-benzyl complex $Os(\eta^5\text{-}C_5H_5)(\eta^3\text{-}CHPhC_6H_5)(P^iPr_3)$ (**3**). At the same temperature, treatment of a tetrahydrofuran solution of **2** with a stoichiometric amount of methyllithium in diethyl ether affords the hydride styrene $OsH(\eta^5\text{-}C_5H_5)(\eta^2\text{-}CH_2{=}CHPh)(P^iPr_3)$ (**4**), whereas the reaction of **2** with allylmagnesium chloride in tetrahydrofuran gives the hydride η^2-phenylbutadiene compound $OsH(\eta^5\text{-}C_5H_5)\{\eta^2\text{-}(E)\text{-}CHPh{=}CHCH{=}CH_2\}(P^iPr_3)$ (**5**).

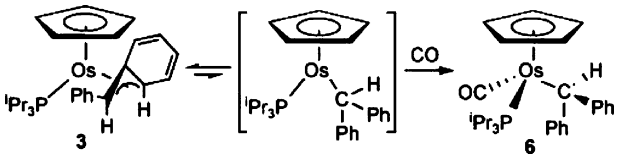
In solution the phenyl groups of **3** exchange their positions. The process takes place via an unsaturated η^1-diphenylmethyl intermediate, which is trapped when a dichloromethane solution of **3** is stirred at room temperature under 1 atm of



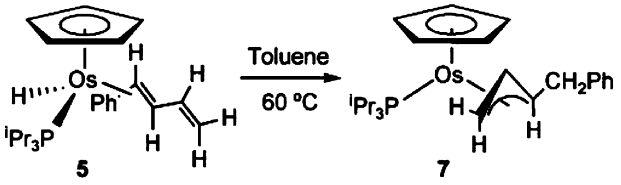
Scheme 1.



Scheme 2.



Scheme 3.

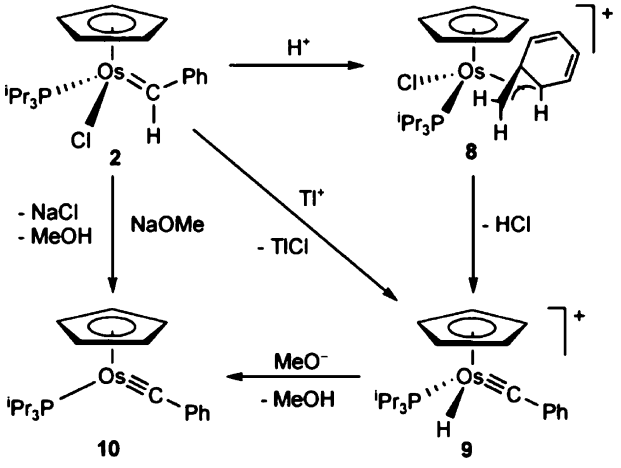


Scheme 4.

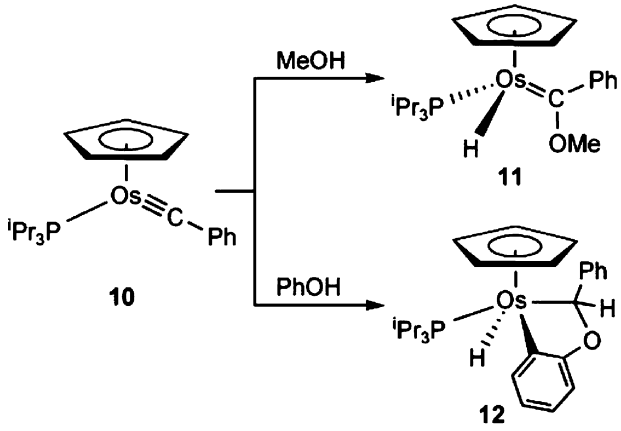
carbon monoxide. Under these conditions, complex Os(η^5-C_5H_5)($CHPh_2$)(CO)(P^iPr_3) (**6**) is formed (Scheme 3).

In solution, at room temperature, the styrene ligand of **4** rotates around the osmium olefin axis. Under the same conditions, the osmium–olefin bond of **5** is rigid. Attempts to force the rotation of the diene led to the formation of the allyl derivative Os(η^5-C_5H_5)(η^3-$CH_2CHCHCH_2Ph$)(P^iPr_3) (**7**) as a result of the migratory insertion of the styryl unit into the Os–H bond (Scheme 4).

Although the reactions shown in Scheme 2 prove the electrophilicity of the carbene carbon atom of **2**, it must be pointed out that this atom also undergoes attack by electrophiles (Scheme 5). Initially, the protonation of the carbene carbon atom of **2** affords [Os(η^5-C_5H_5)(η^3-$CH_2C_6H_5$)Cl(P^iPr_3)]$^+$ (**8**), which eliminates HCl to give [OsH(η^5-C_5H_5)(≡CPh)(P^iPr_3)]$^+$ (**9**). The PF_6 salt of the latter can be obtained by treatment of an acetone solution of **2** with a stoichiometric amount of $TlPF_6$. Reaction of a tetrahydrofuran solution of **2** with sodium methoxide results in the deprotonation of the carbene carbon atom and the formation of the neutral carbyne derivative Os(η^5-C_5H_5)(≡CPh)(P^iPr_3) (**10**). Complex **10** also can be prepared by addition of sodium methoxide to a tetrahydrofuran solution of the cationic hydride carbyne **9**.



Scheme 5.



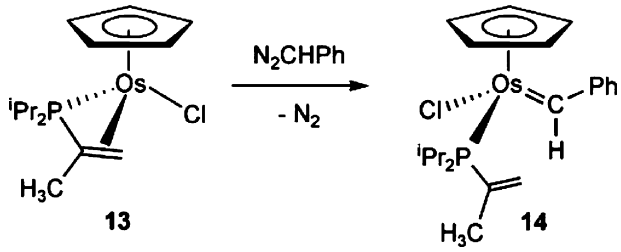
Scheme 6.

In methanol at room temperature, complex **10** is converted into the hydride alkoxycarbene derivative OsH(η^5-C_5H_5){=C(OMe)Ph}(P^iPr_3) (**11**) as a consequence of the addition of the O–H bond of the alcohol to the Os–C triple bond (Scheme 6). The reaction of **10** with phenol gives OsH(η^5-C_5H_5){CH(Ph)OC_6H_4}(P^iPr_3) (**12**).

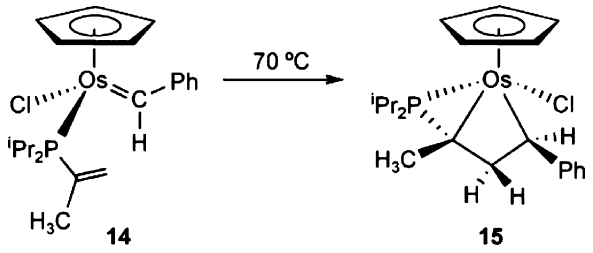
The formation of **12** can be rationalized as a process involving the initial addition of the O–H bond of phenol to the Os–C triple bond of **10**, to give a hydride alkoxycarbene intermediate similar to that isolated from the reaction with methanol. The subsequent migration of the hydride ligand from the metal center to the C_α atom of the carbene should afford an unsaturated species, which could be converted to **12** by C–H activation of one of the *ortho* bonds of the OPh group.

An olefin–alkylidene complex related to **2** has been recently reported [16]. In agreement with the hemilabile character of the α-alkenylphosphine of Os(η^5-C_5H_5)Cl{[η^2-CH_2=$C(CH_3)$]P^iPr_2} (**13**) [17], treatment at room temperature of a toluene solution of this compound with phenyldiazomethane in toluene gives Os(η^5-C_5H_5)Cl(=CHPh){P^iPr_2[$C(CH_3)$=CH_2]} (**14**), according to Scheme 7.

In toluene complex **14** is converted to the osmaphosphabicyclopentane derivative Os(η^5-C_5H_5)Cl{[CH(Ph)$CH_2$$C(CH_3)$]$P^iPr_2$} (**15**). The exclusive formation of the diastereomer shown in Scheme 8 proves that the reaction is diastereoselective and involves a [2 + 2] cycloaddition process between the C–C double bond of the phosphine and the Os–C double bond in the rotamer of **14** containing the phenyl group directed towards the cyclopentadienyl ligand [16].



Scheme 7.

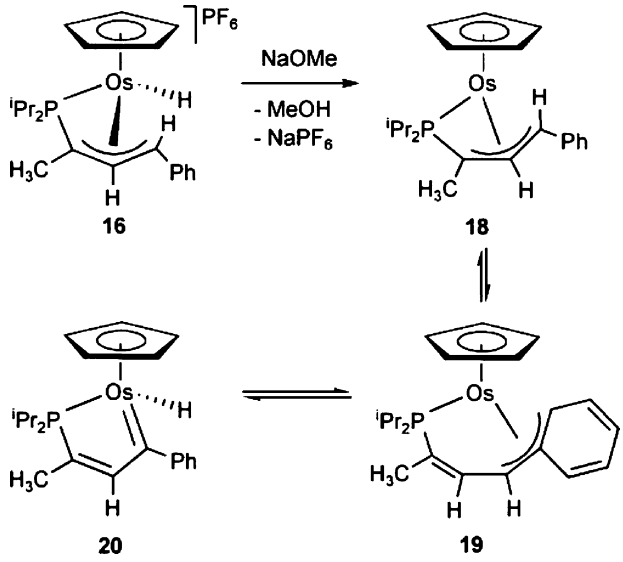


Scheme 8.

The abstraction of the chloride ligand from **15** provokes the destruction of the bicycle (Scheme 9). At room temperature, treatment of an acetone solution of **15** with $TlPF_6$ gives a 1:1 mixture of the α-allylphosphine complex $[OsH(\eta^5\text{-}C_5H_5)\{[\eta^3\text{-}CH(Ph)CHC(CH_3)]P^iPr_2\}]PF_6$ (**16**) and its α-alkenyl-γ-(η^3-benzyl)phosphine isomer $[OsH(\eta^5\text{-}C_5H_5)\{[\eta^3\text{-}C_6H_5CHCH{=}C(CH_3)]P^iPr_2\}]PF_6$ (**17**). The transformation initially affords the hydride η^1-allylphosphine intermediate $[OsH(\eta^5\text{-}C_5H_5)\{[CH(Ph)CH{=}C(CH_3)]P^iPr_2\}]PF_6$, as a result of the Os–$C(CH_3)$P bond cleavage and a β-hydrogen elimination reaction in the CH_2 group of the bicycle.

The hydride ligand of **16** is fairly acidic. Its deprotonation results in an equilibrium mixture of the neutral osmium(II) α-allylphosphine $Os(\eta^5\text{-}C_5H_5)\{[\eta^3\text{-}CH(Ph)CHC(CH_3)]P^iPr_2\}$ (**18**), α-alkenyl-γ-(η^3-benzyl)phosphine $Os(\eta^5\text{-}C_5H_5)\{[\eta^3\text{-}C_6H_5CHCH{=}C(CH_3)]P^iPr_2\}$ (**19**), and α-alkenyl-γ-carbenephosphine $OsH(\eta^5\text{-}C_5H_5)\{[{=}C(Ph)CH{=}C(CH_3)]P^iPr_2\}$ (**20**) isomers (Scheme 10).

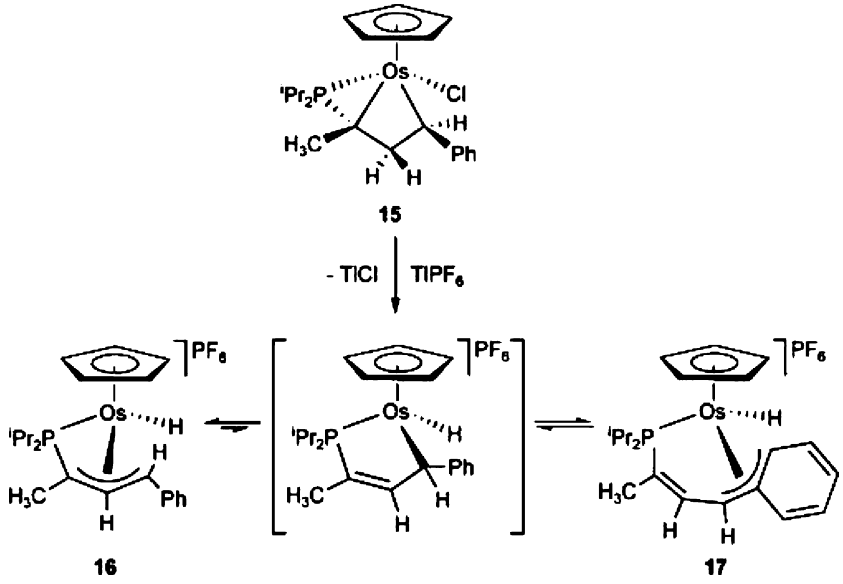
The abstraction of the chloride ligand from **14** provokes the migration of the hydrogen atom of the carbene from the carbon atom to the metal center. As a result, the hydride carbyne derivative $[OsH(\eta^5\text{-}C_5H_5)(\equiv CPh)\{P^iPr_2[C(CH_3){=}CH_2]\}]PF_6$ (**21**) is formed (Scheme 11). In acetone, complex **21** selectively evolves to **16**. According to a kinetic study of the transformation, the isomerization process, that has been rationalized as an intramolecular [2 + 2] cycloaddition, leads to the short-lived intermediate $[OsH(\eta^5\text{-}C_5H_5)\{[{=}C(Ph)CH_2C(CH_3)]P^iPr_2\}]PF_6$, which rapidly affords **16**, by a 1,2-hydrogen shift from the CH_2 group to the $C_\alpha(sp^2)$ atom of the bicycle.



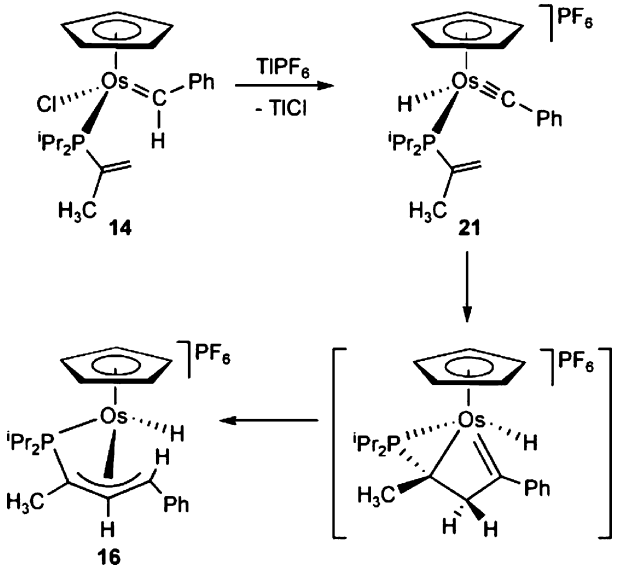
Scheme 10.

The hydride ligand of **21**, as that of **9**, is fairly acidic. Thus, similarly to the latter, the addition of 2.0 equiv of sodium methoxide to a tetrahydrofuran solution of **21** results in its deprotonation, to afford the neutral carbyne derivative $Os(\eta^5\text{-}C_5H_5)(\equiv CPh)\{P^iPr_2[C(CH_3){=}CH_2]\}$ (**22**). In methanol at room temperature, complex **22** is changed to the hydride alkoxycarbene derivative $OsH(\eta^5\text{-}C_5H_5)\{{=}C(OMe)Ph\}\{P^iPr_2[C(CH_3){=}CH_2]\}$ (**23**), as a consequence of the addition of the O–H bond of the alcohol to the Os–C triple bond (Scheme 12).

The carbene carbon atom of **14** has amphiphilic character, as does that of **2**, reacting with both nucleophiles and electrophiles. However, between **14** and **2** there are marked differences in the



Scheme 9.

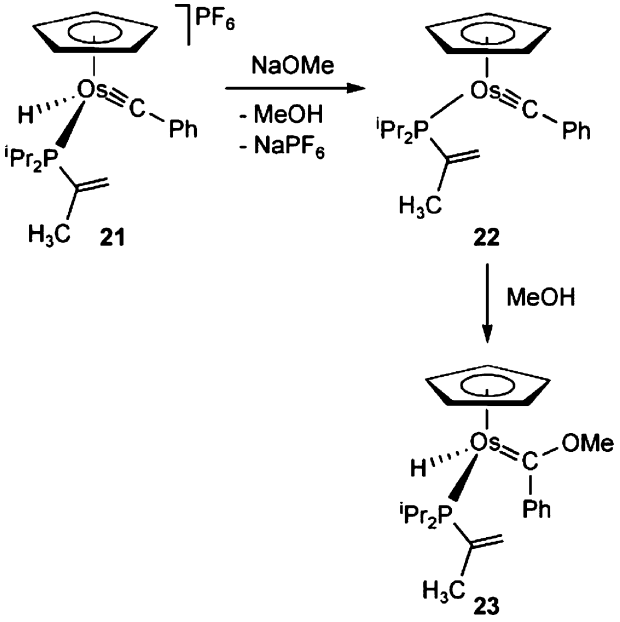


Scheme 11.

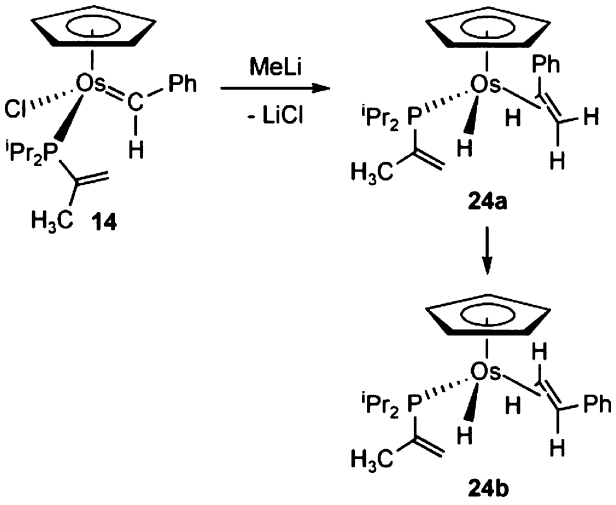
nature of the products resulting from the H^+ addition, which depend on the substituents of the phosphine. The differences are related to the stronger coordinating power of an isopropenyl group with regard to an isopropyl substituent.

Treatment at 0 °C of a tetrahydrofuran solution of **14** with a stoichiometric amount of methyllithium affords the hydride styrene derivative $OsH(\eta^5\text{-}C_5H_5)(\eta^2\text{-}CH_2{=}CHPh)\{P^iPr_2[C(CH_3){=}CH_2]\}$ (**24a**) containing the phenyl group of the styrene ligand *cisoid-anti* with regard to the phosphorous atom of the phosphine. In benzene at 80 °C complex **24a** isomerizes to **24b**, with the phenyl group *cisoid-anti* with regard to the hydride (Scheme 13).

The carbene carbon atom of **14**, like that of **2**, also shows a marked nucleophilicity. At −40 °C, the addition of 1.0 equiv of



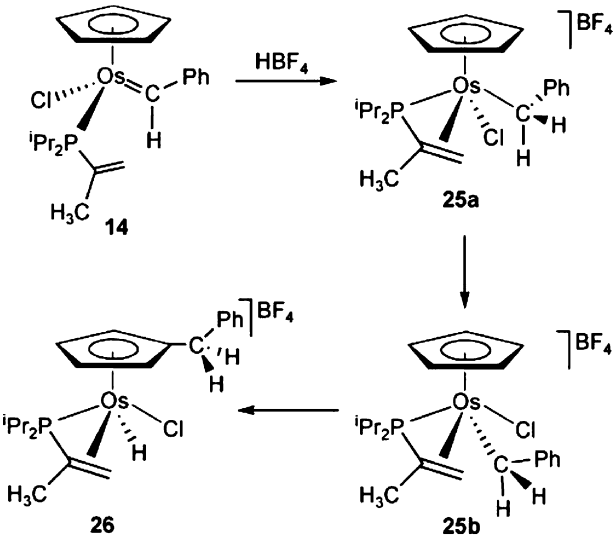
Scheme 12.



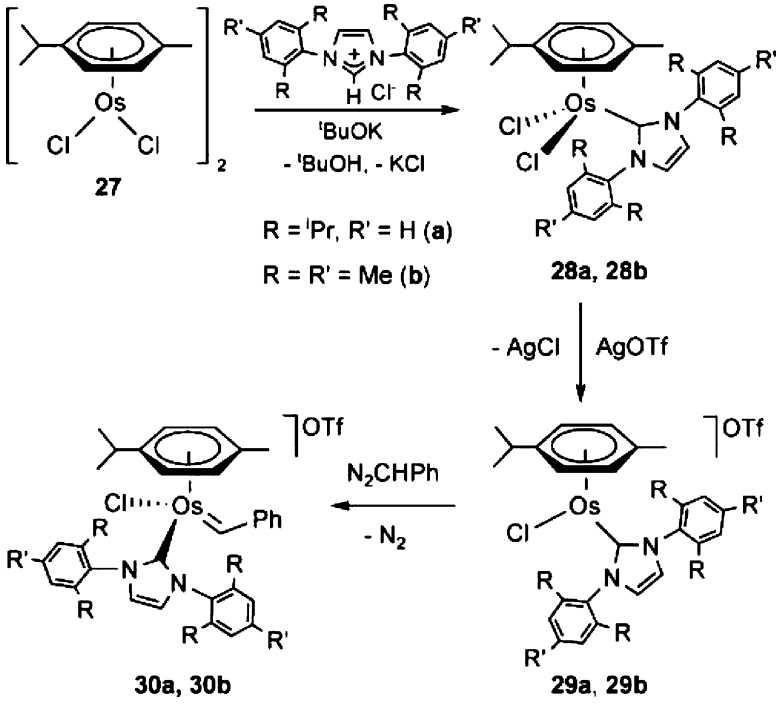
Scheme 13.

HBF_4 to a dichloromethane solution of **14** results in the instantaneous formation of the benzyl-osmium(IV) complex $[Os(\eta^5\text{-}C_5H_5)(CH_2Ph)Cl\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}]BF_4$ (**25a**), as a result of the addition of the proton of the acid to the C_α atom of the carbene ligand, and the coordination of the isopropenyl substituent of the phosphine to the osmium atom (Scheme 14). At room temperature, complex **25a** rapidly isomerizes into **25b**. The benzyl group of the latter and one of the hydrogen atoms of the cyclopentadienyl ring slowly exchange their positions, resulting in a second isomerization to afford $[OsH(\eta^5\text{-}C_5H_4CH_2Ph)Cl\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}]BF_4$ (**26**).

Arene alkylidene–osmium complexes stabilized by an N-heterocyclic carbene (NHC) ligand have been prepared according to Scheme 15 [12g]. The dimer complex $[(\eta^6\text{-}p\text{-cymene})OsCl_2]_2$ (**27**) reacts with 1,3-bis(2,6-diisopropylphenyl)imidazolylidene (IPr) and 1,3-bis(2,4,6-trimethylphenyl)imidazolylidene (IMes) to afford the mononuclear derivatives $(\eta^6\text{-}p\text{-cymene})OsCl_2(NHC)$ (NHC=IPr_2 (**28a**), IMes (**28b**)) in high yield. Treatment of **28a**,**b** with 1.0 equiv



Scheme 14.



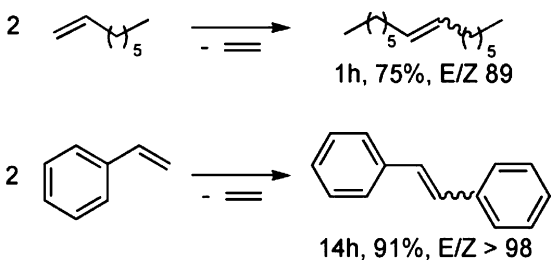
Scheme 15.

of silver trifluoromethanesulfonate (AgOTf) leads to the 16-electron derivatives [(η^6-*p*-cymene)OsCl(NHC)]OTf (**29a**,**b**). The coordination vacancy in these compounds is rapidly occupied by phenylmethylene. The addition at −20 °C of 1.6 equiv of N_2CHPh in toluene to dichloromethane solutions of **29a**,**b** gives the alkylidene derivatives [(η^6-*p*-cymene)OsCl(=CHPh)(NHC)]OTf (**30a**,**b**).

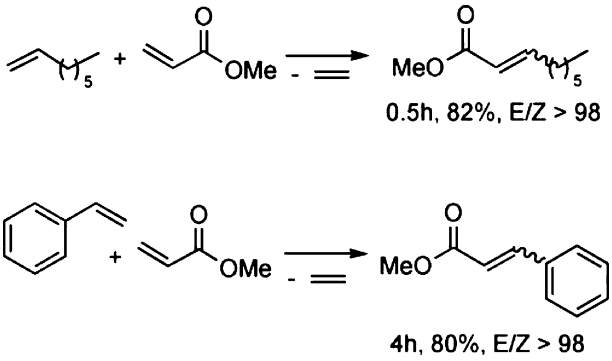
Complexes **30a**,**b** are efficient catalysts precursors for the homometathesis of 1-octene and styrene (Scheme 16), while their activities for the homometathesis of methylacrylate are poor. In agreement with this behavior [18], 1-octene and styrene undergo CM reaction with methylacrylate (Scheme 17) to afford selectively the corresponding cross products in high yield and extremely high stereoselectivities [12g].

Complexes **30a**,**b** are also active catalyst precursors for the RCM of 2,2-diallyl-malonic acid diethyl ester and for the ROMP of cyclooctene (Scheme 18). In 1,2-dichloroethane at 60 °C, and in the presence of 0.1% of metal complex, polyoctenamer with about 30% *cis* content is obtained after 20 h in 99% yield.

It should be mentioned that although the diarylcarbene complexes [(η^6-mes)OsCl(=CR_2)(PPh_3)]PF_6 (R = Ph (**31a**), *p*-Tol (**31b**)) have been isolated [19], all attempts to obtain phosphine

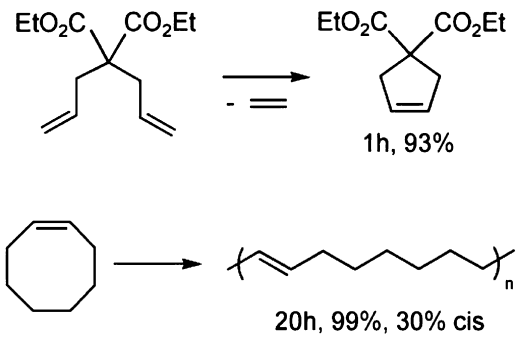


Scheme 16.

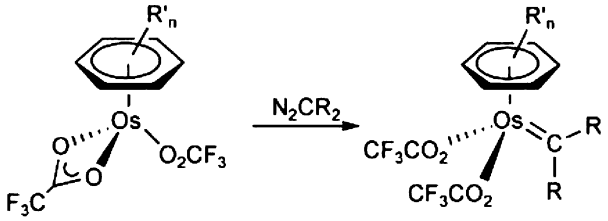


Scheme 17.

complexes related to **30a**,**b** with a hydrogen at the carbene carbon atom have failed until now [20]. Complexes **31a**,**b** have been prepared by reaction of (η^6-mes)$OsCl_2$(=CR_2) (R = Ph (**32a**), *p*-Tol (**32b**)) with $AgPF_6$ in the presence of PPh_3. The successful methodology to obtain **32a**,**b** and related compounds is outlined



Scheme 18.



	Arene
33	1-Me-4-^{i}PrC$_6$H$_4$ (*p*-cym)
34	1,3,5-C$_6$H$_3$Me$_3$ (mes)

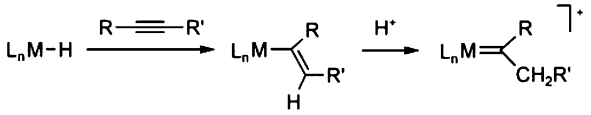
	Arene	R
35a	*p*-cym	Ph
35b	*p*-cym	*p*-Tol
36a	mes	Ph
36b	mes	*p*-Tol
36c	mes	*p*-C$_6$H$_4$Cl
36d	mes	*p*-C$_6$H$_4$OMe

	Arene	R	X
32a	mes	Ph	Cl
32b	mes	*p*-Tol	Cl
32c	mes	*p*-C$_6$H$_4$OMe	Cl
37a-c	*p*-cym	Ph	Cl/Br/I
37d-f	*p*-cym	*p*-Tol	Cl/Br/I

Scheme 19.

in Scheme 19. The bis(trifluoroacetate) compounds **33** and **34** react with diazoalkanes to give **35a**,**b** and **36a–d**. Treatment of **35a**,**b** and **36a–d** with either Me_3SiX or NH_4X (X = Cl, Br, I) leads to a ligand exchange and results in the formation of the dichloro, dibromo and diiodo counterparts **37a–f** and **32a–c**.

The carbene carbon atom of **36a** shows a marked electrophilicity. Thus, it reacts with CH_2=CHMgBr at low temperature to give the allyl derivative (η^6-mes)Os(η^3-CH_2CHCPh_2)Br (**38**). In the presence of trifluoacetic acid the latter affords Ph_2C=$CHCH_3$ and (η^6-mes)OsBr(κ^2-O_2CCF_3). Other carbon–carbon coupling reaction involving the CPh_2 ligand occurs upon treatment of **36a** with ethyl vinyl ether and Na_2CO_3 (Scheme 20). To explain the formation of (η^6-mes)Os(CPh_2CH=$CHOEt$)\{κ^1-OC(O)CF_3\} (**39**), it has been proposed that in the initial step a displacement of one carboxylate ligand by CH_2=CHOEt takes place, which is followed by abstraction of a proton from the less electron-rich part of the bonded olefin with Na_2CO_3. The so-formed vinylic unit could then undergo an intramolecular C–C coupling with the CPh_2 group, similar to what probably occurs during the formation of **38**. Treatment of **39** with trifluoroacetic acid leads to protolytic cleavage of the Os–C bond and to the formation of both the allyl ether Ph_2C=$CHCH_2OEt$ and the bis(trifluoroacetate) complex **34**.

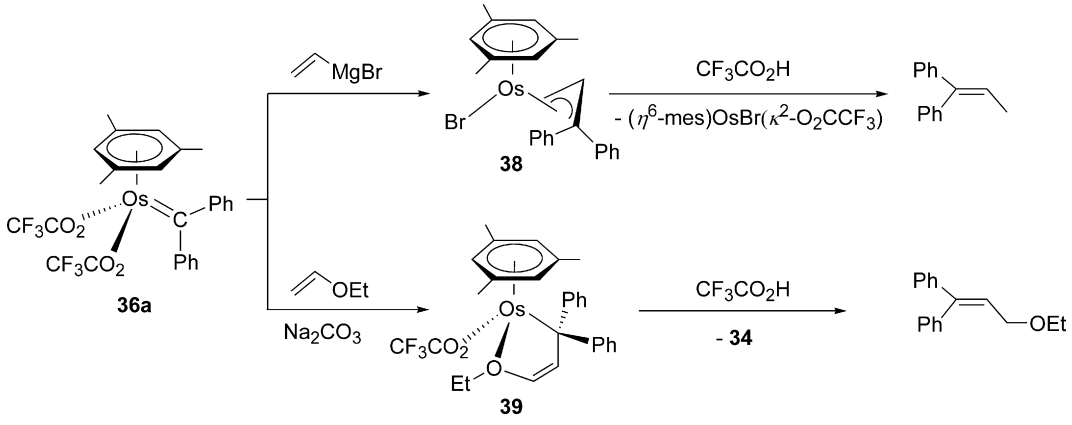


Scheme 21.

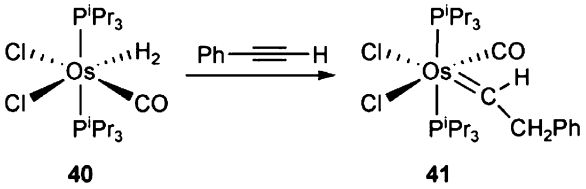
2.2. Carbene compounds derived from alkynes

Electronic structures and reactivities of organic fragments change, often dramatically, when they coordinate to late transition metals to form organometallic compounds. Coordination of [RCH=CH]$^-$ to a metal center transfers the nucleophilicity from C_α to C_β. Thus, the addition of electrophiles to the electron-rich C_β of metal alkenyl derivatives has been described on many occasions as a useful entry to alkylidene complexes [21]. Since one of the most typical reactions of transition metal hydride complexes is the insertion of alkynes into the M–H bond to form alkenyl derivatives, the addition of alkynes to hydride complexes followed by the protonation of the C_β atom of the resulting alkenyl species (Scheme 21) has been a used method to prepare osmium–alkylidene derivatives.

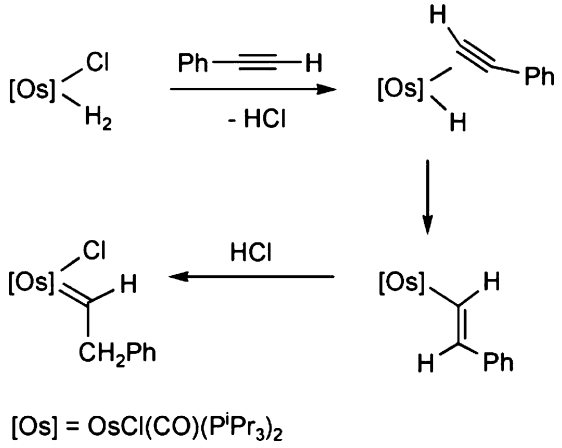
The process shown in Scheme 21 has been performed as a one-pot synthesis by using the elongated dihydrogen complex $OsCl_2(\eta^2$-$H_2)(CO)(P^iPr_3)_2$ (**40**) [22]. Thus, the addition of phenylacetylene to **40** directly gives $OsCl_2$(=$CHCH_2Ph$)$(CO)(P^iPr_3)_2$ (**41**), according to Scheme 22.



Scheme 20.



Scheme 22.



Scheme 23.

The formation of **41** goes by elimination of HCl from **40** to afford initially a six-coordinate hydride π-alkyne intermediate, which evolves to the insertion product. Subsequently, the styryl complex undergoes the electrophilic attack of the HCl proton at the C_β atom to give a cationic alkylidene species, followed by the coordination of the chloride anion to the metallic center (Scheme 23). In favor of this proposal, it has been observed not only that the elongated dihydrogen ligand of **40** is activated towards heterolytic cleavage but also that the styryl complex Os{(*E*)-CH=CHPh}Cl(CO)(P^{i}Pr$_3$)$_2$ (**42**) [23] reacts with HCl to give **41**. Similarly to **42**, in chloroform the carboxylate complex Os{(*E*)-CH=CHPh}(κ^2-O_2CCH_3)(CO)(P^{i}Pr$_3$)$_2$ (**43**) affords [Os(κ^2-O_2CCH_3)(=CHCH$_2$Ph)(CO)(P^{i}Pr$_3$)$_2$]BF$_4$ (**44**) by addition of HBF$_4$·OEt$_2$ [24].

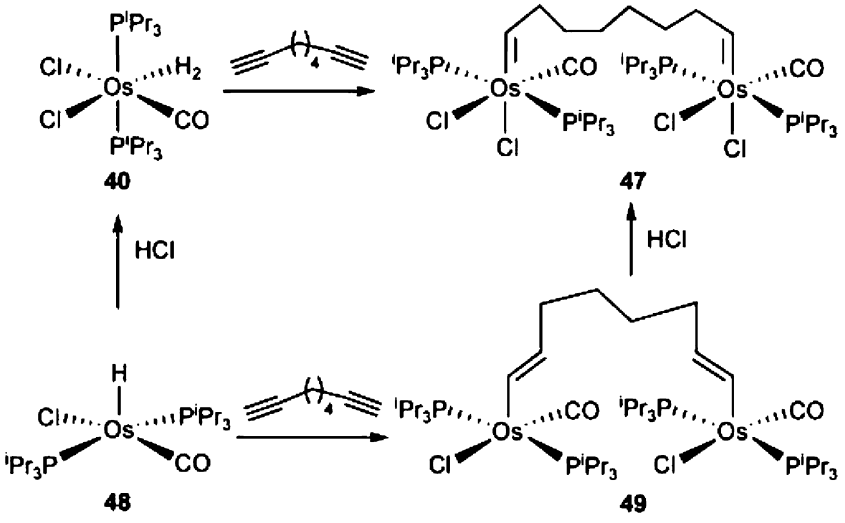
Reaction of **41** with excess carbon monoxide leads to HCl elimination to form Os{(*E*)-CH=CHPh}Cl(CO)$_2$(P^{i}Pr$_3$)$_2$ (**45**), which reacts with the liberated HCl at the C_α atom to yield styrene and OsCl$_2$(CO)$_2$(P^{i}Pr$_3$)$_2$ [25]. The behavior of **45** towards HCl is like that of the ruthenium–methyl complex Ru(CH$_3$){(*E*)-CH=CHPh}(CO)$_2$(P^{i}Pr$_3$)$_2$ towards HBF$_4$, which yields styrene and the five-coordinated cation [Ru(CH$_3$)(CO)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ [26]. Abstraction of chloride from **41** with NaBAr′$_4$ (Ar′ = 3,5-C$_6$H$_3$(CF$_3$)$_2$) gives the unsaturated alkylidene [OsCl(=CHCH$_2$Ph)(CO)(P^{i}Pr$_3$)$_2$]BAr′$_4$(**46**) [25].

The elongated dihydrogen complex **40** also reacts with 1,7-octadiyne in a 2:1 molar ratio. The reaction leads to the dinuclear compound (P^{i}Pr$_3$)$_2$(CO)Cl$_2$Os{=CH(CH$_2$)$_6$-HC=}OsCl$_2$(CO)(P^{i}Pr$_3$)$_2$ (**47**), which has been obtained from the well-known complex OsHCl(CO)(P^{i}Pr$_3$)$_2$ (**48**) [27,13c] via the μ-bis alkenyl intermediate (P^{i}Pr$_3$)$_2$(CO)ClOs{(*E*)-CH=CH(CH$_2$)$_4$CH=CH-(*E*)}OsCl(CO)(P^{i}Pr$_3$)$_2$ (**49**), according to Scheme 24.

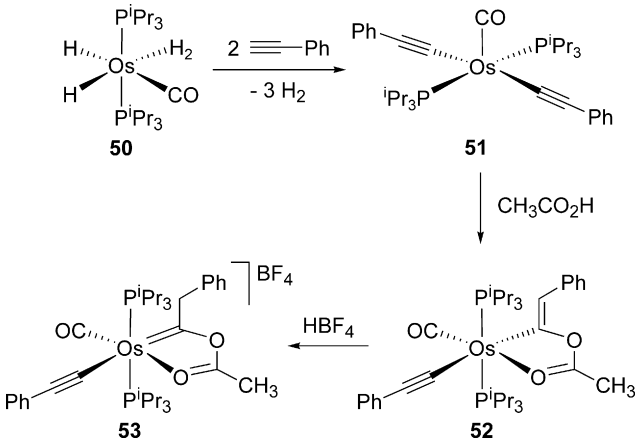
In contrast to **40**, the related dihydride–dihydrogen complex OsH$_2$(η^2-H$_2$)(CO)(P^{i}Pr$_3$)$_2$ (**50**) reacts with phenylacetylene to give the bis-alkynyl derivative Os(C≡CPh)$_2$(CO)(P^{i}Pr$_3$)$_2$ (**51**) [28]. Treatment of **51** with a stoichiometric amount of acetic acid in methanol leads to the alkynyl–alkenyl ester compound Os(C≡CPh){C(=CHPh)OC(O)CH$_3$}(CO)(P^{i}Pr$_3$)$_2$ (**52**), as a result of the addition of the acid to the carbon–carbon triple bond of one of the two alkynyl ligands of **51** (Scheme 25). Complex **52** reacts with HBF$_4$·OEt$_2$ in diethyl ether to give the alkynyl-carbene derivative [Os(C≡CPh){=C(CH$_2$Ph)OC(O)CH$_3$}(CO)(P^{i}Pr$_3$)$_2$]BF$_4$ (**53**). The formation of **53** indicates that the C_β atom of the vinyl ester ligand has a stronger nucleophilic character than the C_β atom of the alkynyl group [29].

2.3. α,β-Unsaturated carbene complexes

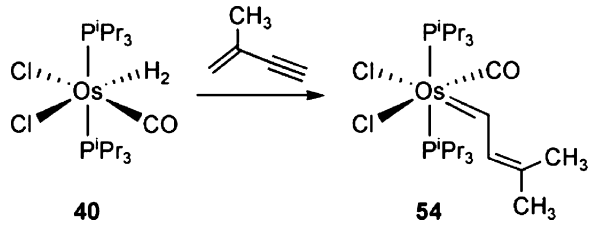
The elongated dihydrogen complex **40** also reacts with 2-methyl-1-buten-3-yne. In toluene at room temperature, the reaction affords the alkenylcarbene derivative



Scheme 24.



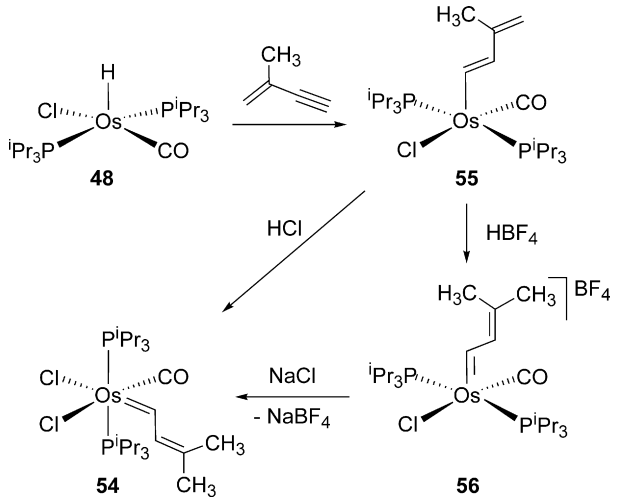
Scheme 25.



Scheme 26.

$OsCl_2\{=CHCH=C(CH_3)_2\}(CO)(P^iPr_3)_2$ (**54**), according to Scheme 26 [22].

Complex **54** can be also prepared via the reaction sequence shown in Scheme 27. The five-coordinate monohydride **48** reacts with 2-methyl-1-buten-3-yne to give the dienyl derivative $Os\{(E)\text{-}CH=CHC(CH_3)=CH_2\}Cl(CO)(P^iPr_3)_2$ (**55**), which is the result of the selective insertion of the C≡C bond of the enyne into the Os–H bond of the starting complex. A behavior similar to **48** has been observed for $RuHCl(CO)(P^iPr_3)_2$ [30] and $RhH(SnPh_3)(acac)(PCy_3)$ [31]. In a similar fashion to the reactions of **42** and **49** with HCl, the reaction of **55** with the stoichiometric amount of a toluene HCl solution affords **54**. X-ray and reactivity studies on dienyl complexes indicate



Scheme 27.

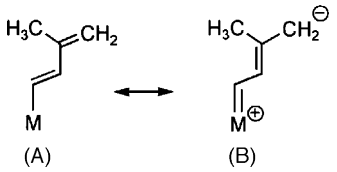


Plate 2.

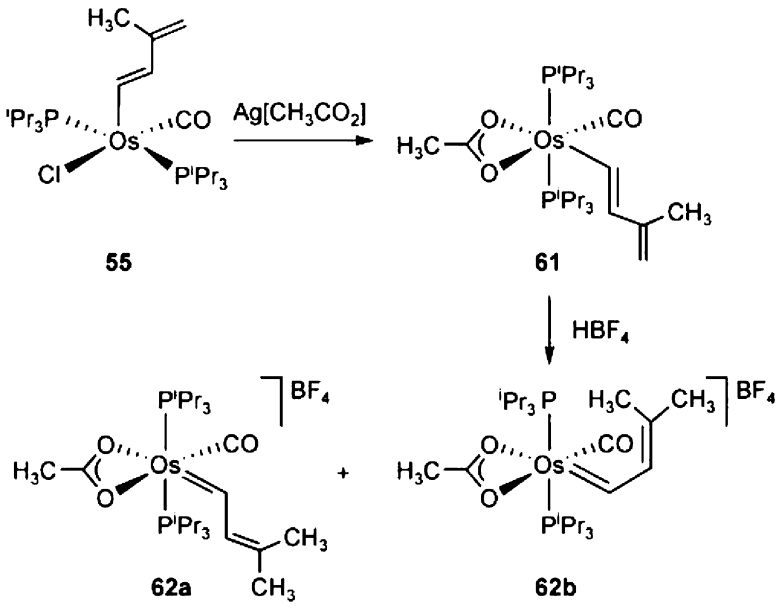
that for an adequate description of the bonding situation in this type of compounds a second zwitterionic resonance (**B** in Plate 2) must be considered [30,32]. Thus, the formation of **54** from **55** has been rationalized as the electrophilic attack of a proton at the C_δ atom of the dienyl ligand to afford an unsaturated alkenylcarbene intermediate, followed by the coordination of a chloride anion. In agreement with these two step processes, it has been observed that the addition of a stoichiometric amount of $HBF_4{\cdot}OEt_2$ to a diethyl ether solution of **55** gives $[OsCl\{=CHCH=C(CH_3)_2\}Cl(CO)(P^iPr_3)_2]BF_4$ (**56**), and that the treatment of the latter with NaCl in methanol affords **54** [22].

Alkynols are also useful organic fragments to prepare α,β-unsaturated carbene compounds related to **54**. Thus, complexes $OsCl_2(=CHCH=CRPh)(CO)(P^iPr_3)_2$ (R = H (**57**), Ph (**58**)) have been separated in 41% (**57**) and 34% (**58**) yield, and characterized by X-ray diffraction analysis, from the mixtures resulting of the addition of 1-phenyl-2-propyn-1-ol and 1,1-diphenyl-2-propyn-1-ol to **48**. The formation of these compounds has been rationalized as the dehydroxylation of the hydroxyalkenyl ligand of $Os\{CH=CHC(OH)RPh\}Cl(CO)(P^iPr_3)_2$ intermediates by action of HCl, which is generated in the reaction media [33]. In agreement with this, Hill and Welton [34] have reported that the reaction of the triphenylphosphine complex $OsHCl(CO)(PPh_3)_3$ (**59**) with 1,1-diphenyl-2-propyn-1-ol and Cl_2PPh_3 gives $OsCl_2(=CHCH=CRPh)(CO)(PPh_3)_2$ (**60**).

The five-coordinate (*E*)-dienyl complex **55** reacts with $Ag[CH_3CO_2]$ in toluene to give $Os\{(E)\text{-}CH=CHC(CH_3)=CH_2\}(\kappa^2\text{-}O_2CCH_3)(CO)(P^iPr_3)_2$ (**61**). The protonation of **61** with $HBF_4{\cdot}OEt_2$ affords $[Os\{=CHCH=C(CH_3)_2\}(\kappa^2\text{-}O_2CCH_3)(CO)(P^iPr_3)_2]BF_4$ (**62**), which is isolated as a mixture of the isomers **a** and **b** shown in Scheme 28 [35].

The *cis*-dicarbonyl (*Z*)-dienyl $Os\{(Z)\text{-}CH=CHC(CH_3)=CH_2\}\{\kappa^1\text{-}OC(O)CH_3\}(CO)_2(P^iPr_3)_2$ (**63**) is also known. In contrast to **61**, the protonation of **63** leads to isoprene and the *cis*-dicarbonyl compound $[Os(\kappa^2\text{-}O_2CCH_3)(CO)_2(P^iPr_3)_2]BF_4$ (**64**). The main difference between **61** and **63** is the presence of a carbonyl group, *trans* disposed to the dienyl ligand, in the latter. So, the difference in behavior between **61** and **63** elegantly proves that, in these systems, the presence of a carbonyl group *trans* disposed to the dienyl ligand reduces its nucleophilicity [13c].

An interesting osmahexatriene complex having the terminal alkene double bond coordinated to the metal center has been prepared from a metallacyclopentatriene (Scheme 29) [36]. When a solution of complex $[Os(C_4Me_4)(en)_2](OTf)_2$ (**65**; en: ethylenediamine) in neat $^tBuNH_2$ is heated under N_2 at 39 °C for 24 h, a base catalyzed 1,2-hydrogen shift within one of the two carbene moieties takes place. As a result com-

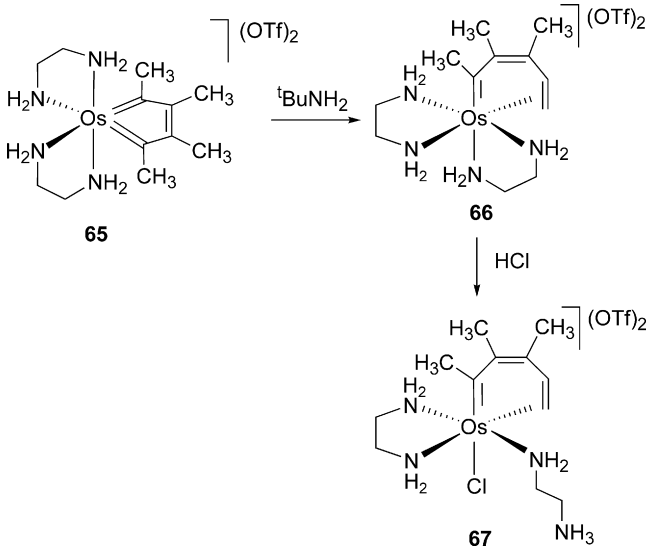


Scheme 28.

plex [Os{=C(CH3)C(CH3)=C(CH3)CH=CH2}(en)2](OTf)2 (**66**) is obtained in about 79% yield. On treatment of **66** with HCl for 12 h, the derivative [OsCl{=C(CH3)C(CH3)=C(CH3)CH=CH2}(en)(NH2CH2CH2NH3)](OTf)2 (**67**) is isolated. Complex **65** is a rare case of bis(alkylidene)–osmium(VI) complex. The only other examples that have been reported are the bis(neopentylidene) derivatives Os(=CH^{t}Bu)2(CH2R)2 (R = ^{t}Bu, SiMe3) [37].

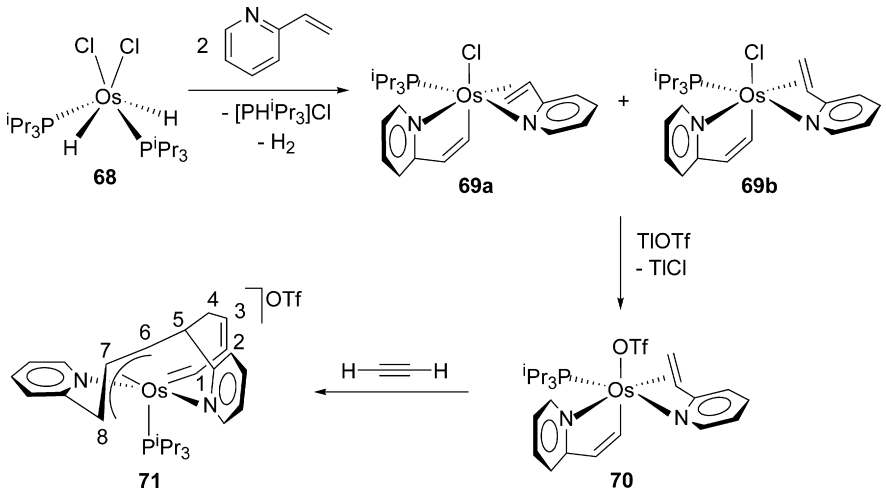
The assembly of two 2-vinylpyridine molecules and two acetylenes has given rise to an unprecedented α,β-unsaturated carbene ligand having an η^3-allyl moiety coordinated to the osmium center (Scheme 30) [38].

Complex OsH2Cl2(P^{i}Pr3)2 (**68**), which has been one of the cornerstones in the development of the modern osmium organometallic chemistry [39], also promotes C–H bond activation and subsequent multiple C–C bond formation [38]. Treatment of **68** with 2 equiv of 2-vinylpyridine in toluene under reflux for 10 h gives rise to the release of H2 and [PH^{i}Pr3]Cl and to the formation of **69**, which is isolated as a 6:4 mixture of the isomers **a** and **b** shown in Scheme 30. The addition at room temperature of 1.0 equiv of TlOTf to a dichloromethane solution of the isomeric mixture of **69** produces the replacement of chloride by trifluoromethane sulfonate to afford selectively **70**, the OTf counterpart of **69b**. Under atmospheric pressure of acetylene, in dichloromethane at room temperature, complex **70** is converted into the spectacular compound **71**, which is obtained in high yield (85%), and that has been characterized by X-ray diffraction. The structure of the cation proves the formation of the py-C(8)H-C(7)H-C(6)H-C(5)H-{C(4)H2–C(3)H=C(2)H-C(l)H}-py ligand, which coordinates to the metal center by the nitrogen atoms of both pyridine rings, by C(8)–C(7)–C(6) in a η^3-allyl manner and by C(1) to form a carbene. The formation of **71** is a one-pot synthesis of multiple complex reactions. In addition to a 1,3-hydrogen shift, three selective C–C coupling processes are assembled to afford this species [38].



Scheme 29.

The migratory insertion of an Os–C triple bond into an Os-alkenyl bond has been found to be also an efficient method to prepare α,β-unsaturated carbene compounds [12c]. In dichloromethane at 0 °C, under 1 atm of acetylene, the dihydride–osmium(IV) complex [OsH2(κ^2-O2CCH3)(H2O)(P^{i}Pr3)2]BF4 (**72**) is a catalyst precursor for the polymerization of acetylene (Scheme 31). The active species appears to be [Os(CH=CH2)(κ^2-O2CCH3)(≡C-CH3)(P^{i}Pr3)2]BF4 (**73**) or a derived of this compound. In fact, the stirring of dichloromethane solutions of **73** under 1 atm of acetylene affords polyacetylene and a yellow solution from which complex **73** is recovered in high yield. The catalytic formation of polyacetylene and the stoichiometric formation of **73** is also observed when dichloromethane



Scheme 30.

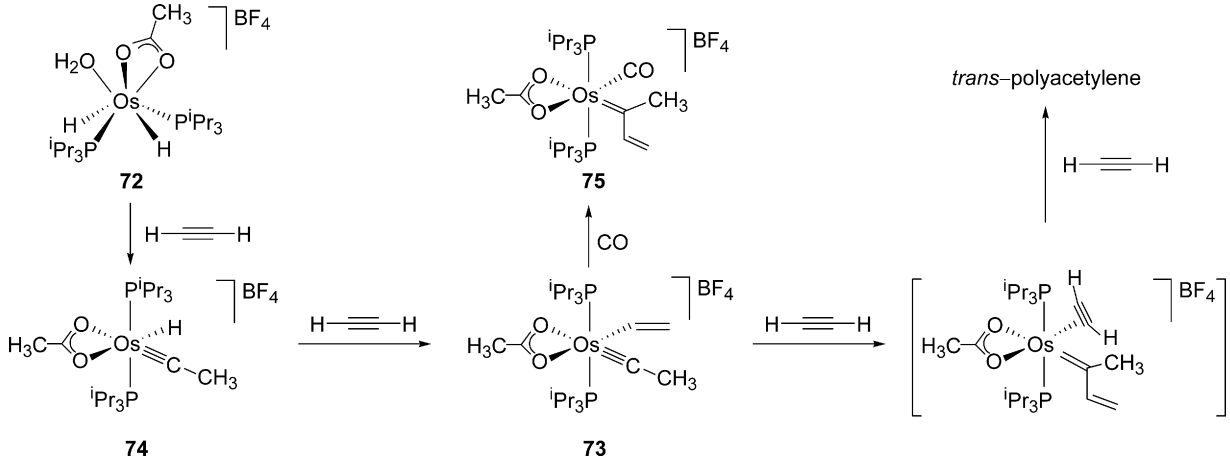
solutions of the hydride–carbyne [OsH(κ^2-O_2CCH_3)(≡C-CH_3)(P^iPr_3)$_2$]BF_4 (**74**) are stirred under 1 atm of acetylene at 0 °C. This indicates that the reaction of **72** with acetylene to give **73** is a two-step process which involves the initial formation of **74** and the subsequent insertion of the alkyne into the Os–H bond of this intermediate. Once complex **73** has been formed, the migratory insertion of the carbyne ligand into the Os–vinyl bond should afford a carbene intermediate, which could be the active species of the catalysis [40]. In favor of the formation of an alkylidene species from **73** and acetylene under an acetylene atmosphere, it has been observed that, under a carbon monoxide atmosphere, complex **73** evolves into [Os(κ^2-O_2CCH_3){=C(CH_3)CH=CH_2}(CO)(P^iPr_3)$_2$]BF_4 (**75**), which is unstable under these conditions and affords, finally, **64** [12c].

2.4. Osmacyclopropene complexes

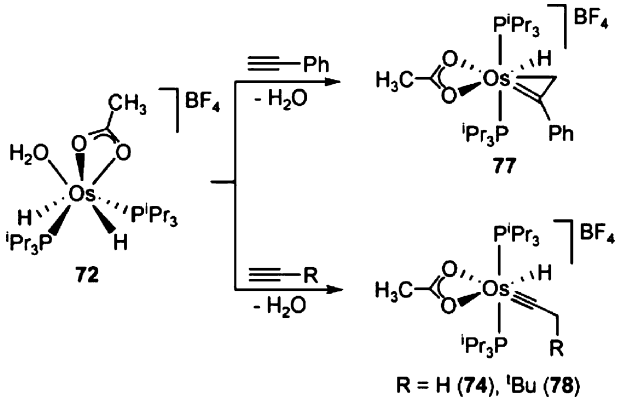
Metallacyclopropene complexes are considered important intermediates in several catalytic reactions. However, few compounds of this type are known. They are limited to early transition metals and, in general, have been prepared by external nucleophilic attack on coordinated alkyne ligands [41].

For osmium, Harman and co-workers [42] have reported that the pentaaminoosmium(II) unit $[Os(NH_3)_5]^{2+}$, despite its divalent character, acts as an electron donor through a substantial interaction with the olefin π^* orbital. Thus, in the case of vinyl ether or vinyl ester complexes, coordination by osmium(II) facilitates the loss of the oxygen substituent through the stabilization of the resulting osmacyclopropene. When the Os=C carbon atom carries a methyl group, the complex Os{=C(CH_3)CH_2}(NH_3)$_5$](OTf)$_3$ (**76**) can be isolated. In contrast, when the Os=C carbon atom bears a hydrogen atom the metallacyclopropene evolves into the carbyne isomer by an intramolecular 1,2-hydrogen shift.

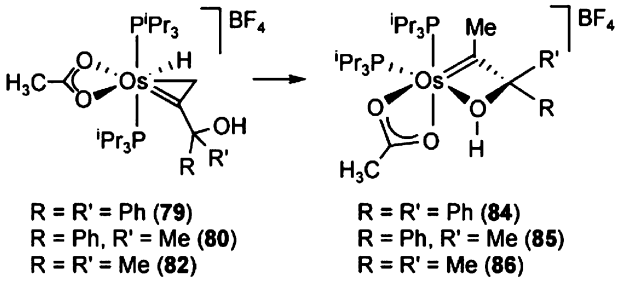
In addition to Harman's work, we have observed [43] that the hydride–osmium(IV) complex **72** reacts with phenylacetylene to give the hydride-osmacyclopropene derivative [OsH{=C(Ph)CH_2}(κ^2-O_2CCH_3)(P^iPr_3)$_2$]BF_4 (**77**) and with *tert*-butylacetylene and (trimethylsilyl)acetylene to afford the hydride–carbyne complexes [OsH(κ^2-O_2CCH_3)-(≡CCH_2R)(P^iPr_3)$_2$]BF_4 (R = H (**74**), CMe_3 (**78**)) (Scheme 32).



Scheme 31.



Scheme 32.

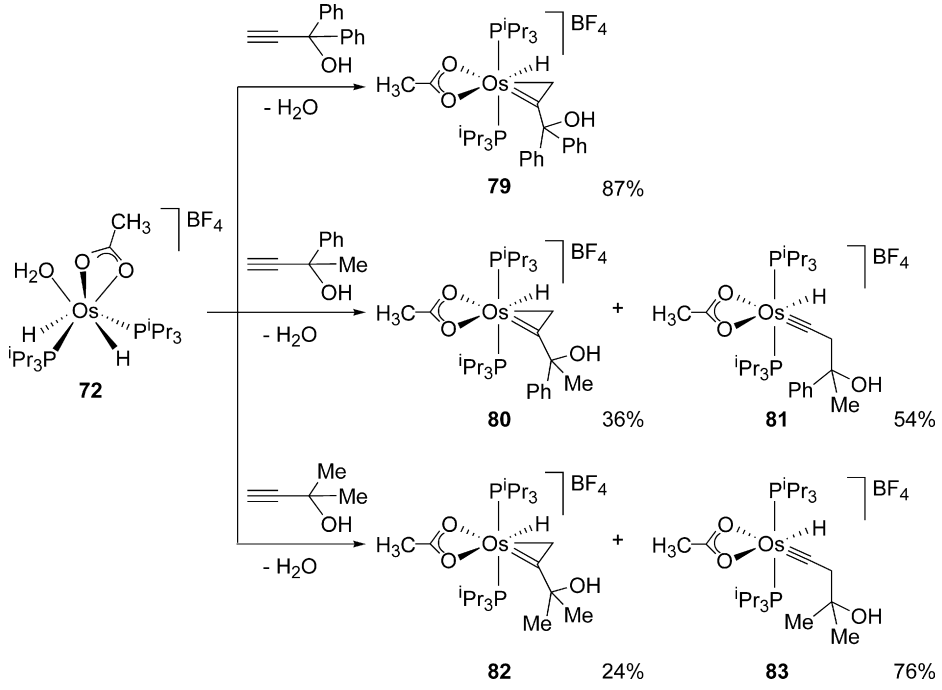


Scheme 34.

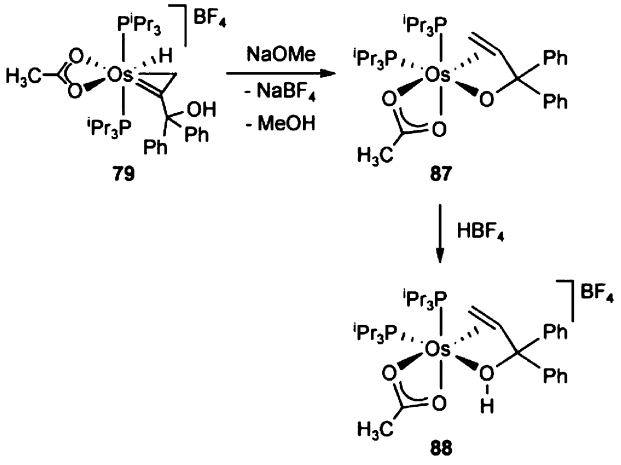
In agreement with these observations, theoretical calculations indicate that the relative stabilities of the metallacyclopropene and carbyne structures depend on the substituent of the alkyne precursor. There is a strong energy preference for the carbyne for R = H, and any substitution stabilizes the metallacyclopropene form more than the carbyne. The stabilization already operative for alkyl substitution through hyperconjugation of the alkyl group is magnified for a phenyl group, where conjugation with a true π system is possible [43].

The reactions of **72** with alkynols (Scheme 33) lead to isomeric mixtures of hydride–hydroxyosmacyclopropenes and hydride–hydroxycarbynes [44]. The molar ratio of the isomers in the mixture depends on the nature of the substituents at the C–OH carbon atom of the alkynol. With 1,1-diphenyl-2-propyn-1-ol the hydroxyosmacyclopropene isomer $[OsH\{=C[C(OH)Ph_2]CH_2\}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2]BF_4$ (**79**) is the only reaction product. The consecutive substitution of phenyl by methyl groups produces an increase in the amount of the hydroxycarbyne isomer and a decrease in the amount of the hydroxyosmacyclopropene isomer. Thus, with 2-phenyl-3-butyn-1-ol $[OsH\{=C[C(OH)MePh]CH_2\}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2]BF_4$ (**80**) and $[OsH(\kappa^2\text{-}O_2CCH_3)\{\equiv CCH_2C(OH)MePh\}(P^iPr_3)_2]BF_4$ (**81**) are obtained in 36% and 54% yield, respectively, while with 2-methyl-3-butyn-2-ol $[OsH\{=C[C(OH)Me_2]CH_2\}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2]BF_4$ (**82**) and $[OsH(\kappa^2\text{-}O_2CCH_3)\{\equiv CCH_2C(OH)Me_2\}(P^iPr_3)_2]BF_4$ (**83**) are formed in 24 and 76% yield.

At room temperature, in dichloromethane, complexes **79**, **80**, and **82** are unstable and evolve into the corresponding cyclic hydroxycarbene compounds $[Os(\kappa^2\text{-}O_2CCH_3)\{=C(CH_3)C(OH)RR'\}(P^iPr_3)_2]BF_4$ (**84–86** in Scheme 34). The transformation involves a 1,2-migration of the hydride ligand from the osmium atom to the CH_2 group of the osmacyclopropene and subsequent coordination of the hydroxy group of the resulting carbene ligand. During this process a significant rearrangement of the coordination environment at the osmium atom takes place. The phosphine



Scheme 33.



Scheme 35.

ligands, mutually *trans*-disposed in the starting materials, lie mutually *cis* in the isomerization products.

Treatment of **79** with 1.4 equiv of sodium methoxide in tetrahydrofuran at room temperature leads to the η^2-vinyl alcoxide compound $Os\{\eta^2\text{-}CH_2{=}CHC(Ph)_2O\}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ (**87**). Its formation has been rationalized as the deprotonation of the OH group of the hydroxyosmacyclopropene ligand, together with a 1,2-hydrogen shift from the metal to the Os=C carbon atom. Similarly to the isomerization of **79**, **80**, and **82** to **84**–**86**, the transformation of **79** to **87** involves a significant rearrangement of the coordination environment at the osmium atom. The phosphine ligands, which were mutually *trans* in **79**, are now mutually *cis*. The reaction is not reversible. Addition of $HBF_4{\cdot}OEt_2$ to dichloromethane solutions of **87** affords $[Os(\kappa^2\text{-}O_2CCH_3)\{\eta^2\text{-}CH_2{=}CHC(OH)Ph_2\}(P^iPr_3)_2]BF_4$ (**88**), as a result of the protonation of the oxygen atom of the η^2-vinyl alcoxide ligand of **87** (Scheme 35).

2.5. Hydride–carbyne versus carbene

A large number of carbene complexes have been prepared by protonating carbyne compounds [45]. However, not in all cases it has been clear the participation of the metallic center. Evidences for 1,2-hydrogen shift from the metal to the carbyne carbon atom have been found in the tungsten complex $WH(\equiv C\text{-}Mes)(CO)\{P(OMe)_3\}_3$, which affords $W(=CHMes)(CO)L\{P(OMe)_3\}_3$ (L = CO, $P(OMe)_3$, PMe_3) via a five-coordinate carbene intermediate [46]. The 1,2-hydrogen shift has been mainly observed in the opposite sense. Like is shown in Schemes 5 and 11, the extraction of the chloride ligand from the carbene complexes **2** and **14** gives rise to the hydride–carbyne derivatives **9** and **21**, respectively. The related compounds $[OsH(\eta^5\text{-}C_5H_5)(\equiv CCH_2Ph)(P^iPr_3)]BF_4$ (**89**) [47] and $[OsH(\eta^5\text{-}C_5H_4SiPh_3)\{\equiv CCH(Ph)R\}(P^iPr_3)]BF_4$ (R = H (**90**), Me (**91**)) [48] are also known.

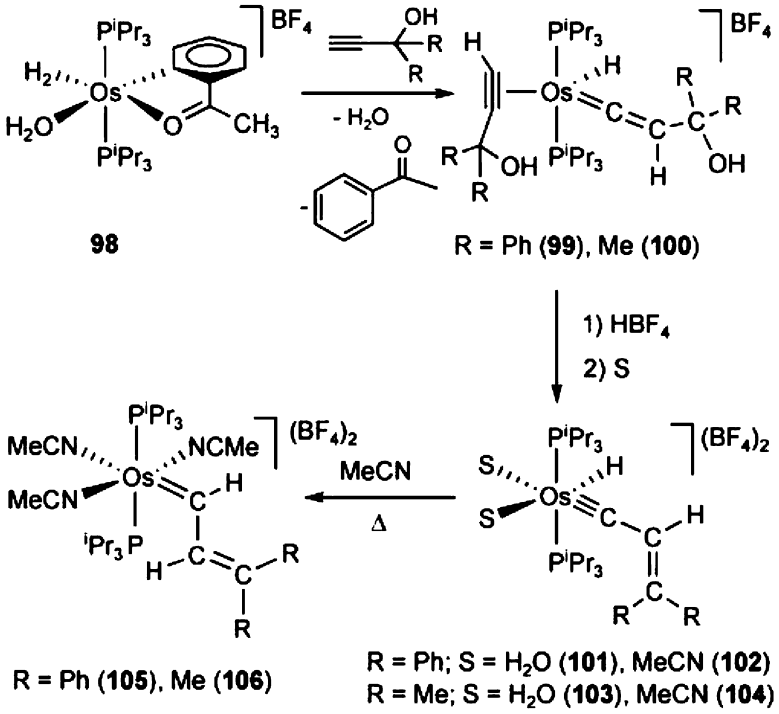
The formation of **9** and **21** by means of the creation of a coordination vacancy in **2** and **14** agrees well with the existence of $[OsH\{\kappa\text{-}N,\ \kappa\text{-}O[ON{=}C(CH_3)_2)]\}(\equiv CCH_2R)(P^iPr_3)_2]BF_4$ (R = CH_3 (**92**), ^{t}Bu (**93**), Cy (**94**), Ph (**95**)) [49], **74**, **78**, $[OsHX(\equiv CCH_2Ph)(Hpz)(P^iPr_3)_2]BF_4$ (X = F (**96**), Cl (**97**)) [50] and $OsHCl_2(\equiv CR)(PR'_3)_2$ [51]. The latter are isomers of the unknown compounds $OsCl_2(=CHR)(PR'_3)_2$, which should be the osmium counterparts to the Grubbs-type carbene ruthenium derivatives $RuCl_2(=CHR)(PR'_3)_2$ [52]. The complexes $OsHCl_2(\equiv CR)(PR'_3)_2$ are obtained by reaction of $OsCl_2H_2(PR'_3)_2$ with terminal alkynes. In contrast, the reaction of the ruthenium counterpart $RuCl_2H_2(P^iPr_3)_2$ with PhC≡CH gives a mixture of $RuCl_2(=C{=}CHPh)(P^iPr_3)_2$ (90%) and $RuCl_2(=CHCH_2Ph)(P^iPr_3)_2$ (10%) [52e]. This difference between osmium and ruthenium could be due to the fact that the 5d metal derivatives are generally more reducing than the 4d analogues.

The elongated dihydrogen complex $[Os\{C_6H_4C(O)CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$ (**98**) [53] is a synthon of the 12-valence electron monohydride $[OsH(P^iPr_3)_2]^+$ [49a], which coordinates two alkynol molecules to afford the novel hydride-hydroxyvinylidene-π-alkynol species $[OsH\{=C{=}CHC(OH)R_2\}\{\eta^2\text{-}HC{\equiv}CC(OH)R_2\}(P^iPr_3)_2]BF_4$ (R = Ph (**99**), Me (**100**)), where the π-alkynol acts as a four-electron donor ligand (Scheme 36). These species are the entry to the dicationic hydride–alkenylcarbyne complexes $[OsH(\equiv CCH{=}CR_2)S_2(P^iPr_3)_2][BF_4]_2$ (**101**–**104**) which, in contrast to the neutral hydride–carbyne compounds $OsHCl_2(\equiv CR)(PR'_3)_2$, undergo 1,2-hydrogen from the osmium to the carbyne carbon atom. Thus, in acetonitrile, they evolve into the corresponding dicationic alkenylcarbene derivatives $[Os(=CHCH{=}CR_2)(CH_3CN)_3(P^iPr_3)_2][BF_4]_2$ (R = Ph (**105**), Me (**106**)) [54].

Kinetic studies suggest that the formation of these six-coordinate alkenyl–carbene complexes takes place via the five-coordinate intermediates $[Os(=CHCH{=}CR_2)(CH_3CN)_2(P^iPr_3)_2]^{2+}$, which coordinate an acetonitrile molecule. In agreement with the kinetic results, DFT calculations on the model system $[OsH(\equiv CCH{=}CH_2)(CH_3CN)_2(PH_3)_2]^{2+}$ have located the transition state connecting the hydride alkenylcarbyne and the five-coordinate alkenylcarbene intermediate $[Os(=CHCH{=}CH_2)(CH_3CN)_2(PH_3)_2]^{2+}$ at 19.4 kcal mol^{-1} above the starting compound. It can be described as an η^2-carbene species ($Os{=}C(R)H$) [54].

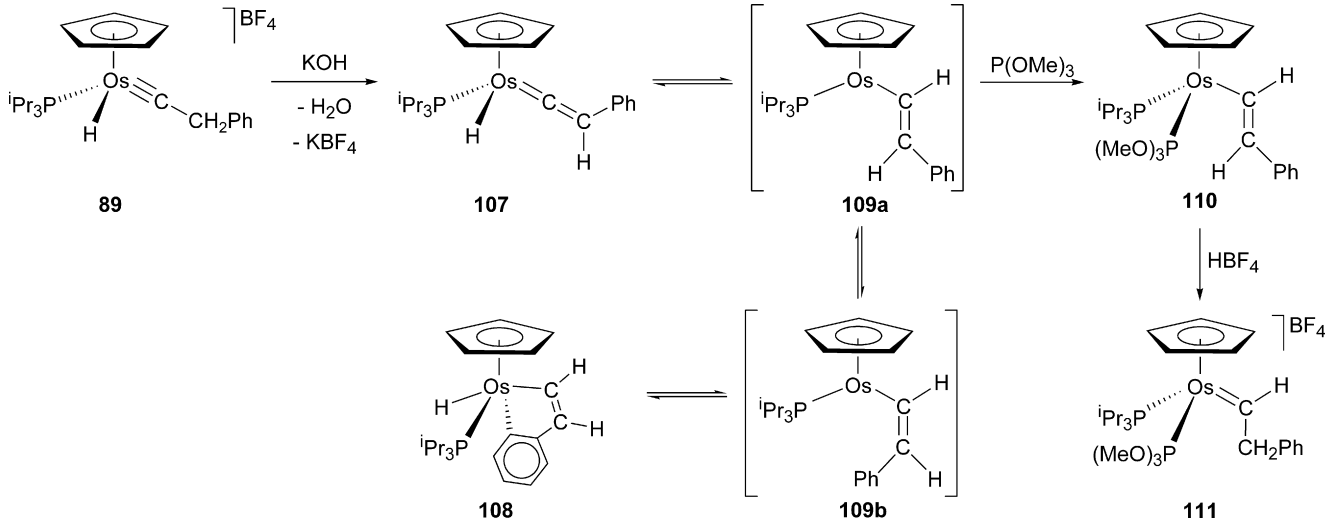
The sequential substitution of acetonitrile molecules by chloride ligands in the dicationic hydride-alkenylcarbyne compounds produces a sequential increase in the activation energy for the hydride migration. This is a consequence of the gradual increase of the electron richness of the metal center. While two chloride ligands inhibit the hydride-alkenylcarbyne to carbene transformation, the latter is favored by a carbonyl group [25,51b,54].

When a carbyne ligand bears a CHR_2 substituent, the Lewis base-assisted hydride–carbyne to carbene transformation can also take place via an ionic mechanism involving: (i) dissociation of a proton from the CHR_2 group of the carbyne, (ii) hydride migration to the C_α atom of the resulting vinylidene, (iii) stabilization of the alkenyl intermediate by coordination of the Lewis base, and (iv) protonation of the C_β atom of the alkenyl. In agreement with this, the transforma-

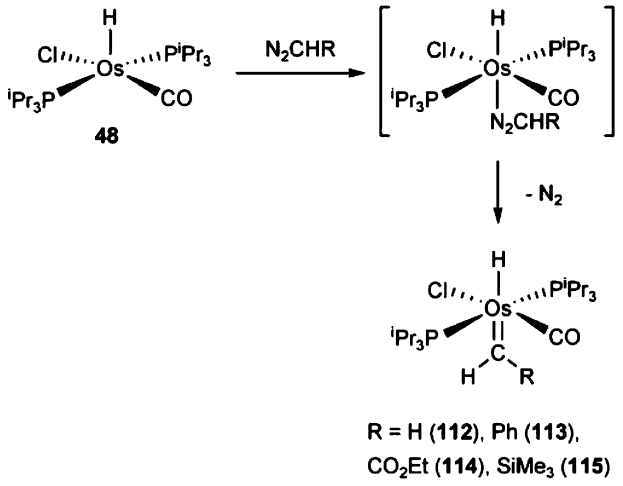


Scheme 36.

tion summarized in Scheme 37 has been reported [47]. The substituent of the carbyne of **89** is fairly acidic and can easily be deprotonated. Thus, treatment of a methanol solution of this compound with KOH affords the hydride vinylidene $OsH(\eta^5\text{-}C_5H_5)(=C=CHPh)(P^iPr_3)$ (**107**) in equilibrium with its metalated isomer $OsH(\eta^5\text{-}C_5H_5)(C_6H_4CH=CH)(P^iPr_3)$ (**108**). The isomerization of **107** to **108** occurs via the spectroscopically undetected (*Z*)-alkenyl intermediate **109b**, which is transformed into **108** by C–H activation of one of the *o*-CH bonds of the aryl group. Intermediate **109b** is in equilibrium with its *E* isomer **109a**. The formation of **109a** and **109b** could be the result of the migration, in **107**, of the hydride to the C_α atom of the vinylidene ligand, which should be rotating around the osmium vinylidene axis. Alternatively, the equilibrium between **109a** and **109b** could be a consequence of an isomerization process via a zwitterionic carbene form. The presence of spectroscopically undetected amounts of **109a** in the isomeric mixture is strongly supported by the reaction of the latter with trimethyl phosphite, which affords the (*E*)-styryl derivative $Os(\eta^5\text{-}C_5H_5)\{(E)\text{-}CH=CHPh\}\{P(OMe)_3\}(P^iPr_3)$ (**110**). The protonation of the C_β atom of the styryl ligand of **110** yields the carbene derivative $[Os(\eta^5\text{-}C_5H_5)(=CHCH_2Ph)\{P(OMe)_3\}(P^iPr_3)]BF_4$ (**111**). In contrast to trimethyl phosphite, bromide ion promotes the hydride–carbyne to olefin transformation [55].



Scheme 37.



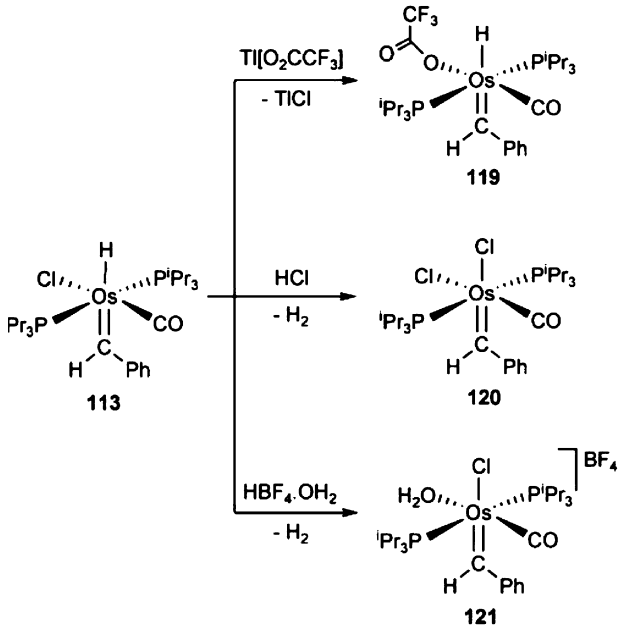
Scheme 38.

2.6. Hydride–carbene

The five coordinate compound **48** (Scheme 38) reacts with CH_2N_2 and other diazoalkanes $RCHN_2$ (R = Ph, CO_2Et, $SiMe_3$) to give the hydride–carbene derivatives $OsHCl(=CHR)(CO)(P^iPr_3)_2$ (R = H (**112**), Ph (**113**), CO_2Et (**114**), $SiMe_3$ (**115**)) in excellent yields. With Me_3SiCHN_2 as the substrate, the intermediate $OsHCl(N_2CHSiMe_3)(CO)(P^iPr_3)_2$ (**116**) has been detected at low temperature. The reactions of **48** with Ph_2CN_2 and $Cl_4C_5N_2$ afford $OsHCl(N_2CR_2)(CO)(P^iPr_3)_2$ compounds related to **116**. However, in contrast to the latter, they appear to be quite stable and do not eliminate N_2 to give the corresponding hydride–carbene derivatives [56].

In benzene at 25 °C complex **112** decomposes unselectively to give a mixture of several products, between them **48** and ethylene. In contrast to **112**, the related $^tBu_2MeP$-derivative $OsHCl(=CH_2)(CO)(P^tBu_2Me)_2$ (**117**) isomerizes into the five-coordinate methyl derivative $Os(CH_3)Cl(CO)(P^tBu_2Me)_2$ (**118**) [57]. In agreement with the isomerization, *ab initio* MP_2 calculations show that the unsaturated methyl species is considerably more stable than both the *trans* and *cis* six-coordinate hydride–carbene isomers [58].

Complex **113**, which has been also prepared by reaction of **48** with $Ph_2S{=}CHPh$ [59], reacts with $Tl[O_2CCF_3]$ to give the trifluoroacetate compound $OsH(\kappa^1\text{-}O_2CCF_3)(=CHPh)(CO)(P^iPr_3)_2$ (**119**). Treatment of **113** with either HCl or $HBF_4{\cdot}OH_2$ leads to the cleavage of the Os–H bond and results in the formation of $OsCl_2(=CHPh)(CO)(P^iPr_3)_2$ (**120**) and $[OsCl(=CHPh)(CO)(H_2O)(P^iPr_3)_2]BF_4$ (**121**), respectively (Scheme 39) [56b].



Scheme 39.

2.7. Osmafurane, osmapyrrole, and related compounds

There are osmium complexes containing a five-membered heterometallacycle with an Os–C distance between those expected for single and double Os–C(sp^2) bonds. Thus, for an adequate description of the bonding situation in the ring, the resonance forms shown in Plate 3 should be taken into account. In agreement with the presence of a partial Os–C double bond, the

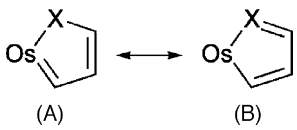
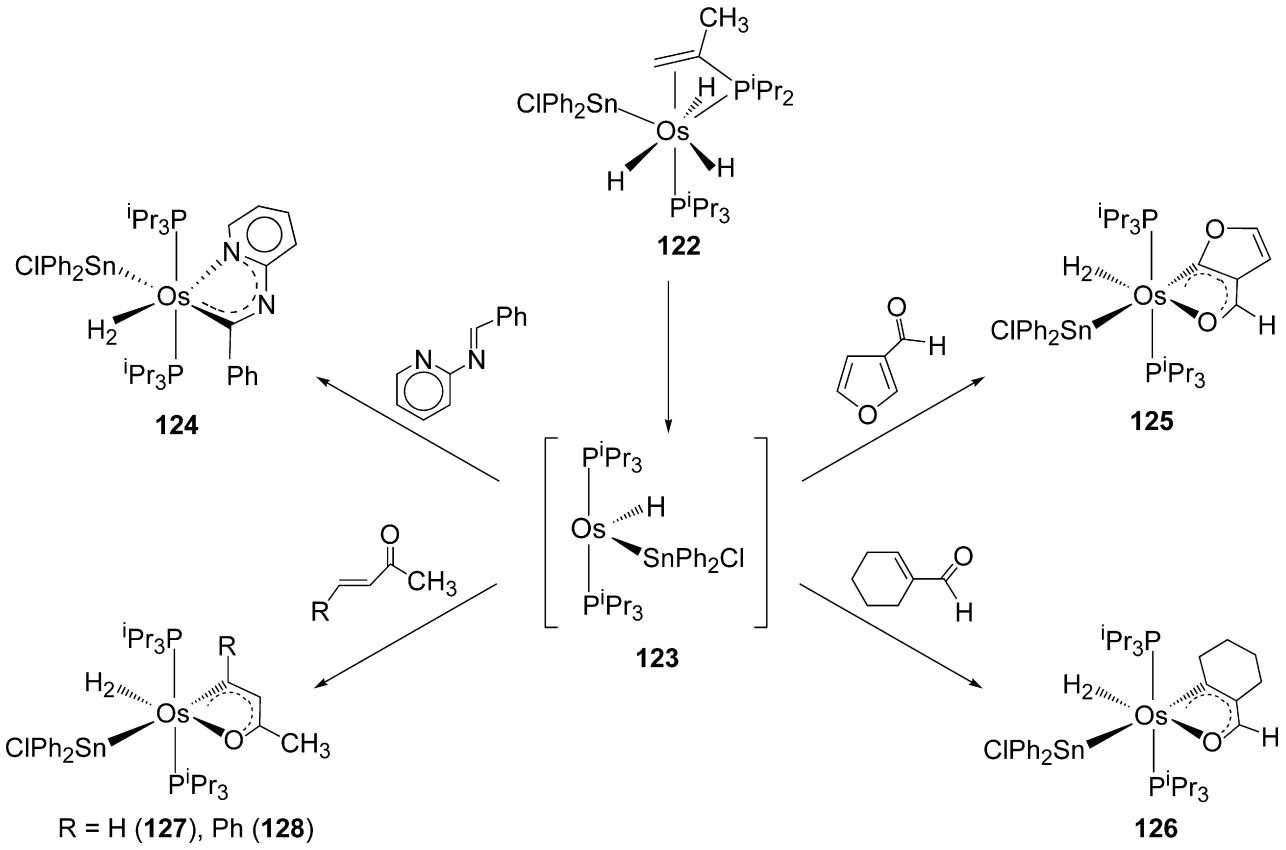


Plate 3.

OsC resonance in the $^{13}C\{^1H\}$ NMR spectra appears between 220 and 260 ppm. These compounds have been generally prepared by means of C–H bond activation reactions, and have received a great deal of attention in recent years.

In an effort to introduce the advantages of the tin ligands into the osmium-polyhydride chemistry, we have prepared a family of polyhydride-tin-osmium complexes [60], including the trihydride-isopropenyldiisopropylphosphine derivative $OsH_3(SnPh_2Cl)\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}(P^iPr_3)$ (**122**), which is a synthon for the 14-valence-electron monohydride $OsH(SnPh_2Cl)(P^iPr_3)_2$ (**123**) (Scheme 40). This highly unsaturated species activates C(sp^2)–H bonds of a wide range of organic molecules [61]. Treatment at room temperature of toluene solutions of **122** with (*E*)-N-(phenylmethylene)-2-pyridinamine leads after 5 days to the elongated dihydrogen complex $Os(SnPh_2Cl)(NC_5H_4\text{-}o\text{-}NCPh)(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**124**). Its formation involves the C(sp^2)–H activation of the vinylic CHPh group of the substituent of the pyridine by the monohydride **123**. In agreement with a significant contribution of the amino-carbene resonance form to the structure of the five-membered ring, the OsC resonance in the $^{13}C\{^1H\}$ NMR spectrum of **124** appears at 237.1. The reactions of **123** with 3-furaldehyde and 1-cyclohexene-1-carboxaldehyde afford $Os(SnPh_2Cl)\{C_4H_2(O)C(O)H\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**125**; δ_{OsC}, 230.6) and $Os(SnPh_2Cl)\{C_6H_8C(O)H\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**126**; δ_{OsC}, 242.9), respectively [61b], as a consequence of the activation of C(sp^2)–H bonds β-disposed to the carbonyl group of the aldehydes. In this context, it must be pointed out that

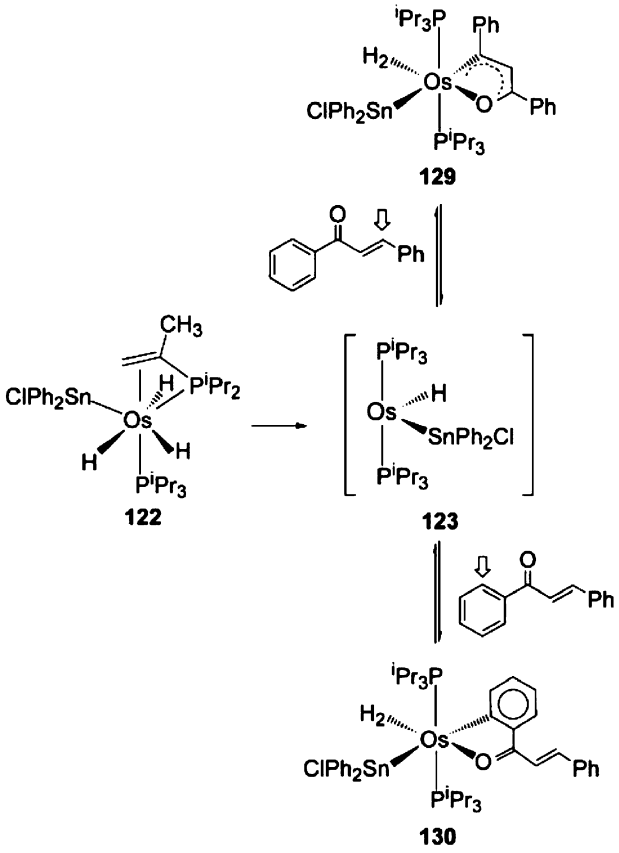


Scheme 40.

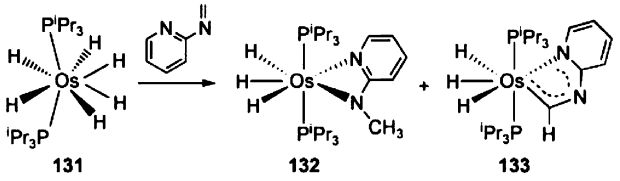
although 3-furaldehyde has two carbon atoms β-disposed with regard to the carbonyl group, only the C_β–H bond adjacent to the oxygen atom of the heterocycle is activated. Monohydride **123** also activates a $C_\beta(sp^2)$–H bond of α,β-unsaturated ketones [61c]. Thus, treatment at room temperature of toluene solutions of **122** with methyl vinyl ketone and benzylideneacetone leads to the osmafurane derivatives $Os(SnPh_2Cl)\{C(R)CHC(O)CH_3\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (R = H (**127**); δ_{OsC}, 233.1. R = Ph (**128**); δ_{OsC}, 241.4).

Monohydride **123** activates both the $C_\beta(sp^2)$–H of the olefinic moiety and an *o*-CH bond of the phenyl group of benzylideneacetophenone, to give $Os(SnPh_2Cl)\{C(Ph)CHC(O)Ph\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**129**) and $Os(SnPh_2Cl)\{C_6H_4C(O)CH{=}CHPh\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**130**), respectively (Scheme 41). The activation of the $C_\beta(sp^2)$–H bond of the olefin is kinetically favored with regard to the *o*-CH bond activation of the phenyl group. However, complex **130** is thermodynamically more stable than **129** [61c]. The lower strength of a H–vinyl bond with regard to a H–Ph bond appears to be the reason for the kinetic preference for the olefin bond activation over the *o*-CH bond activation, whereas the Os–Ph bond being stronger than the Os–vinyl bond appears to be the driving force for the thermodynamic preference for the formation of **130** over the formation of **129** [24,61c,62].

The C–H bond activation reactions with high-valent metal complexes are rare, in particular those using hydride compounds. Despite this, it has been shown that the thermal activation of the hexahydride $OsH_6(P^iPr_3)_2$ (**131**) affords a short-lived species



Scheme 41.



Scheme 42.

$OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$ which activates an *o*-CH bond of aromatic ketones [63] and imines [64], the C(sp^2)–H_α bond of aldehydes [12f], a vinylic CH bond of N-methylene-2-pyridinamine [65], and C(sp^3)–H bonds of cyclohexyl methyl ketone [66].

The reaction of **131** with N-methylene-2-pyridinamine leads to a mixture of the trihydride derivatives $OsH_3(NC_5H_4\text{-}o\text{-}NCH_3)(P^iPr_3)_2$ (**132**) and $OsH_3(NC_5H_4\text{-}o\text{-}NCH)(P^iPr_3)_2$ (**133**) in a 3:1 molar ratio (Scheme 42). In agreement with the partial double character of the Os–C bond in the five-membered ring of **133**, the OsC resonance in the $^{13}C\{^1H\}$ NMR spectrum of this compound is observed at 251.7 ppm. Complex **132** is the result of the insertion of the C=N double bond of N-methylene-2-pyridinamine into one of the Os–H bonds of the short lived intermediate $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$, while complex **133** is a consequence of the C–H activation of the terminal CH_2 group. The replacement of a hydrogen atom in the latter by a phenyl group favors the insertion with regard to the C–H activation. Thus, the treatment under reflux of toluene solutions of **131** with (*E*)-N-(phenylmethylene)-2-pyridinamine selectively affords the trihydride $OsH_3(NC_5H_4\text{-}o\text{-}NCH_2Ph)(P^iPr_3)_2$ [65].

The reaction of **131** with cyclohexyl methyl ketone affords $OsH_3\{C_6H_8C(O)CH_3\}(P^iPr_3)_2$ (**134**; δ_{OsC}, 255.9), as a result of a triple C(sp^3)–H bond activation (Scheme 43). The cyclohexyl group of the ketone undergoes the cleavage of both C–H bonds of one of the two CH_2 groups β-disposed to the carbonyl and the activation of the C–H bond of the α-CH group [66].

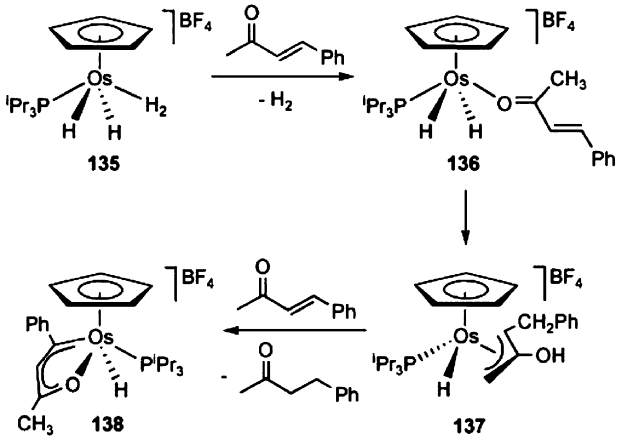
Several alkylidene- and alkylidyne-osmium complexes have been prepared by C(sp^3)–H bond activation. Gusev et al. have observed that cyclometalation of bis(di-*tert*-butylphosphino)pentane (D^tBPP) and subsequent product dehydrogenation take place in the reaction of D^tBPP with $[OsCl_6]^{2-}$ to give the osmium(IV) dihydride $OsH_2Cl\{CH(C_2H_4P^tBu_2)_2\}$ and the alkylidene derivative $OsHCl\{=C(C_2H_4P^tBu_2)_2\}$ [67]. Girolami and co-workers have reported that the reaction of the hydride complex $OsH(\eta^5\text{-}C_5Me_5)$(dppm) (dppm = bis(diphenylphosphino)methane) with 2 equiv of MeOTf affords the methylidene derivative $[Os(\eta^5\text{-}C_5Me_5)(=CH_2)$(dppm)] OTf, via a hydride-methyl intermediate which loses molecular hydrogen [68]. Caulton and co-workers have observed that the three benzylic methyl hydrogens of *p*-cymene are cleaved by ligating $[N(SiMe_2CH_2P^tBu_2)_2]^{2-}$ (PNP) to **27**, to give the carbyne compound (PNP)$OsH_2(\equiv CC_6H_4\text{-}p\text{-}^iPr)$ [69a]. In contrast with this reaction, the analogous reaction with ruthenium leads to (PNP)RuCl [69b,c].

In the presence of α,β-unsaturated ketones, the dihydride–dihydrogen complex $[OsH_2(\eta^5\text{–}C_5H_5)(\eta^2\text{-}H_2)(P^iPr_3)]BF_4$ (**135**) loses a hydrogen molecule, subsequently it reduces 1 equiv of substrate, and finally the resulting $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)]^+$ metal fragment activates a C(sp^2)–H bond to give half-sandwich osmafurane derivatives [70].

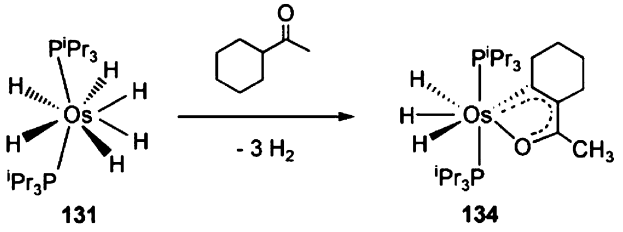
The reaction with benzylideneacetone leads initially to $[OsH_2(\eta^5\text{-}C_5H_5)\{\kappa^1\text{-}OC(CH_3)CH{=}CHPh\}(P^iPr_3)]BF_4$ (**136**). In dichloromethane complex **136** is converted to the hydroxyallyl derivative $[OsH(\eta^5\text{-}C_5H_5)\{\eta^3\text{-}CH_2C(OH)CHCH_2Ph\}(P^iPr_3)]BF_4$ (**137**), which affords the osmafurane $[OsH(\eta^5\text{-}C_5H_5)\{C(Ph)CHC(O)CH_3\}(P^iPr_3)]BF_4$ (**138**) by addition of benzylideneacetone (Scheme 44).

Complex **138** can be deprotonated by reaction with sodium methoxide. The addition of this base to a tetrahydrofuran solution of **138** gives rise to the formation of the neutral compound $Os(\eta^5\text{-}C_5H_5)\{C(Ph)CHC(O)CH_3\}(P^iPr_3)$ (**139**), as a result of the extraction of the hydride ligand (Scheme 45).

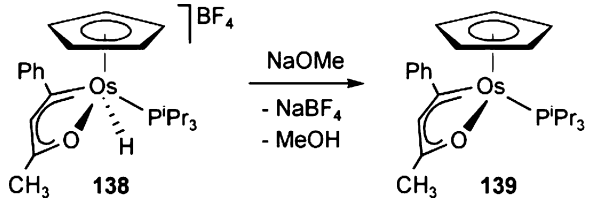
The $^{13}C\{^1H\}$ NMR spectrum of **139** reveals an increase of the contribution of the resonance form **A** (Plate 3) to the bonding in the five-membered ring, as a consequence of the deprotonation of the metal center. Thus, the OsC resonance is observed at 249.0 ppm, shifted about 12 ppm to lower field with regard to that of **138** (δ_{OsC}, 236.9). This increase of the carbene resonance form



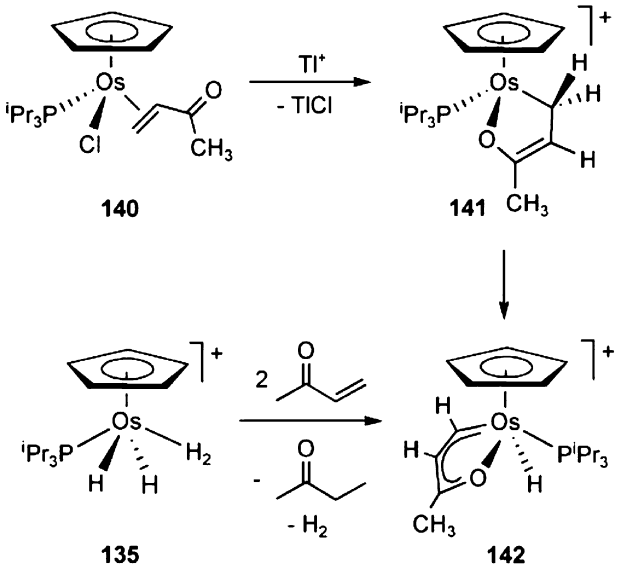
Scheme 44.



Scheme 43.



Scheme 45.



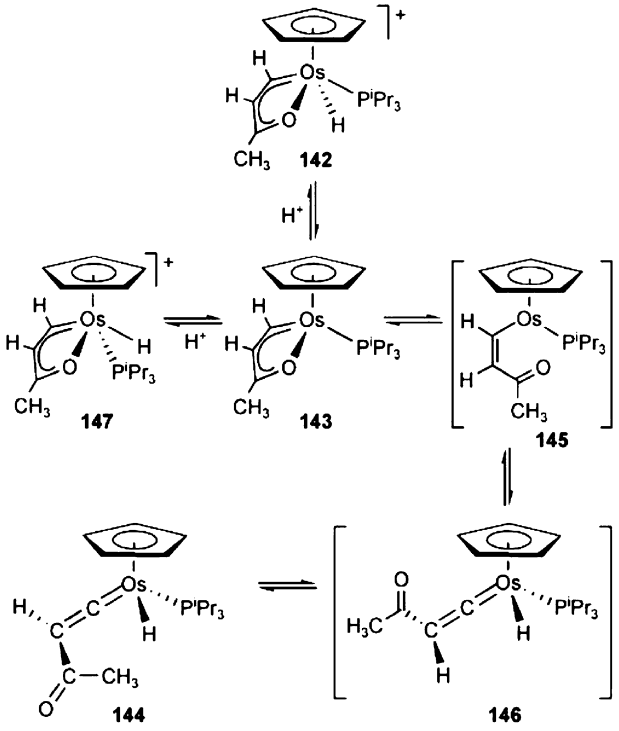
Scheme 46.

is in agreement with the formal reduction of the metal center, which increase the back-bonding Os(dπ) → C(pπ) interaction.

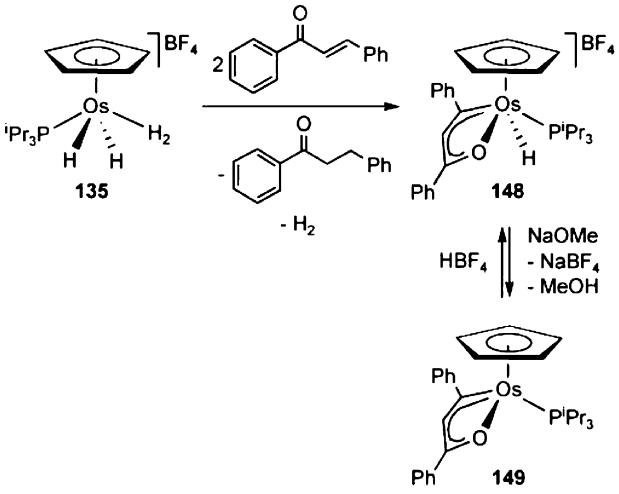
The formation of **138** involves the coordination of benzylideneacetone to the osmium atom, after the release of 4-phenylbutan-2-one from **137**, as a previous step to the C(sp^2)–H bond activation. In agreement with this, treatment of the methyl vinyl ketone complex Os(η^5-C_5H_5)Cl{η^2-CH_2=CHC(O)CH_3}(P^iPr_3) (**140**) with $TlPF_6$ produces the abstraction of the chloride ligand and the intramolecular coordination of the carbonyl group of the ketone to give the intermediate [Os(η^5-C_5H_5){$CH_2CHC(O)CH_3$}(P^iPr_3)]PF_6 (**141**), which in dichloromethane at room temperature is rapidly converted into the osmafurane **142** (δ_{OsC}, 222.8). The isomerization has been rationalized as a 1,2-hydrogen shift from the $OsCH_2$ carbon atom of the coordinated substrate to the unsaturated metal center of **141** (Scheme 46).

Like **138**, complex **142** can be deprotonated with sodium methoxide. In this case, the deprotonation leads to an equilibrium mixture of Os(η^5-C_5H_5){CHCHC(O)CH_3}(P^iPr_3) (**143**; δ_{OsC}, 237.8) and its hydride–vinylidene isomer OsH(η^5-C_5H_5){=C=CHC(O)CH_3}(P^iPr_3) (**144**). The formation of the latter has been rationalized according to Scheme 47. The decoordination of the oxygen atom in **143** should give an unsaturated alkenyl intermediate **145**, which could evolve into the hydride–vinylidene **146** by 1,2-hydrogen shift from the η^1-carbon donor ligand to the metal center. Finally, the rotation of the vinylidene of **146** around the Os–vinylidene bond should afford **144**. The deprotonation of **142** is reversible. The addition of HBF_4 to a dichloromethane solution of the equilibrium mixture of **143** and **144** initially leads to a mixture of **142** and its isomer **147** (δ_{OsC}, 210.0). After 12 h at room temperature, the quantitative isomerization of **147** into **142** occurs.

Although the metal fragment [Os(η^5-C_5H_5)(P^iPr_3)]$^+$ activates a C$_\beta$(sp^2)–H olefinic bond of α,β-unsaturated ketones and an *o*-CH bond of aromatic ketones, in contrast to **123**, the exclusive activation of the olefinic C$_\beta$(sp^2)–H bond is observed with



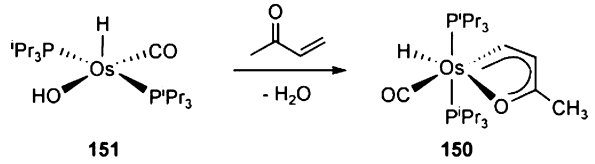
Scheme 47.



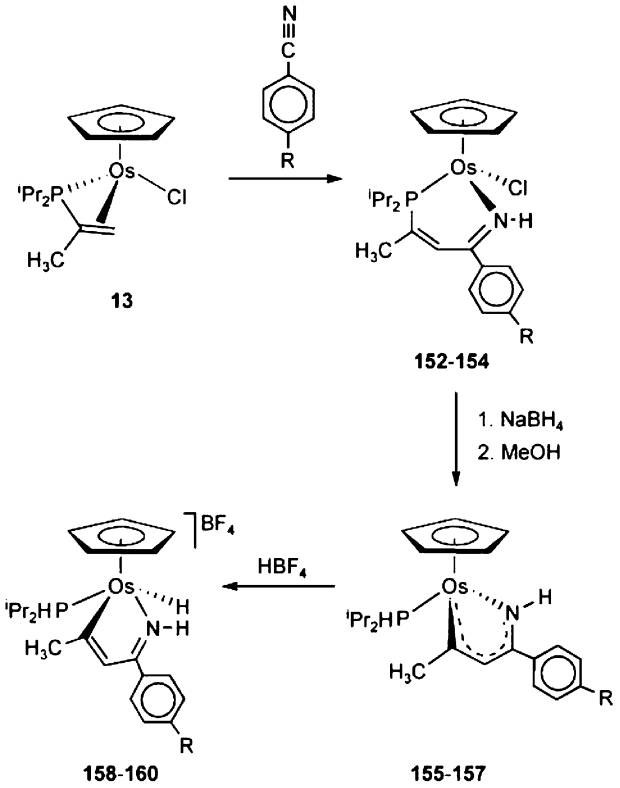
Scheme 48.

135 in substrates such as benzylideneacetophenone, which contains both types of organic moieties bonded to the carbonyl group (Scheme 48) [70].

The osmium(II)–bisphosphine complex OsH{CHCHC(O)CH_3}(CO)(P^iPr_3)$_2$ (**150**), related to the osmium(II) derivatives **139**, **143**, and **149**, has been also reported [71]. It results from the reaction of the hydride-hydroxo complex OsH(OH)(CO)(P^iPr_3)$_2$ (**151**) with methyl vinyl ketone (Scheme 49). In agreement with the osmium(II) half-sandwich osmafurane compounds, the OsC resonance in the $^{13}C\{^1H\}$ NMR spectrum of **150** (δ, 250.8) appears significantly shifted to lower field with regard to the osmium(IV) derivatives.



Scheme 49.



Scheme 50.

Although further work needs to be done in order to develop the methodology, it seems to be clear that alkenylphosphines can be successfully used to prepare osmapyrrole complexes [72]. The insertion of the carbon–nitrogen triple bond of benzonitriles into one of the C(sp^2)–H bonds of the isopropenyl group of the phosphine of **13** (Scheme 50) affords the iminophosphine compounds $Os(\eta^5\text{-}C_5H_5)Cl\{NH{=}C(p\text{-}C_6H_4R)CH{=}C(CH_3)P^iPr_2\}$ (R = CH_3 (**152**), H (**153**), Cl (**154**)). Treatment of the latter with $NaBH_4$ and methanol produces the rupture of the P–C bond of the iminophosphine ligands and the formation of $Os(\eta^5\text{-}C_5H_5)\{NHC(p\text{-}C_6H_4R)CHC(CH_3)\}(PH^iPr_2)$ (R = CH_3 (**155**), H (**156**), Cl (**157**)), containing an osmapyrrole unit (δ_{OsC}, 222–224). The protonation of the metallic center of the osmapyrrole complexes leads to the hydride-azabutadienyl-osmium(IV) derivatives $[OsH(\eta^5\text{-}C_5H_5)\{NH{=}C(p\text{-}C_6H_4R)CH{=}C(CH_3)\}(PH^iPr_2)]BF_4$ (R = CH_3 (**158**), H (**159**), Cl (**160**)). The oxidation of the metallic center provokes a decrease of the contribution of the carbene resonance form to the Os–C bond of **158–160**, which is evident in the OsC resonance in the $^{13}C\{^1H\}$ NMR spectra of these compounds (δ, 194–197).

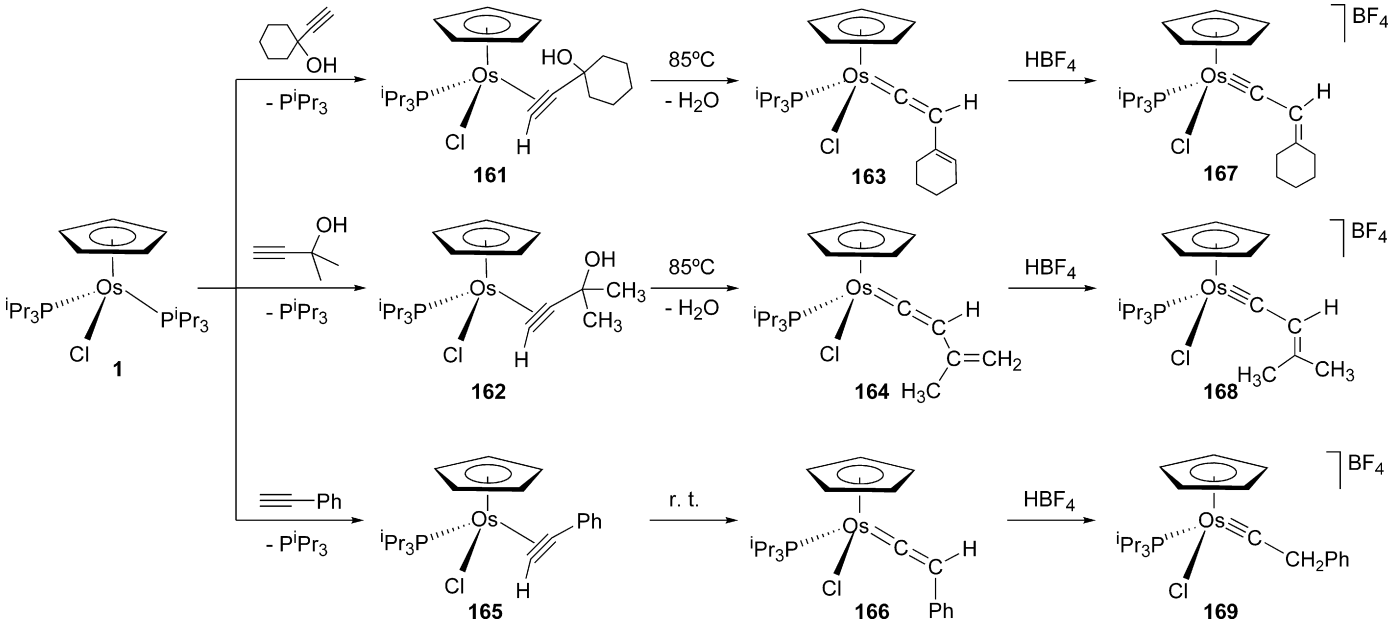
3. Os=C=CR_2 complexes

3.1. Half-sandwich derivatives

In agreement with the tendency shown by **1** to release a triisopropylphosphine ligand, treatment of this compound with 1-ethynyl-1-cyclohexanol and 2-methyl-3-butyn-2-ol in pentane leads to the π-alkyne compounds $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HC{\equiv}CC(OH)(CH_2)_4CH_2\}(P^iPr_3)$ (**161**) and $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HC{\equiv}CC(OH)(CH_3)_2\}(P^iPr_3)$ (**162**), which are converted to the corresponding alkenyl–vinylidene derivatives $Os(\eta^5\text{-}C_5H_5)Cl\{{=}C{=}CHC{=}CH(CH_2)_3CH_2\}(P^iPr_3)$ (**163**) and $Os(\eta^5\text{-}C_5H_5)Cl\{{=}C{=}CHC(CH_3){=}CH_2\}(P^iPr_3)$ (**164**) by loss of a water molecule (Scheme 51). The formation of **163** and **164** most probably involves hydroxyvinylidene intermediates, which spontaneously undergo dehydration [73]. Complex **164** can be also prepared from 2-methyl-1-buten-3-yne. In this case a π-alkyne intermediate related to **161** and **162** has not been detected, even at −60 °C. In contrast to the enyne, the reaction with phenylacetylene initially yields $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HC{\equiv}CPh\}(P^iPr_3)$ (**165**), which rapidly is changed to the vinylidene $Os(\eta^5\text{-}C_5H_5)Cl\{{=}C{=}CHPh\}(P^iPr_3)$ (**166**). Treatment of **163** and **164** with $HBF_4{\cdot}OEt_2$ give the alkenylcarbyne complexes $[Os(\eta^5\text{-}C_5H_5)Cl\{{\equiv}CCH{=}C(CH_2)_4CH_2\}(P^iPr_3)]BF_4$ (**167**) and $[Os(\eta^5\text{-}C_5H_5)Cl\{{\equiv}CCH{=}C(CH_3)_2\}(P^iPr_3)]BF_4$ (**168**), respectively. The protonation of **166** affords $[Os(\eta^5\text{-}C_5H_5)Cl({\equiv}CCH_2Ph)(P^iPr_3)]BF_4$ (**169**).

The vinylidene ligand of **166** is not only nucleophile at C_β but also electrophile at C_α. Thus, complex **166** reacts with organomagnesium compounds RMgCl (R = Me, Et, Ph) to give initially hydride–osmaindene derivatives $OsH(\eta^5\text{-}C_5H_5)\{C(R){=}CHC_6H_4\}(P^iPr_3)$ (R = Me (**170**), Et (**171**), Ph (**172**)), as a consequence of the addition of the nucleophile to the C_α atom of the vinylidene followed by *o*-CH bond activation of the phenyl substituent at the C_β atom. When R is Me and Et, the hydride-osmaindene moiety rearranges to afford d^6-*exo*-allyl derivatives, $Os(\eta^5\text{-}C_5H_5)\{\eta^3\text{-}CH(R')CHCHPh\}(P^iPr_3)$ (**173** (R′ = H) and **174** (R′ = Me) in Scheme 52). The transformation involves the reductive elimination of phenyl in the metallacycle and a 1,2-hydrogen shift, through the metal center, from the alkyl substituent to the C_α atom of the resulting unsaturated alkenyl intermediate [74].

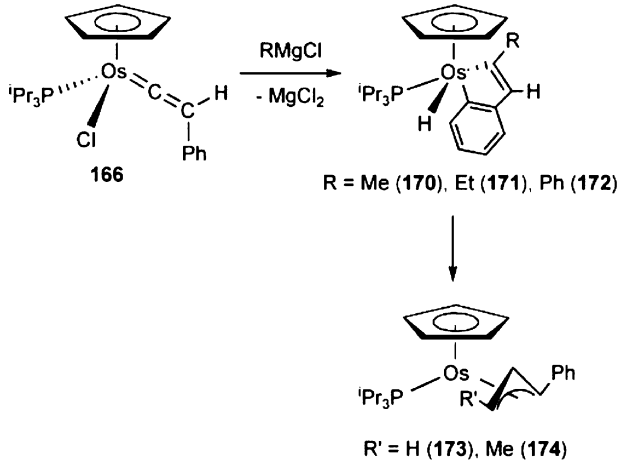
In the presence of $TlPF_6$ the abstraction of the chloride ligand of **1** and the C(sp)–H bond activation of alkynes take place [75]. Thus, the combined treatment of **1** with alkynes such as phenylacetylene and cyclohexylacetylene and $TlPF_6$ gives the hydride-alkynyl-osmium(IV) complexes $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(P^iPr_3)_2]PF_6$ (R = Ph (**175**), Cy (**176**); Scheme 53). *Ab initio* calculations on the model complexes $[Os(\eta^5\text{-}C_5H_5)(\eta^2\text{-}HC{\equiv}CH)(PH_3)_2]^+$ and $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CH)(PH_3)_2]^+$ show that the π-alkyne model complex is 4.0 kcal mol^{-1} more stable than the hydride-alkynyl



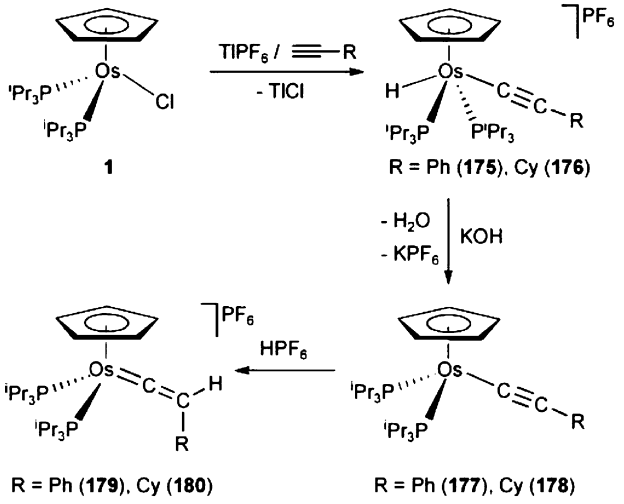
Scheme 51.

compound [76]. This means that π-alkyne species, [Os(η^5-C$_5$H$_5$)(η^2-HC≡CR)(P^{i}Pr$_3$)$_2$]$^+$, are not intermediates in the formation of **175** and **176**, since they are thermodynamically more stable than the products of the oxidative addition. The formation of **175** and **176** must be rationalized by assuming that the oxidative addition of the C(sp)–H bond of the alkynes is a kinetically favored process with regard to the coordination of the carbon–carbon triple bond [75]. *Ab initio* calculations also indicate that the vinylidene model complex [Os(η^5-C$_5$H$_5$)(=C=CH$_2$)(PH$_3$)$_2$]$^+$ is 22 kcal mol^{-1} more stable than [OsH(η^5-C$_5$H$_5$)(C≡CH)(PH$_3$)$_2$]$^+$. However, complexes **175** and **176** do not convert into the corresponding vinylidene compounds in the solid state or in solution. The formation of the vinylidenes [Os(η^5-C$_5$H$_5$)(=C=CHR)(P^{i}Pr$_3$)$_2$]PF$_6$ (R = Ph (**179**), Cy (**180**)) requires the deprotonation of **175** and **176** with a strong base and the subsequent protonation of the resulting alkynyl-osmium(II) intermediates [Os(η^5-C$_5$H$_5$)(C≡CR)(P^{i}Pr$_3$)$_2$] (R = Ph (**177**), Cy (**178**)) [76].

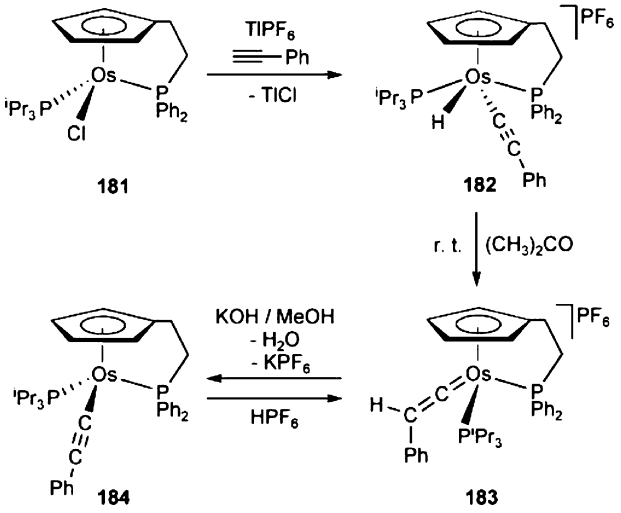
The kinetic inertness of **175** and **176** has been attributed to the basicities of **177** and **178**, which impose a high activation barrier for the isomerization of the hydride-alkynyl-osmium(IV) complexes to the corresponding vinylidene derivatives. The replacement of a triisopropylphosphine ligand and the cyclopentadienyl group by [2-(diphenylphosphino)-ethyl]cyclopentadienyl increases the acidity of the hydride-alkynyl intermediate [77]. At −20 °C, treatment of Os{[η^5-C$_5$H$_4$(CH$_2$)$_2$]PPh$_2$}Cl(P^{i}Pr$_3$) (**181**) with phenylacetylene in the presence of TlPF$_6$ initially leads to [OsH{[η^5-C$_5$H$_4$(CH$_2$)$_2$]PPh$_2$}(C≡CPh)(P^{i}Pr$_3$)]PF$_6$ (**182**). In contrast to **175** and **176**, complex **182** isomerizes into the vinyli-



Scheme 52.



Scheme 53.

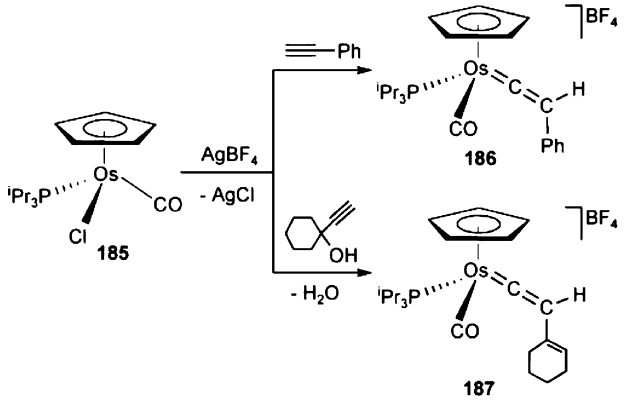


Scheme 54.

dene [Os{[η^5-$C_5H_4(CH_2)_2$]PPh_2}(=C=CHPh)(P^iPr_3)]PF_6 (**183**). In acetone at room temperature, the transformation is quantitative after 12 h (Scheme 54). Because the rate-determining step for the isomerization of the hydride alkynyl to the vinylidene complex is the H^+ dissociation from the hydride-alkynyl and, therefore, the protonation of the neutral alkynyl intermediate is very fast, the Os{[η^5-$C_5H_4(CH_2)_2$]PPh_2}(C≡CPh)(P^iPr_3) (**184**) species is not detected during the isomerization of **182**–**183**. However, compound **184** can be prepared by deprotonation of the vinylidene ligand of **183** with potassium hydroxide in methanol. In agreement with the higher stability of **183** compared to **182**, the addition of 1.2 equiv of $HPF_6{\cdot}H_2O$ to diethyl ether solutions of **184** produces the instantaneous precipitation of **183** in almost quantitative yield.

The increase of acidity in the hydride alkynyl intermediates, and therefore the falling off in stability, is a consequence of the decrease of the electron density at the metal center. Replacement of [2-(diphenylphosphino)ethyl]cyclopentadienyl by a carbonyl group and a cyclopentadienyl ligand, a more acidic combination than the cyclopentadienyl pendant phosphine moiety, produces a destabilization of the hydride alkynyl-osmium(IV) intermediates, which have not been observed during the fast formation of the vinylidene complexes [78]. Treatment of Os(η^5-C_5H_5)Cl(CO)(P^iPr_3) (**185**) with $AgBF_4$ and phenylacetylene or 1-ethynyl-1-cyclohexanol gives the stable vinylidene [Os(η^5-C_5H_5)(=C=CHPh)(CO)(P^iPr_3)]BF_4 (**186**) or alkenylvinylidene [Os(η^5-C_5H_5){=C=CHC=CH$(CH_2)_3$$CH_2$}(CO)($P^iPr_3$)]$BF_4$ (**187**), respectively (Scheme 55). A similar behavior has been observed for the carbonyl-pentamethylcyclopentadienyl complex Os(η^5-C_5Me_5)I(CO)(PPh_3) [79], and for the bis(triphenylphosphine)indenyl derivatives Os(η^5-C_9H_7)X(PPh_3)$_2$ (X = Cl, Br, I) [80].

Neutral hydride-alkynyl-silyl- and hydride-alkynyl-germyl-osmium(IV) species are also useful starting materials to prepare vinylidene–osmium(II) derivatives. In all the cases, the synthetic strategy involves the deprotonation of the starting compound and the subsequent electrophilic addition to the C_β atom the alkynyl ligand [48].



Scheme 55.

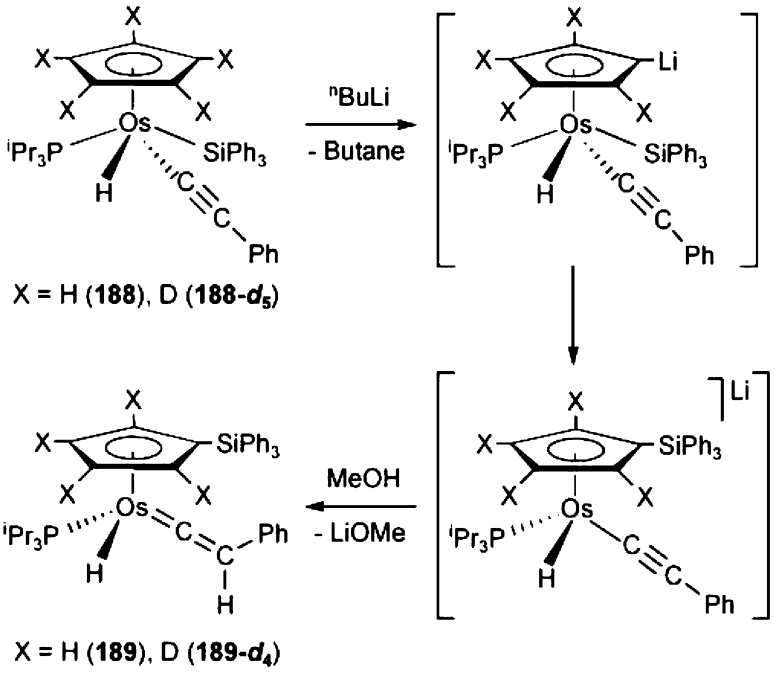
Treatment of tetrahydrofuran solutions of OsH(η^5-C_5X_5)(C≡CPh)($SiPh_3$)(P^iPr_3) (X = H (**188**), D (**188-*d*$_5$**)) with 3.0 equiv of *n*-butyllithium gives solutions that react with methanol to afford OsH(η^5-$C_5X_4SiPh_3$)(=C=CHPh)(P^iPr_3) (X = H (**189**), D (**189-*d*$_4$**)). The formation of these compounds has been rationalized according to Scheme 56. The deprotonation of **188** occurs selectively at the cyclopentadienyl ligand. The resulting species undergoes migration of the silyl group from the osmium atom to the cyclopentadienyl ligand to afford the anion [OsH(η^5-$C_5X_4SiPh_3$)(C≡CPh)(P^iPr_3)]$^-$. Subsequently, the acidic proton of methanol attacks the C_β atom of the alkynyl group.

In agreement with Scheme 56, the addition of methanol-d_4 to the solution resulting from the treatment of **188** with ^{n}BuLi gives OsH(η^5-$C_5H_4SiPh_3$)(=C=CDPh)(P^iPr_3) (**189-*d*$_1$**), according to Scheme 57.

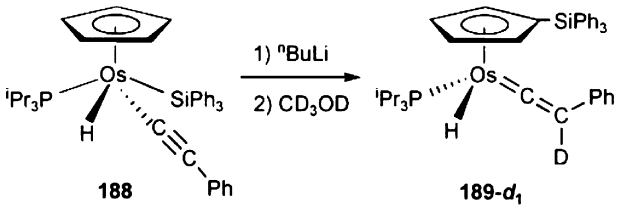
Interestingly, the treatment of a tetrahydrofuran solution of OsH(η^5-C_5H_5)(C≡CPh)($GePh_3$)(P^iPr_3) (**190**) with 3.0 equiv of *n*-butyllithium gives a solution that reacts with methanol, methanol-d_4 and methyl iodide to afford Os(η^5-C_5H_5)($GePh_3$)(=C=CHPh)(P^iPr_3) (**191**), Os(η^5-C_5H_4D)($GePh_3$)(=C=CDPh)(P^iPr_3) (**191-*d*$_2$**), and Os(η^5-$C_5H_4CH_3$)($GePh_3$){=C=C(CH_3)Ph}(P^iPr_3) (**192**), respectively (Scheme 58). The formation of these compounds indicates that treatment of **190** with *n*-butyllithium results in a double deprotonation: at the metal center and at the cyclopentadienyl ligand. Furthermore, in contrast to **188**, the deprotonation of the cyclopentadienyl ligand of **190** does not give way to the migration of the germyl group from the osmium atom to the cyclopentadienyl ligand.

In agreement with the nucleophilic character of the C_β atom of the vinylidene ligands, complex **189** reacts with $HBF_4{\cdot}OEt_2$ in diethyl ether to give the previously mentioned hydride–carbyne **90**. Similarly, the vinylidene ligands of **191** and **192** are prone to attack by electrophiles. Thus, the addition of HBF_4 to a diethyl ether solution of these compounds gives the corresponding germyl carbyne derivatives [Os(η^5-C_5H_5)($GePh_3$)(≡CCH_2Ph)(P^iPr_3)]BF_4 (**193**) and [Os(η^5-$C_5H_4CH_3$)($GePh_3$){≡CCH(CH_3)Ph}(P^iPr_3)]BF_4 (**194**), respectively (Scheme 59).

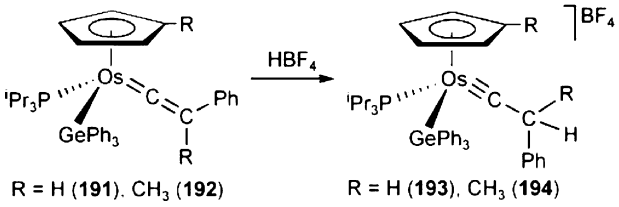
We have previously mentioned that both **1** and **13** react with phenyldiazomethane to give a chloro-phosphine-carbene



Scheme 56.



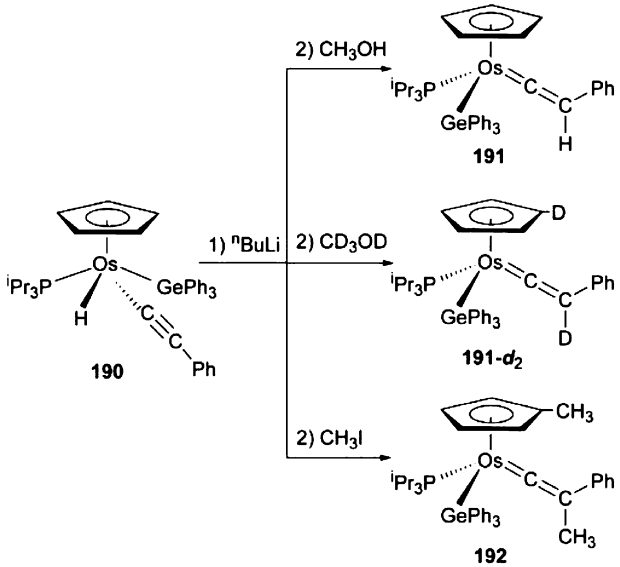
Scheme 57.



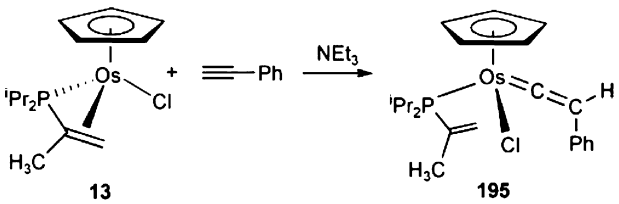
Scheme 59.

derivative (Schemes 1 and 7). However, in the reaction with phenylacetylene, there is a significant difference in behavior between them. While **1** affords the vinylidene **166** (Scheme 51), the isopropenyldiisopropylphosphine complex **13** gives the dienylphosphine compound $Os(\eta^5\text{-}C_5H_5)Cl\{[\eta^2\text{-}(E)\text{-}PhCH{=}CHCH_2C(=CH_2)]P^iPr_2$ as a result of an ene-type reaction between the isopropenyl substituent of the phosphine of **13** and the alkyne. The formation of the vinylidene complex $Os(\eta^5\text{-}C_5H_5)Cl(=C{=}CHPh)\{P^iPr_2[C(CH_3){=}CH_2]\}$ (**195**), related to **2**, **14**, and **166**, requires the presence of triethylamine which accelerates the alkyne-vinylidene transformation (Scheme 60) [81]. In the absence of the chloride ligand the coupling between the alkyne and the isopropenyl substituent of the phosphine gives rise to a dihydronaphthylphosphine derivative [82].

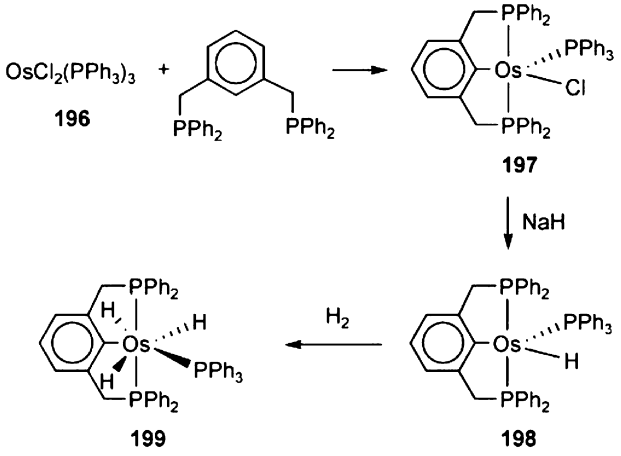
Cationic arene-osmium(II)-vinylidene compounds $[(\eta^6\text{-}C_6H_6)Os(=C{=}CHR)(PR'_3)X]^+$ can be obtained both directly from $(\eta^6\text{-}C_6H_6)Os(PR'_3)X_2$ (X = Cl, I), $AgPF_6$, and



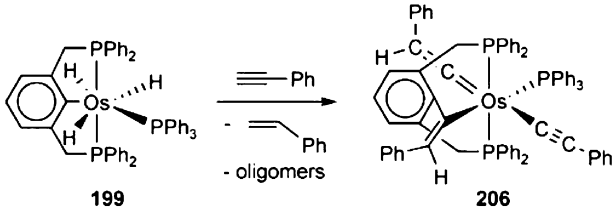
Scheme 58.



Scheme 60.



Scheme 61.



Scheme 63.

1-alkynes or from the alkynyls (η^6-C_6H_6)Os(C≡CR)(PR'_3)X on protonation [83]. Related osmium(0) derivatives, (η^6-C_6H_6)Os(=C=CHR)(PR'_3), have been prepared from halogeno alkenyl starting materials by α-deprotonation with *tert*-butyllithium at low temperature [84].

3.2. PCP "pincer" derivatives

Complex $OsCl_2(PPh_3)_3$ (**196**) reacts with 1,3-$(CH_2PPh_2)_2$-C_6H_4 to afford the unsaturated derivative Os(PCP)Cl(PPh_3) (**197**; PCP = 2,6-$(CH_2PPh_2)_2C_6H_3$) [85]. Treatment of **197** with NaH in THF under argon atmosphere produces a mixture of the monohydride OsH(PCP)(PPh_3) (**198**) and the trihydride OsH_3(PCP)(PPh_3) (**199**). The H_2 needed for the formation of **199** in the reaction is presumably generated in situ from the reaction of NaH with the trace water present in the solution. When the reaction is performed under an H_2 atmosphere, the trihydride **199** is obtained quantitatively (Scheme 61) [86].

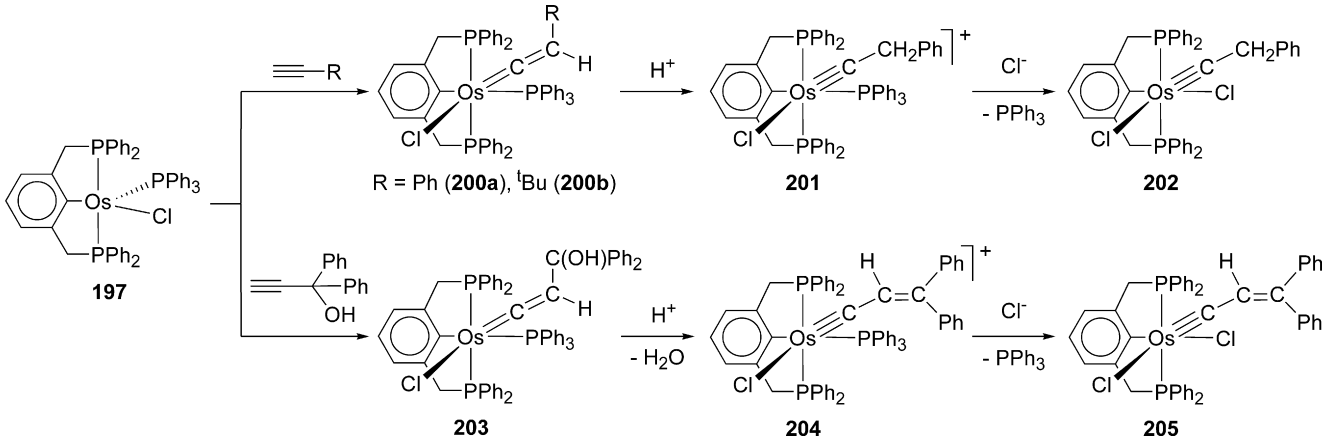
Complex **197** reacts with phenylacetylene and *tert*-butylacetylene to give the vinylidene compounds Os(PCP)Cl(=C=CHR)(PPh_3) (R = Ph (**200a**), ^{t}Bu (**200b**)). In agreement with the nucleophilic character of the C_β atom of the vinylidene ligands, the addition of HBF_4·OEt_2 to a dichloromethane solution of **200a** affords the cationic carbyne derivative [Os(PCP)Cl(≡CCH_2Ph)(PPh_3)]BF_4 (**201**), which by treatment with [NEt_3CH_2Ph]Cl gives Os(PCP)Cl_2(≡CCH_2Ph) (**202**). Complex **197** also reacts with 1,1-diphenyl-2-propyn-1-ol. The reaction leads to the hydroxyvinylidene Os(PCP)Cl{=C=CHC(OH)Ph_2}(PPh_3) (**203**), which dehydrates to give the alkenylcarbyne derivative [Os(PCP)Cl{≡CCH=CPh_2}(PPh_3)]BF_4 (**204**) in the presence of HBF_4·OEt_2. Similarly to **201**, the triphenylphosphine ligand of **204** can be displaced by chloride. Thus, treatment of the latter complex with [NEt_3CH_2Ph]Cl yields Os(PCP)Cl_2\{≡CCH=CPh_2\} (**205** in Scheme 62) [85].

Treatment of **199** with excess phenylacetylene produces the coupling product Os{C(=CHPh)C_6H_3(CH_2PPh_2)$_2$}-(C≡CPh)(=C=CHPh)(PPh_3) (**206**). The reaction also gives ca. 1.7 equiv of styrene and some oligomers of phenylacetylene (Scheme 63) [86].

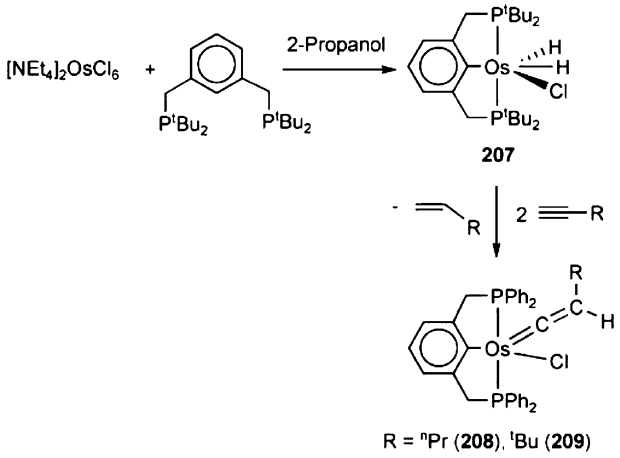
Five-coordinate vinylidene-osmium(II) complexes containing the PCP' "pincer" ligand 2,6-$(CH_2P^tBu_2)_2C_6H_3$ have been prepared according to Scheme 64. Reaction in 2-propanol between $[Et_4N]_2OsCl_6$ and 1,3-$(CH_2P^tBu_2)_2C_6H_4$ affords the dihydride-osmium(IV) starting material OsH_2Cl(PCP′) (**207**) [87]. Treatment of this complex with terminal alkynes such as 1-pentyne and *tert*-butylacetylene leads to the corresponding olefins and the vinylidene derivatives Os(PCP′)Cl(=C=CHR) (R = ^{n}Pr (**208**), ^{t}Bu (**209**)) [88].

3.3. Hydride–vinylidene compounds

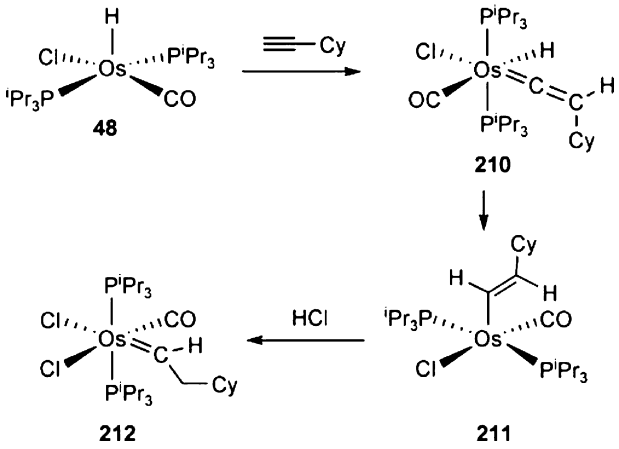
The five-coordinate complex **48** reacts with cyclohexylacetylene at room temperature to give the hydride–vinylidene deriva-



Scheme 62.



Scheme 64.



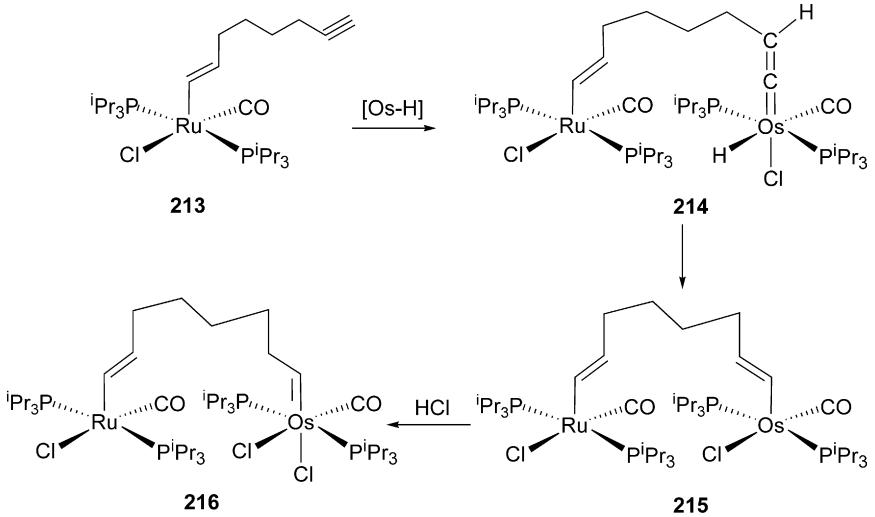
Scheme 65.

tive OsHCl(=C=CHCy)(CO)(P^iPr_3)$_2$ (**210**). In toluene, this complex evolves after 3 days into the alkenyl compound Os{(*E*)-CH=CHCy}Cl(CO)(P^iPr_3)$_2$ (**211**), which reacts with a stoichiometric amount of a toluene–HCl solution to afford the dichlorocarbene $OsCl_2$(=CHCH$_2$Cy)(CO)(P^iPr_3)$_2$ (**212** in Scheme 65) [89].

The metalloalkyne compound Ru{(*E*)-CH=CH(CH$_2$)$_4$C≡CH}Cl(CO)(P^iPr_3)$_2$ (**213**) exhibits a behavior similar to cyclohexylacetylene (Scheme 66). It reacts with **48** to give the hydride–vinylidene derivative (P^iPr_3)$_2$(CO)ClRu{(*E*)-CH=CH(CH$_2$)$_4$CH=C=}OsHCl(CO)(P^iPr_3)$_2$ (**214**), which evolves in toluene into the heterodinuclear-μ-bis(alkenyl) complex (P^iPr_3)$_2$(CO)ClRu{(*E*)-CH=CH-(CH$_2$)$_4$-CH=CH-(*E*)}OsCl(CO)(P^iPr_3)$_2$ (**215**). In agreement with the nucleophilic character shown by the C$_\beta$ atom of the alkenyl group of **211**, the heterodinuclear-μ-bisalkenyl complex **215** reacts with HCl. Interestingly, only the C$_\beta$ atom of the Os-alkenyl unit is attacked. Thus, treatment of **215** with the stoichiometric amount of a toluene–HCl solution selectively affords (P^iPr_3)$_2$(CO)-ClRu{(*E*)CH=CH–(CH$_2$)$_5$CH=}$OsCl_2$(CO)(P^iPr_3)$_2$ (**216**) [90].

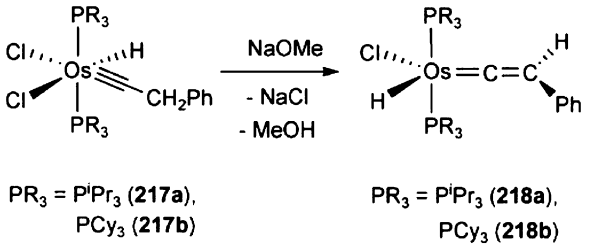
Five-coordinate hydride compounds related to **48** but containing a vinylidene ligand instead of a carbonyl group have been prepared from Os≡CCH$_2$R carbyne complexes by deprotonation of the CH$_2$R substituent. Treatment of the six-coordinate hydride–carbyne derivatives $OsHCl_2$(≡CCH$_2$Ph)(P^iPr_3)$_2$ ($PR_3 = P^iPr_3$ (**217a**), PCy_3 (**217b**)) with sodium methoxide gives the five-coordinate hydride–vinylidene complexes OsHCl(=C=CHPh)(PR_3)$_2$ ($PR_3 = P^iPr_3$ (**218a**), PCy_3 (**218b**)), according to Scheme 67 [51c,91].

In contrast to **48**, the distribution of ligands around the osmium atom of these compounds can be described as a distorted trigonal bipyramid with apical phosphines and inequivalent angles within the Y-shaped equatorial plane. The preference for this structure originates from neutral vinylidene being a potent π-acceptor in the C$_\beta$R$_2$ plane, but a weak π-donor in the orthogonal plane. The donating property of π_{CC} disfavors a *trans* relationship of the chloride and vinylidene ligands since this maximizes the overlaps between the occupied orbitals of



[Os-H] = OsHCl(CO)(P^iPr_3)$_2$ (**48**)

Scheme 66.



Scheme 67.

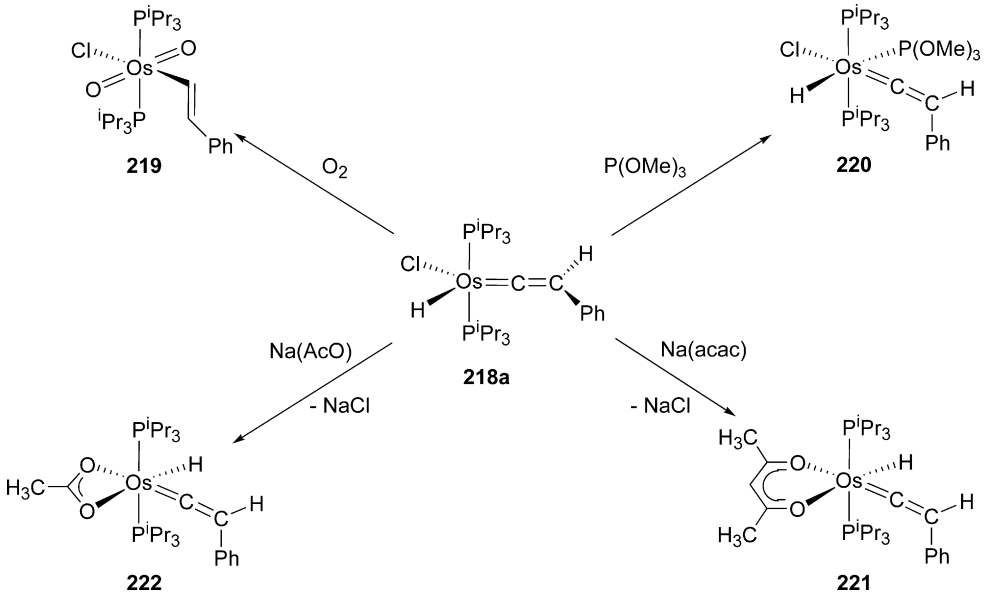
the metal (d) and the two ligands (π_{CC} and π_{Cl}). Two stabilizing interactions occur when $C_\beta R_2$ lies in the H-M-Cl plane. In addition to the usual M–Cl π bond characteristic of a Y-shaped d^6ML_5 species, the x^2–y^2 orbital is back-bonding into the $\pi_{C\alpha}$ empty orbital [92].

In solution the vinylidene ligand of these compounds rotates around the C–C axis [91,93]. Jia, Lin and co-workers have studied the vinylidene rotational barriers in MXCl(=C=CHR)$(PH_3)_2$ (M = Ru, Os; X = H, CH_3, SiH_3, SiF_3, CH=CH_2, Cl; R = H, SiH_3, SiF_3) model compounds by density functional theory calculations at the B3LYP level. The results show that the rotational barriers increase with X from having π-acceptor, σ-donor to having π-donor properties. Ligands X with π-acceptor properties stabilize the transition state structures through interaction with the d orbital used for metal-vinylidene π bonding in the most stable conformation and, therefore, give smaller rotational barriers. Studies of the influence of different substituents R show that the rotational barriers also increase with the electron donation abilities of R. The rotational barriers for osmium complexes are generally higher in comparison to those of the ruthenium analogues [94]. Ariafard and Zare have also examined, by density functional molecular orbital calculation at the BP86 level, the influence of the phosphine ligand in OsHCl(=C=CH_2)$(PR_3)_2$ (PR_3 = PMe_3, PH_3, PF_3). The results indicate that the rotational barrier increases with the increasing π-accepting ability of phosphine [95].

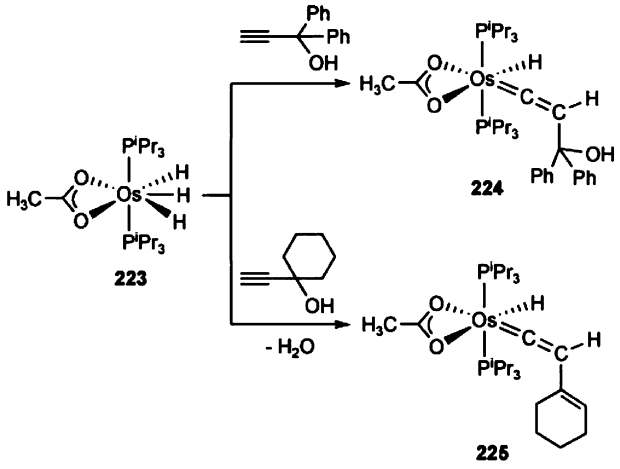
In the solid state and in solution complex **218a** is stable if kept under argon. However under air, it is capable of activating the oxygen–oxygen double bond of O_2 to give the dioxo compound OsCl{(*E*)-CH=CHPh}$(O)_2(P^iPr_3)_2$ (**219**). In pentane at −78 °C, complex **218a** adds $P(OMe)_3$ to form the six-coordinate hydride–vinylidene OsHCl(=C=CHPh){$P(OMe)_3$}$(P^iPr_3)_2$ (**220**). Using complex **218a** as the starting material, octahedral six-coordinate hydride–vinylidene complexes are also prepared by displacement of the chloride by acetylacetonato (acac) and acetato anions (Scheme 68) [91].

The acetato complex **222** has been also obtained from the reaction of the trihydride acetato $OsH_3(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ (**223**) with phenylacetylene [96]. Hydroxyvinylidene and alkenylvinylidene complexes can be similarly prepared by reaction of **223** with alkynols. Thus, complexes $OsH(\kappa^2\text{-}O_2CCH_3)\{=C=CHC(OH)Ph_2\}(P^iPr_3)_2$ (**224**) and $OsH(\kappa^2\text{-}O_2CCH_3)\{=C=CHC=CH(CH_2)_3CH_2\}(P^iPr_3)_2$ (**225**) have been synthesized starting from 1,1-diphenyl-2-propyn-1-ol and 1-ethynyl-1-cyclohexanol, respectively (Scheme 69) [91]. The related alkenylvinylidene complex $OsH(\kappa^2\text{-}O_2CCH_3)\{=C=CHC(Ph)=CH_2\}(P^iPr_3)_2$ (**226**) has been prepared in a one-pot synthesis, by deprotonation and dehydration of the hydride-alkoxy-carbyne **81** [44].

When the deprotonation of **217a** is carried out in the presence of pyrazole (HPz), the six-coordinate hydride–vinylidene complex OsH(pz)(=C=CHPh)(Hpz)$(P^iPr_3)_2$ (**227**), containing pyrazole and pyrazolate ligands, is obtained [50]. From a structural point of view, it should be mentioned that the N–H hydrogen atom of the pyrazole lies between the azole group and the pyrazolate, forming an intramolecular N···H–N hydrogen bond [97]. Treatment of a diethyl ether solution of **227** with 2 equiv of $HBF_4{\cdot}OEt_2$ leads to the fluoro derivative [OsHF(≡CCH_2Ph)(Hpz)$(P^iPr_3)_2$]BF_4 (**228**). The formation of



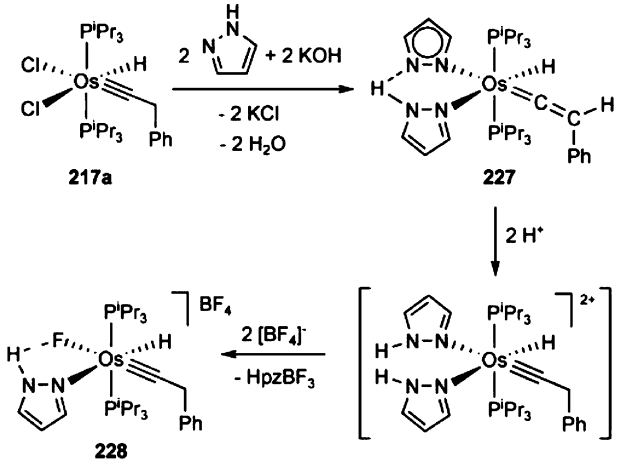
Scheme 68.



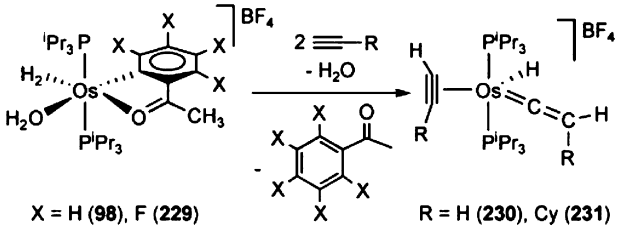
Scheme 69.

the latter has been rationalized according to Scheme 70 [50]. One equivalent of acid protonates the C_β atom of the vinylidene to give a carbyne ligand, whereas the protonation of the pz–H···pz unit by the other equivalent affords two pyrazole groups. Subsequently, the decomposition of a $[BF_4]$ anion gives a fluoride, which displaces one of the pyrazole ligands. The X-ray structure analysis of **228** shows that the N–H hydrogen atom of the pyrazole and the fluoride ligand are involved in intra- and intermolecular F···H–N hydrogen bonding. In polar solvents the intermolecular hydrogen bond is broken. However, the intramolecular interaction is retained. The strength of this interaction appears to depend on the polarity of the solvent decreasing in the sequence chloroform > dichloromethane > acetone [50].

In dichloromethane under 1 atm of acetylene, the elongated dihydrogen complexes $[Os\{C_6X_4C(O)CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$ (X = H (**98**), F (**229**)) eliminate ketone. The resulting unsaturated metallic fragment coordinates two acetylene molecules to afford the novel hydride–vinylidene-π-alkyne derivative $[OsH(=C=CH_2)(\eta^2\text{-}HC\equiv CH)(P^iPr_3)_2]BF_4$ (**230**), with the alkyne acting as a four-electron donor ligand and parallel disposed to the P–Os–P vector. At 233 K, similarly to acetylene, the reactions of **98**



Scheme 70.



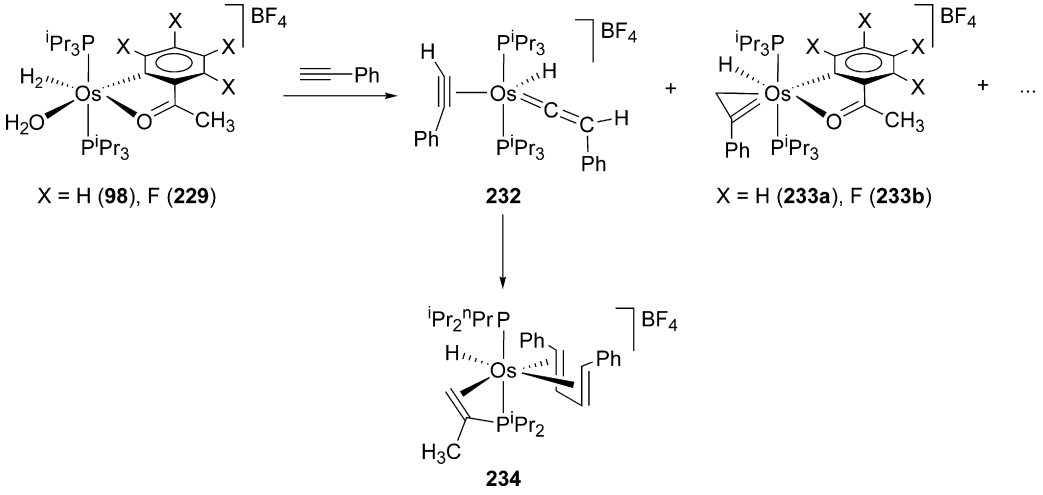
Scheme 71.

and **229** with cyclohexylacetylene give $[OsH(=C=CHCy)(\eta^2\text{-}HC\equiv CCy)(P^iPr_3)_2]BF_4$ (**231**). The stability of **231** is lower than that of **230**. This is consistent with the parallel disposition of the carbon–carbon triple bond of the alkyne with regard to the P–Os–P direction, which imposes a high steric hindrance between the substituent of the alkyne and the isopropyl groups of the phosphines (Scheme 71).

At room temperature, the reactions of **98** and **229** with phenylacetylene lead to complex mixtures of products (Scheme 72). Initially, the main components of mixtures are the hydride–vinylidene-π-alkyne complex $[OsH(=C=CHPh)(\eta^2\text{-}HC\equiv CPh)(P^iPr_3)_2]BF_4$ (**232**) and the hydride-metallacyclopropene compounds $[Os\{C_6X_4C(O)CH_3\}\{=C(Ph)CH_2\}(P^iPr_3)_2]BF_4$ (X = H (**233a**), F (**233b**)). At this temperature complex **232** evolves into the 1,4-diphenylbutadiene derivative $[OsH(\eta^4\text{-}C_4H_4Ph_2)\{[\eta^2\text{-}CH_2=C(CH_3)]P^iPr_2\}(P^iPr_2{}^nPr)]BF_4$ (**234**). The formation of the diene is the result of the reductive condensation of the vinylidene and π-alkyne ligands of **232**. The reductor is one of the triisopropylphosphine ligands, which undergoes dehydrogenation of one of the isopropyl groups, to afford a monoisopropenylphosphine [49b]. In addition to the dimerization–reduction tandem process, the carbon skeleton isomerization of one of the isopropyl groups, to *n*-propyl, of the other phosphine takes place [98].

Complex **230** reacts with MeMgCl and acetone oxime (Scheme 73). Treatment at room temperature of this compound with 1.2 equiv of MeMgCl leads to the allyl derivative $OsH(\eta^3\text{-}C_3H_5)(=C=CH_2)(P^iPr_3)_2$ (**235**), whereas the addition of 2.4 equiv of acetone oxime to dichloromethane solutions of **230** affords the oximate-carbyne compound $[OsH\{\kappa\text{-}N,\kappa\text{-}O[ON=C(CH_3)_2]\}(\equiv CCH_3)(P^iPr_3)_2]BF_4$ (**236**) [49b].

Each osmium-elongated dihydrogen derivative appears to have a particular behavior in the presence of alkynes. In contrast to **98**, complex $[Os\{C_6H_4C(O)CH_3\}(\eta^2\text{-}H_2)\{N(OH)=C(CH_3)_2\}(P^iPr_3)_2]BF_4$ (**237**) gives carbyne derivatives, related to **236**. In the presence of phenylacetylene, cyclohexylacetylene, and *tert*-butylacetylene, the oxime-elongated dihydrogen compound **237** eliminates acetophenone and the resulting unsaturated monohydride intermediate gives $[OsH\{\kappa\text{-}N,\kappa\text{-}O[ON=C(CH_3)_2]\}(\equiv CCH_2R)(P^iPr_3)_2]BF_4$ (R = Ph (**238**), Cy (**239**), ^{t}Bu (**240**)). The transformation alkyne-carbyne seems to occur via alkynyl species involving two dissociation-addition processes, where the oxime ligand plays a main role [49a]. Complexes **238–240** are a novel type of bifunctional organometallic derivatives, which have amphoteric nature reacting with



Scheme 72.

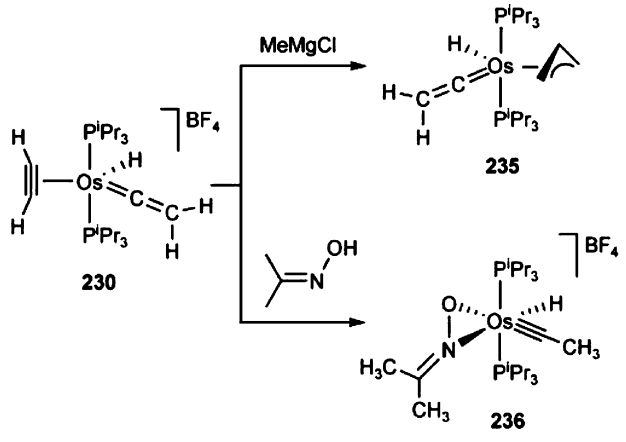
both KOH and HBF_4 (Scheme 74). The reactions with KOH afford the neutral hydride–vinylidene derivatives $OsH\{\kappa\text{-}N, \kappa\text{-}O[ON{=}C(CH_3)_2]\}(=C{=}CHR)(P^iPr_3)_2$ (R = Ph (**241**), Cy (**242**), ^{t}Bu (**243**)), as a result of the deprotonation of the CH_2 group of the carbyne ligand. The reactions with HBF_4 give fluoro-oxime compounds $[OsH\{F\cdots HON{=}C(CH_3)_2\}(\equiv CCH_2R)(P^iPr_3)_2]BF_4$ (R = Ph (**244**), Cy (**245**), ^{t}Bu (**246**)), where a strong F···H hydrogen bond between the fluorine and the OH proton of the oxime appears to stabilize the Os–F bond.

3.4. Azavinylidene–vinylidene and related compounds

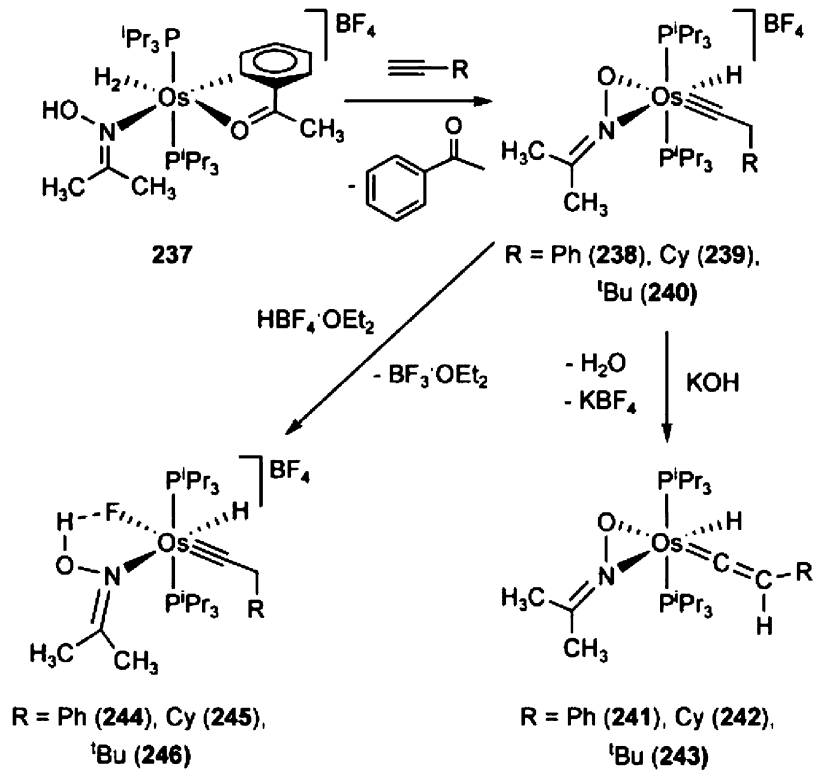
The dihydride-dichloro-osmium(IV) complex $OsH_2Cl_2(P^iPr_3)_2$ reacts with acetone oxime and cyclohexanone oxime, in the presence of Et_3N, to give the dihydride derivatives $OsH_2Cl_2(\kappa^2\text{-}ON{=}CR_2)(P^iPr_3)_2$ ($CR_2 = CMe_2$ (**247**), $\overline{C(CH_2)_4CH_2}$ (**248**)) [99], which afford the corresponding hydride-azavinylidene compounds $OsHCl_2(=N{=}CR_2)(P^iPr_3)_2$ ($CR_2 = CMe_2$ (**249**), $\overline{C(CH_2)_4CH_2}$ (**250**)) by addition of HCl [100]. Although the imido groups [$R_2C{=}N$] are strong bases, the azavinylidene ligands of **249** and **250** are stable towards hydrolysis when they are treated with AgOTf in the presence of water. The reactions lead to the cationic hydride-azavinylidene-osmium(IV) complexes $[OsHCl(=N{=}CR_2)(H_2O)(P^iPr_3)_2]OTf$. The related compounds $[OsHCl(=N{=}CR_2)(CO)(P^iPr_3)_2]OTf$ and $[OsHCl(=N{=}CR_2)\{P(OMe)_3\}(P^iPr_3)_2]OTf$ ($CR_2 = CMe_2$, $\overline{C(CH_2)_4CH_2}$) are formed in the presence of CO and $P(OMe)_3$, respectively [101]. Treatment at room temperature of dichloromethane solutions of the hydride-azavinylidene **249** and **250** with AgOTf, and the subsequent addition at −25 °C of phenylacetylene to the resulting solutions, affords the alkenyl-azavinylidene derivatives $[Os\{(E)\text{-}CH{=}CHPh\}Cl(=N{=}CR_2)(P^iPr_3)_2]OTf$ ($CR_2 = CMe_2$ (**251**), $\overline{C(CH_2)_4CH_2}$ (**252**)), where the H_β atom of the alkenyl ligand interacts with the osmium atom to form an agostic bond. The addition at −30 °C of NaCl to tetrahydrofuran solutions of **251** and **252** produces the split of the agostic interaction and the formation of the neutral six-coordinate alkenyl-azavinylidene compounds $Os\{(E)\text{-}CH{=}CHPh\}Cl_2(=N{=}CR_2)(P^iPr_3)_2$ ($CR_2 = CMe_2$ (**253**), $\overline{C(CH_2)_4CH_2}$ (**254**)). In dichloromethane at room temperature complexes **253** and **254** evolve into the imine-vinylidene derivatives $OsCl_2(=C{=}CHPh)(NH{=}CR_2)(P^iPr_3)_2$ ($CR_2 = CMe_2$ (**255**), $\overline{C(CH_2)_4CH_2}$ (**256**)), as a result of the novel hydrogen transfer from the styryl ligand to the azavinylidene groups (Scheme 75) [102].

In contrast to phenylacetylene, the reactions of the hydride-azavinylidene complex **249** with AgOTf and alkynes such as acetylene, cyclohexylacetylene, and 1-pentyne lead, in a one-pot synthesis, to the five-coordinate azavinylidene-carbyne compounds $[OsCl\{=N{=}C(CH_3)_2\}(\equiv CCH_2R)(P^iPr_3)_2]OTf$ (R = H (**257**), Cy (**258**), ^{n}Pr (**259**)), which react with methyllithium to afford the five-coordinate azavinylidene–vinylidene derivatives $OsCl\{=N{=}C(CH_3)_2\}(=C{=}CHR)(P^iPr_3)_2$ (R = H (**260**), Cy (**261**), ^{n}Pr (**262**)) [103], as a result of the deprotonation of the CH_2R substituent of the carbyne ligands (Scheme 76).

The formation of the carbyne ligands of **257**–**259** is the result of the extraction of a chloride from **249** and the subsequent addition of the Os–H bond to the alkynes. The reactions initially give azavinylidene-alkenyl intermediates, which evolve by a formal 1,2-hydrogen shift within the alkenyl group into the



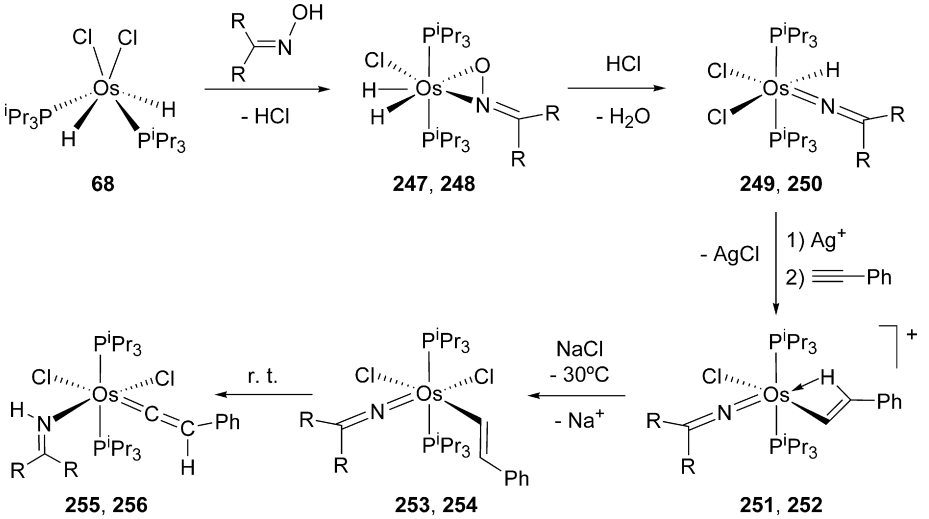
Scheme 73.



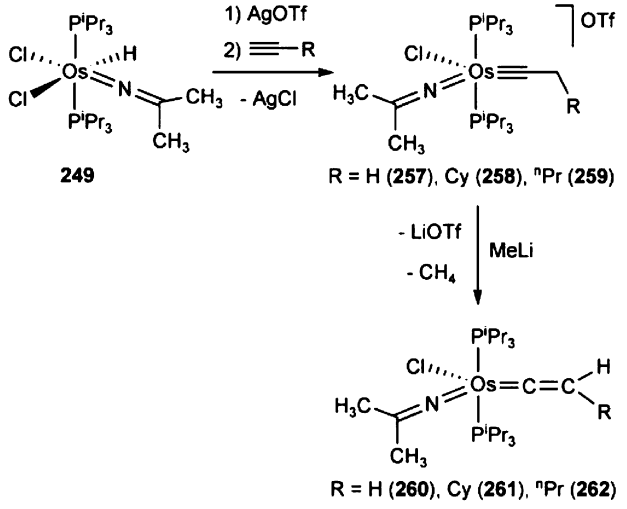
Scheme 74.

carbynes. This hydrogen shift involves: (i) the hydrogen transfer from the C_α atom of the alkenyl ligand to the nitrogen atom of the azavinylidene group to afford imine-vinylidene species and (ii) the NH hydrogen migration from the imine to the C_β atom of the vinylidene. In agreement with this, it has been observed that at −25 °C the addition of cyclohexylacetylene to the solution resulting from the treatment of **249** with AgOTf affords $[Os\{(E)\text{-}CH{=}CHCy\}Cl\{{=}N{=}C(CH_3)_2\}(P^iPr_3)_2]OTf$ (**263**), related to **251** and **252**. Similarly to the latter, at −30 °C the addition of NaCl to tetrahydrofuran solutions of **263** gives rise to the imine-vinylidene devivative $OsCl_2(=C{=}CHCy)\{NH{=}C(CH_3)_2\}(P^iPr_3)_2$ (**264**), as a result of the hydrogen transfer from the alkenyl group to the azavinylidene ligand. In contrast to **255** and **256**, complex **264** is not stable in dichloromethane at room temperature. It dissociates a chloride and evolves into **258** by hydrogen transfer from the imine to the C_β atom of the vinylidene (Scheme 77).

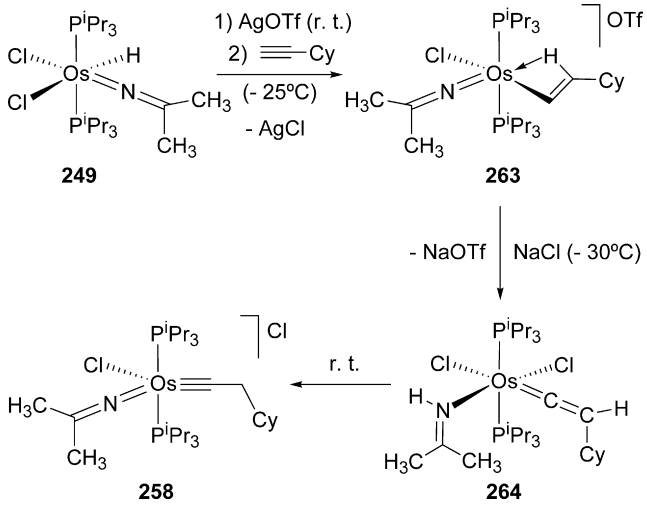
The azavinylidene-alkenylcarbyne derivatives $[OsCl\{{=}N{=}C(CH_3)_2\}\{{\equiv}CCH{=}C(CH_3)_2\}(P^iPr_3)_2]OTf$ (**265**) and $[OsCl\{{=}N{=}C(CH_3)_2\}\{{\equiv}CCH{=}CRPh\}(P^iPr_3)_2]OTf$ (R = H



Scheme 75.

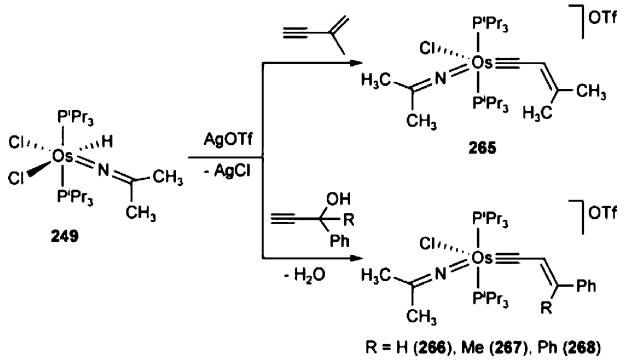


Scheme 76.

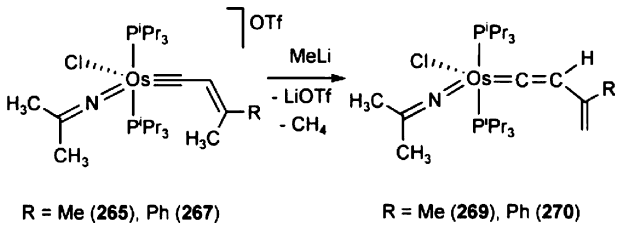


Scheme 77.

(**266**), CH_3 (**267**), Ph (**268**)) are similarly formed from enynes and alkynols, respectively (Scheme 78). In this case the reactions initially give azavinylidene-butadienyl or azavinylidene-hydroxyalkenyl intermediates, which evolve into imine-alkenylvinylidene or imine-hydroxyvinylidene species, respectively. The imine-alkenylvinylidenes afford



Scheme 78.



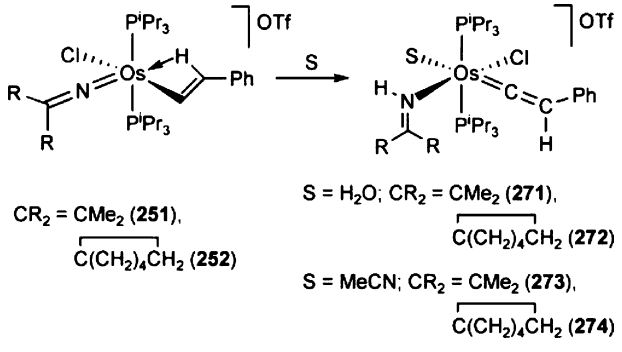
Scheme 79.

azavinylidene-alkenylcarbynes by migration of the NH hydrogen from the imine to the C_δ atom of the alkenylvinylidene ligand, whereas the imine-hydroxyvinylidenes afford azavinylidene-alkenylcarbynes by protonation of the OH group of the hydroxyvinylidene with the NH of the imine [103].

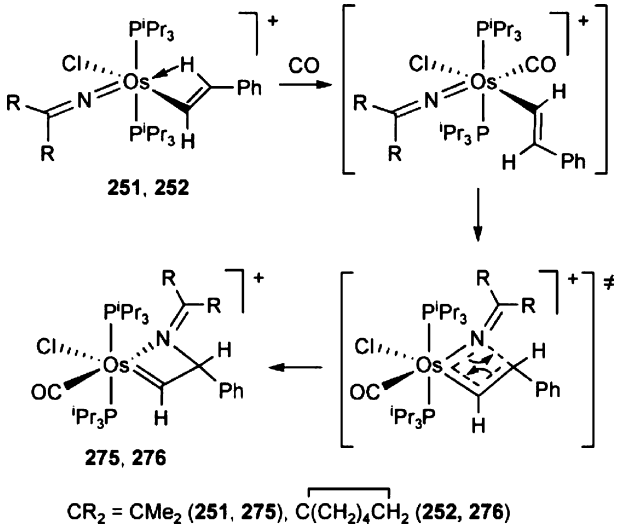
Treatment at room temperature of tetrahydrofuran solutions of **265** and **267** with methyllithium affords the azavinylidene-alkenylvinylidene complexes $OsCl\{=N=C(CH_3)_2\}\{=C=CHC(R)=CH_2\}(P^iPr_3)_2$ (R = CH_3 (**269**), Ph (**270**)), as a result of the deprotonation of the methyl group of the alkenyl substituent of the carbyne ligands (Scheme 79).

Cationic imine-vinylidene derivatives, related to **255**, **256** and **264**, have been prepared by addition of weak Lewis bases to **251** and **252** (Scheme 80). The formation of $[OsCl\{=C=CHPh\}S(NH=CR_2)(P^iPr_3)_2]OTf$ (S = H_2O; CR_2 = CMe_2 (**271**), $C(CH_2)_4CH_2$ (**272**). S = CH_3CN; CR_2 = CMe_2 (**273**), $C(CH_2)_4CH_2$ (**274**)) takes place via alkenyl-azavinylidene intermediates which, similarly to **253** and **254**, evolves into **271**–**274** by hydrogen transfer from the styryl ligand to the azavinylidene groups [102].

Under atmospheric pressure of carbon monoxide, complexes **251** and **252** afford the Δ^2-1,2-azaosmetine compounds $[OsCl\{=CHCH(Ph)N=CR_2\}(CO)(P^iPr_3)_2]OTf$ (CR_2 = CMe_2 (**275**), $C(CH_2)_4CH_2$ (**276**)). The formation of these compounds has been rationalized as intramolecular [2 + 2] cycloaddition reactions between the osmium azavinylidene bonds and the carbon–carbon double bond of the styryl ligands (Scheme 81). The first step of these transformations appears to be the coordination of carbon monoxide *trans* to the azavinylidene ligands. Thus, the strong π-acceptor power of the carbonyl could excite the π-donor nature of the azavinylidene groups increasing the double bond character of the osmium–azavinylidene bonds and, in this way, activate the intramolecular cycliza-



Scheme 80.

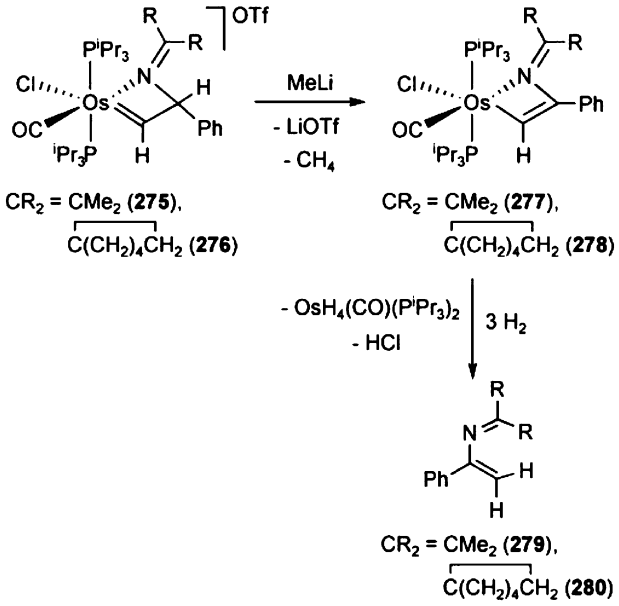


Scheme 81.

tion between the Os–N and C–C double bonds. The very low π-acceptor capacity of the chloride, water, and acetonitrile ligands could explain why the previously mentioned complexes Os{(*E*)-CH=CHPh}Cl_2(=N=CR_2)(P^iPr_3)$_2$ and [Os{(*E*)-CH=CHPh}Cl(=N=CR_2)S(P^iPr_3)$_2$]OTf evolve into imine-vinylidene species (**255**, **256,** or **271**–**274**) instead of Δ^2-1,2-azaosmetine derivatives [104].

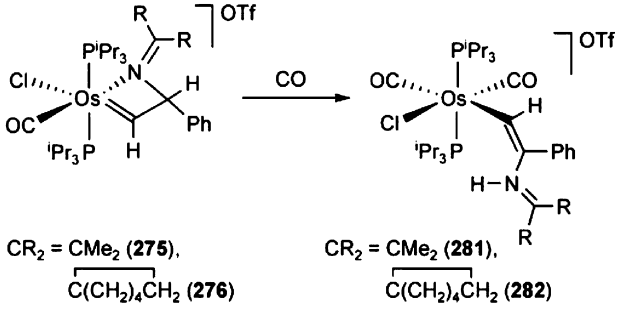
The formation of **275** and **276** is the key step to form 2-aza-1,3-butadienes by means of the stoichiometric imination of phenylacetylene with acetone oxime and cyclohexanone oxime, in the presence of **68** (Scheme 82). Thus, it has been observed that the deprotonation of **275** and **276** with methyllithium afford the Δ^3-1,2-azaosmetine compounds Os{CH=C(Ph)N=CR_2}Cl(CO)(P^iPr_3)$_2$ (CR_2 = CMe_2 (**277**), $C(CH_2)_4CH_2$ (**278**)), which react with molecular hydrogen to give the well known complex $OsH_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ [105] and CH_2=C(Ph)N=CR_2 (CR_2 = CMe_2 (**279**), $C(CH_2)_4CH_2$ (**280**)) [104], according to Scheme 83.

Complexes **275** and **276** are also intermediate species to form η^1-azoniabutadienyl derivatives (Scheme 84). Their carbonylation produces the ring opening of the Δ^2-1,2-azaosmetine units and the 1,2-hydrogen shift from

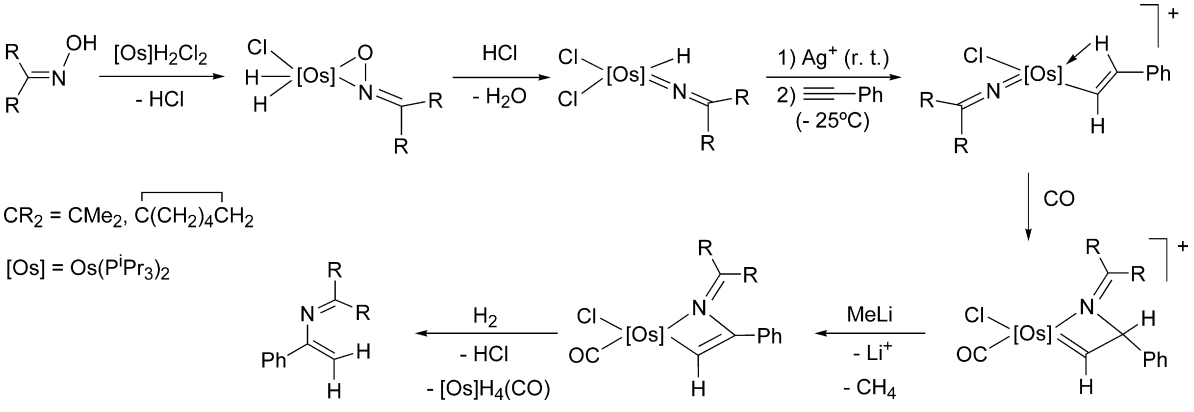


Scheme 83.

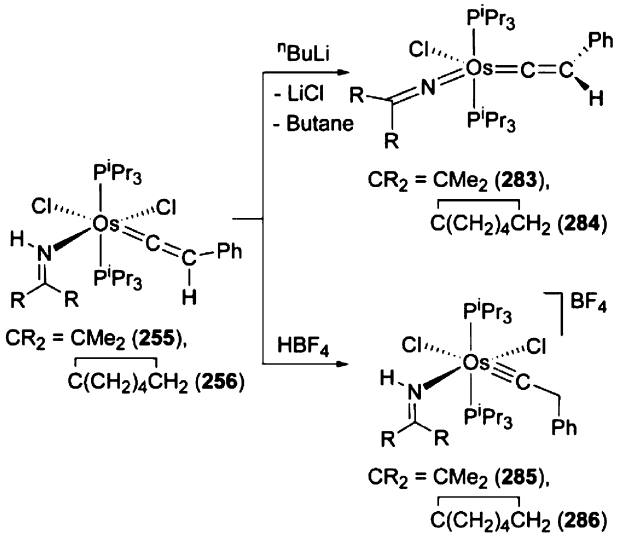
the CHPh carbon atom to the nitrogen to give [Os{(*Z*)-CH=C(Ph)NH=CR_2}Cl(CO)$_2$(P^iPr_3)$_2$]OTf (CR_2 = CMe_2 (**281**), $C(CH_2)_4CH_2$ (**282**)). These compounds are also obtained starting from the Δ^3-1,2-azaosmetine complexes **277**, and **278** by initial carbonylation and subsequent protonation of the resulting η^1-azabutadienyl species [104].



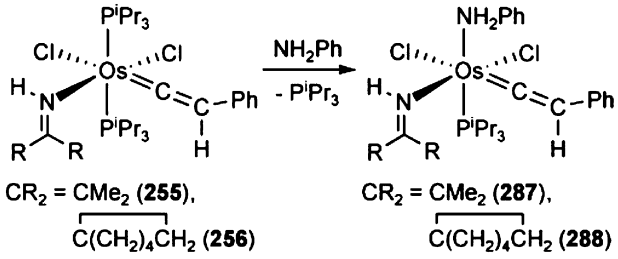
Scheme 84.



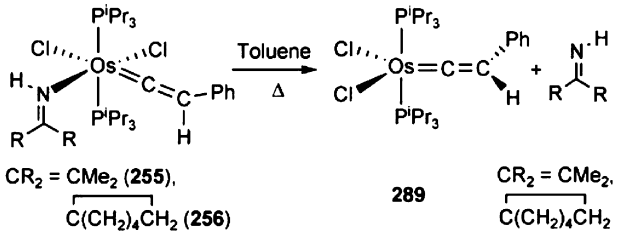
Scheme 82.



Scheme 85.



Scheme 86.



Scheme 87.

The reactivity of the imine-vinylidene compounds **255** and **256** is the result of: (i) the electrophilic character of the NH-hydrogen atom of the imines and the nucleophilic character of the vinylidene ligand, (ii) the electronegativity of the chloride ligand, which favors the formation of hydrogen bonds, and (iii) the weak Lewis basicity of the imine nitrogen atom [106].

As a consequence of the electrophilic character of the NH-hydrogen atom of the imine and the nucleophilic character of the vinylidene, complexes **255** and **256** have amphoteric nature, transferring the NH-hydrogen proton to bases such as amines and ^{n}BuLi and accepting the proton from HBF_4 (Scheme 85). In their reactions as acids, the conjugated bases are the five-coordinate azavinylidene–vinylidene compounds $OsCl(=N=CR_2)(=C=CHPh)(P^iPr_3)_2$ ($CR_2 = CMe_2$ (**283**), $\overline{C(CH_2)_4CH_2}$ (**284**)). In their reactions as bases the conjugated acids are the imine-carbyne derivatives $[OsCl_2(\equiv CCH_2Ph)(NH=CR_2)(P^iPr_3)_2]^+$ ($CR_2 = CMe_2$ (**285**), $\overline{C(CH_2)_4CH_2}$ (**286**)).

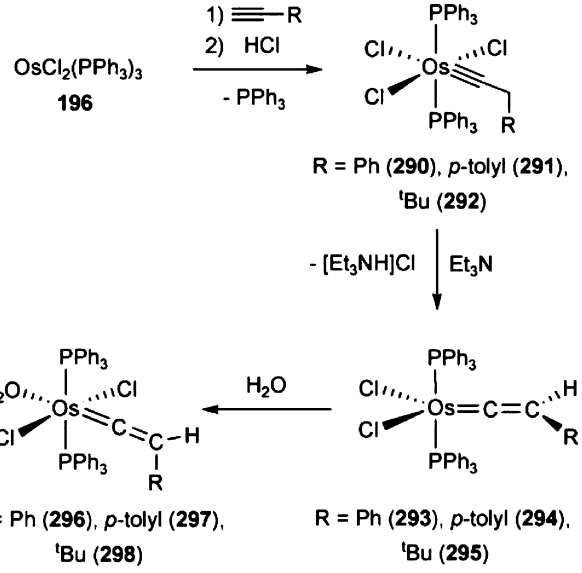
The high electronegativity of the chlorine makes this ligand efficient for forming inter- and intramolecular hydrogen bonds with ligands containing hydrogen atoms bonded to the donor atom. The additional stabilization resulting from these H···Cl interactions appears to be the reason for the surprising formation of the mixed amine-phosphine complexes $OsCl_2(=C=CHPh)(NH=CR_2)(NH_2Ph)(P^iPr_3)$ ($CR_2 = CMe_2$ (**287**), $\overline{C(CH_2)_4CH_2}$ (**288**)), which are obtained as a result of the displacement of a triisopropylphosphine ligand from **255** and **256** by aniline (Scheme 86).

As a result of the weak Lewis basicity of the nitrogen atom of the imines, complexes **255** and **256** dissociate the N-H ketenimine in toluene under reflux to give $OsCl_2(=C=CHPh)(P^iPr_3)_2$ (**289** in Scheme 87).

Triphenylphosphine-osmium-vinylidene complexes, related to **289**, have been prepared according to Scheme 88 [107]. Treatment of **196** with HC≡CR(R = Ph, *p*-tolyl, ^{t}Bu) in the presence of HCl gives the corresponding trichlorocarbyne compounds $OsCl_3(\equiv CCH_2R)(PPh_3)_2$ (R = Ph (**290**), *p*-tolyl (**291**), ^{t}Bu (**292**)) in good yields. The vinylidene derivatives $OsCl_2(=C=CHR)(PPh_3)_2$ (R = Ph (**293**), *p*-tolyl (**294**), ^{t}Bu (**295**)) are prepared from the reactions of **290–292** with Et_3N. These new vinylidene compounds are hygroscopic and react with water to give the aqua-vinylidene complexes $OsCl_2(=C=CHR)(H_2O)(PPh_3)_2$ (R = Ph (**296**), *p*-tolyl (**297**), ^{t}Bu (**298**)). The six-coordinate vinylidene derivatives $OsF_2(=C=CH_2)(CO)(P^tBu_2Me)_2$ [108] and $OsCl_2(=C=CHPh)\{\kappa\text{-}P,N[^iPr_2PCH_2CH_2NMe_2]\}(P^iPr_3)$ [109] are also known.

3.5. Cyclic metallaallenes and related compounds

1,2,4-Cyclohexatriene (**Ia** in Plate 4) is a short-lived strained allene isomer of benzene. The cyclic **Ia** structure has been proposed as the key intermediate in Diels-Alder reactions of enynes



Scheme 88.

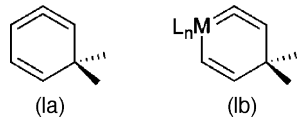


Plate 4.

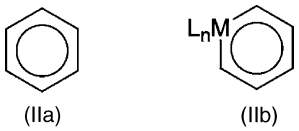
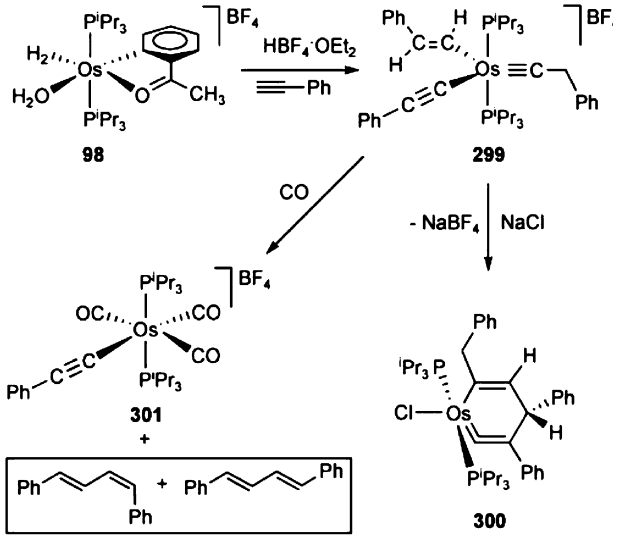


Plate 5.



Scheme 89.

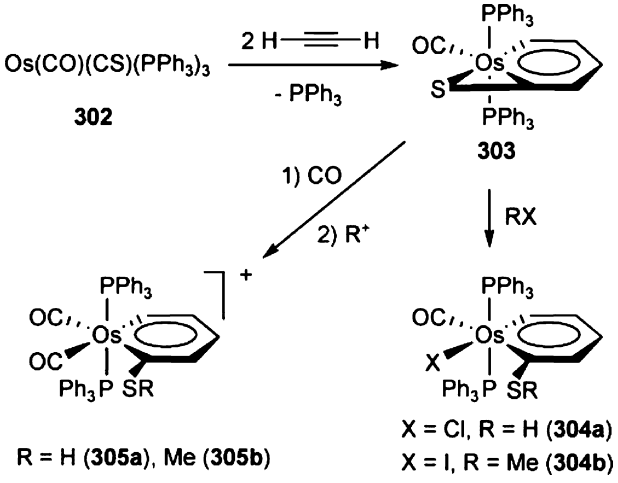
with alkynes. Conclusive evidence of **Ia** was obtained by the isolation of trapping products, after **Ia** had been generated in the presence of activated olefins. Metalla-**Ia** structures in which the 3-CH group is formally replaced by a L_nM transition metal fragment (**Ib** in Plate 4) appears to be more stable than **Ia**. Thus, the first isometallabenzene with structure of 1,2,4-cyclohexatriene has been recently prepared (Scheme 89), and characterized by X-ray diffraction analysis [110].

Treatment at −50 °C of dichloromethane solutions of **98** with 2.0 equiv of $HBF_4{\cdot}OEt_2$ and 4.5 equiv of phenylacetylene affords the 16e⁻-alkenyl-alkynyl-carbyne intermediate $[Os\{(E)\text{-}CH{=}CHPh\}(C{\equiv}CPh)(\equiv CCH_2Ph)(P^iPr_3)_2]BF_4$ (**299**). In dichloromethane at temperatures higher than −30 °C, complex **299** is unstable and evolves into a complex mixture of unidentified products. However, in the presence of an excess of NaCl, the evolution takes place in a controlled way, and the cyclic allene derivative $OsCl\{=C=C(Ph)CH(Ph)CH=C(CH_2Ph)\}(P^iPr_3)_2$ (**300**) is formed. Complex **300** is the result of the coordination of a chloride ligand to the osmium atom of **299** and the migration of the alkenyl group from the metallic center to both the alkynyl and the carbyne ligands. The addition is regiospecific: the C_α atom of the alkenyl group is coupled with the C_α atom of the carbyne, while the C_β atom of the alkenyl is coupled with the C_β atom of the alkynyl. In contrast to chloride, CO only promotes the coupling between the alkenyl group and the carbyne ligand. Under a carbon monoxide atmosphere, complex **299** affords *cis*,*trans*- and *trans*,*trans*-1,4-diphenylbutadiene and the alkynyl-tricarbonyl derivative $[Os(C{\equiv}CPh)(CO)_3(P^iPr_3)_2]BF_4$ (**301**).

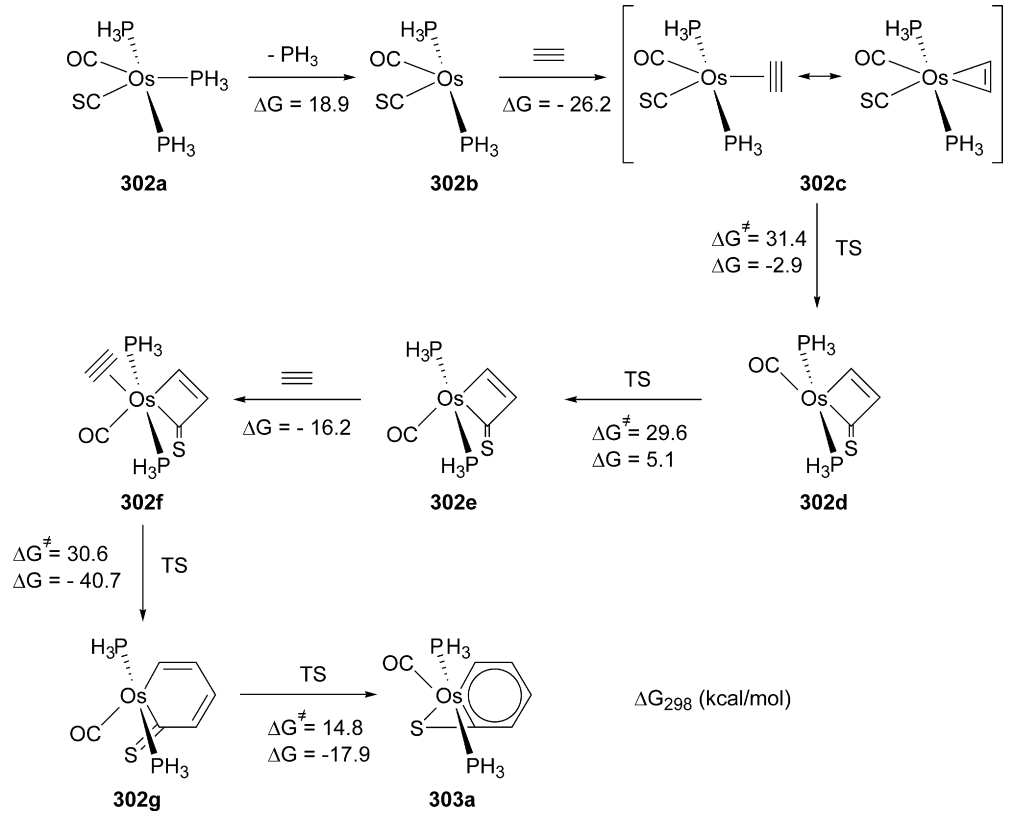
Structure **Ib** is related to a metal vinylidene complex just as structure **IIb** (Plate 5) is related to a carbene complex. Metallabenzenes (**IIb**) are a class of benzene analogues on which a CH group has been formally replaced by a transition metal and its associated ligands [111].

The first example of a stable, isolable, metallabenzene was reported by Roper and co-workers in 1982 [112]. Osmabenzene $[Os\{C(S)CHCHCHCH\}(CO)(PPh_3)_2$ (**303** in Scheme 90) was synthesized by a cyclization reaction involving the thiocarbonyl ligand of the precursor $Os(CO)(CS)(PPh_3)_3$ (**302**) and two acetylene molecules. Closely related molecules $Os\{C(SR)CHCHCHCH\}X(CO)(PPh_3)_2$ (X = Cl, R = H (**304a**); X = I, R = Me (**304b**)) were generated by protonation or methylation of **303**, while osmabenzenes $[Os\{C(SR)CHCHCHCH\}(CO)_2(PPh_3)_2]^+$ (R = H (**305a**), Me (**305b**)) were prepared by treatment of **303** with carbon monoxide, followed by protonation or methylation [112]. The reaction of **302** with propyne gives a complex mixture of products from which can be separated the osmabenzene $[Os\{C(S)C(CH_3)CHCHC(CH_3)\}(CO)(PPh_3)_2$ [113].

The mechanism for the formation of **303** has been examined by computational methods [114], starting from the model complex $Os(CO)(CS)(PH_3)_3$ (**302a** in Scheme 91). The reaction pathway appears to involve phosphine dissociation, η^2-coordination of the first acetylene molecule followed by C–C coupling to give an osmacyclobutenthianone complex. From this complex, **302d**, CO migration to the other *cis*-coordination site, η^2-coordination of the second acetylene followed by C–C coupling and C=S activation of the resulting osmacyclohexadienthione **302g** yields in the end the osmabenzene **303a**.



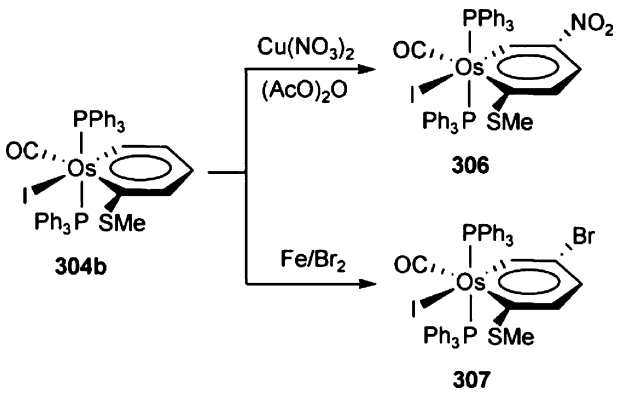
Scheme 90.



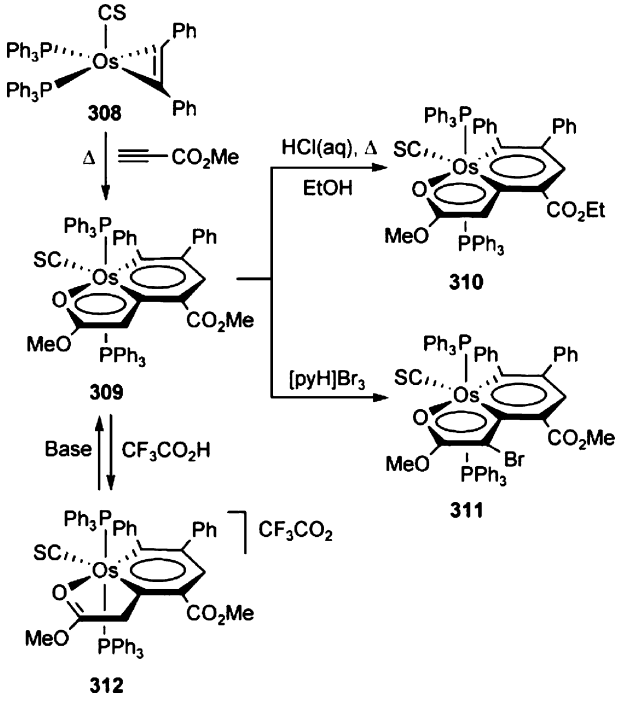
Scheme 91.

In agreement with the aromatic character of this type of derivatives, it has been observed that complex **304b** undergoes electrophilic aromatic substitution reactions (Scheme 92), specifically mononitration and monohalogenation, to produce Os{C(SMe)CHCHC(NO_2)CH}I(CO)(PPh_3)$_2$ (**306**) and Os{C(SMe)CHCHC(Br)CH}I(CO)(PPh_3)$_2$ (**307**), respectively. In both cases the SMe ring substituent exerts a strong *para*-directing effect [115].

The diphenylacetylene complex Os(η^2-PhC≡CPh)(CS)(PPh_3)$_2$ (**308** in Scheme 93), similarly to **302**, reacts with two molecules of methyl propiolate to give the osmabenzofuran [Os{C[CHC(OMe)O]C(CO_2Me)CHC(Ph)C(Ph)}(CS)(PPh_3)$_2$ (**309**), which is a tethered osmabenzene [116]. The bicyclic ring



Scheme 92.



Scheme 93.

system is remarkably robust and heating this compound in ethanol at reflux with aqueous HCl effects only a transesterification of the ester function in the six-membered ring, forming [Os{C[CHC(OMe)O]C(CO_2Et)CHC(Ph)C(Ph)}(CS)(PPh_3)$_2$ (**310**).

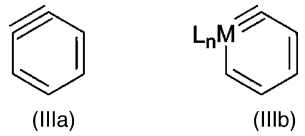


Plate 6.

Reactions of **309** with pyridinium tribromide effects bromination in the five-membered ring of the osmabenzofuran to form $[Os\{C[C(Br)C(OMe)O]C(CO_2Me)CHC(Ph)C(Ph)\}(CS)(PPh_3)_2$ (**311**). Treatment of **309** with trifluoroacetic acid results the cationic tethered osmabenzene $[Os\{C[CH_2C(OMe)=O]C(CO_2Me)CHC(Ph)C(Ph)\}(CS)(PPh_3)_2][CF_3CO_2]$ (**312**).

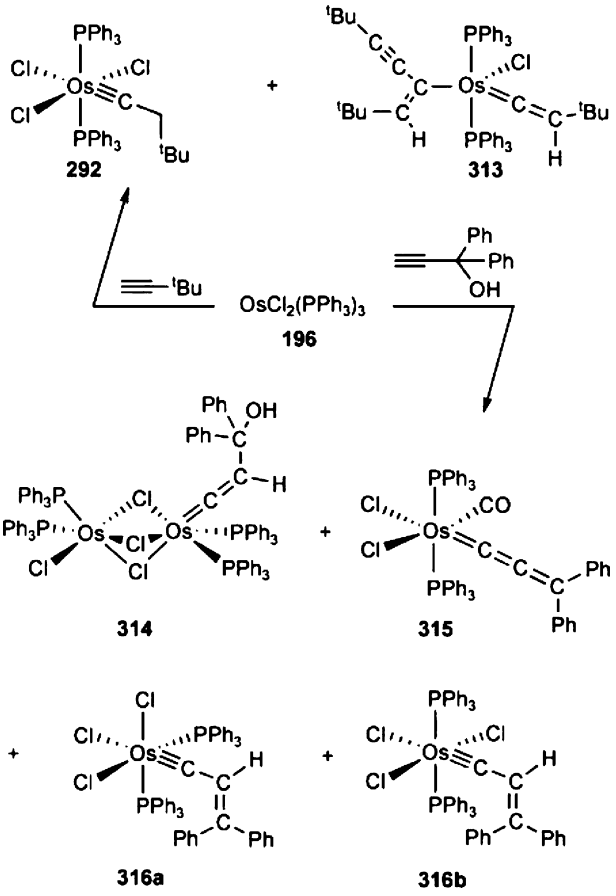
The six-membered organic compounds with a C≡C triple bond in the ring, in particular benzynes (**IIIa** in Plate 6), are usually unstable at room temperature. The formal replacement of one of the C(sp) atoms in **IIIa** by a transition metal and its associated ligands (**IIIb**) increases the stability of the six-membered ring. Thus, the first stable metallabenzyne has been recently prepared by Jia and co-workers [117].

The isolable products from the reactions of **196** with terminal alkynes are strongly dependent on the substituent of the alkyne. Reactions of **196** with *tert*-butylacetylene lead to the trichloro-carbyne **292** and the alkenyl vinylidene $Os\{C(C{\equiv}C^tBu){=}CH^tBu\}Cl(=C=CH^tBu)(PPh_3)_2$ (**313** in Scheme 94) [118]. Reactions of **196** with 1,1-diphenyl-2-propyn-1-ol produce the dinuclear vinylidene $(PPh_3)_2ClOs(\mu\text{-}Cl)_3Os\{=C=CHC(OH)Ph_2\}(PPh_3)_2$ (**314**), the allenylidene $OsCl_2(=C=C=CPh_2)(CO)(PPh_3)_2$ (**315**) and the trichloro carbyne isomers $OsCl_3(\equiv CCH=CPh_2)(PPh_3)_2$ (**316a**,**b**) [119].

Under similar conditions, reactions of **196** with trimethylsilylacetylene (Scheme 95) produces the osmabenzyne $Os\{\equiv CC(SiMe_3){=}C(Me)C(SiMe_3){=}CH\}Cl_2(PPh_3)_2$ (**317**) along with other complexes such as the trichloro-carbyne $OsCl_3(\equiv CCH_3)(PPh_3)_2$ (**318**) and the alkenyl-vinylidene derivatives $Os\{C(C{\equiv}CSiMe_3){=}CHSiMe_3\}Cl(=C=CHSiMe_3)(PPh_3)_2$ (**319**) and $Os\{C(C{\equiv}CSiMe_3){=}CHSiMe_3\}(C{\equiv}CSiMe_3)(=C=CHSiMe_3)(PPh_3)_2$ (**320**) [120].

The cycloaddition of $HC{\equiv}CSiMe_3$ on the vinylidene intermediate $OsCl_2(=C=CH_2)(PPh_3)_2$ has been proposed as the key step for the formation of **317** [117,121]. In agreement with this, it has been observed that the vinylidene **293** reacts with phenylacetylene to give the allenylcarbene compound $OsCl_2\{=C[\eta^2\text{-}CH=C=CHPh]Ph\}(PPh_3)_2$ (**321** in Scheme 96), which can be also prepared from the one-pot reaction of **196** and phenylacetylene. Treatment of **321** with phenylacetylene in the presence of triethylamine yields the osmabenzyne $Os\{\equiv CC(Ph){=}C(CH_2Ph)CH{=}C(Ph)\}Cl_2(PPh_3)_2$ (**322**) [122].

Complex **322** can be also obtained from the reaction of **321** with $(PPh_3)AuC{\equiv}CPh$. This chemistry has been extended to prepare osmabenzyne complexes, using different gold(I) acetylide derivatives (Scheme 97). Treatment of **321** with $(PPh_3)AuC{\equiv}C$-tolyl produces $Os\{\equiv CC(tolyl){=}C(CH_2Ph)CH{=}C(Ph)\}Cl_2(PPh_3)_2$ (**323**), treatment with $(PPh_3)AuC{\equiv}C^nBu$ produces

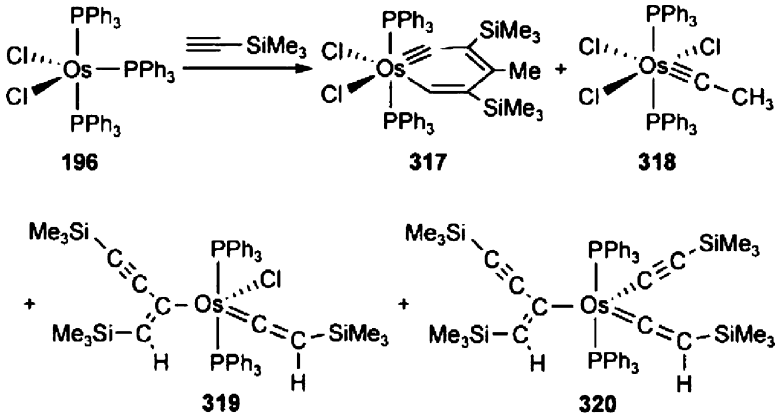


Scheme 94.

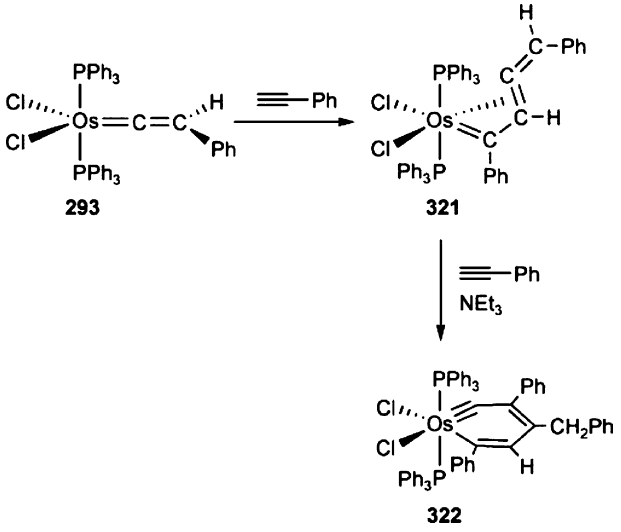
$Os\{\equiv CC(^nBu){=}C(CH_2Ph)CH{=}C(Ph)\}Cl_2(PPh_3)_2$ (**324**) and treatment with $(PPh_3)AuC{\equiv}CSiMe_3$ gives $Os\{\equiv CC(SiMe_3){=}C(CH_2Ph)CH{=}C(Ph)\}Cl_2(PPh_3)_2$ (**325**).

Theoretical calculations at the B3LYP level of density functional theory have been carried out to study the stability of the osmabenzyne complexes. The ring strain energy was found to be small, primarily because of the relatively small angle of bending at the carbyne carbon (149.3°). The conjugation energy is comparable to those of benzene and osmabenzene. The effect of the substituents at the ring carbons on the stabilities has been also examined. π-Electron accepting groups at the carbon atoms disposed in β position with regard to the osmium atom are found to increase the HOMO–LUMO gaps and are good stabilizing substituents [123].

The osmabenzyne complexes undergo electrophilic substitution reactions (Scheme 98). Complex **317** reacts with 2 equiv of HBF_4 in wet dichloromethane to give the cationic osmabenzyne $[Os\{\equiv CC(SiMe_3){=}C(Me)C(SiMe_3){=}CH\}Cl(H_2O)(PPh_3)_2]BF_4$ (**326**), which is presumably formed by protonation of one of the chloride ligands followed by trapping the intermediate with water present in the reaction medium. In the presence of NaCl the dissociation of the chloride is supressed and the protonation reaction gives the neutral desilylated osmabenzyne $[Os\{\equiv CCH{=}C(Me)CH{=}CH\}Cl_2(PPh_3)_2$ (**327**). Complex **326** can be also desilylated to give



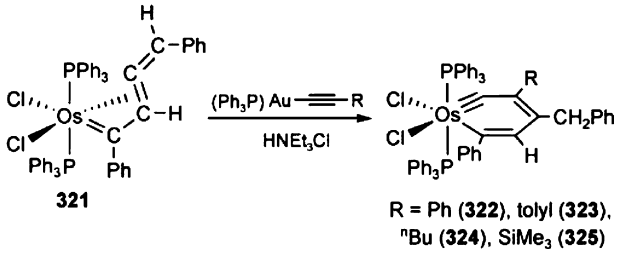
Scheme 95.



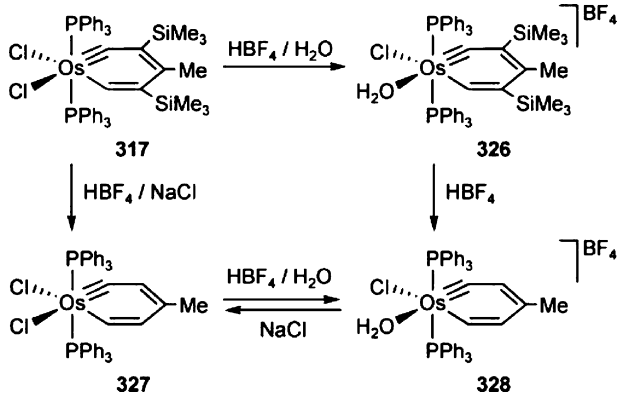
Scheme 96.

$[Os\{\equiv CCH=C(Me)CH=CH\}Cl(H_2O)(PPh_3)_2]BF_4$ (**328**) when treated with excess of HBF_4 [124].

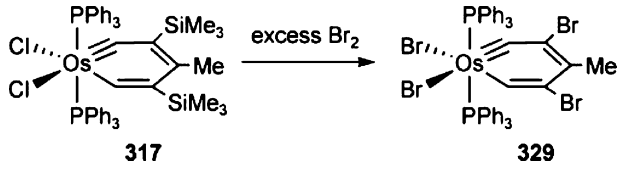
The reactions of **317** and **326** with HBF_4 to give **327** and **328** are similar to the reactions of $C_6H_5SiMe_3$ with acids. Reactions of the latter with bromine are known to give C_6H_5Br. Like $C_6H_5SiMe_3$, complex **317** also reacts with excess Br_2 to give $[Os\{\equiv CC(Br)=C(Me)C(Br)=CH\}Br_2(PPh_3)_2$ (**329**) as the predominant species (Scheme 99).



Scheme 97.



Scheme 98.

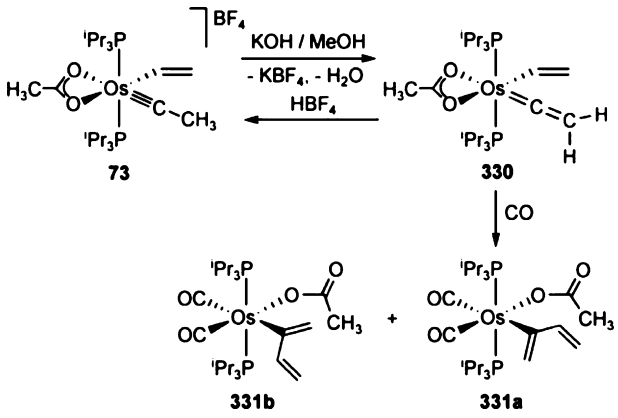


Scheme 99.

3.6. Vinylidene complexes as intermediates in the preparation of butadienyl derivatives

The vinyl–carbyne complex **73** reacts with a stoichiometric amount of KOH in methanol to yield the vinyl–vinylidene derivative $Os(CH=CH_2)(\kappa^2\text{-}O_2CCH_3)(=C=CH_2)(P^iPr_3)_2$ (**330**), as a result of the deprotonation of the carbyne ligand [12c]. Under carbon monoxide atmosphere, complex **330** evolves by migratory insertion of the vinylidene into the osmium–vinyl bond to afford the butadienyl derivative $Os\{C(CH=CH_2)=CH_2\}\{\kappa^1\text{-}OC(O)CH_3\}(CO)_2(P^iPr_3)_2$ (**331**), which in solution exists as a mixture of the isomers **a** and **b** shown in Scheme 100.

The vinyl–vinylidene complex **330** is the key species to prepare dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate, by coupling of two molecules of acetylene and one molecule of dimethyl acetylendicarboxylate, using the $Os(O_2CCH_3)(P^iPr_3)_2$ moiety as a template. This unit is introduced in the form of



Scheme 100.

the dihydride-acetate complex **72**. Scheme 101 summarizes the steps of the process.

In agreement with Scheme 101, it has been observed that, at 45 °C the benzene solutions of the isomeric mixture **331** react with dimethyl acetylenedicarboxylate to give $Os\{C{=}CHCH_2C(CO_2Me){=}C(CO_2Me)CH_2\}\{\kappa^1\text{-}OC(O)CH_3\}(CO)_2(P^iPr_3)_2$ (**332**), as the result of a Diels-Alder reaction between the butadienyl ligand of **331** and the activated alkyne. In solution, complex **332** also exists as a mixure of the isomers **a** and **b** shown in Scheme 102. This isomeric mixture reacts in chloroform with $HBF_4{\cdot}OEt_2$ to give the previously mentioned complex **64** and dimethyl 1,4-cylohexadiene-1,2-dicarboxylate in quantitative yield. Complex **331** also reacts with maleic anhydride. In this case, the cycloaddition reactions lead to an isomeric mixture of $Os\{C{=}CHCH_2CH[C(O)OC(O)]CHCH_2\}\{\kappa^1\text{-}OC(O)CH_3\}(CO)_2(P^iPr_3)_2$ (**333**). Attempts to separate the bicycle from the metallic fragment, by reaction of the isomeric mixture with H_2 or I_2, have been unsuccessful.

A chloro-osmium-butadienyl complex related to **331** has been prepared by the procedure shown in Scheme 103. The trihydride-chloro-osmium(IV) complex $OsH_3Cl(P^iPr_3)_2$ (**334**) is dehydrogenated in the presence of 2 equiv of trimethylsilylacetylene to give the silylated olefin and the hydride–vinylidene derivative $OsHCl(=C{=}CHSiMe_3)(P^iPr_3)_2$ (**335**) [125]. The reaction of the latter with a new molecule of trimethylsilylacetylene affords the alkenyl-vinylidene $Os\{(E)\text{-}CH{=}CHSiMe_3\}Cl(=C{=}CHSiMe_3)(P^iPr_3)_2$ (**336**). Similarly to **330**, carbon monoxide induces migration of the vinylidene into the osmium–alkenyl bond to give the butadienyl compound $Os\{C(CH{=}CHSiMe_3){=}CHSiMe_3\}Cl(CO)_2(P^iPr_3)_2$ (**337**) [126].

The migratory insertion of a vinylidene ligand into an osmium alkenyl bond can be also promoted by chloride (Scheme 104). The dihydride–dihydrogen complex $OsH_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ (**50**) reacts with 2 equiv of methylpropiolate to give the alkynyl-alkenyl derivative $Os\{CH{=}CHC(O)OMe\}(C{\equiv}CCO_2Me)(CO)(P^iPr_3)_2$ (**338**) [28]. The addition of 1 equiv of $HBF_4{\cdot}OEt_2$ to diethyl ether solutions of **338** affords the alkenyl-vinylidene $[Os\{CH{=}CHC(O)OMe\}(=C{=}CHCO_2Me)(CO)(P^iPr_3)_2]BF_4$ (**339**), which by treatment with NaCl, gives the butadienyl $Os\{C(CH{=}CHCO_2CH_3){=}CHC(O)OCH_3\}Cl(CO)(P^iPr_3)_2$ (**340**) [127].

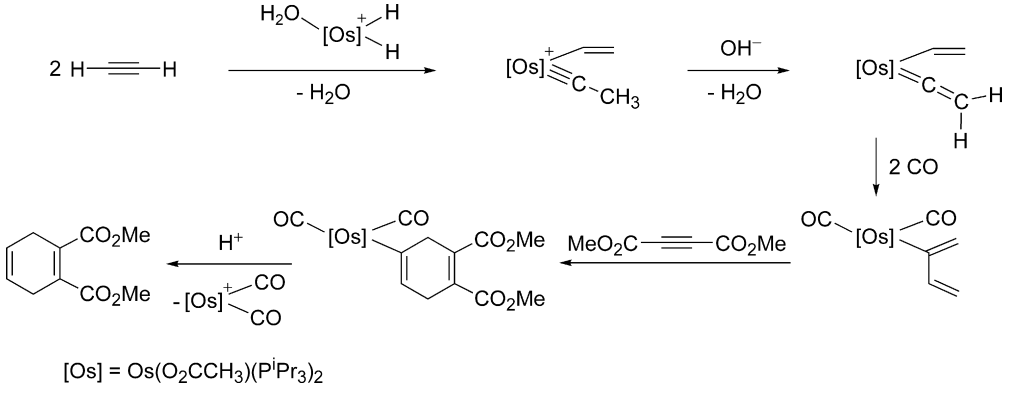
The C_β atom of the OsC=CH unit of the butadienyl ligand of **340** also shows nucleophilic character. Thus, the reaction of this complex with 1 equiv of $HBF_4{\cdot}OEt_2$ in diethyl ether leads to the α,β-unsaturated carbene derivative $[OsCl\{=C[CH_2C(O)OCH_3]CH{=}CHCO_2CH_3\}(CO)(P^iPr_3)_2]BF_4$ (**341**), according to Scheme 105.

4. Os=C=C=CR_2 complexes

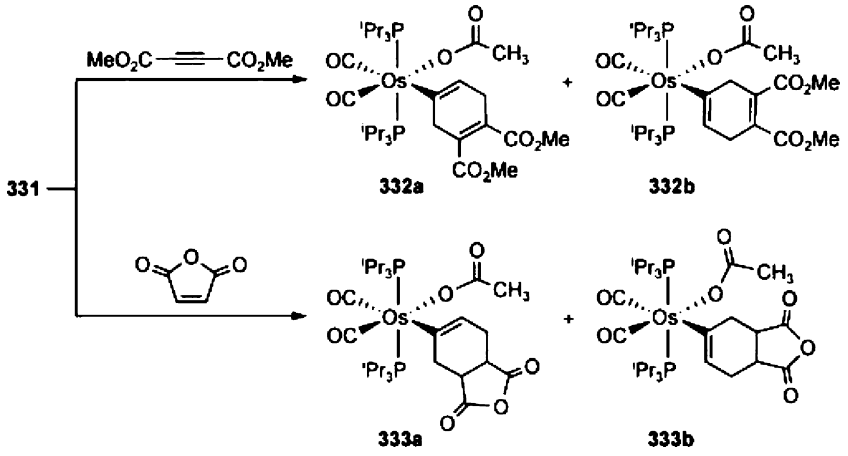
4.1. Half-sandwich derivatives

In agreement with 1-ethynyl-1-cyclohexanol and 2-methyl-3-butyn-2-ol, the addition of 1,1-diphenyl-2-propyn-1-ol to a pentane solution of the cyclopentadienyl bisphosphine complex **1** causes the displacement of one of the phosphine ligands and the formation of the π-alkyne compound $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HC{\equiv}CC(OH)Ph_2\}(P^iPr_3)$ (**342**), which affords the allenylidene derivative $Os(\eta^5\text{-}C_5H_5)Cl(=C{=}C{=}CPh_2)(P^iPr_3)$ (**343**) in toluene at 85 °C (Scheme 106) [128].

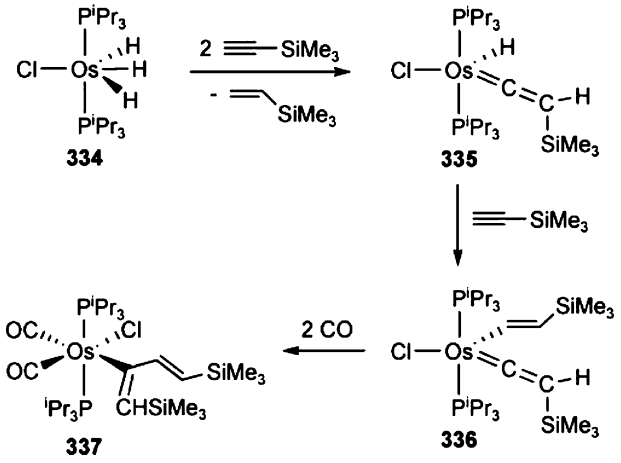
The allenylidene ligand of **343** has a marked nucleophilic character which is demonstrated in its reactions with HBF_4 and dimethyl acetylenedicarboxylate (Scheme 107), which give $[Os(\eta^5\text{-}C_5H_5)Cl(\equiv CCH{=}CPh_2)(P^iPr_3)]BF_4$ (**344**) and $Os(\eta^5\text{-}C_5H_5)Cl\{=C{=}C(CO_2Me)C(CO_2Me){=}C{=}CPh_2\}(P^iPr_3)$ (**345**), respectively. The alkenylcarbyne complex is the result of the



Scheme 101.

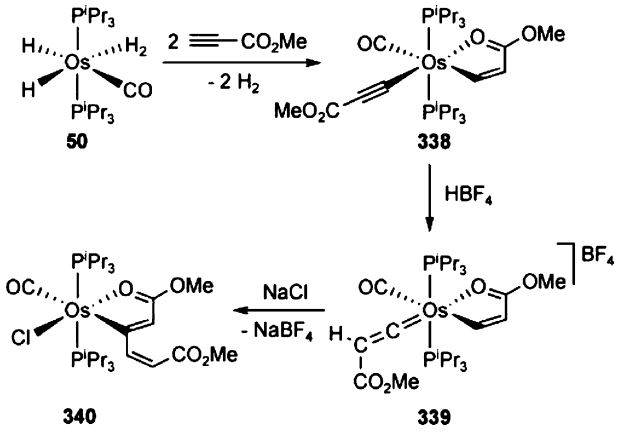


Scheme 102.

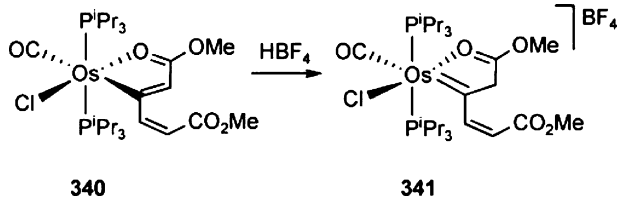


Scheme 103.

attack of the proton of the acid at the C_β atom of the allenylidene ligand, whereas the formation of **345** involves the insertion of the electronwithdrawing alkyne into the C_α–C_β double bond of the allenylidene ligand. The process has been rationalized as a stepwise cycloaddition to form a η^1-cyclobutenyl intermediate, which rapidly ring opens to give the allenylvinylidene product.

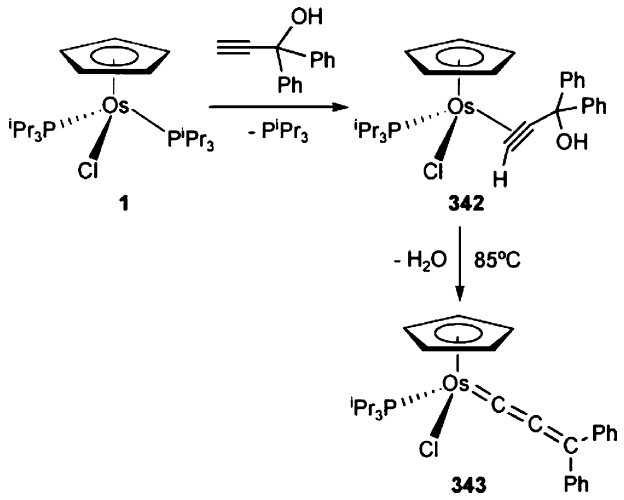


Scheme 104.

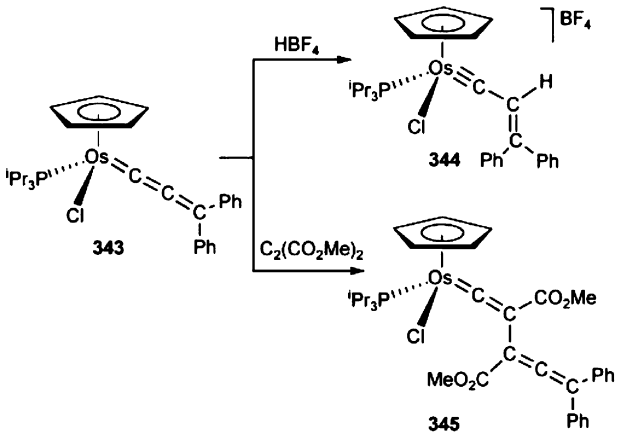


Scheme 105.

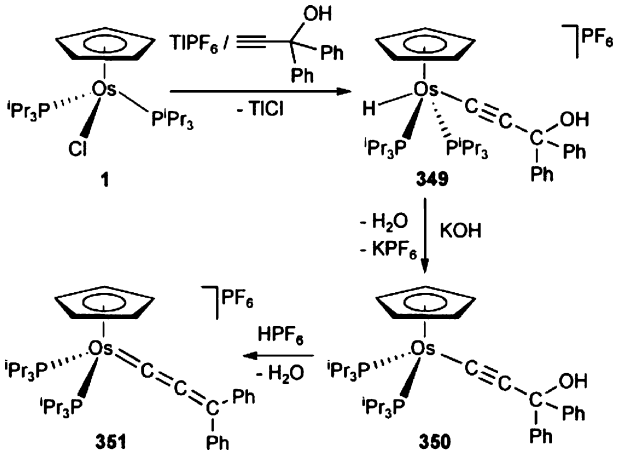
The reactivity of **343** is not limited to the nucleophilic power of the C_β atom of the allenylidene, but the chloride ligand is also activated towards nucleophilic substitution (Scheme 108), as shown by its reaction with KI to give Os(η^5-C_5H_5)I(=C=C=CPh_2)(P^iPr_3) (**346**). This property is most probably responsible for the formation of the pentatrienyl derivative Os(η^5-C_5H_5)(η^3-CH_2CHC=C=CPh_2)(P^iPr_3) (**347**), as a result of the reaction of **343** with $CH_2CHMgBr$. With regard to the mechanism of formation of **347**, it has been proposed that initially nucleophilic substitution of the chloride ligand takes place and a vinyl–metal intermediate is generated. This should rearrange by migratory insertion of the allenylidene ligand into the Os–vinyl bond to give **347**. Also noteworthly is the reduction



Scheme 106.



Scheme 107.

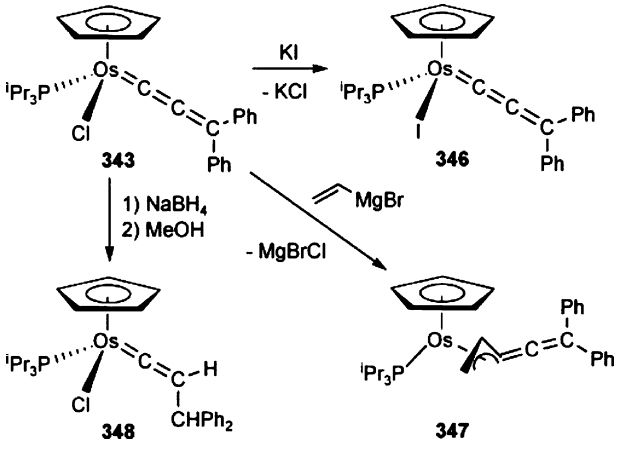


Scheme 109.

of the C_β–C_γ double bond of the allenylidene ligand of **343** by action of $NaBH_4$ and some drops of methanol, which affords the vinylidene derivative $Os(\eta^5\text{-}C_5H_5)Cl(=C=CHCHPh_2)(P^iPr_3)$ (**348**).

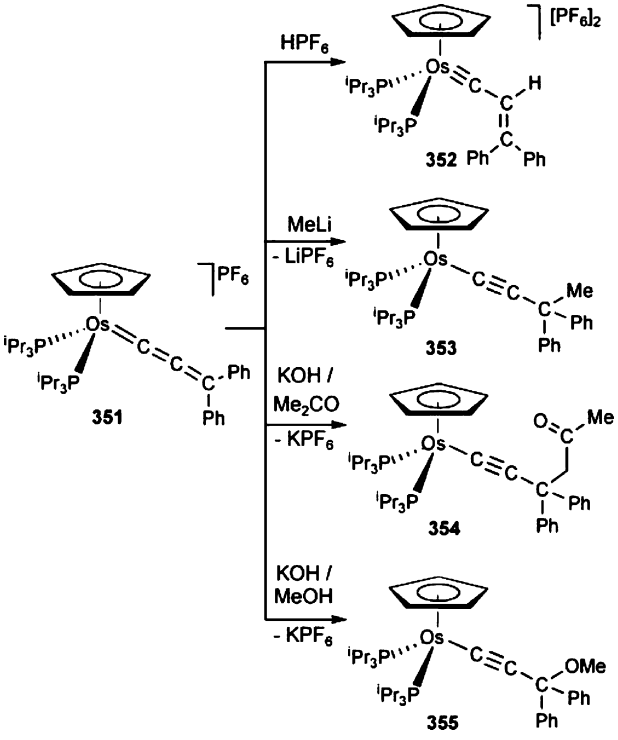
1,1-Diphenyl-2-propyn-1-ol reacts with **1** in the presence of $TlPF_6$ to give $[OsH(\eta^5\text{-}C_5H_5)\{C\equiv CC(OH)Ph_2\}(P^iPr_3)_2]PF_6$ (**349**). The addition of KOH to a methanol solution of this complex gives the neutral hydroxyalkynyl compound $Os(\eta^5\text{-}C_5H_5)\{C\equiv CC(OH)Ph_2\}(P^iPr_3)_2$ (**350**), which reacts with HPF_6 to afford the allenylidene derivative $[Os(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(P^iPr_3)_2]PF_6$ (**351**), as a result of the protonation of the OH group of the hydroxyalkynyl ligand of **350** (Scheme 109) [75].

In agreement with the neutral compound **343**, the proton of HPF_6 adds to the C_β atom of the C_3 chain of **351**. The addition gives the dicationic carbyne derivative $[Os(\eta^5\text{-}C_5H_5)(\equiv CCH=CPh_2)(P^iPr_3)_2](PF_6)_2$ (**352**) (Scheme 110). Complex **351** also reacts with methyllithium and with acetone and methanol solutions of KOH to afford the alkynyl compound $Os(\eta^5\text{-}C_5H_5)\{C\equiv CC(R)Ph_2\}(P^iPr_3)_2$ (R = CH_3 (**353**), $CH_2C(O)CH_3$ (**354**), OCH_3 (**355**)), as a result of the regioselective addition of the nucleophiles to the C_γ atom of the allenylidene ligand.

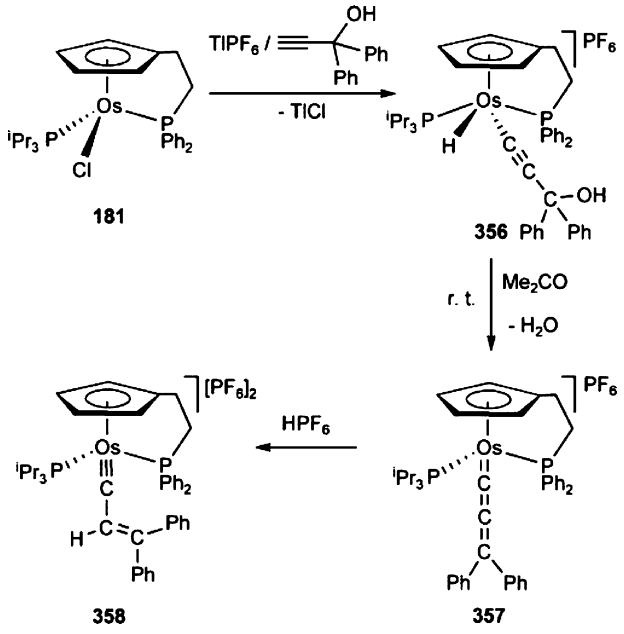


Scheme 108.

The replacement of the cyclopentadienyl ring and a triisopropylphosphine ligand by the [2-(diphenylphosphino)-ethyl]cyclopentadienyl group destabilizes the hydride-hydroxy-alkynyl-osmium(IV) intermediates and facilitates the formation of the allenylidene derivatives. Thus, the treatment of an acetone solution of **181** with 1,1-diphenyl-2-propyn-1-ol and $TlPF_6$ at −10 °C leads to $[OsH\{[\eta^5\text{-}C_5H_4(CH_2)_2]PPh_2\}\{C\equiv CC(OH)Ph_2\}(P^iPr_3)]PF_6$ (**356**) which, in contrast to **349**, loses a molecule of water to afford the allenylidene $[Os\{[\eta^5\text{-}C_5H_4(CH_2)_2]PPh_2\}(=C=C=CPh_2)(P^iPr_3)]PF_6$ (**357** in Scheme 111). Similarly to **351**, complex **357** reacts with HPF_6 to give the dicationic carbyne derivative $[Os\{[\eta^5\text{-}C_5H_4(CH_2)_2]PPh_2\}(\equiv CCH=CPh_2)(P^iPr_3)](PF_6)_2$ (**358**) [77].

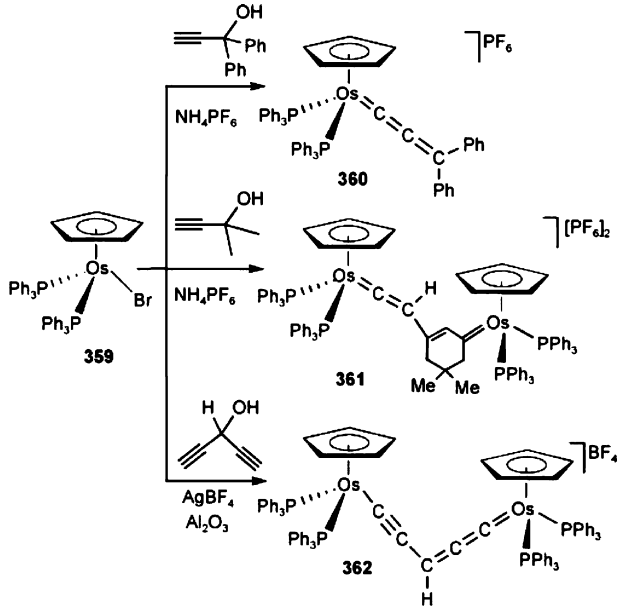


Scheme 110.

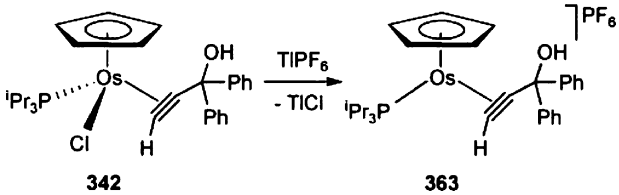


Scheme 111.

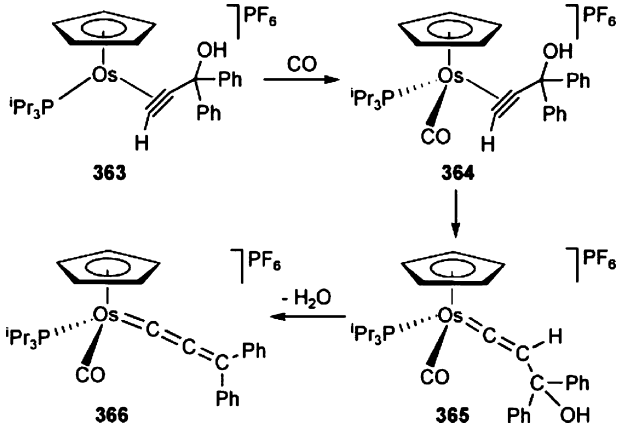
The reaction of the bis(triphenylphosphine) complex Os(η^5-C_5H_5)Br(PPh_3)$_2$ (**359** in Scheme 112) with 1,1-diphenyl-2-propyn-1-ol and NH_4PF_6 directly forms the allenylidene compound [Os(η^5-C_5H_5)(=C=C=CPh_2)(PPh_3)$_2$]PF_6 (**360**). Under the same conditions, 2-methyl-3-butyn-2-ol affords a dicationic diosmium vinylidene alkylidene complex of formula [{(η^5-C_5H_5)Os(PPh_3)$_2$}$_2$(μ-$C_{10}H_{12}$)](PF_6)$_2$ (**361**) [129], whereas treatment of **359** with $AgBF_4$, 0.5 equiv of HC≡CCH(OH)C≡CH, and Al_2O_3 gives [Os(η^5-C_5H_5)(PPh_3)$_2$(=C=C=CHC≡C)Os(PPh_3)$_2$(η^5-C_5H_5)]BF_4 (**362**) [130]. The indenyl complexes [Os(η^5-C_9H_7)(=C=C=CR_2)(PPh_3)$_2$]PF_6 (R_2 = Ph_2, C_8H_{12}) have been prepared by reaction of Os(η^5-C_9H_7)Cl(PPh_3)$_2$ with the corresponding HC≡CC(OH)R_2 substrate and $NaPF_6$ in refluxing methanol [131].



Scheme 112.



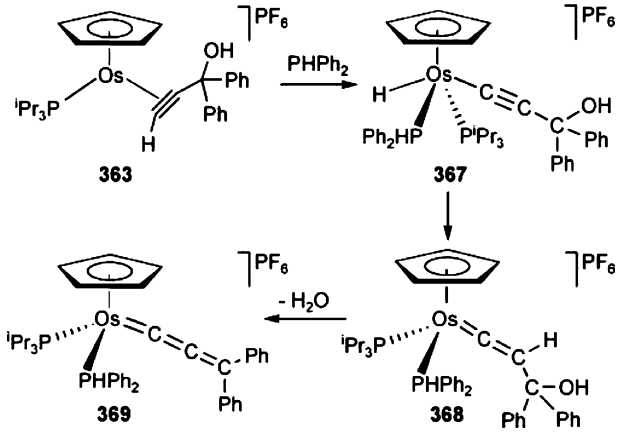
Scheme 113.



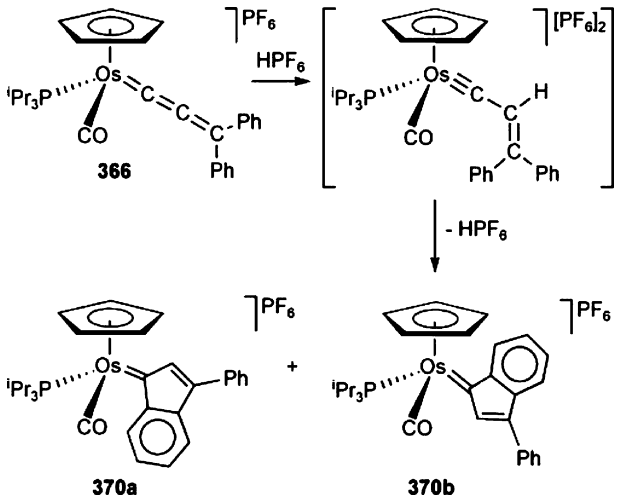
Scheme 114.

Treatment of the π-alkyne complex **342** with $TlPF_6$ produces the abstraction of the chloride ligand and the formation of [Os(η^5-C_5H_5){η^2-HC≡CC(OH)Ph_2}(P^iPr_3)]PF_6 (**363**), with the alkynol acting as a four-electron donor ligand (Scheme 113) [132]. This four-electron alkyne complex affords a general method to prepare mixed-ligand allenylidene derivatives (Schemes 114 and 115) [133].

Under 1 atm of carbon monoxide, complex **363** rapidly coordinates a carbon monoxide molecule to give the carbonyl intermediate [Os(η^5-C_5H_5){η^2-HC≡CC(OH)Ph_2}(CO)(P^iPr_3)]PF_6 (**364**), according to Scheme 114. In dichloromethane under argon, complex **364** is converted to the hydroxyvinylidene derivative [Os(η^5-C_5H_5){=C=CHC(OH)Ph_2}(CO)(P^iPr_3)]PF_6 (**365**), which undergoes dehydration to afford the allenyli-



Scheme 115.

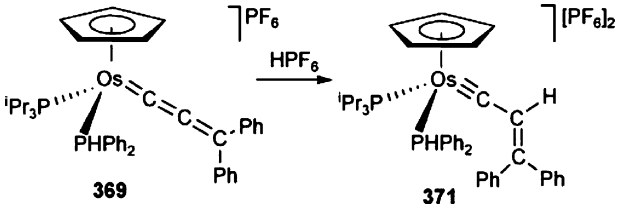


Scheme 116.

dene compound $[Os(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]PF_6$ (**366**).

In contrast to carbon monoxide, diphenylphosphine reacts with **363** to give the hydride-hydroxyalkynyl-osmium(IV) complex $[OsH(\eta^5\text{-}C_5H_5)\{C{\equiv}CC(OH)Ph_2\}(PHPh_2)(P^iPr_3)]PF_6$ (**367** in Scheme 115). In dichloromethane, the latter slowly changes to its hydroxy-vinylidene isomer $[Os(\eta^5\text{-}C_5H_5)\{=C=CHC(OH)Ph_2\}(PHPh_2)(P^iPr_3)]PF_6$ (**368**). At 55 °C, complex **368** dehydrates to give the allenylidene $[Os(\eta^5\text{-}C_5H_5)\{=C=C=CPh_2\}(PHPh_2)(P^iPr_3)]PF_6$ (**369**).

Treatment at room temperature of dichloromethane solutions of **366** with HPF_6 gives the indenylidene derivative $[Os(\eta^5\text{-}C_5H_5)$(3-phenyl-1-indenylidene)$(CO)(P^iPr_3)]PF_6$ (**370**), which has been isolated as a 1:1 mixture of the two possible rotamers resulting from a high barrier to the rotation of the indenylidene group around the Os–indenylidene bond. Isotope labeling experiments suggest that its formation involves the initial attack of the proton of the acid at the C_β atom of the allenylidene of **366**. The



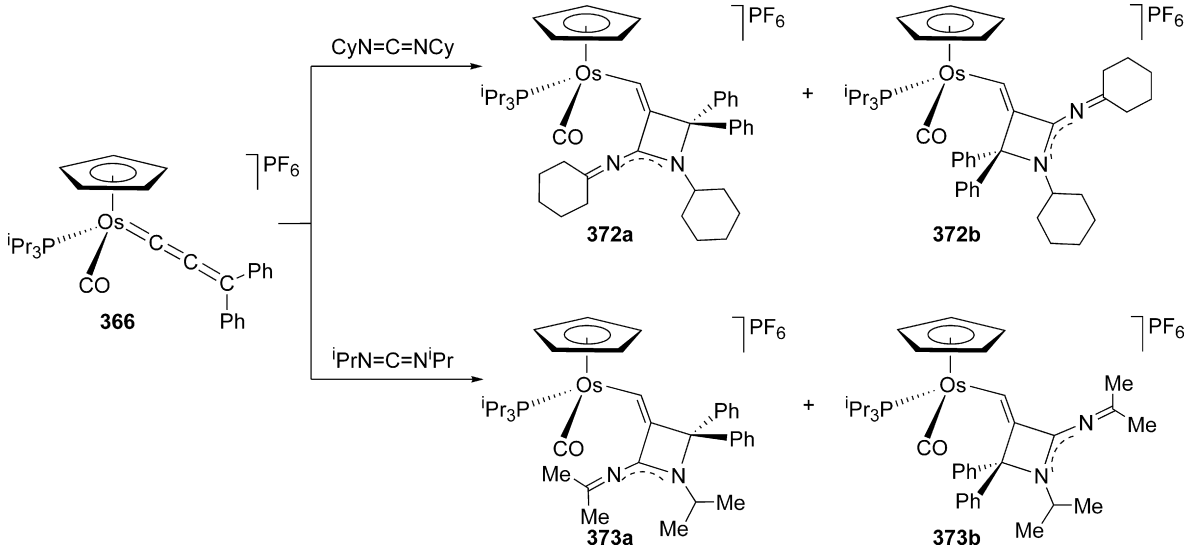
Scheme 117.

addition affords a dicationic carbyne intermediate, related to **352** and **358**, which is converted to **370** by electrophilic substitution of an ortho proton of one of the phenyl groups by the C_α atom of the alkenylcarbyne unit (Scheme 116) [133].

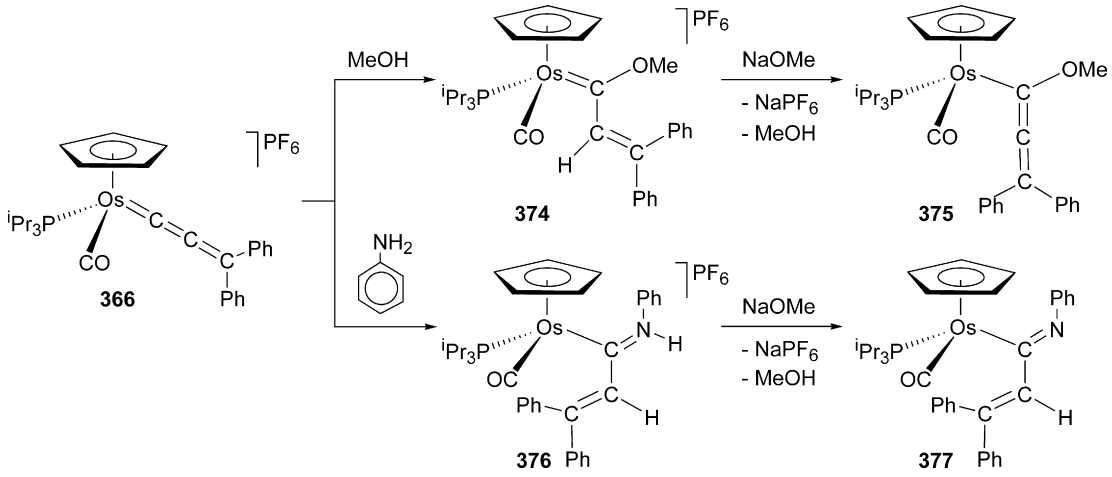
In agreement with this, and with the behavior previously mentioned for **343**, **351**, and **357**, complex **369** reacts with HPF_6 to give $[Os(\eta^5\text{-}C_5H_5)(\equiv CCH{=}CPh_2)(PHPh_2)(P^iPr_3)](PF_6)_2$ (**371**), according to Scheme 117.

Complexes **366** and **369** show significant differences of behavior not only in the presence of HPF_6 but also in the presence of carbodiimides. While, in agreement with its ruthenium counterpart [134], complex **366** reacts with *N*,*N*′-dicyclohexylcarbodiimide and *N*,*N*′-diisopropylcarbodiimide to give the iminiumazetidinylidene methyl derivatives $[Os(\eta^5\text{-}C_5H_5)\{CH{=}\overline{CC(Ph_2)N(Cy){=}C{=}N{=}C(CH_2)_4CH_2}\}(CO)(P^iPr_3)]PF_6$ (**372**) and $[Os(\eta^5\text{-}C_5H_5)\{CH{=}\overline{CC(Ph_2)N(^iPr){=}C}{=}N{=}C(CH_3)_2\}(CO)(P^iPr_3)]PF_6$ (**373**), respectively, which are isolated as mixtures of the isomers *Z* and *E* shown in Scheme 118, complex **369** is inert [133].

Complex **366** shows the typical behavior of a diarylallenylidene compound with α-electrophilic character [135], adding RXH molecules at the C_α–C_β double bond to afford Fischer-type alkenylcarbene derivatives (Scheme 119). Thus, in methanol solutions it is converted to the α,β-unsaturated alkoxycarbene derivative $[Os(\eta^5\text{-}C_5H_5)\{=C(OCH_3)CH{=}CPh_2\}(CO)(P^iPr_3)]PF_6$ (**374**). Treatment of **374** with sodium methoxide in tetrahydrofuran causes deprotonation of the



Scheme 118.



Scheme 119.

alkenyl group of the alkoxycarbene ligand to give the allenyl derivative $Os(\eta^5\text{-}C_5H_5)\{C(OCH_3)=C=CPh_2\}(CO)(P^iPr_3)$ (**375**). Complex **366** also reacts with aniline. The reaction gives the azoniabutadienyl complex $Os(\eta^5\text{-}C_5H_5)\{C(CH=CPh_2)=NHPh\}(CO)(P^iPr_3)]PF_6$ (**376**). As for **374**, complex **376** undergoes deprotonation in the presence of bases. However, the deprotonation does not take place at the $CH=CPh_2$ group but at the nitrogen atom. Treatment of a tetrahydrofuran solution of **376** with sodium methoxide yields the azabutadienyl derivative $Os(\eta^5\text{-}C_5H_5)\{C(CH=CPh)=NPh\}(CO)(P^iPr_3)$ (**377**) [133].

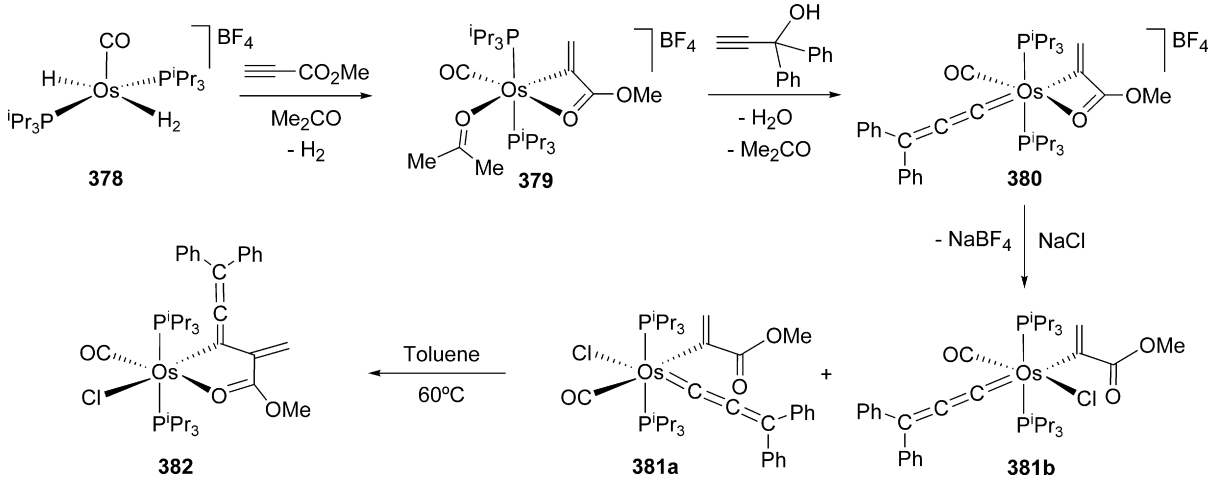
Cationic arene derivatives of the type $[Os(\eta^6\text{-arene})Cl(=C=C=CPh_2)L]^+$ ($L = PMe_3$, PCy_3, As^iPr_3, Sb^iPr_3) have been reported by Werner and co-workers [136]. Like **366**, complex $[Os(\eta^6\text{-mes})Cl(=C=C=CPh_2)(PMe_3)]PF_6$ reacts with alcohols. The reactions with methanol and ethanol leads to the Fischer-type carbene compounds $[Os(\eta^6\text{-mes})Cl\{=C(OR)CH=CPh_2\}(PMe_3)]PF_6$ ($R = Me$, Et).

Treatment of $[Os(\eta^6\text{-mes})Cl\{=C(OMe)CH=CPh_2\}(PMe_3)]PF_6$ with NaH affords the neutral allenyl derivative $Os(\eta^6\text{-mes})Cl\{C(OMe)=C=CPh_2\}(PMe_3)$.

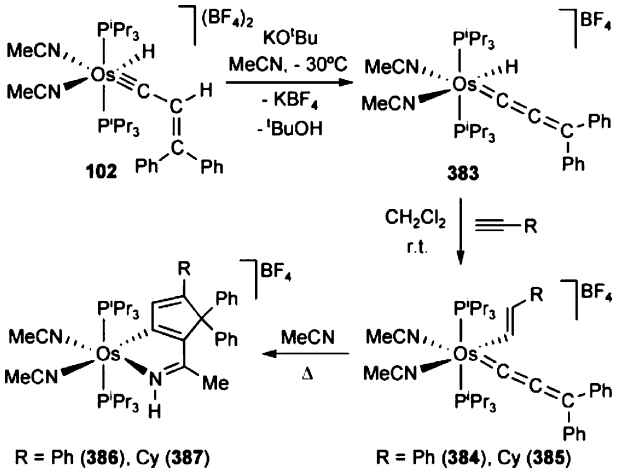
4.2. Non-half-sandwich compounds

Complexes of this type are also very scarce. The five-coordinate compound $OsCl_2(=C=C=CPh_2)(PPh_3)_2$ has been prepared by reaction of $OsCl_2(PPh_3)_3$ (**196**) with 1,1-diphenyl-2-propyn-1-ol [137]. Treatment of the dihydrogen complex $[OsBr(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]BF_4$ with propargyl alcohols leads to the corresponding cationic six-coordinate allenylidene derivatives $[OsBr(=C=C=CRR')\{PPh(OEt)_2\}_4]BF_4$ ($R = Ph$; $R' = Ph$, Me) [138].

The hydride-dihydrogen complex $[OsH(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2]BF_4$ (**378**) allows the access of methyl propiolate and 1,1-diphenyl-2-propyn-1-ol to the osmium atom, and the coupling between them via an allenylidene intermediate (Scheme 120). In an initial stage the alkyne molecules are introduced in a sequential manner. Thus, complex **378** reacts with methyl propiolate in acetone to give the alkenyl derivative $[Os\{C[C(O)OCH_3]=CH_2\}\{\kappa^1\text{-}OC(CH_3)_2\}(CO)(P^iPr_3)_2]BF_4$ (**379**), which by addition of 1,1-diphenyl-2-propyn-1-ol affords the alkenyl-allenylidene $[Os\{C[C(O)OCH_3]=CH_2\}(=C=C=CPh_2)(CO)(P^iPr_3)_2]BF_4$ (**380**).



Scheme 120.

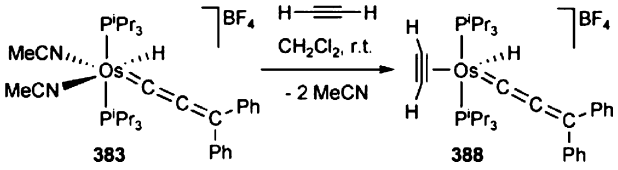


Scheme 121.

Despite the fact that **380** is stable in solution and does not evolve by migratory insertion of the allenylidene ligand into the Os–alkenyl bond, in the subsequent stage of the process, it is shown that the addition of NaCl produces the carbon–carbon coupling to give the allenyl derivative $Os\{C[C(=CH_2)C(O)OCH_3]=C=CPh_2\}Cl(CO)(P^iPr_3)_2$ (**382**) via the intermediate $Os\{C(CO_2CH_3)=CH_2\}Cl(=C=C=CPh_2)(CO)(P^iPr_3)_2$ (**381**), which is isolated as the two different isomers shown in Scheme 120 [139].

The assembly of an allenylidene ligand, a terminal alkyne, and an acetonitrile molecule to form osmacyclopentapyrrole derivatives has been recently reported (Scheme 121) [140]. The selective deprotonation of the alkenyl substituent of the alkenylcarbyne group of the hydride complex **102** affords the novel hydride-allenylidene derivative $[OsH(=C=C=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (**383**), which is the key species to assemble the organic fragments, in a LEGO manner, until the osmabicycles are obtained. The hydride ligand of this cumulene compound is an efficient anchor to nail terminal alkynes beside the allenylidene ligand. Thus, complex **383** reacts with phenylacetylene and cyclohexylacetylene to give the alkenyl-allenylidene derivatives $[Os\{(E)\text{-}CH=CHR\}(=C=C=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (R = Ph (**384**), Cy (**385**)), which in acetonitrile are converted into $Os\{C=C(CPh_2CR=CH)C(CH_3)=NH\}(CH_3CN)_2(P^iPr_3)_2]BF_4$ (R = Ph (**386**), Cy (**387**)) by means of the formation of three carbon–carbon bonds involving the three carbon atoms of the cumulene. The C_α and C_γ atoms of the allenylidene ligand are coupled with the C_α and C_β atoms, respectively, of the alkenyl group, while the C_β atom of the allenylidene is added to the C(sp) atom of the acetonitrile molecule.

Complex **383** also reacts with acetylene. However, there are marked differences in behavior between the latter and the mono substituted alkynes. In contrast to phenylacetylene and cyclohexylacetylene, the reaction of **383** with acetylene affords the hydride-π-alkyne-allenylidene derivative $[OsH(=C=C=CPh_2)(\eta^2\text{-}HC\equiv CH)(P^iPr_3)_2]BF_4$ (**388**), according to Scheme 122. Complex **388** is the first member of the



Scheme 122.

novel $[OsH\{=C(=C)_n=CRR'\}(\eta^2\text{-}HC\equiv CR'')(P^iPr_3)_2]^+$ series with $n > 0$ [140].

5. Conclusions

The success in ruthenium chemistry during the last decade has, in part, eclipsed the findings with osmium. However, in spite that the efforts in osmium have been much less than in ruthenium, it should be clear for the reader that the osmium chemistry is more versatile than that of ruthenium, in particular from a stoichiometric point of view.

Efficient catalytic systems with osmium are known [12,13,141], recently complexes **30** for olefin metathesis have been reported. On the other hand, it is evident that the catalytic osmium chemistry is poor, at least in comparison with ruthenium. Why? Probably, because osmium is more reducing than ruthenium and prefers coordination saturation and redox isomers with more metal–carbon bonds [52a]. A clear example are the hydride–carbyne complexes $OsHCl_2(\equiv CR)(PR'_3)_2$. They are oxidized isomers of the unknown compounds $OsCl_2(=CHR)(PR'_3)_2$. This apparent handicap, from a catalytic point of view, is the reason of the versatility of the stoichiometric osmium chemistry.

One of the first things learnt by the organometallic chemist is that the kinetic and thermodynamic of the redox equilibria depend critically on the electronic properties of the ligands of the complexes and, therefore, both are easily governable. The sequential substitution of acetonitrile molecules in $[OsH(\equiv CCH=CR_2)(CH_3CN)_2(P^iPr_3)_2]^{2+}$ (R = Ph, Me) by chloride ligands produces a sequential increase of the activation energy for the hydride migration from the metal center to the carbyne carbon atom and, in fact, this is a consequence of the gradual increase of the electron richness of the metal center. While two chloride ligands inhibit the hydride-alkenylcarbyne to carbene transformation, the latter is favored by a carbonyl group.

The tendency of osmium to stabilize the oxidized isomers facilitates assembly processes of organic fragments. For instance, the presence of a hydride ligand beside the allenylidene group in the complex $[OsH(=C=C=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ allows to build osmacyclopentapyrrole derivatives in a LEGO manner, with the allenylidene, a terminal alkyne, and an acetonitrile molecule. This tendency also facilitates sequential processes of C–H bond activation and C–C coupling, which allow to develop complex assembly procedures, as the fascinating synthesis of the spectacular complex **71**. In connection with the allenylidene ligands, it should be again remarked the promising future of the complexes containing these ligands. The scarce work carried out with osmium points out in the same

direction as the ruthenium chemistry appears to indicate: their potentiality can become greater than that of the classical carbene derivatives.

In conclusion, because osmium is reductant and prefers coordination saturation and redox isomers with more metal carbon bonds, the α-substituent migration equilibria in carbon donor ligands are, in general, shifted towards the oxidized form. As a consequence, the formation of C–C bonds by insertion processes of unsaturated organic molecules into the bond between the carbon donor atom and one of its α-substituents can be easily achieved with this metal.

Acknowledgements

We thank the Ministerio de Educatión y Ciencia of Spain (Project CTQ2005-00656) and the Diputación General de Aragón (E35) for financial support.

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