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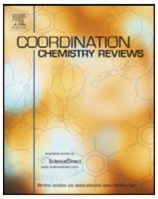

Review

Insertion reactions of allenes with transition metal complexes

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ABSTRACT

Recently, allenes have been widely used as starting materials to synthesize various organic compounds and polymeric materials, especially through reactions catalyzed by transition metal catalysts. In many of the catalytic reactions, insertion of allenes is one of the most important elementary steps. In this review, stoichiometric insertion reactions of transition metal complexes with allenes affording well-defined inserted products are summarized, which may help chemists to understand the mechanisms of catalytic reactions of allenes and to design new catalytic reactions of allenes.

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1. Introduction

Allenes are a unique class of organic compounds with two cumulated double bonds. There has been much interest in using them as starting materials for the syntheses of various organic compounds and polymeric materials, especially through reactions catalyzed by transition metal catalysts. In the past, many interesting transition metal catalyzed reactions of allenes have been developed. Excellent updated reviews on catalytic reactions of allenes are now available [1].

Allenes also have rich coordination and organometallic chemistry. It has been well established that allenes can form transition metal complexes with one of their double bonds. Upon coordination, allenes are activated and can participate in various organometallic reactions, for example, insertion into M–R bonds, oxidative coupling with other unsaturated substrates [2], nucleophilic addition [3] and abstraction [4] reactions, and electrophilic addition reactions [5]. These fundamental organometallic reactions play very important roles in metal catalyzed/mediated reactions of allenes.

This review mainly concerns the insertion of allenes into an M–X bond where X is a main group element. Stoichiometric insertion reactions of allenes to give well-defined metal complexes were first reported in the literature in early 1960s. Since then, many examples of stoichiometric allene insertion reactions have been discovered. However, there are only a few reviews dealing with coordination and organometallic chemistry of allenes and there appear no reviews dealing specifically with stoichiometric allene insertion reactions. The early work on the coordination and organometallic chemistry was summarized in excellent reviews in 1973 [6] and 1976 [7]. A review dealing with coordination chemistry of arynes, strained cyclic alkynes and cumulenes appeared in 1998 [8]. In view of the increasing interest in organometallic and catalytic reactions of allenes, it would be of interest to have an overview on the stoichiometric allene insertion reactions with transition metal complexes.

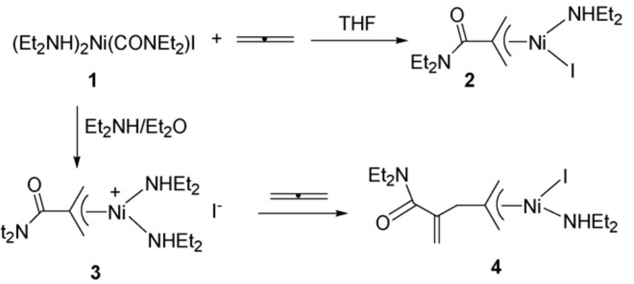
In this review, the work on insertion of allenes into M–X bonds (X = a main group element) to give well-defined metal complexes are summarized. The related work on the reactions of allenes with complexes containing an M=X double bond, and organometallic transformations involving insertion of allenes will also be mentioned. The reactions are relevant to many catalytic reactions of allenes, for example, polymerization, hydrogenation, hydrosilylation and hydroformylation of allenes; coupling of allenes with halides and unsaturated substrates. Knowledge on these stoichiometric insertion reactions of allenes may be helpful for the mechanistic comprehension of transition metal-catalyzed reactions of allenes and for design of new catalytic reactions of allenes. We apologize to those whose work was not cited.

2. Reactions of allenes with mononuclear transition metal complexes

2.1. Reactions of group 10 metal complexes

2.1.1. Reactions with nickel complexes

Insertion reactions of allenes have been reported for carbamoyl and allyl complexes of nickel. The σ-carbamoyl-nickel(II) complex **1** undergoes an insertion reaction with one equivalent of 1,2-propadiene in THF and Et_2NH/Et_2O to form the neutral and cationic 2-carbamoyl η^3-allylnickel(II) complexes **2** and **3**, respectively (Scheme 1) [9]. The allyl complex **3** can undergo further insertion with 1,2-propadiene to give the neutral allyl complex **4** [9b].



Scheme 1.

Bisallyl nickel complexes such as α,ω-octadienediylnickel and α,ω-dodecatrienediylnickel undergo mono or multiple insertion reactions with 1,2-propadiene to give a series of new bis-π-allyl nickel intermediates, which undergo coupling reactions to give hydrocarbon products on treatment with carbon monoxide, or cyclic imines on treatment with alkyl isocyanides [10].

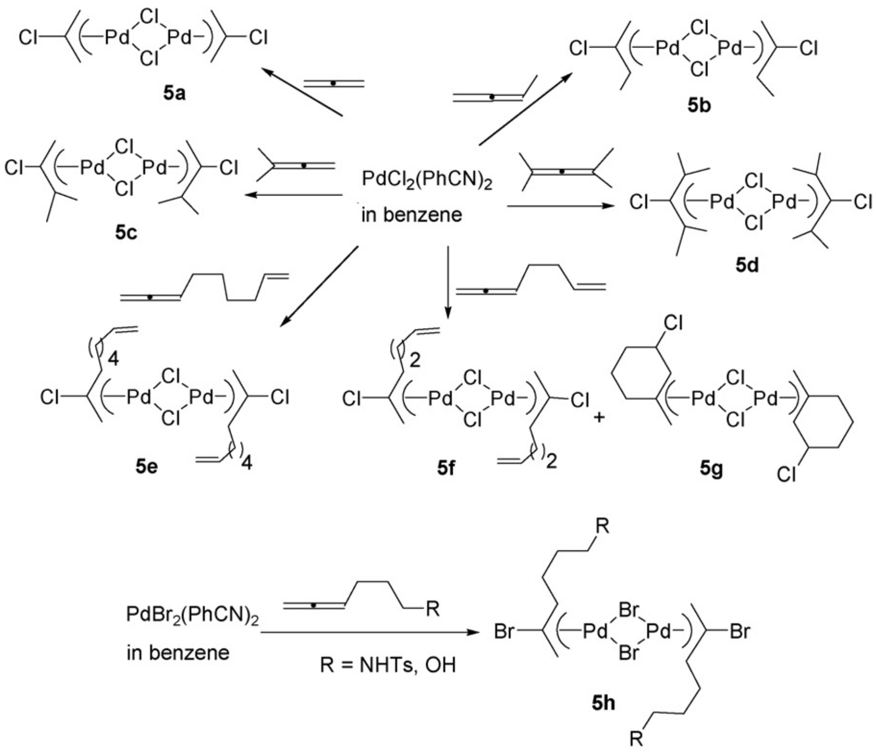
2.1.2. Reactions of palladium complexes

2.1.2.1. Reactions of $PdX_2(PhCN)_2$ (X = Cl, Br), Na_2PdCl_4 and $Pd(OAc)_2$. Many allene insertion reactions of palladium complexes are known. Such reactions were first observed in 1960s in the reactions of allenes with simple palladium complexes such as $PdCl_2(PhCN)_2$, Na_2PdCl_4 and $Pd(OAc)_2$. The reactions of allenes with $PdCl_2(PhCN)_2$ were found to give various allyl complexes (Schemes 2 and 3) [11,12], depending on the allenes, and the polarity of the solvents and the order of adding reactants. When 1,2-propadiene was bubbled into a solution of $PdCl_2(PhCN)_2$ in a non-polar solvent such as benzene, a rapid formal insertion of 1,2-propadiene into a Pd—Cl bond occurred and the product is the dimeric (2-chloro)allyl palladium chloride **5a** (Scheme 2) [11]. Similar products were obtained when $CH_2{=}C{=}CHMe$ [12], $CH_2{=}C{=}CMe_2$ [12], $Me_2C{=}C{=}CMe_2$ [11], $CH_2{=}C{=}CH(CH_2)_4CH{=}CH_2$ [13] and $C_5H_{11}CH{=}C{=}CH(CH_2)_2CO_2H$ [14a] were used as illustrated in Scheme 2. The reaction of $PdCl_2(PhCN)_2$ with 1,2,6-heptatriene gives a mixture of **5f** and **5g** (Scheme 2) [13]. Similarly, reaction of $PdBr_2(PhCN)_2$ with allenes functionalized with NHTs or OH was found to give allyl complexes **5h** [14b].

When $PdCl_2(PhCN)_2$ was introduced as a solid to a solution of 1,2-propadiene in benzene, the major product is **6a** (Scheme 3) [11]. When 1,2-propadiene was bubbled into a benzonitrile solution of $PdCl_2(PhCN)_2$, the product is **6b**. Two products **6b** (30%) and **6c** (46%) were isolated when 1,2-propadiene was bubbled into a methanolic solution of $PdCl_2(PhCN)_2$ [11]. In these reactions, the π-allyl palladium complexes **6a**, **6b** and **6c** can be thought as being formed by insertion of 1,2-propadiene into the Pd—C bonds of the vinyl palladium intermediates **6d** formed by external attack of coordinated 1,2-propadiene by Cl^- or methanol. A higher yield of complex **6b** (88%) was obtained when 1,2-propadiene was bubbled into a methanolic solution of Na_2PdCl_4 (Scheme 3) [12]. Reaction of 1,2-propadiene with Na_2PdCl_4 in acetic acid in the presence of NaOAc gives the 2-acetoxy allyl complex **7** [15].

Palladium acetate reacts with 1,2-propadiene in benzene to give the bis-π-allyl dipalladium complex **9**, which was isolated in 18% yield by chromatography on silica gel (Scheme 4). Complex **9** could also be obtained in high yield by bubbling 1,2-propadiene into a dichloromethane solution of di-μ-acetato-2,2′-bi-π-allyldipalladium(II) (**8**) [16].

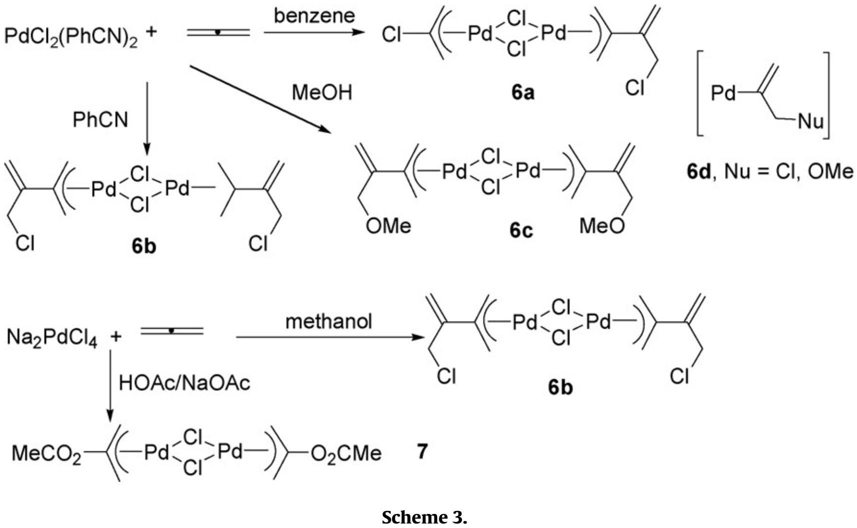
2.1.2.2. Reactions of allyl and alkyl complexes supported with Cl and O-donor ligands. Carbometalation reactions of allenes have been demonstrated with well-defined allyl, alkyl, aryl, acyl and vinyl



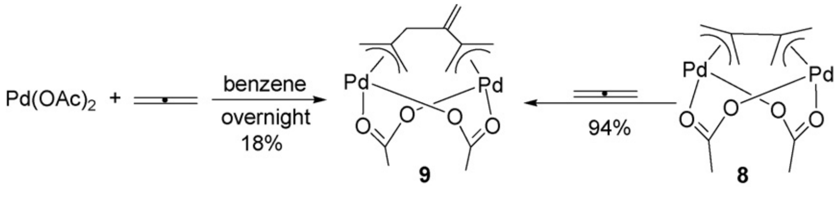
Scheme 2.

palladium complexes in various ligand environments. The dimeric η^3-allyl palladium complexes [(π-allyl)PdCl]$_2$ (**10**) undergo double insertion reactions with 1,2-propadiene to give the new dimeric allyl palladium complexes **11** as illustrated in Scheme 5 [17,18].

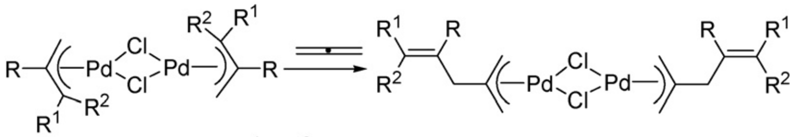
The monomeric η^3-allyl palladium complexes (π-allyl)Pd(acac) (**12**) show similar reactivity toward 1,2-propadiene, producing mainly the allyl complexes **13** along with trace amounts of the bimetallic complex **14** with a 2,2′-bis-π-allyl ligand (Scheme 6)



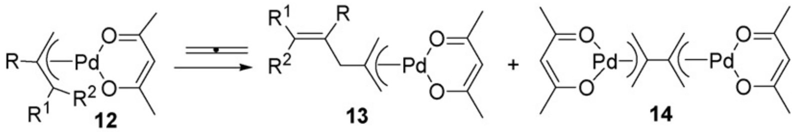
Scheme 3.



Scheme 4.


10 (**a**) R = R^1 = R^2 = H (**c**) R = R^2 = H, R^1 = Me (**b**) R = Me, R^1 = R^2 = H (**d**) R = H, R^1 = R^2 = Me **11**

Scheme 5.

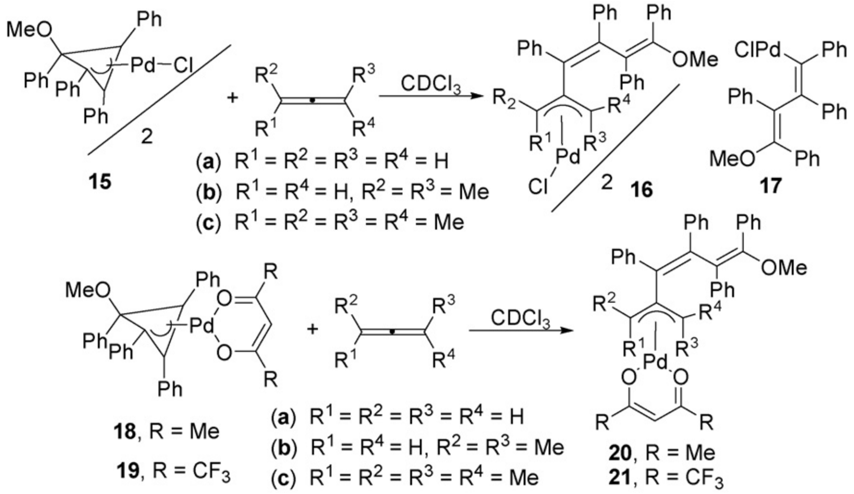

12 **13** **14**

(**a**) R = R^1 = R^2 = H, (**b**) R = Me, R^1 = R^2 = H,
(**c**) R = R^2 = H, R^1 = Me, (**d**) R = H, R^1 = R^2 = Me

Scheme 6.

[17]. Related η^3-allyl palladium complexes (π-allyl)Pd(Hfacac) are more reactive than **12** and react with both 1,2-propadiene and substituted allenes such as 1-methylallene, 1,1-dimethylallene and 1,3-dimethylallene to produce complexes analogous to **13**. In these reactions, the insertion took place at the unsubstituted terminal carbon of the allylic moiety in the starting complexes.

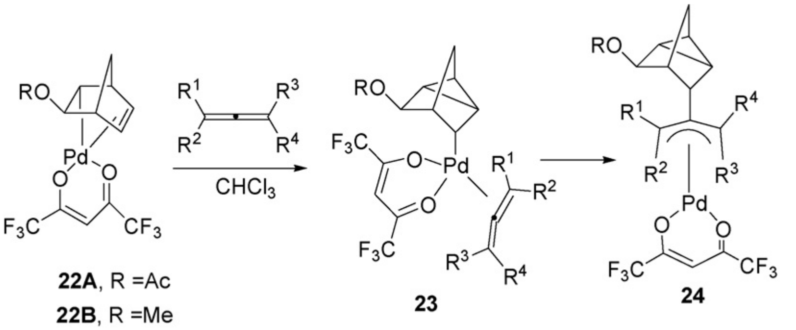
Insertion of allenes into a Pd–C(vinyl) bond was observed in the reactions of the cyclic π-allyl chloropalladium complex **15** with allenes. When a stoichiometric amount of allenes was added into a $CDCl_3$ solution of the cyclic π-allyl chloropalladium complex **15**, ring-opening and insertion reactions occurred to give allyl complexes **16** (Scheme 7) [19]. It was suggested that


15 **16** **17**

(**a**) R^1 = R^2 = R^3 = R^4 = H
(**b**) R^1 = R^4 = H, R^2 = R^3 = Me
(**c**) R^1 = R^2 = R^3 = R^4 = Me

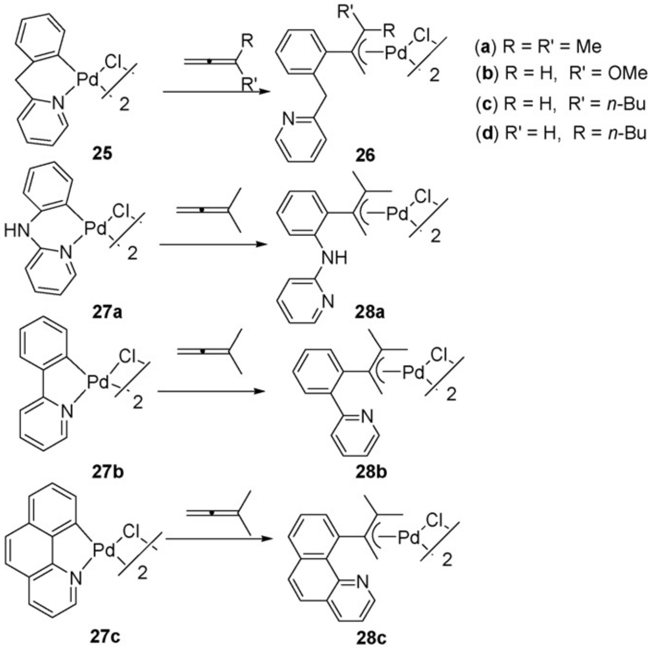
18, R = Me
19, R = CF$_3$
20, R = Me
21, R = CF$_3$

Scheme 7.


22A, R =Ac
22B, R =Me
23 **24**

(**a**) R^1 = R^2 = R^3 = R^4 = H, R = Ac; (**b**) R^1 = Me, R^2 = R^3 = R^4 = H, R = Ac;
(**c**) R^1 = R^2 = Me; R^3 = R^4 = H, R = Ac; (**d**) R^1 = R^3 =Me, R^2 = R^4 = H, R = Ac;
(**e**) R^1 = R^2 = R^3 = R^4 = Me, R = Ac; (**f**) R^1 = R^2 = R^3 = R^4 = H, R = Me;
(**g**) R^1 = R^2 = Me, R^3 = R^4 = H, R = Me

Scheme 8.

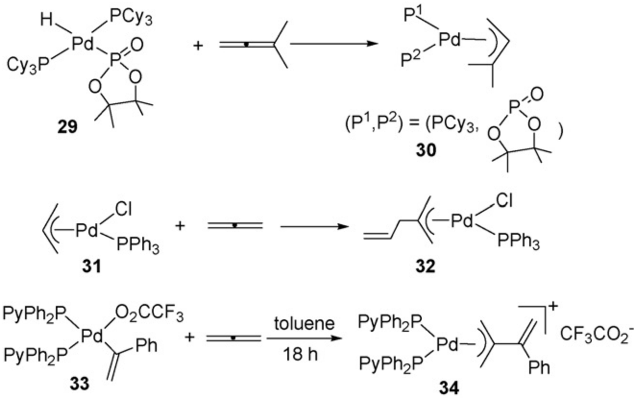


Scheme 9.

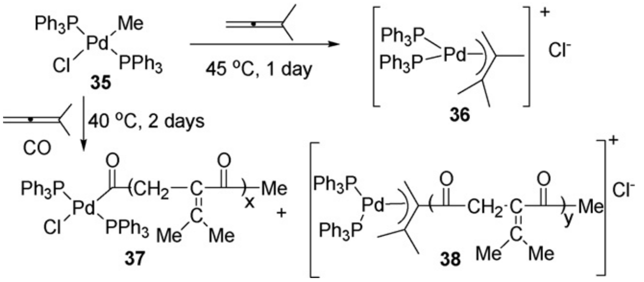
the reactions proceed by initial ring-opening of the cyclobutenyl moiety to give vinyl intermediate **17**. The intermediate then undergoes insertion reactions with allenes to give **16** [19]. Analogous reactions also occurred for the acac and Hfacac complexes **18** and **19** to give allyl complexes **20** and **21**, respectively. For a given anionic ligand, the rate of the insertion reactions is roughly in the order of 1,1-dimethylallene ≫ 1,2-propadiene > 1,3-dimethylallene ≫ tetramethylallene; for a given allene, the reactivity of the complexes follows the order of Hfacac > acac ≫ Cl. Here both steric and electronic factors may play an important role in determining the rate of these insertion reactions.

Insertion of allenes into a Pd–C(alkyl) bond was observed in the reactions of the Hfacac norbornenyl complexes **22** with allenes. Complexes **22** readily react with 1,2-propadiene, 1-methylallene, 1,1-dimethylallene, and 1,3-dimethylallene in $CHCl_3$ to form the corresponding π-allyl palladium complexes **24** (Scheme 8) via nortricyclenyl–allene intermediates **23** (Scheme 8) [20]. The rate of the insertion reactions decreases in the order of 1,1-dimethylallene > 1,2-propadiene > tetramethylallene, probably due to the electronic and steric effect of the substituents of allenes.

Insertion of allene into Pd–C(aryl) bonds was observed in the reactions of cyclopalladated dimeric aryl compounds **25** and **27** with allenes. Complex **25** reacts with both symmetrically and unsymmetrically substituted allenes to give the dimeric allyl complexes **26**. The related cyclometallated complexes **27** similarly react with $CH_2{=}C{=}CMe_2$ to give the dimeric allyl complexes **28** (Scheme 9) [21]. There are reports that insertion reactions of other cyclometallated aryl palladium complexes give unstable organometallic compounds that readily undergo reductive elimination to give heterocycles or metallacycles [21,22].

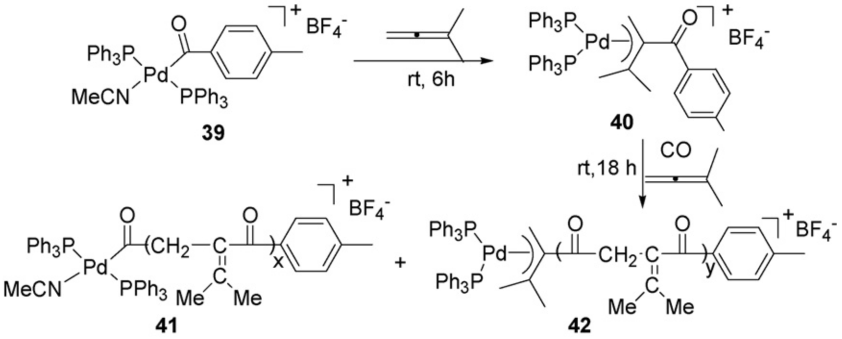


Scheme 10.

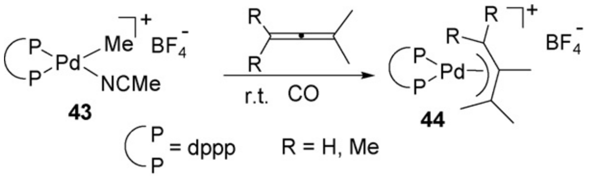


Scheme 11.

2.1.2.3. Reactions of palladium complexes supported with P-donor ligands. A few allene insertion reactions of hydride, allyl, alkyl, vinyl, aryl and acyl palladium complexes containing phosphine as the supporting ligands have been investigated. The palladium hydride complex **29** was found to react with $CH_2{=}C{=}CMe_2$ to give the allyl complex **30** [23]. However, the reaction of π-allyl palladium complex **31** with 1,2-propadiene is extremely slow at room temperature and takes a year to go to completion (Scheme 10) [17]. The vinyl palladium complex **33** in toluene also slowly reacts with 1,2-propadiene to give the insertion product **34** (Scheme 10) [24].



Scheme 12.



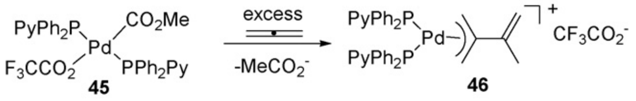
Scheme 13.

In 1970, Stevens and Shier briefly reported the reaction of $RPd(PR'_3)_2X$ (R = alkyl, Ph) with 1,2-propadiene in the presence of silver tetrafluoroborate to give the cationic η^3-allyl palladium complexes $[Pd(PR_3)_2(\eta^3\text{-}CH_2CRCH_2)]BF_4$ [25]. More recently, Kacker and Sen reported that the neutral complex $Pd(Me)Cl(PPh_3)_2$ (**35**) reacts with 3,3-dimethylallene to give the methylpalladation product **36**, although high reaction temperature and long reaction time are required. In the presence of carbon monoxide, **35** slowly reacts with 3,3-dimethylallene to form complexes **37** and **38**, due to successive insertion of CO and the allene (Scheme 11) [26].

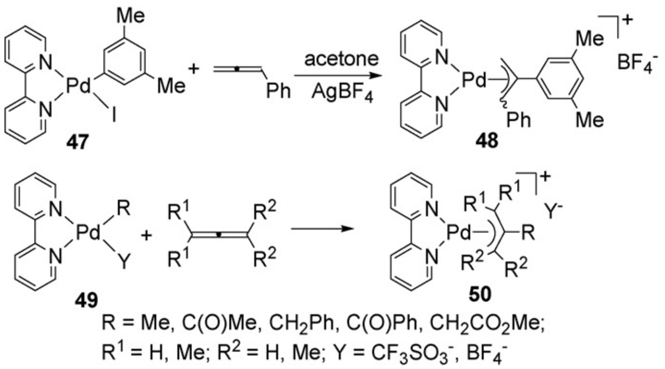
The cationic acyl complex *trans*-$[Pd(PPh_3)_2(C(O)C_6H_4Me\text{-}p)(MeCN)](BF_4)$ (**39**) readily reacts with 3,3-dimethylallene in $CDCl_3$ to form the 2-acyl substituted π-allyl palladium complex **40** (Scheme 12), which upon exposure to carbon monoxide in the presence of a few equivalents of 1,1-dimethylallene is converted to the acyl palladium complex **41** and the π-allyl palladium complex **42** with a polymeric chain [26].

Under similar condition, the cationic dppp complex $[PdMe(MeCN)(dppp)]BF_4$ (**43**) reacts with allenes to yield the corresponding mono insertion products, π-allyl palladium complexes **44**, as the only products (Scheme 13) which do not undergo insertion with carbon monoxide. This is consistent with the poor catalytic activity exhibited by complexes with a bidentate ligand in the alternating copolymerization of 3,3-dimethylallene with carbon monoxide [26].

The expected allene insertion product was not obtained in the reaction of the alkoxycarbonyl complex **45** with 1,2-propadiene. Instead, the reaction produces the unexpected allyl complex **46** (Scheme 14) [27].



Scheme 14.

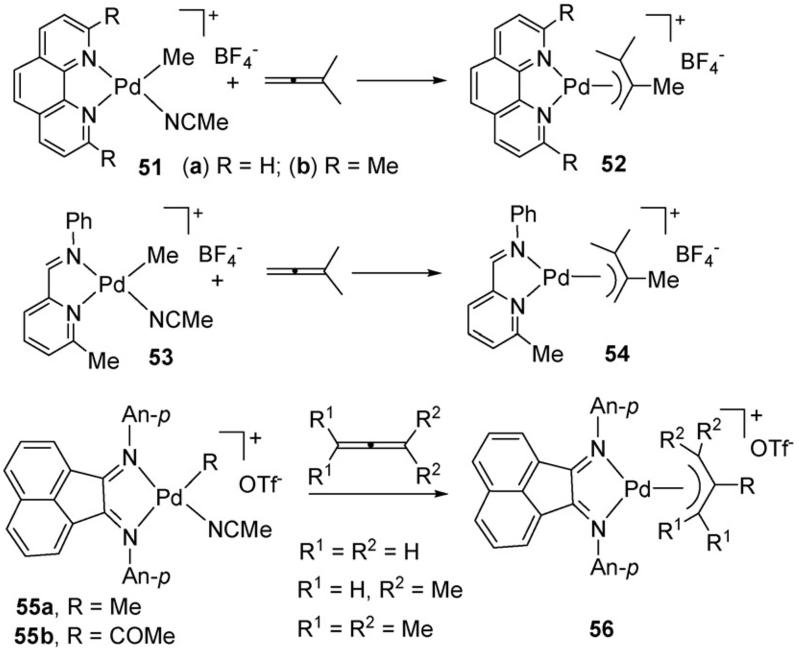


Scheme 15.

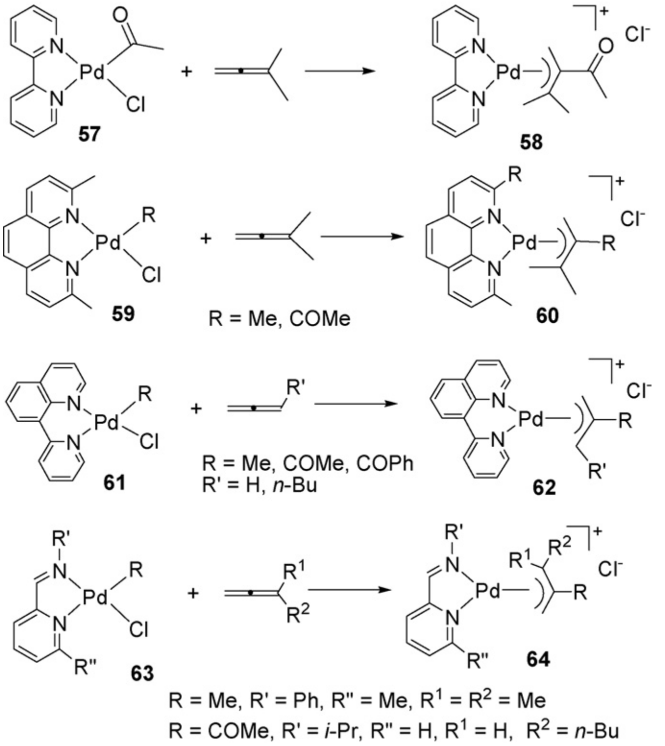
2.1.2.4. Reactions of palladium complexes supported with N-, S-donor ligands. A number of allene insertion reactions of alkyl, vinyl, aryl and acyl palladium complexes containing N-, S-donor ligands have been reported.

Several allene insertion reactions have been reported for palladium complexes containing a bidentate nitrogen donor ligand. Carbopalladation of the bipyridine aryl palladium complex **47** in the presence of $AgBF_4$ with phenylallene produces the cationic π-allyl complex **48** (*syn*:*anti* = 2:1) (Scheme 15) [28]. Similar π-allyl complexes **50** were obtained from the reactions of the bipyridine palladium complexes **49** containing a weakly coordinating ligand with allenes such as 1,2-propadiene, 1,1-dimethylallene and tetramethylallene [29].

The cationic alkyl or acyl complexes **51** [30], **53** [30] and **55** [31] undergo insertion reactions with allenes to give cationic π-allyl complexes **52**, **54** and **56**, respectively (Scheme 16).

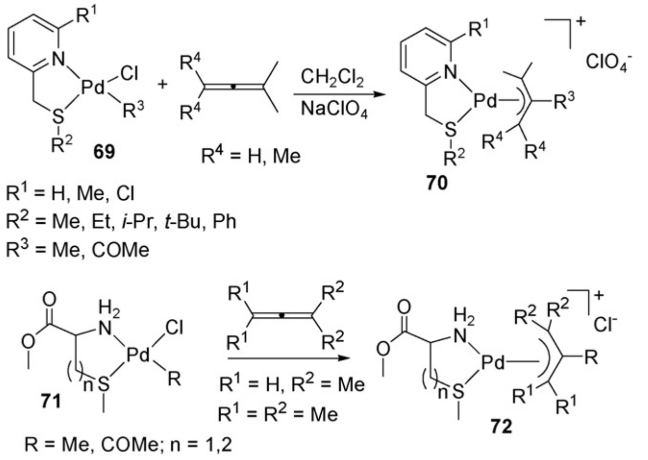


Scheme 16.



Scheme 17.

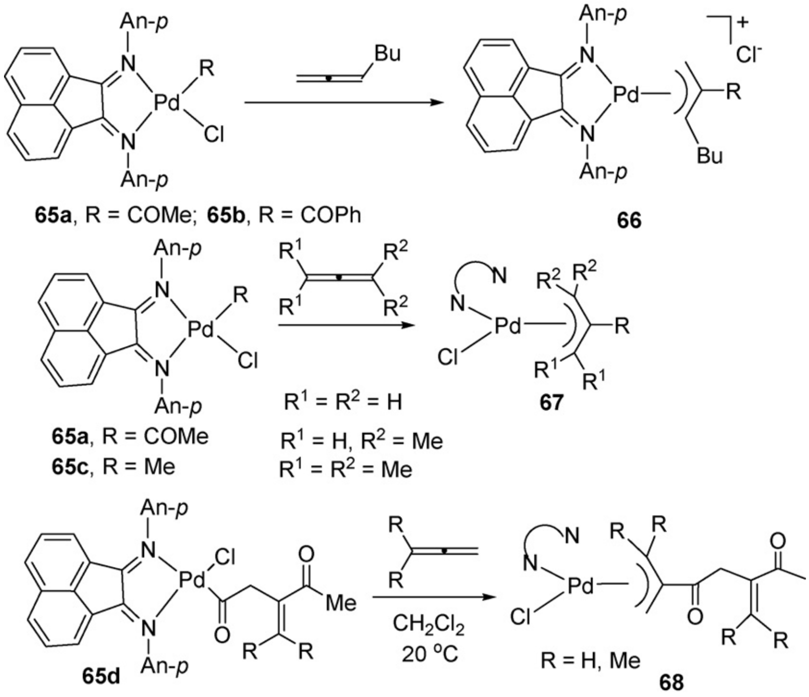
The neutral alkyl or acyl complexes **57** [29], **59** [30], **61** [32] and **63** [30,32] also undergo insertion reactions with allenes to give the cationic π-allyl complexes **58**, **60**, **62** and **64**, respectively (Scheme 17). Kinetic studies indicate that flexible bidentate ligands greatly facilitate the insertion reactions because of the easier generation of an accessible site on the metal center for substrates [32].



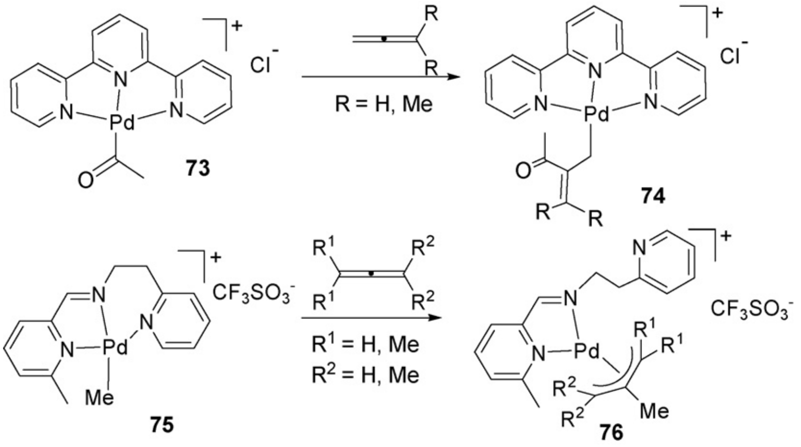
Scheme 19.

The products of the reactions of analogous Pd(*p*-An-BIAN) complexes **65** with allenes vary depending on allenes. Thus, the acyl complexes **65a** and **65b** react with 1,2-heptadiene to yield the cationic allyl complexes **66**, due to dissociation of the chloride (Scheme 18) [32]. In contrast, complexes **65a** and **65c** react with 1,2-propadiene, 1,1-dimethylallene and tetramethylallene to give neutral allyl complexes **67**, due to dissociation of one of the N-donor [31]. Similar reactions occur between **65d** and 1,2-propadiene and 1,1-dimethylallene to give the neutral complexes **68** [31].

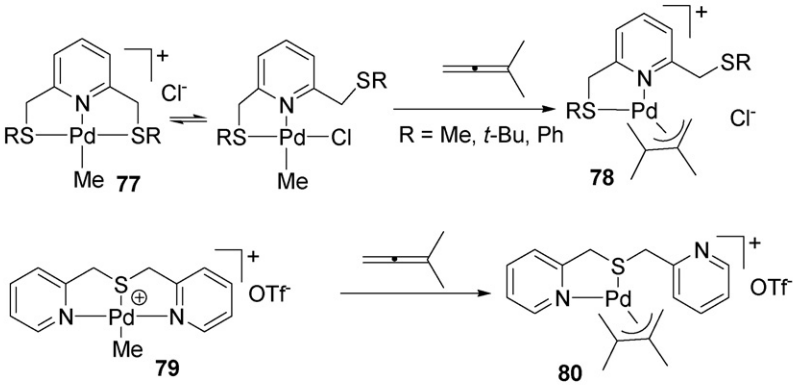
Allene insertion reactions with palladium complexes containing a bidentate N-, S-ligand have also been reported. For example, the methyl and acylpalladium complexes **69** with a bidentate pyridinylmethylthioether ligand were found to react with 1,1-dimethylallene and tetramethylallene in the presence of $NaClO_4$ to yield the corresponding π-allyl palladium complexes **70** (Scheme 19) [33]. The rates of the insertion reactions are strongly influenced by the electronic and steric effect of the bidentate ligands. The



Scheme 18.



Scheme 20.



Scheme 21.

related complexes **71** react rapidly with allenes such as 1,1-dimethylallene and tetramethylallene to give the cationic allyl complex **72** [34].

Square planar palladium alkyl complexes with tridentate ligands could also undergo insertion reactions with allenes. Treatment of the acyl palladium complex **73** containing a terpy ligand with $CH_2{=}C{=}CR_2$ (R = H, Me) resulted in the formation of η^1-allyl complexes **74**, due to the strong tendency of the terpy ligand to maintain terdentate coordination. Under similar condition, reactions of palladium complexes **75** containing a more flexible tridentate ligand with allenes form the *N*,*N*-bidentate η^3-allyl palladium complexes **76** (Scheme 20) [29].

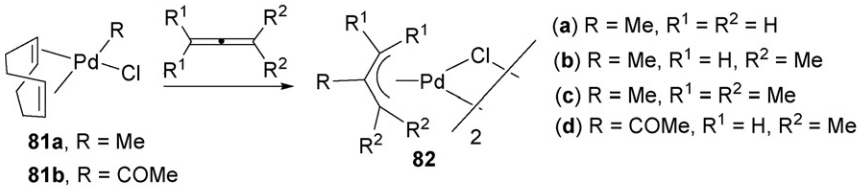
Similarly, palladium methyl complexes **77** and **79** containing a terdentate pyridylbisthioether ligand can undergo insertion reactions with 1,1-dimethylallene to afford the corresponding η^3-allyl products **78** and **80**, respectively (Scheme 21) [35].

2.1.2.5. Reactions of PdCl(R)(COD). The alkyl and acyl complexes PdCl(R)(COD) (**81**) undergo insertion reactions with 1,2-propadiene, 1,1-dimethylallene, and tetramethylallene at room temperature to give the dimeric allyl complexes **82** (Scheme 22) [34,33c].

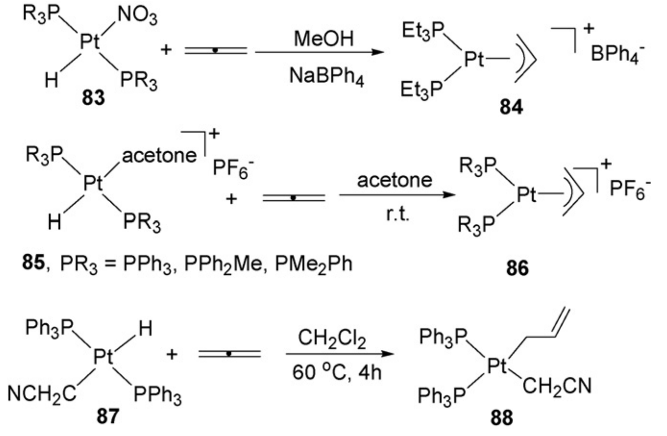
2.1.3. Reactions with platinum complexes

Insertions of allenes into Pt–H, Pt–alkyl, Pt–vinyl and Pt–aryl bonds have been demonstrated. The hydride complex **83** reacts with 1,2-propadiene in the presence of $NaBPh_4$ in methanol to afford the π-allyl complex **84** [36]. The cationic hydride complexes **85** readily react with 1,2-propadiene to give the η^3-allyl complexes **86** (Scheme 23) [37]. The related hydridoalkyl complex **87** also undergoes an insertion reaction with 1,2-propadiene to produce the η^1-allyl complex **88** (Scheme 23) [38].

The vinylplatinum complexes **90**, prepared by hydrometallation of alkynes with platinum hydride complexes **89**, react with 1, 2-propadiene to afford the π-allyl complexes **91** (Scheme 24) [39]. Surprisingly, the methanol complex **92** reacts with allene to give a six-membered metallacycle **93** [40]. The detailed mechanism for the interesting transformation is not well-defined.



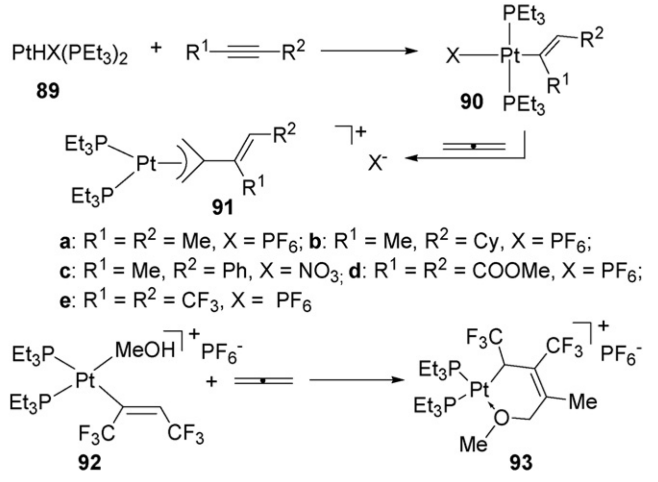
Scheme 22.



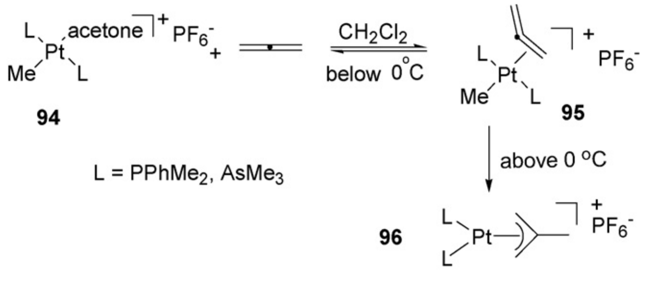
Scheme 23.

The methyl complexes *trans*-[PtMe(acetone)L_2]PF_6 (L = $PPhMe_2$, $AsMe_3$) (**94**) react, at temperature below 0 °C, with 1,2-propadiene to form the allene–Pt complexes **95**, which undergo methylplatination to afford the η^3-allyl complexes **96** at a higher temperature (Scheme 25) [41]. The addition of neutral or anionic ligands such as I^-, NO_3^-, CO, PPh_3 was found to inhibit the insertion reactions. A theoretical study suggests that the insertion reactions most likely proceed through a four-coordinate intermediate and that the regioselectivity of the insertion reactions could be caused by steric effect [42].

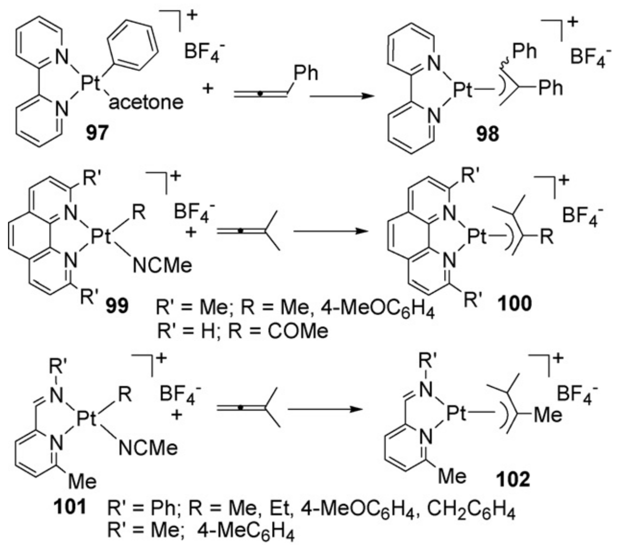
The 2,2′-bipyridine phenyl platinum complex **97** reacts with phenylallene to give a 52:48 mixture of *syn*- and *anti*-isomers of the π-allyl complex **98** (Scheme 25) [43]. The related cationic complexes **99** and **101** react with 1,1-dimethylallene to give analogous π-allyl complexes **100** and **102**, respectively (Scheme 26) [30].



Scheme 24.



Scheme 25.



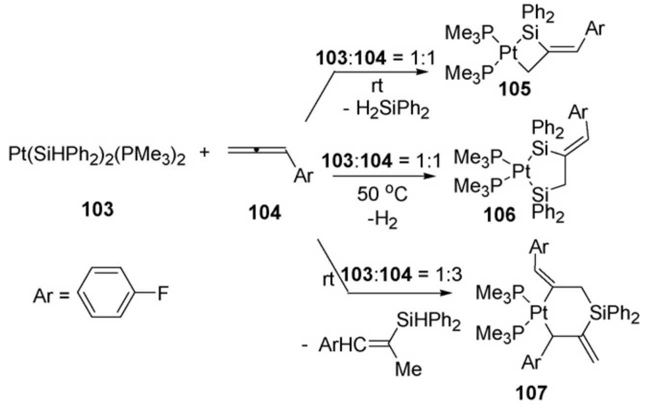
Scheme 26.

The platinum complex $Pt(SiHPh_2)_2(PMe_3)_2$ (**103**) reacts with arylallene **104** to give **105–107**, depending on the ratio of the reactants and the reaction temperature (Scheme 27) [44]. The formation of **107** may involve insertion of allene into a Pt—Si bond, although the mechanism has not been defined.

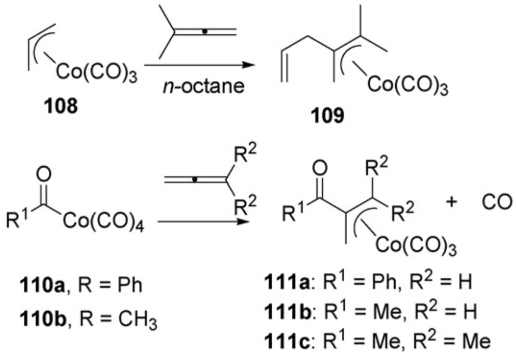
2.2. Reactions of group 9 metal complexes

Carbometallation of allenes has been reported for allyl and acyl cobalt complexes. For example, the η^3-allyl cobalt complex **108** reacts with 1,2-propadiene to produce the (η^3-2-allyl-1,1-dimethylallyl) cobalt tricarbonyl complex **109** (Scheme 28) [45]. The acetyl and benzoyl cobalt tetracarbonyl complexes **110** react with 1,2-propadiene to give the π-allyl cobalt tricarbonyl complexes **111a–b** and carbon monoxide (Scheme 28) [45,46]. The reaction between the acetyl complex **110b** and 1,1-dimethylallene similarly gives **111c** [45].

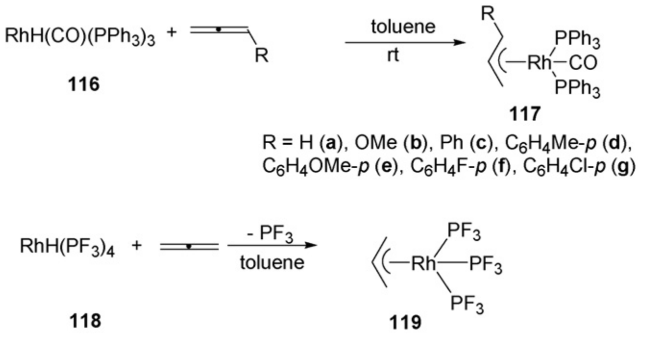
The octacarbonyl dicobalt complex **112** undergoes carbonylative metallation with 1,1-dimethylallene to give **113–115**, depending on the applied equivalents (from 1:2 to 1:4) of the 1,1-dimethylallene (Scheme 29) [45]. The reactions can be regarded as additional examples of allene insertion into Co–acyl and Co–allyl bonds.



Scheme 27.



Scheme 28.

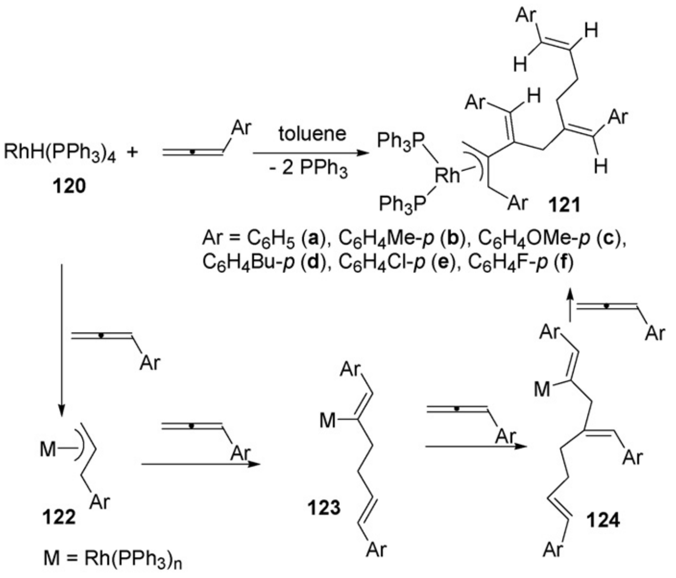


Scheme 30.

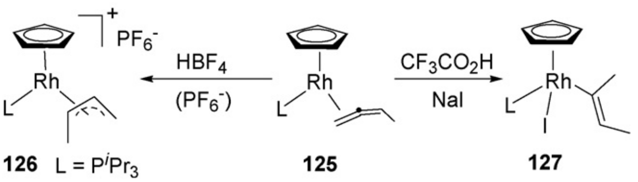
A computational study on the reaction of $HCo(CO)_3$ with 1,2-propadiene to give $Co(\eta^3\text{-}C_3H_5)(CO)_3$ in connection with mechanism of hydroformylation of allene has been reported [47].

There are several reports on the insertion reactions of rhodium hydride complexes with allenes. Reactions of $RhH(CO)(PPh_3)_3$ (**116**) with 1,2-propadiene [48,49], methoxyallene [49], and arylallene [49,50b] result in the formation of π-allyl rhodium complexes **117** (Scheme 30). The Rh–H complex **118** containing trifluorophosphine as the ligand similarly reacts with 1,2-propadiene to form the π-allyl complex **119** (Scheme 30) [51].

Interestingly, the Rh–H complex without CO ligand, i.e., $RhH(PPh_3)_4$ (**120**), reacts with arylallenes in a 1:5 molar ratio at room temperature to give the multi-insertion products **121** in high yields (>80%) (Scheme 31) [50]. It is suggested that the reaction proceed by first insertion of a molecule of arylallene into the Rh—H bond to afford the allyl complex **122**, followed by insertion reactions yielding vinyl Rh intermediates **123**, **124** and finally the allyl complex **121**. Complexes **116** and **117c** could also react with phenylallene to give **121a** [50b].



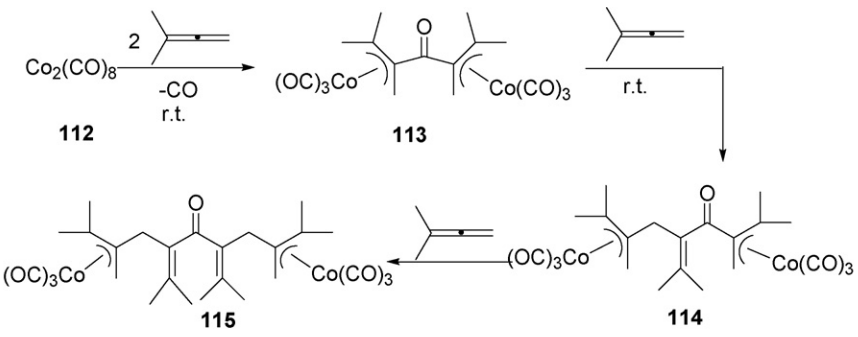
Scheme 31.



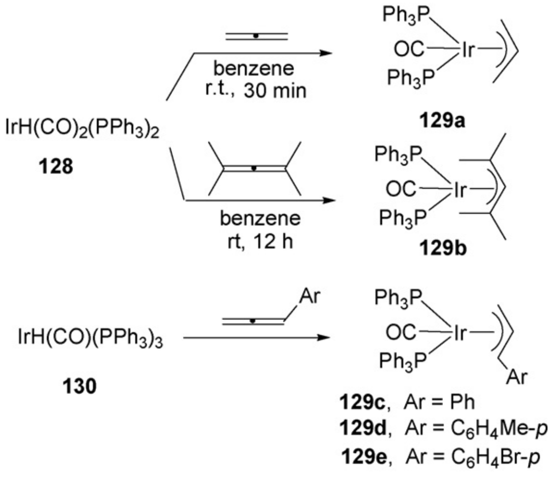
Scheme 32.

Insertion of allenes into a Rh—H bond also occurred in the protonation reaction of the allene complex **125**, which is expected to give initially a hydrido-allene complex [52]. Complex **125** is converted to the allyl complex **126** when treated with HPF_6, but to the vinyl complex **127** when treated with CF_3CO_2H in the presence of NaI (Scheme 32). The dihydride complex $[RhH_2Cl(P^iPr_3)]_2$ reacts with allene to give $[RhCl(MeCH{=}CH_2)\text{-}(P^iPr_3)]_2$ [53].

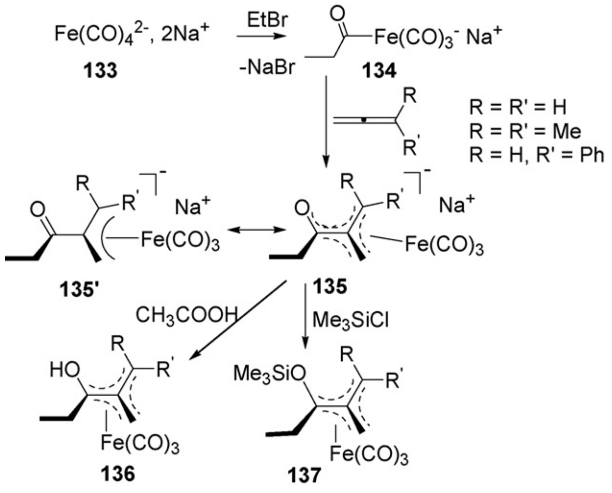
Insertion reactions of allenes with iridium complexes are rare and have only been reported for $IrH(CO)_2(PPh_3)_2$ (**128**) and $IrH(CO)(PPh_3)_3$ (**130**). The iridium hydride complex **128** reacts with allene and tetramethylallene to afford the π-allyl complexes **129a** and **129b**, respectively (Scheme 33) [48]. Analogous π-allyl complexes **129c–e** were obtained when **130** was treated with arylallenes [54].



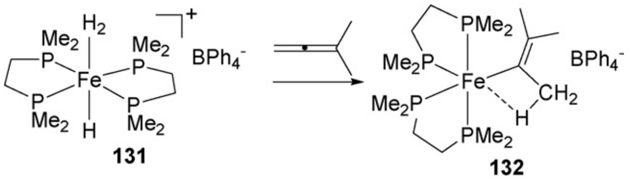
Scheme 29.



Scheme 33.



Scheme 35.



Scheme 34.

2.3. Reactions of group 8 metal complexes

2.3.1. Reactions of iron complexes

Insertion reactions of allenes into Fe—H and Fe–acyl bonds have been documented. As a rare example of insertion of allenes into a Fe—H bond, the dihydrogen iron hydride complex **131** reacts with 1,1-dimethylallene to give the vinyl complex **132** with an agostic C–H interaction (Scheme 34) [55]. A similar vinyl complex was obtained when 1,2-propadiene was used. The reaction is interesting as it represents a rare example of insertion of allene into an M–R bond to give a vinyl complex.

There are several reports on the insertion reactions of allenes with acyl iron complexes. For example, sodium tetracarbonyl ferrate (**133**) reacts with ethyl bromide and allenes to give allyl complexes **135** which are formed by insertion of allenes into the Fe–acyl bond of intermediate **134** (Scheme 35) [56]. The η^4-heterodiene iron tricarbonyl complexes **136** and **137** can be prepared by treating **135** with acid or Me_3SiCl.

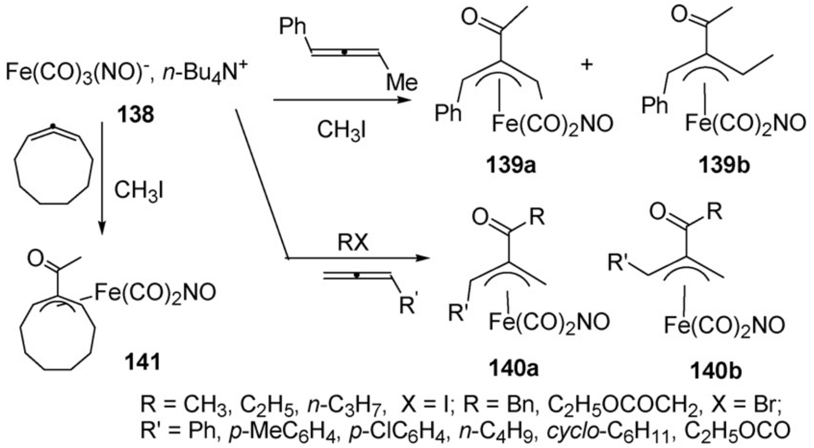
Similar acylmetallation of allenes occurs in the reactions of [*n*-Bu_4N]$Fe(CO)_3(NO)$] (**138**) with allenes and alkyl halides to give allyl iron complexes **139–141** (Scheme 36) [57].

Besides the intermolecular reactions mentioned above, an intramolecular version of the reaction has also been observed. The sodium dicarbonyl ferrate complex $[CpFe(CO)]^-Na^+$ (**142**) reacts with 3,4-allenylic bromides to afford the 3,4-allenyl complexes **143**, which undergo CO and allene insertion to give the final cyclic allyl complexes **144** (Scheme 37) [58]. Similarly, $Na_2Fe(CO)_4$ (**133**) reacts with 3,4-allenylic bromide to give complex **145**, which is converted to **146** on treatment with Me_3SiCl [59].

Insertion of allene into a Fe–acyl bond was also noted in the nucleophilic addition reactions of **147** [60]. Nuclophiles such as $NaBH_4$, $NHEt_2$, PPh_3 attack the coordinated allene to give vinyl complexes **148** (Scheme 38). Interestingly when NaOEt was used, the allyl iron complex **150** was obtained presumably through ethoxycarbonyl iron intermediate **149**.

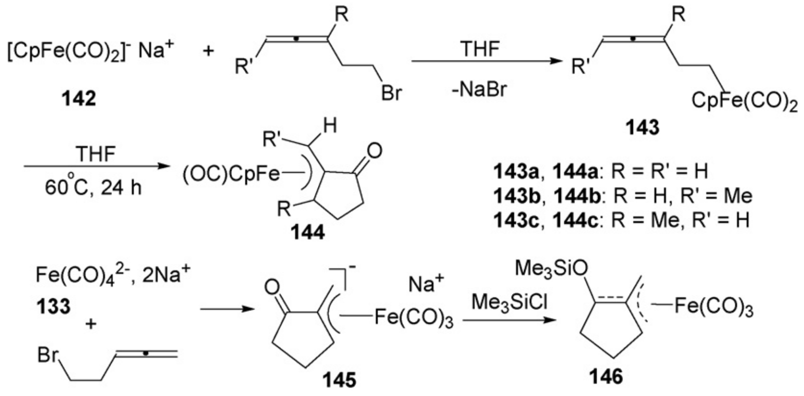
2.3.2. Reactions of ruthenium and osmium complexes

A few hydrometallation reactions of allene with ruthenium hydrides are known. Hydrometallation of the ruthenium hydride complex $RuHCl(CO)(PPh_3)_3$ (**151**) with 1,2-propadiene [61], phenylallene [62] and $CH_2{=}C{=}CHCO_2Me$ [63] gives the π-allyl

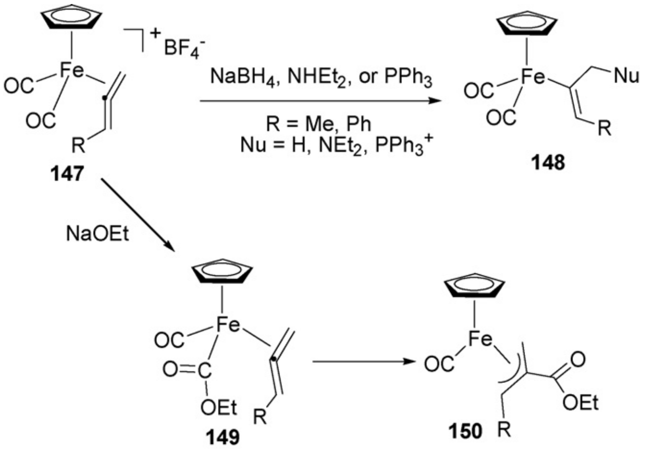


R = CH_3, C_2H_5, *n*-C_3H_7, X = I; R = Bn, $C_2H_5OCOCH_2$, X = Br;
R' = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *n*-C_4H_9, *cyclo*-C_6H_{11}, C_2H_5OCO

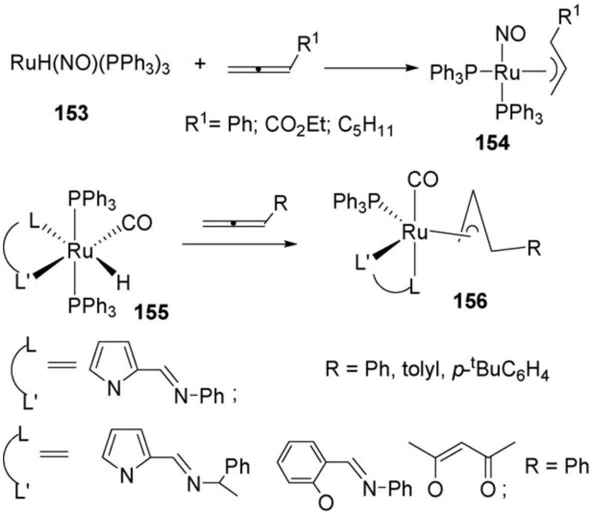
Scheme 36.



Scheme 37.



Scheme 38.

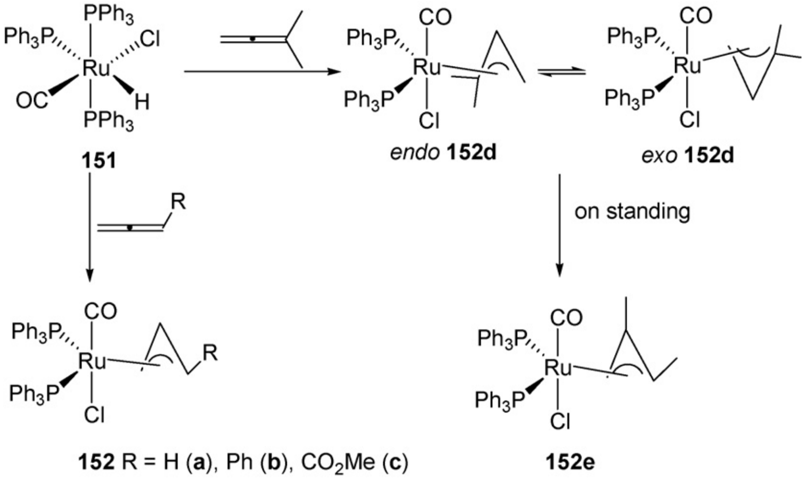


Scheme 40.

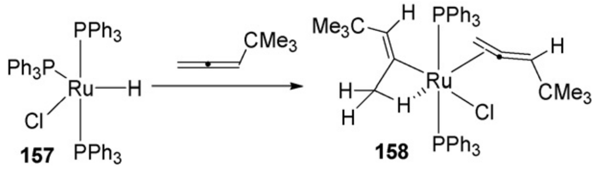
complexes **152a–c** (Scheme 39). Reaction of complex **151** with 1,1-dimethylallene yields the π-allyl complex **152d**, which slowly isomerizes to form the isomeric η^3-allyl complex **152e** in solution or in the solid state [62].

Similarly, $RuH(NO)(PPh_3)_3$ (**153**) reacts with terminal allenes to afford the η^3-allyl complex **154** (Scheme 40) [64]. The corresponding insertion products were not formed when disubstituted allenes were used as the substrates. The hydride complexes **155** with a chelating bidentate ligand could also undergo allene insertion reactions to give allyl complexes **156** as illustrated in Scheme 40 [65].

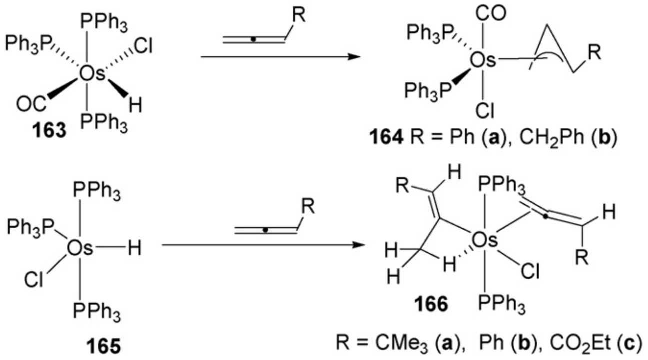
In contrast, the CO-free ruthenium hydride complex **157** reacts with $CH_2{=}C{=}CHCMe_3$ to give the vinyl complex **158** (Scheme 41) [63].



Scheme 39.



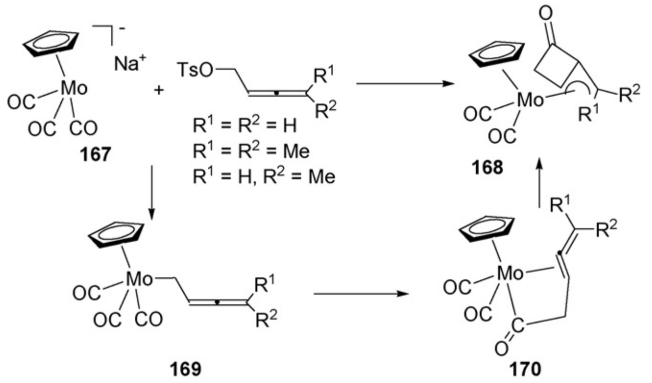
Scheme 41.



Scheme 43.

Carbometallation reactions of allenes have been reported with ruthenium vinyl complexes of the type RuCl(CH═CHR)(CO)$(PPh_3)_2$. The alkenyl ruthenium complexes RuCl(CH═CHR^1)(CO)$(PPh_3)_2$ (R^1 = Ph, (**159a**), CO_2Me (**159b**)) react with allenes to give η^3-allyl ruthenium complexes Ru(η^3-2-alkenylallyl)(Cl)(CO)$(PPh_3)_2$ (**160** and **161**) as the only products in good yields (Scheme 42). However, analogous complexes with R^1 = trimethylsilyl (**159c**) and *t*-butyl (**159d**), react with phenylallene to give the carbometallated η^3-allyl complex **162** as the major products along with the hydrometallation product **152b** as a minor product (Scheme 42) [66a]. The reactions have been recently used to make roraxanes [66b].

Insertion reactions of allenes with osmium complexes have rarely been studied. Recently, it was reported that the CO coordinating osmium hydride complex OsHCl(CO)$(PPh_3)_3$ (**163**) reacts with allenes CH_2═C═CHR (R = Ph, CH_2Ph) to give allyl complexes **164** [63], while the related CO-free osmium hydride complex OsHCl$(PPh_3)_3$ (**165**) reacts with allenes to give the vinyl complexes **166** (Scheme 43) [67]. The results clearly show that the ligand environment has a dramatic effect on the reaction pathways of allene insertion reactions.



Scheme 44.

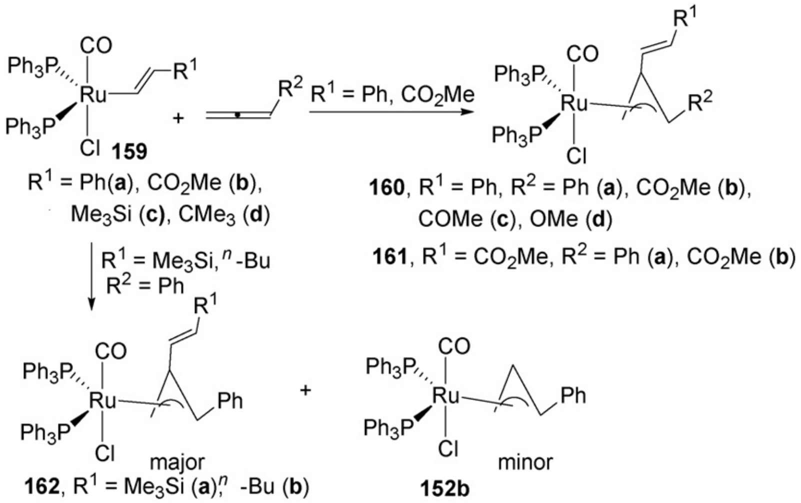
2.4. Reactions with group 5–7 metal complexes

Little work has been carried out for these metals. There appear no reported examples of insertion of allenes with mononuclear metal complexes of group 7 metals.

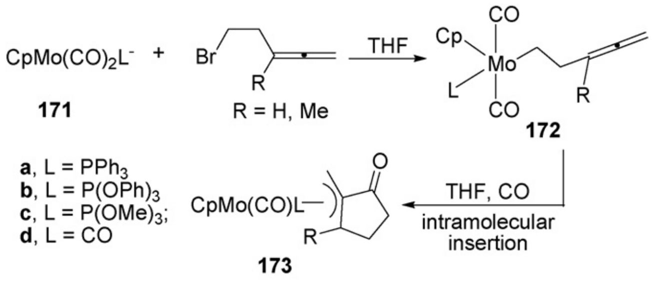
A few reports on the insertion of allenes into metal–acyl bond of complexes of group 6 metals have appeared. The anionic Mo complexes $[CpMo(CO)_3]^-$ (**167**) react with a variety of allenic electrophiles to produce η^3-2-alkylidene cyclobutanone complexes **168** (Scheme 44) [68]. It is postulated that the complexes are formed via a CO insertion (alkyl migration) to form intermediates **170** followed by intramolecular allene insertion.

Similarly, the anionic Mo complexes $[CpMo(CO)_2L]^-$ (**171**) undergo oxidative addition reactions with 3,4-allenyl bromides in THF at ambient temperature to afford the 3,4-allenyl Mo complexes **172**, which undergo CO and allene insertion to generate the allyl complexes with a cyclopentanone unit **173** (Scheme 45) [69].

The cationic allene complex $[CpMo(CO)_3(\eta^2\text{-}CH_2CCHCPh_3)]BF_4$ (**174**) can be transformed to the anti-η^3-allyl complex **175** when treated with NMe_3 and water, and to the η^3-2-hydroxycarbonylallyl complex **176** when treated with KSCN and water (Scheme 46) [70]. The common intermediate **177** may extrude CO_2 to give a hydride intermediate, which can undergo an allene insertion to give **175**. Complex **178** also undergoes insertions with CO and



Scheme 42.

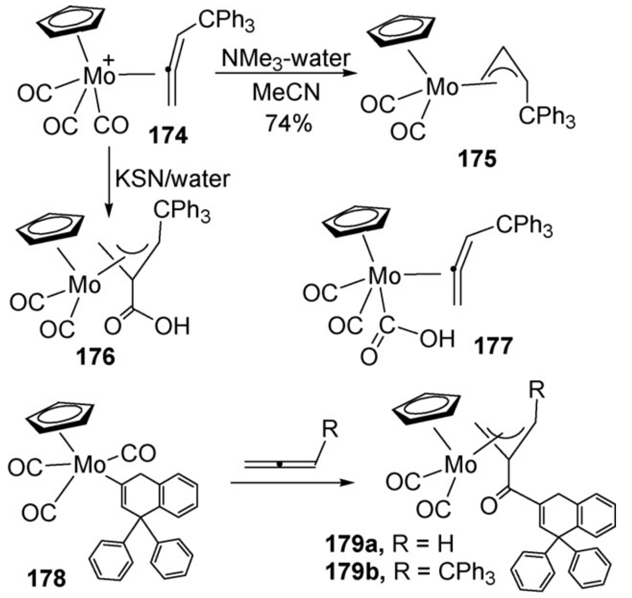


Scheme 45.

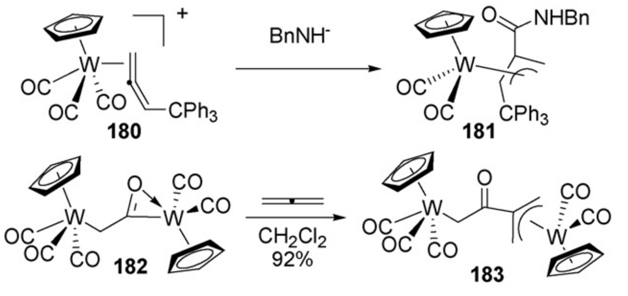
CH_2=C=CHR (R = H, CPh_3) to give allyl complexes **179** via an acyl metallation.

Two reports on allene insertion into W–acyl bonds have appeared. The tungsten allene complex $[CpW(CO)_3(\eta^2\text{-}CH_2CCHCPh_3)]BF_4$ (**180**), like Mo complex **174**, reacts with $BnNH^-$ to give the η^3-allyl complex **181** (Scheme 47) [71]. The bimetallic tungsten acyl complex **182** undergoes an insertion reaction with gaseous allene to give the dinuclear acylmetallated allyl complex **183** [72].

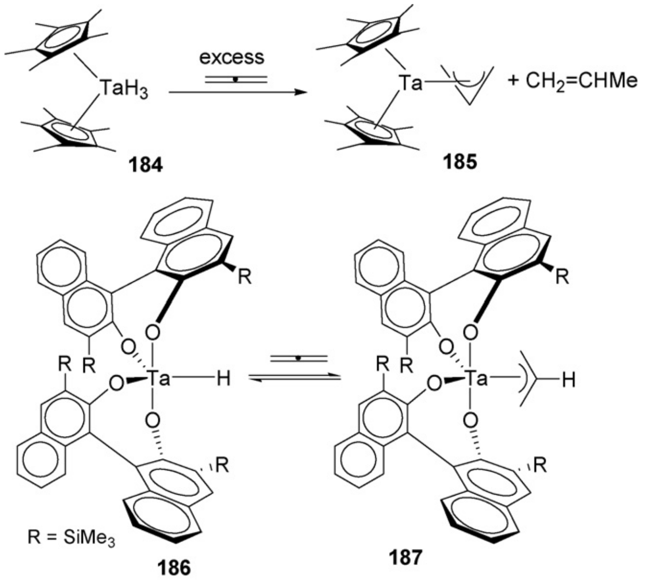
There are reported examples of insertion of allene into a Ta—H bond. The trihydride complex $Cp^*_2TaH_3$ (**184**) reacts with allene at 80 °C in benzene or toluene to give the η^3-allyl complex **185** along with H_2 and propene (Scheme 48) [73]. The insertion reaction of the tantalum hydride complex (*R*,*R*)-**186** with 1,2-propadiene in C_6D_6 to give the allyl complex **187** was observed by in situ NMR (Scheme 48) [74]. However, a preparative attempt was not successful because the allyl complex was not stable in the absence of an allene atmosphere.



Scheme 46.



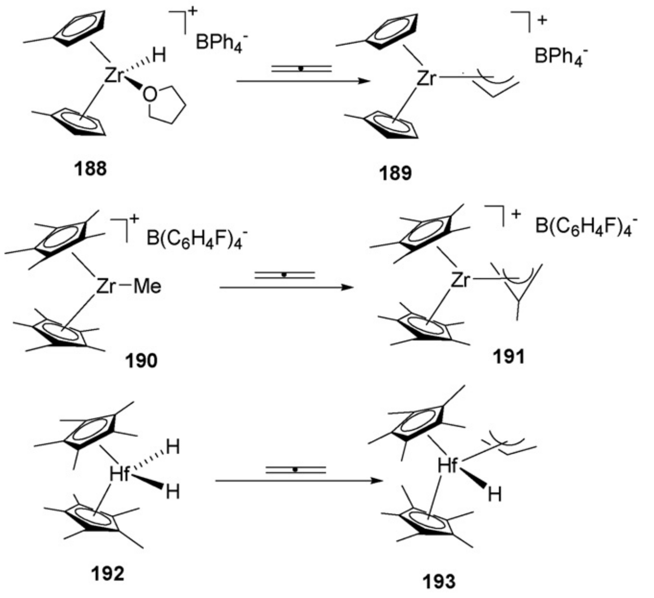
Scheme 47.



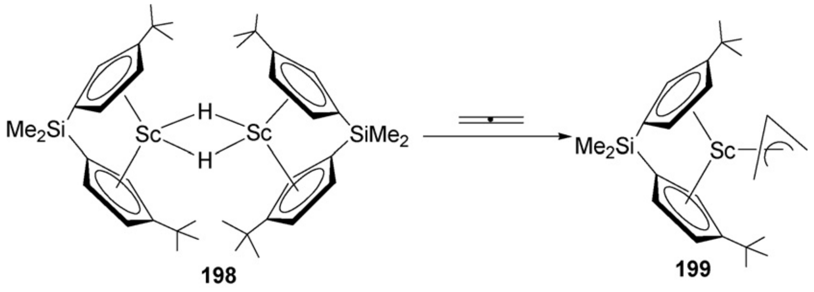
Scheme 48.

2.5. Reactions of group 4 metal complexes

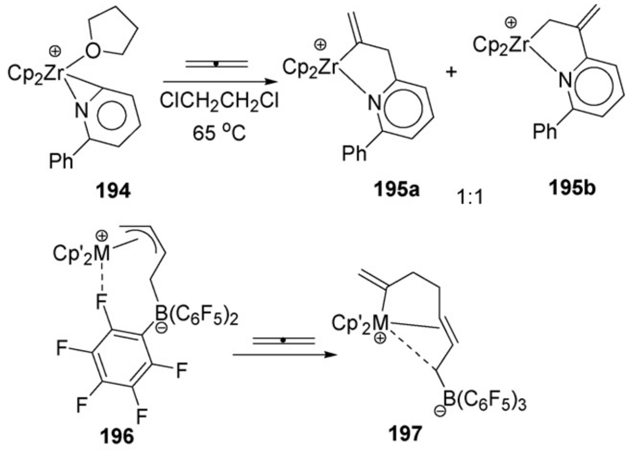
There appear no reported examples of insertion of allenes into Ti—H or Ti—C bonds. On the other hand, several reactions involving hydride and alkyl complexes of Zr and Hf have been reported. Hydrozirconation of allenes with Cp_2ZrHCl has often been used in organic synthesis to generate allylzirconocenes in situ [75]. The cationic Zr hydride complexes **188** [76] and methyl complex **190** [77] undergo rapid reactions with 1,2-propadiene to afford π-allyl complexes **189** and **191**, respectively (Scheme 49) [41]. The hafnium dihydride complex $Cp^*_2HfH_2$ (Cp^* = (η^5-C_5Me_5)) (**192**) reacts with



Scheme 49.



Scheme 51.



Cp'$_2$M = Cp$_2$Zr (**a**), (MeCp)$_2$Zr (**b**), Cp$_2$Hf (**c**)

Scheme 50.

1,2-propadiene in a 1:1 ratio to generate the π-allyl complex **193** (Scheme 49) [78].

Insertion of allene into Zr–alkyl bonds was also observed in the reactions of the cyclometallated 6-phenylpyridyl complex **194** with 1,2-propadiene. Treatment of complex **194** with excess 1,2-propadiene afforded a 1:1 mixture of vinyl complex **195a** and allyl complex **195b** (Scheme 50) [79]. The Zr and Hf allyl complexes $Cp'_2M(CH_2CHCHCH_2B(C_6F_5)_3)$ (**196**) were reported to react with 1,2-propadiene to give the vinyl metal complexes **197** [80].

2.6. Reactions with group 3 metal complexes

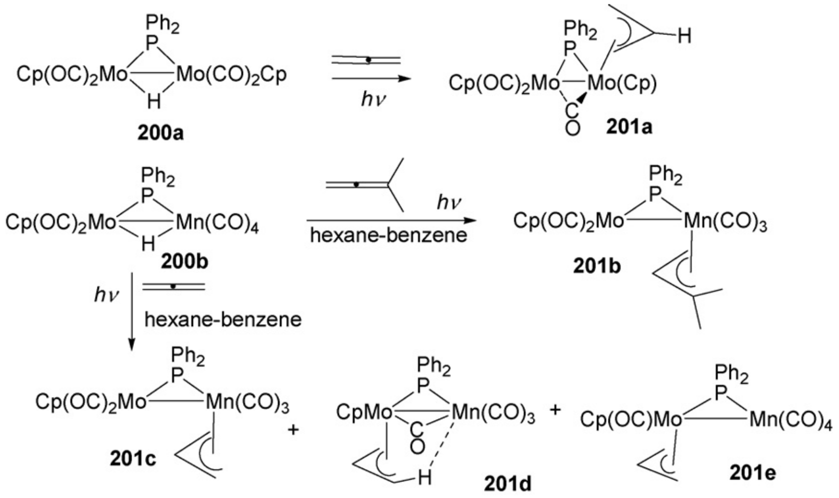
Treatment of the hydride complex **198** with excess allene produced the η^3-allyl complex **199** (Scheme 51) [81]. The analogous allyl complex $Cp^*_2Sc(\eta^3\text{-}CH_2CHCH_2)$ was similarly obtained from the reaction of allene with the unstable hydride complex $[Cp^*_2ScH]_n$ [82].

3. Reactions of allenes with dinuclear transition metal complexes

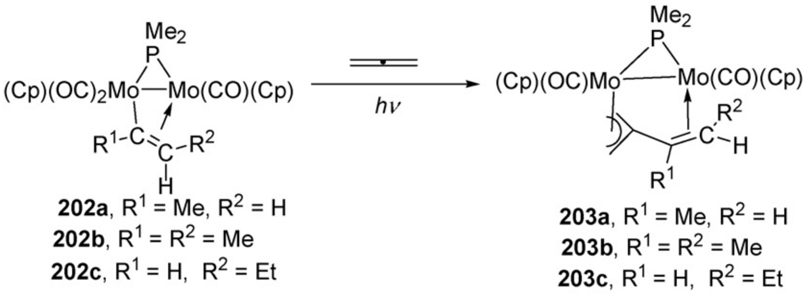
There has also been much interest in the reactivity of dinuclear transition metal complexes with allenes. Inserted products have been isolated especially from the reactions of allenes with dinuclear complexes with bridging or terminal ligands such as hydride, alkyls, carbenes (methylenes), CO and phosphides. The insertion reactions usually lead to allyl complexes, and occasionally also vinyl complexes.

3.1. Reactions of dinuclear complexes with allenes giving π-allyl complexes only

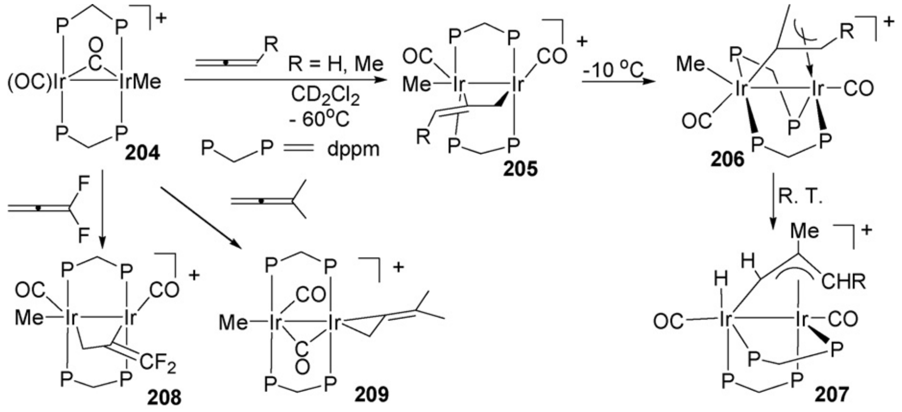
The hydrido-bridged dimolybdenum complex **200a** reacts, upon photolysis, with two-fold excess of 1,2-propadiene to give the η^3-allyl dimolybdenum complex **201a** as the only product (Scheme 52) [83]. The related hydrido-bridged bimetallic complex **200b** reacts with 1,2-propadiene under photolysis to give a mixture of allyl complexes **201c–e**. When 1,1-dimethylallene was used, complex **201b** can be isolated as the only product (Scheme 52) [84].



Scheme 52.



Scheme 53.



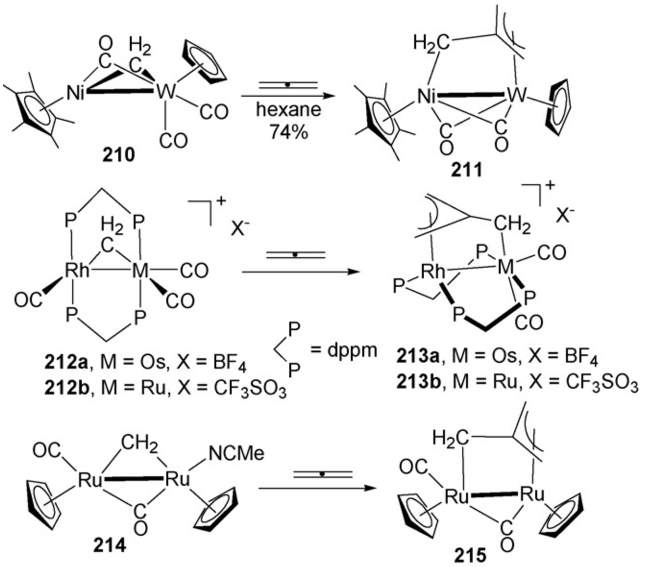
Scheme 54.

Photochemically induced reactions of the vinyl-bridged dimolybdenun complexes **202** with 1,2-propadiene were also found to give the vinylmetallated η^3-allyl dimolybdenum complexes **203** (Scheme 53) [85].

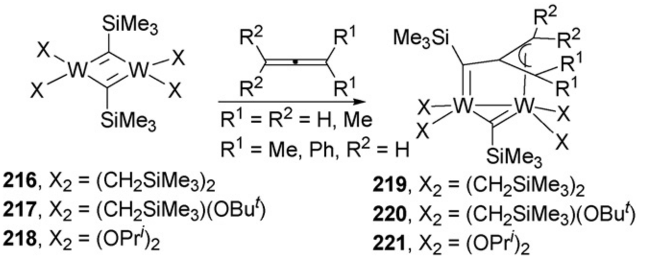
Insertion of allene into an iridium–methyl bond appears to occur in the reaction of $[Ir_2(CH_3)(CO)(\mu\text{-}CO)(dppm)_2][CF_3SO_3]$ (**204**) with monosubstituted allenes. Complex **204** reacts with allenes $CH_2{=}C{=}CHR$ (R = H, Me) to afford the η^2-allene complexes **205** at −60 °C, which transform to 2-metallated allyl iridium complexes **206** upon warming to −10 °C (Scheme 54). At room temperature, the complexes evolve to the 2-methylated allyl complex **207** [86]. Reactions of **204** with $CH_2{=}C{=}CF_2$ and $CH_2{=}C{=}CMe_2$ only give the simple coordination complexes **208** and **209**, respectively.

Several insertion reactions involving alkylidene and alkylidyne bridged complexes are known. When the methylene bridged Ni–W dinuclear complex **210** was treated with 1,2-propadiene, the allene formally inserts into the Ni—CH2 bond to generate the trimethylenemethane complex **211** chemoselectively (Scheme 55) [87]. Similar reactions occur between 1,2-propadiene and the methylene bridged dinuclear Rh–M (M = Os, Ru) complexes **212** [88] and Ru–Ru complex **214** [89] to give the corresponding trimethylenemethane-bridged products (Scheme 55). The dinuclear complexes $[RhOs(CO)_3(\mu\text{-}CH_2)(\mu\text{-}dppm)_2][X]$ (M = Os, X = BF4 (**212a**) also reacts with methylallene to yield the trimethylenemethane-bridged complex $[RhOs(CO)_2(\mu\text{-}\eta^3,\eta^1\text{-}C(CH_2)_2CH_2Me)(\mu\text{-}dppm)_2]BF_4$ with a structure analogous to that of **213a** [88].

The alkylidyne bridged complexes **216–218** react with allenes to give bimetallic complexes **219–221**, via C–C coupling between the central carbons of the allenes and one of the bridging carbon of $CSiMe_3$ (Scheme 56) [90].

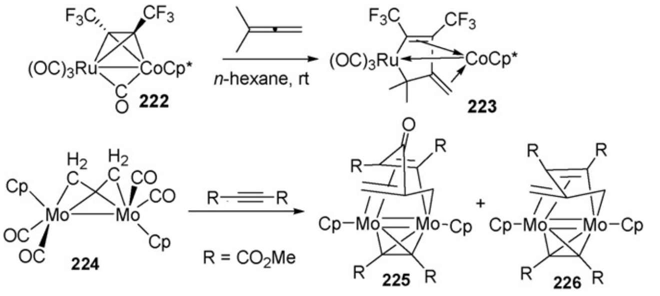


Scheme 55.



Scheme 56.

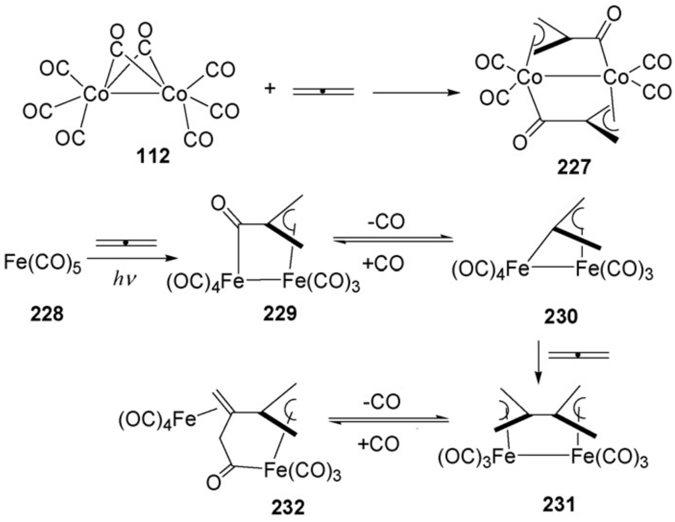
The alkyne bridged Ru–Co binuclear complex **222** reacts with 1,1-dimethylallene to afford complex **223**, as a result of C—C bond



Scheme 57.

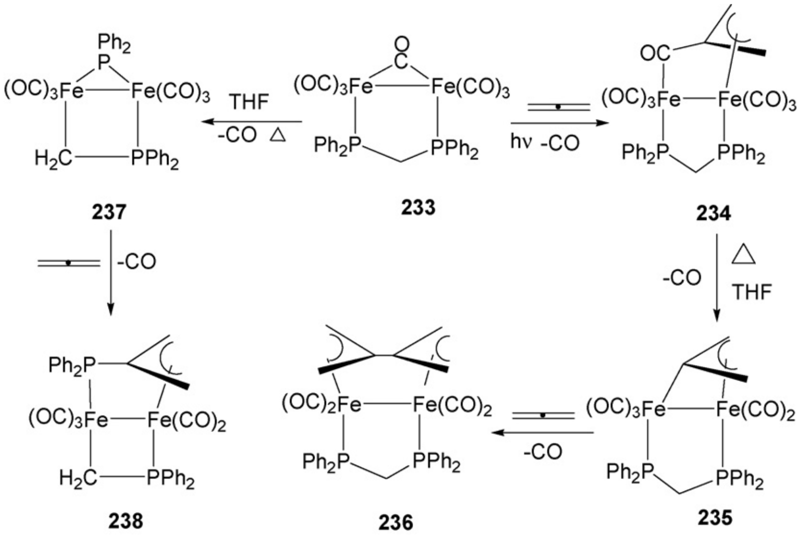
formation between the central allene carbon and one of the hexafluorobutyne sp-carbons (Scheme 57) [91]. Coupling of allene with alkyne is also observed when the dinuclear complex **224** is refluxed in octane for 16 h with RC≡CR (R = CO_2Me), giving complexes **225** and **226**, which can be isolated in 19% and 24% yield, respectively [92]. Other examples of C—C bond formation reactions of allene with a bridging alkyne ligand include the reactions of allene with the dinuclear complex $W(OR)_6(Py)(\mu\text{-}HC{\equiv}CH)$ [93] and the cluster complex $Os_4(CO)_{11}(\mu\text{-}HC{\equiv}CCO_2Me)(\mu_4\text{-}S)$ [94].

There are few reported reactions involving formal insertion of allene into a M–CO (bridging) bond. The reaction of $Co_2(CO)_8$ (**112**) with allene to give the acyl–allyl complex **227** [95] and the reaction of iron carbonyl complex $Fe(CO)_5$ (**228**) with allene to generate complexes **229** and **232** via intermediates **230** and **231** [96] are the examples of such reactions (Scheme 58). Complexes analogous to **229** and **232** were also obtained from the reaction of $Fe(CO)_5$ with phenylallene [96].

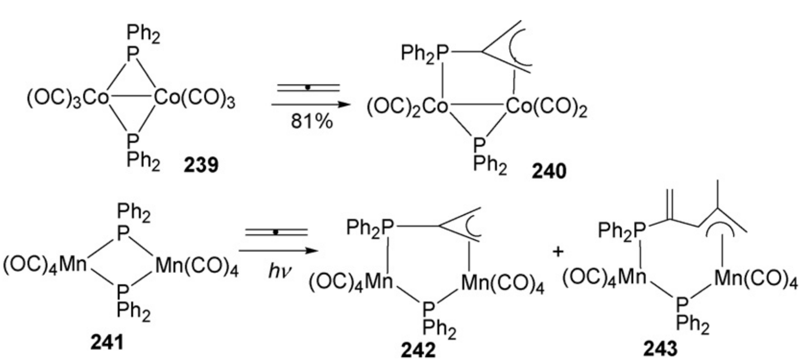


Scheme 58.

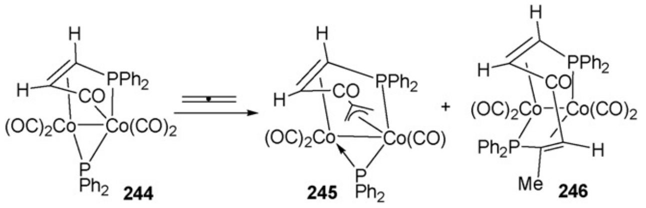
As another example of carbonylative insertion reaction of allenes, $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)]$ (**233**) reacts, upon photolysis, with 1,2-propadiene to form the π-allyl complex **234**, which decar-



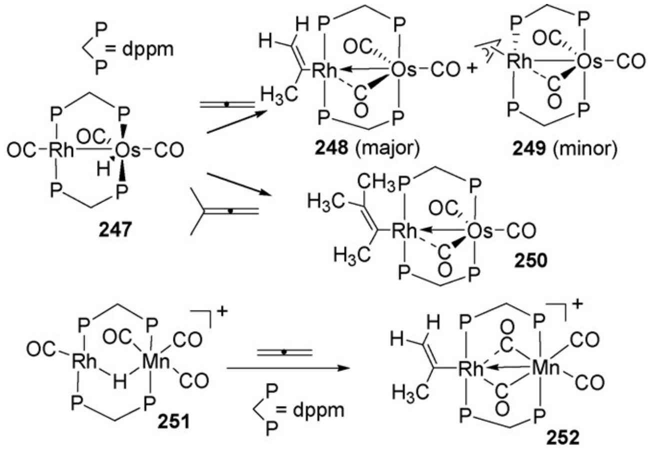
Scheme 59.



Scheme 60.



Scheme 61.



Scheme 62.

bonylates to give complex **235** when heated (Scheme 59). Complex **235** can react with another molecule of 1,2-propadiene to give carbometallated 2, 2′-bisallyl iron complex **236** [97].

Allenes could also insert into a M–P bond of phosphido-bridged bimetallic complexes. As shown in Scheme 59, complex **233** can be decarbonylated to give the phosphido-bridged complex **237**. Interestingly, complex **237** reacts with 1,2-propadiene to generate the π-allyl complex **238**, by insertion of allene into the Fe—P bond, rather than the Fe—CH_2 bond (Scheme 59) [98].

Additional examples of insertion of allene into a M–P bond of phosphido-bridged complexes include the reaction of phosphido-bridged dicobalt complex **239** with 1,2-propadiene to give **240** [98] and the photochemical reaction of dimanganese complex **241** with 1,2-propadiene to give **242** and **243** (Scheme 60). The latter reaction produced at least 15 compounds of which complexes **242** and **243** (Scheme 54) were isolated in 5% and 12%, respectively [99].

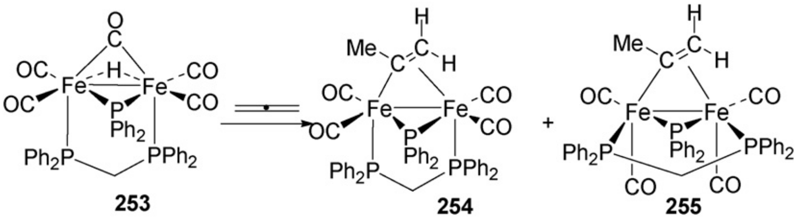
Insertion of allene into a Co—P bond may also occur in the reaction of the bimetallic complex **244** with allene. Slowly bubbling allene through a toluene solution of the phosphido-bridged complex **244** heated at 338 K produced complexes **245** and **246** which can be isolated in 13% and 35% yield, respectively (Scheme 61) [100]. Complex **245** can be regarded as being formed by insertion of allene into the Co–C(O) bond, while **246** may be formed by insertion of allene via its central carbon atom into the Co–P bond of the phosphido bridge, followed by 1,3-H shift and coupling.

Formal insertion of an allene molecule into a M–Cp bond was observed in the thermolysis of CpNi(μ-η^1,η^3-CH_2=C=CMe_2)W$(CO)_2$(η^5-C_5H_4Me), which gives the cyclopentadienyl-1,1-dimethylallyl species (η^5-C_5H_4Me)W$(CO)_2$(η^3-$CH_2C(C_5H_4)CMe_2$) [101]. A related transformation is the isomerization of CpPd(L)-Pd(L)(η^3-CH_2CClCH_2) (L = P^iPr_3) to (η^3-$CH_2C(C_5H_5)CH_2$)PdL_2 [102].

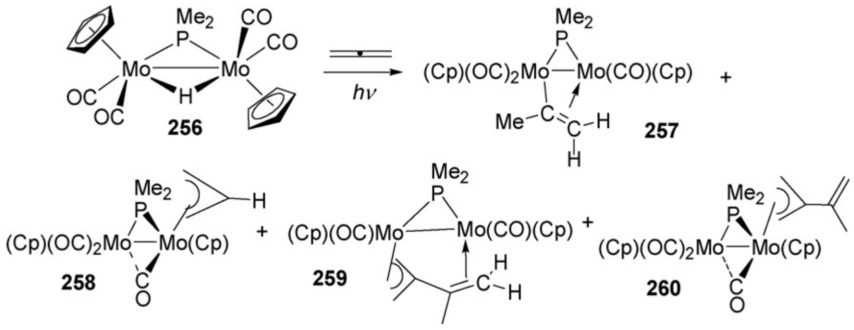
3.2. *Reactions of dinuclear complexes with allenes giving vinyl complexes or a mixture of vinyl and allyl complexes*

Some dinuclear hydride complexes can react with allenes to give vinyl or a mixture of vinyl and allyl complexes. The dinuclear Os–Rh hydride complex [RhOsH$(CO)_3$$(dppm)_2$] (**247**) reacts with 1,2-propadiene to give the vinyl complex [RhOs(C(CH_3)═CH_2)$(CO)_3$$(dppm)_2$] (**248**) as the major product along with approximately 10% (by ^{31}P NMR) of the η^3-allyl complex **249** (Scheme 62) [103]. Inter-conversion between **248** and **249** was not observed even under heating. The vinyl complex **250** was obtained as the only product when 1,1-dimethylallene was used. Reaction of the Mn–Rh binuclear complex **251** with allene similarly gives the vinyl complex **252** [104].

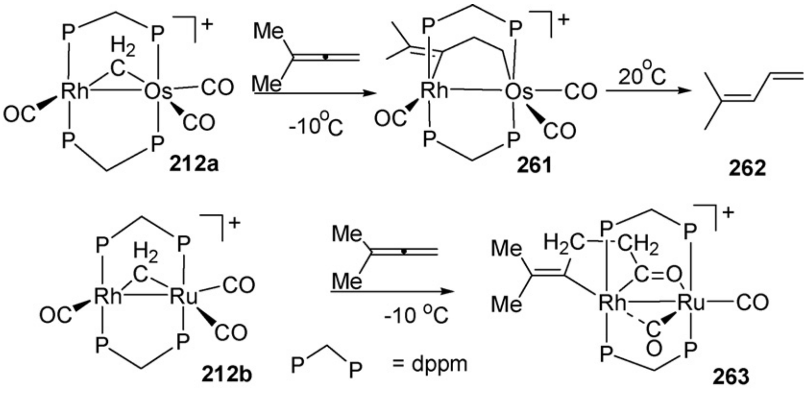
As additional examples, 1,2-propadiene reacts with hydrido-bridged dinuclear iron complex [$Fe_2(CO)_4$(μ-CO)(μ-H)(μ-PPh_2)(μ-



Scheme 63.



Scheme 64.



Scheme 65.

dppm)] (**253**) to give the 2-propenyl iron complexes **254** and **255** in 70% combined yield (2:1) as indicated by ^{1}H NMR (Scheme 63) [105]. The related complex $[Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}H)(\mu\text{-}PCy_2)(\mu\text{-dppm})]$ also reacts with 1,2-propadiene to give a vinyl complex with a structure similar to that of **254** (PPh_2 being replaced with PCy_2) [106].

Under prolonged photolysis, the hydrido-bridged dimolybdenum complex **256** reacts with two-fold excess of 1,2-propadiene to give a mixture of species, including 2-propenyl dimolybdenum complex **257**, and η^3-allyl dimolybdenum complexes **258–260** (Scheme 64).

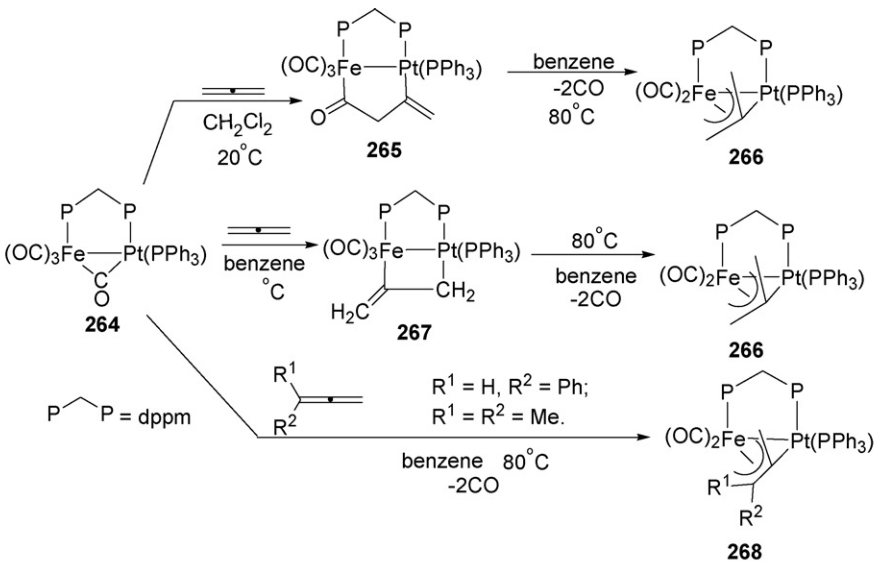
Complex **259** can be obtained from the reaction of **257** with 1,2-propadiene [85]. Reaction of the related hydrido-bridged dimolybdenum complex **200a** with 1,2-propadiene only give allyl complex **201a** (see Scheme 52).

As mentioned previously (Scheme 55), binuclear complexes $[RhM(CO)_3(\mu\text{-}CH_2)(\mu\text{-dppm})_2][X]$ (M = Os, X = BF_4 (**212a**); M = Ru, X = CF_3SO_3 (**212b**); dppm = $Ph_2PCH_2PPh_2$) react with 1,2-propadiene to yield trimethylenemethane-bridged products $[RhM(CO)_2(\mu\text{-}\eta^3\text{:}\eta^1\text{-}C(CH_2)_3)(\mu\text{-dppm})_2][X]$ (M = Os (**213a**), Ru (**213b**)). However, very different products were obtained when **212a** were treated with 1,1-dimethylallene. Complex $[RhOs(CO)_3(\mu\text{-}CH_2)(dppm)_2]^+$ (**212a**) reacts with 1,1-dimethylallene at −10 °C to give the vinyl dinuclear complex **261** (Scheme 65). At ambient temperature this species decomposes to give 4-methyl-1,3-pentadiene (**262**) via β-H elimination. Interestingly, the related Rh–Ru bimetallic complex **212b** reacts with 1,1-dimethylallene to yield **263** [88]. Obviously, one carbonyl ligand is migratorily inserted.

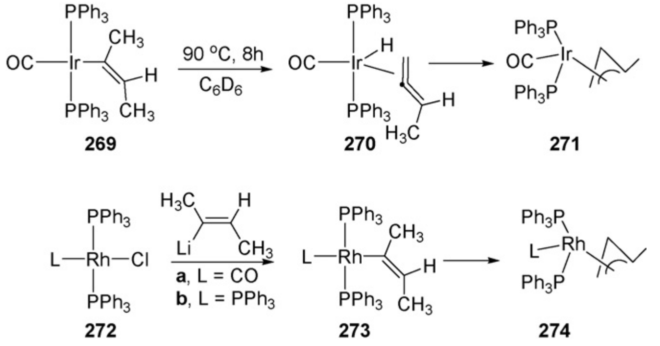
The Fe–Pt dinuclear complex $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-}CO)Pt(PPh_3)]$ (**264**) (dppm = $Ph_2PCH_2PPh_2$) was reported to undergo carbonylative platination with 1,2-propadiene at 20 °C in dichloromethane to gave the vinyl Pt–Fe dinuclear complex **265** in moderate yield after several days (Scheme 66) [107]. However, other products were obtained when the reaction was carried out under different conditions. Treatment of complex **264** with 1,2-propadiene at 80 °C gives the dimetalation product $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C({=}CH_2)CH_2\}Pt(PPh_3)]$ (**266**) in moderate yield. When complex **265** or **267** was further heated at 80 °C in benzene, allyl complex $[(OC)_2Fe(\mu\text{-dppm})\{\eta^4\text{-}(CH_2)_2CPt(PPh_3)\}]$ (**266**) can be obtained in high yield. Allyl complexes $[(OC)_2Fe(\mu\text{-dppm})\{\eta^4\text{-}(CH_2)(CRR')CPt(PPh_3)\}]$ (**268**) were obtained directly by treatment of complex **264** with substituted allenes ($PhCH{=}C{=}CH_2$ and $Me_2C{=}C{=}CH_2$) (Scheme 66) in benzene at 80 °C.

4. Organometallic transformations involving allene insertion reactions

The insertion reaction of allene can be an important step in transformations between organometallic species. Some examples of these transformations are given in this section,



Scheme 66.



Scheme 67.

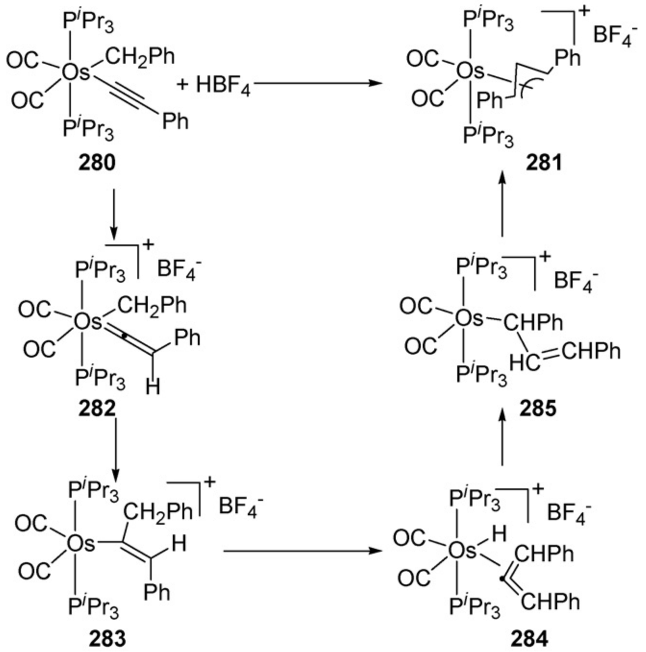
4.1. Conversion of vinyl complexes to allyl complexes

A vinyl complex could be converted to an η^3-allyl complex via insertion reaction of a hydrido-allene intermediate. For example, the iridium vinyl complex **269** slowly isomerizes to give the allyl complex **271** after heated at 90 °C in benzene for 8 h (Scheme 67) [108]. It was suggested that the vinyl complex **269** first undergoes β-H elimination to give the allene complex **270**, which undergoes a migratory insertion reaction to give **271**. Similar reactions occur more readily for related rhodium complexes. Thus, treatment of rhodium complexes **272** with *trans*-2-lithio-2-butene yielded the allyl complexes **274** directly, and the expected vinyl intermediates **273** could not be isolated.

As additional examples, the η^2-vinyl complexes of the type Tp′W(CO)$_2$(η^2-$H_2C{=}CCH_2R$) (Tp′ = hydridotris(3,5-dimethyl-1-pyrazolyl)borate; R = H, Pr, Ph, CH$_2$Ph) were reported to convert to the corresponding η^3-allyl complexes Tp′W(CO)$_2$(η^3-$H_2CCHCHR$) at room temperature or heated in toluene [109,110]. The vinyl-to-allyl transformation can account for the observation that photochemically induced insertion reactions of Tp′WH(CO)$_3$ (Tp′ = hydridotris(3,5-dimethyl-1-pyrazolyl)borate) with alkynes MeC≡CR (R = Me, SiMe$_3$) give the η^3-allyl complexes Tp′W(CO)$_2$(η^3-$H_2CCHCHR$) [110,111], and that the reactions of Cp′WH(CO)$_3$ (Cp′ = C_5H_5, C_5Me_5) with MeC≡CR (R = H, Me) give the η^3-complexes Cp′W(CO)$_2$(η^3-$H_2CCHCHR$) [112].

The vinylidene complex **275** reacts with CH_3I at room temperature to give the allyl complex **279** (Scheme 68). The transformation involves initial formation of the vinylidene complex **276** and the vinyl complex **277**, which was observed spectroscopically (Scheme 68) [113]. The vinyl complex **277** then rearranges to the hydrido-allene complex **278**, which undergoes an insertion reaction to give η^3-allyl complex **279**.

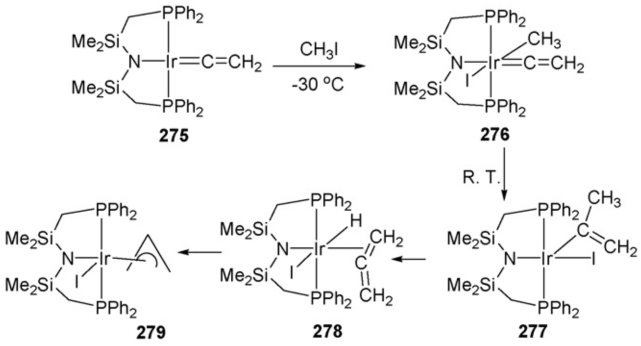
Protonation of **280** with HBF_4 produces the allyl complex **281** (Scheme 69) [114]. A deuterium labeling experiment suggests that the transformation proceeds through intermediates **282–285**. Thus, allene insertion reaction is responsible for the formation of the allyl complex **281**.



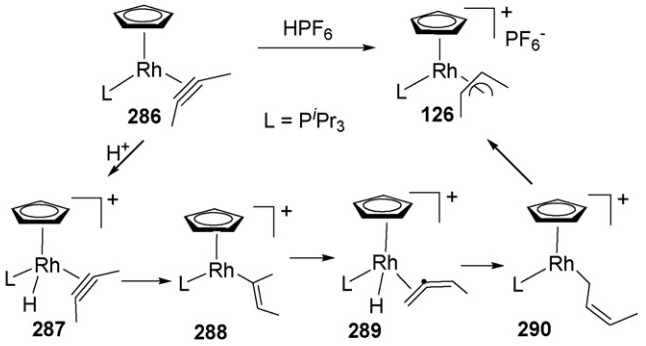
Scheme 69.

Protonation of the alkyne complex **286** with HPF_6 produces the η^3-allyl complex **126** (Scheme 70). It is suggested that the reaction proceed by initial protonation at the metal to give the hydrido-alkyne intermediate **287**, which undergoes an insertion reaction to give the vinyl complex **288**. Complex **288** then rearranges to the hydrido-allene complex **289**. Complex **126** is then formed by an insertion reaction of **289** [52].

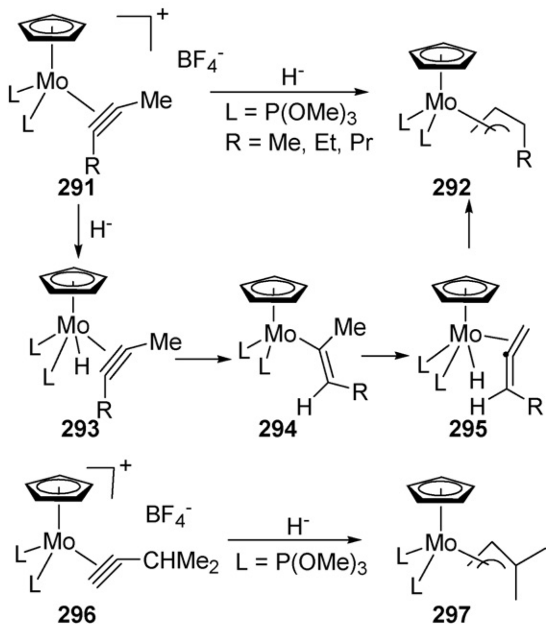
Reactions of the cationic alkyne complexes of the type [CpMoLL′(η^2-MeC≡CR)]BF$_4$ (R = Me, Et, Pr; LL′ = (P(OMe)$_3$)$_2$, Ph$_2$PCH=CHPPh$_2$, (PEt$_3$)(CO)) with hydride donors such as NaBH$_4$, K[BHBu$_3$] produce the allyl complexes [CpMoLL′(η^3-CH_2CHCHR)]BF$_4$, as illustrated by the formation of the allyl Mo complexes **292** from [CpMo(P(OMe)$_3$)$_2$(η^2-MeC≡CR)]BF$_4$ (**291**) shown in Scheme 71 [115]. The hydrido-alkyne complex **293** and the hydrido-allene complex **295** are the key intermediates for the formation of **292**. Complex [CpMoLL′(η^2-HC≡CCHMe$_2$)]BF$_4$ (**296**) also reacts with H$^-$ to give the analogous η^3-allyl complex **297**. The tungsten complexes Tp′W(CO)$_2$(η^2-RC≡CMe) (R = Me, Ph) react with LiBHEt$_3$ to give the allyl complex Tp′W(CO)$_2$(η^3-$H_2CCHCHR$) [116].



Scheme 68.



Scheme 70.



Scheme 71.

Reaction of the acetylide complex **298** with HCl and MeI produced the coupled products **299** and **300**, respectively (Scheme 72). Insertion reaction of the hydrido-allene complex **303** was proposed to be involved in the formation of **299** and **300** as illustrated in Scheme 72 [117].

Protonation of the iridium acetylide complex **304** gives complex **305** and organic compounds **306** and **307** (Scheme 73). Deuterium labeling experiments suggest that an allene insertion reaction is involved in the formation of **307** as illustrated in Scheme 72 [118].

Conversion of vinyl complexes to allyl complexes is not limited to mononuclear complexes and can also occur for bimetallic complex. Thus, reaction of the bimetallic complex **312** with alkynes such as MeC≡CH, MeC≡CMe, EtC≡CH and MeC≡CPh gives a mixture of vinyl complexes and η^3-allyl complexes as illustrated by the formation of **313** and **314** (Scheme 74) [119]. Reactions of the bimetallic complex Cp(CO)$_2$Mo(μ-PPh$_2$)(μ-H)Mn(CO)$_4$ (**200b**) with alkynes such as MeC≡CH, MeC≡CMe and EtC≡CH give η^3-allyl complexes with a structure similar to those of **201c–d** (see Scheme 52 for structures **200b** and **201c–d**). The formation of the allyl complexes was also thought to involve isomerization of vinyl complexes via hydrido-allene intermediates.

4.2. *Conversion of allyl complexes to alkyne complexes*

When the allyl complex **185** was heated at 60 °C for 3 days, the hydrido-alkyne complex **315** was formed (Scheme 75) [73]. The reaction is interesting because it represents a rare example of conversion of an allyl complex to hydrido-alkyne complex. It was suggested that the reaction may proceed by first deinsertion of **185** to give an hydrido-allene complex **317**, which then undergoes an insertion reaction to give the vinyl intermediate **318** and then to the alkyne complex **315** by β-H elimination of **318**. A related transformation is the formation of the alkyne complex **320** from the reaction of the hydride complex **184** with butadiene. Treatment of **184** with butadiene produced several complexes including Cp$^*_2$TaH(η^2-CH$_2$=CH—CH=CH$_2$), allene complex Cp$^*_2$TaH(η^2-CH$_2$=C=CHMe) (**319**), and alkyne complex **320**, depending on the reaction condition. Complex **320** is formed in high yield upon prolonged warming of the reaction mixture and that allene complex **319** is one of the intermediate. Thus **320** was likely formed through the vinyl intermediate **321**.

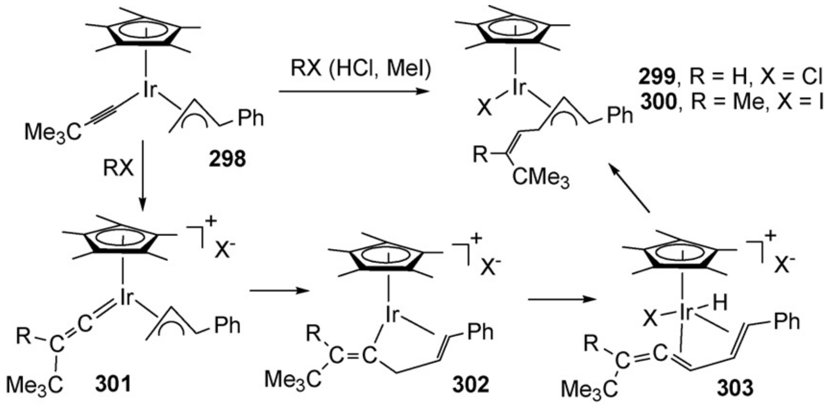
When heated, the allyl complex **322** isomerizes to the vinyl complex **323** (Scheme 76) [120]. The isomerization proceeds through intermediates of allene complex **324**, vinyl complex **325** and alkyne complex **326** as monitored by NMR.

4.3. *Isomerization of alkynes*

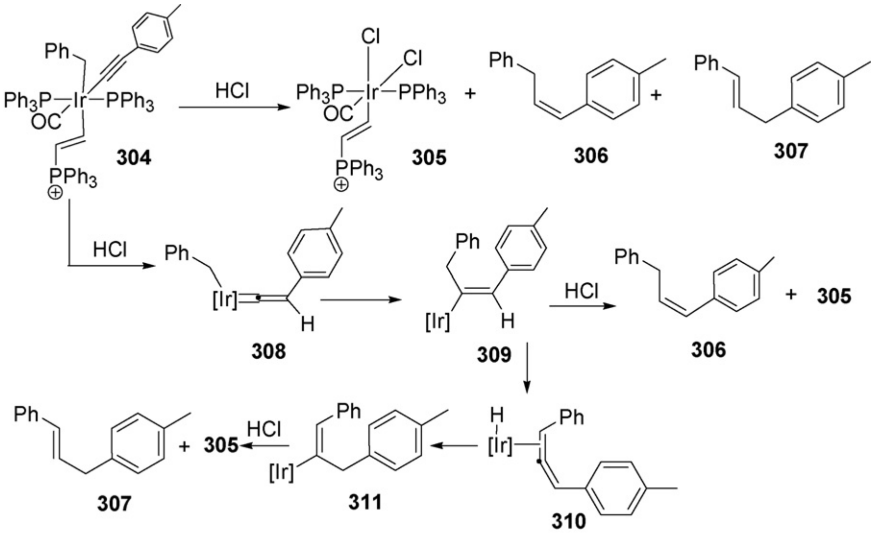
Walton and co-workers show that the hydride complex **327** can react, in the presence of an electrophile (e.g. HPF$_6$, Ph$_3$CPF$_6$), with both internal and terminal alkynes to give carbyne complexes as illustrated by the formation of **328** and **329** (Scheme 77) [121]. The reactions starting from internal alkynes involve isomerization of internal alkynes to terminal alkynes through allene complexes. The isomerization process involves vinyl intermediates formed by insertion/deinsertion reactions of allenes and alkynes. A general mechanism for the formation of carbyne complexes from the reactions of internal alkynes with **327** is illustrated by the formation of **328** via intermediates **330–334** shown in Scheme 77.

4.4. *C–H activation*

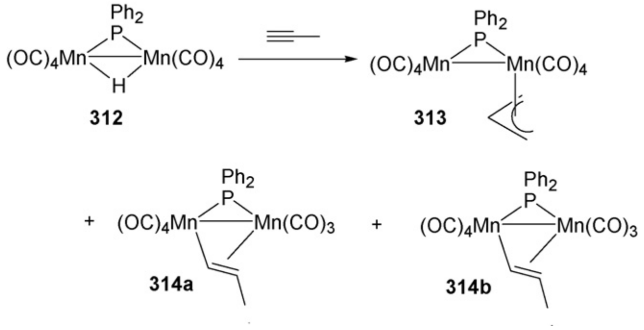
The tungsten complex **335** undergoes C—H bond activation with a variety of hydrocarbons, for example, with SiMe$_4$ to give allyl complex **338**, and with benzene to give allyl complex **339** (Scheme 78) [122]. The key intermediate of the reaction is the allene complex **336**, which can be trapped with PMe$_3$ to give allene complex **337**. A theoretical study shows that the C–H addition process involves a transition state like **340** [123].



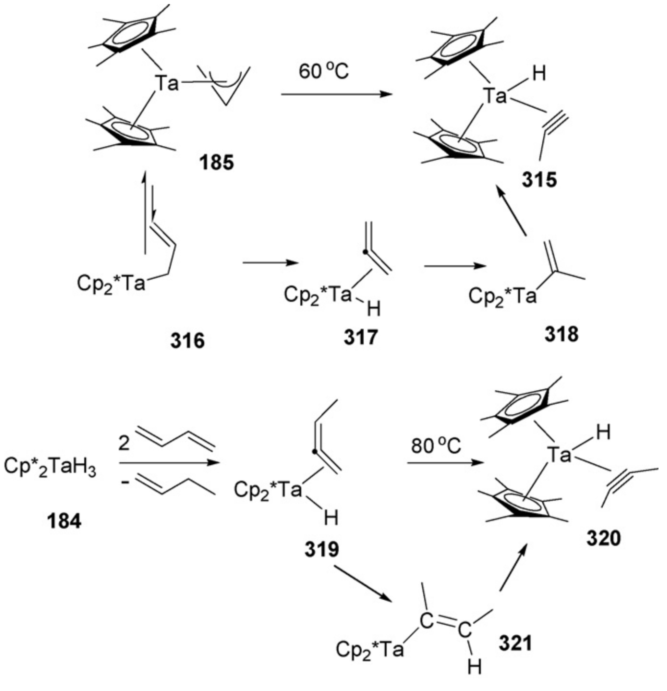
Scheme 72.



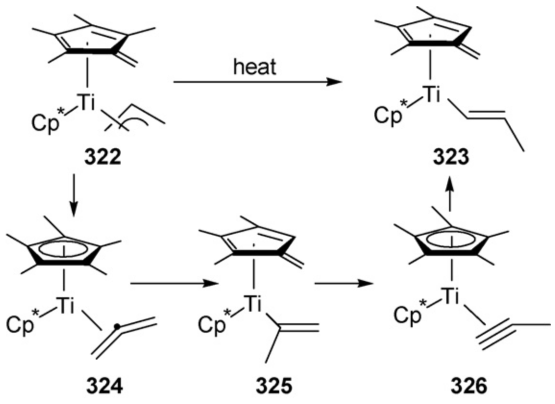
Scheme 73.



Scheme 74.



Scheme 75.



Scheme 76.

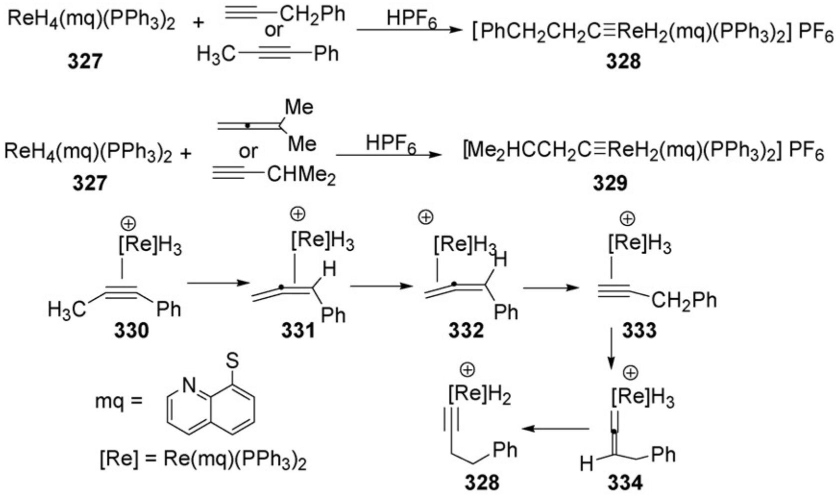
5. Reactions of allenes with complexes containing a M=X double bond

Very limited work has been carried out on the isolation of stable complexes from the reactions of allenes with complexes containing a M=X double bond (e.g. carbene, oxo, imido complexes). There appear no reports on the stoichiometric reactions of allenes with mononuclear complexes containing an M≡X triple bond (e.g. carbyne complexes).

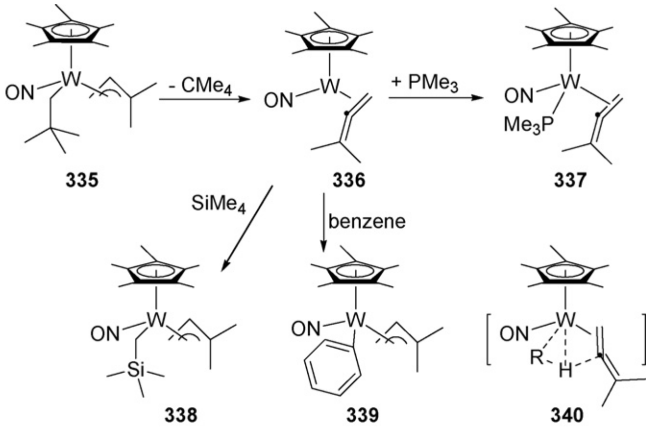
5.1. Reactions with carbene complexes

[2 + 2] cycloaddition reactions of allenes and metal carbene complexes have been proposed as one of the key step in several catalytic and stoichiometric reactions of allenes, for example, cross metathesis catalyzed by $(PCy_3)_2Cl_2Ru{=}CHPh$ [124] and $(OCMe_2CF_3)_2(N(2,6\text{-}^iPr_2C_6H_3))Mo{=}CMe_2Ph$ [125], metathesis and cycloaddition reactions of alkenyl Fischer carbenes with allenes [126], formal ene reaction of Fischer chromium carbene complexes with vinylidenecyclopropenes [127].

Well-defined complexes have been isolated in a few reactions of allenes with carbenes. In 1987, Aumann reported the isolation of the trimethylenemethane complex **343** from the reactions of carbene complexes $(CO)_5M{=}C(OEt)Ph$ (M = Cr, Mo, W; **341**) with phenylallene. The reaction was proposed to proceed through inter-

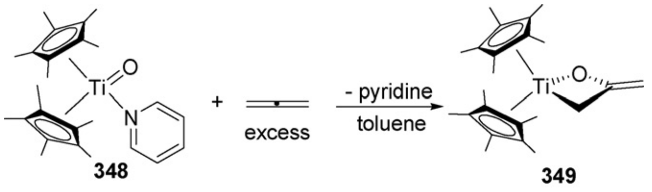


Scheme 77.



Scheme 78.

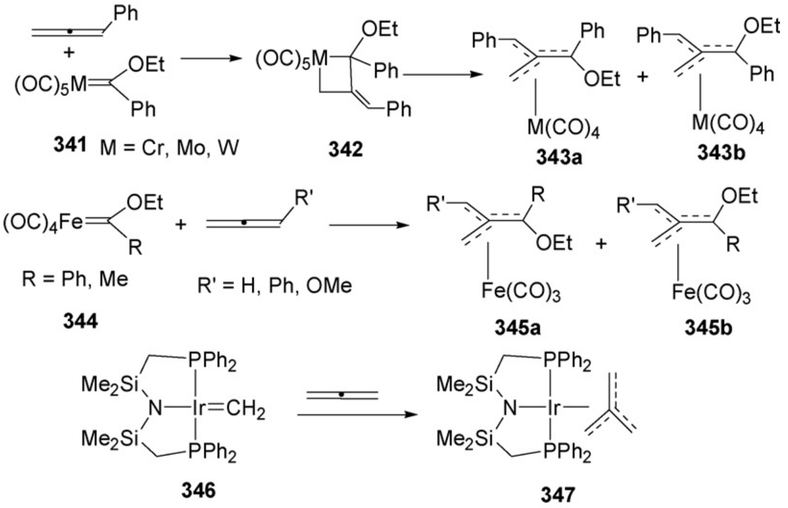
mediate **342** (Scheme 79) [128]. The chromium carbene complex $(CO)_5Cr{=}C(OEt)Ph$ also reacts with functionalized allenes such as $CH_2{=}C{=}CHCH_2R$ (R = OH, CO_2Et, CH_2OH). In these cases, a small amount of enol ether $CH_2{=}C(OEt)Ph$ was also obtained due to metathesis reaction [129]. The iron carbenes $Fe(CO)_4{=}C(OEt)R$ (**344**, e.g. R = Ph, Me) can also react with allenes to give η^4-trimethylenemethane complexes (e.g. **345**) [129,130]. The related iron trimethylenemethane complex $(\eta^4\text{-}C(CH_2)_3)Fe(CO)_3$ has been obtained from the reaction of $Fe_2(CO)_8(\mu\text{-}CH_2)$ with allene [131]. Reaction of the iridium carbene complex **346** with allene also gives the η^4-trimethylenemethane complex **347** [132].



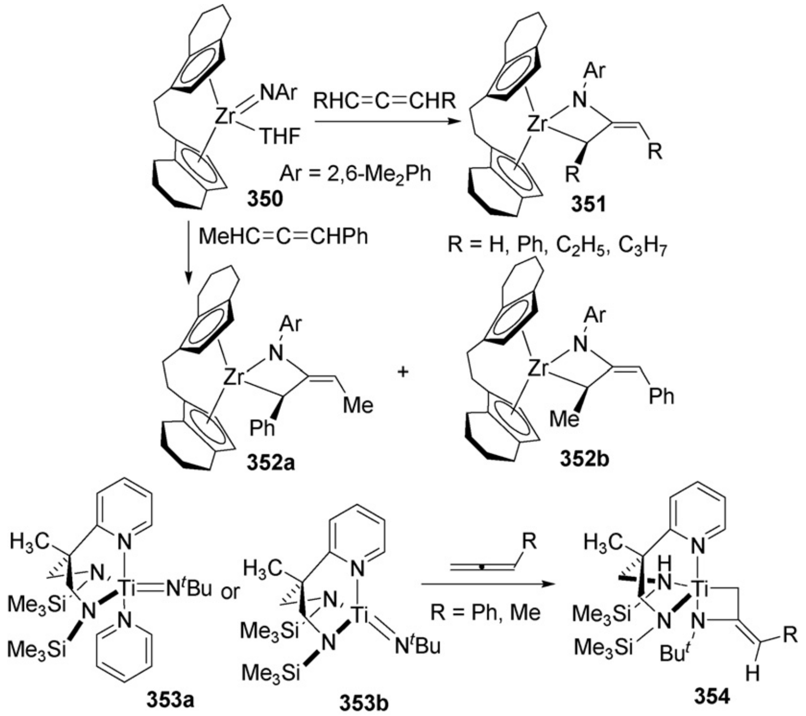
Scheme 80.

5.2. Reactions with oxo and imido complexes

The monomeric oxo compound **348** readily undergoes a [2 + 2] cycloaddition reaction with excess allene to give oxametallacyclobutane complex **349** (Scheme 80) [133].



Scheme 79.



Scheme 81.

[2 + 2] cycloaddition reactions of allenes with metal imido complexes have been suggested as one of the key step in early transition metal catalyzed hydroamination of allenes [134,135]. A few cycloaddition products have been isolated. Bergman and co-workers discovered that the imidozirconium complexes $Cp_2Zr{=}NAr(THF)$ and $(ebthi)Zr{=}NAr(THF)$ (ebthi = bis(tetrahydroindenylethene) (**350**) [136] undergo [2 + 2] cycloaddition reactions with allenes to give azametallacycles as illustrated by the production of **351** and **352** from **350** (Scheme 81). The azametallacycles are the key intermediate in zirconium mediated stereoselective inversion of allenes. Gade and co-workers show that the imidotitanium complexes **353a** or **354b** can undergo [2 + 2] cycloaddition reactions with 1-methylallene and phenylallene to give the azametallacyclic complex **354** [137].

6. Conclusion and outlook

Substantial amount of work have been carried out on the insertion reactions of allenes. It is clear that many transition metal complexes can react with allenes to form carbometallation, hydrometallation, or heteroatom-metallation products. For insertion of allenes into an M–X single bond of mononuclear complexes, the prevailing reaction products are the η^3-allyl complexes while vinyl complexes were only observed occasionally. The insertion reaction of allenes has been found to be an important step in catalytic reactions and in transformations between organometallic species. In view of the important roles of mononuclear allyl complexes, especially those with a hemilabile bidentate ligand [138], in catalytic reactions, it is expected that new catalytic reactions based on allene insertions will be discovered.

For insertion of allenes into an M–X single bond of dinuclear complexes, both η^3-allyl and vinyl complexes can be produced. Further work is still needed especially in the area of detailed understanding of the insertion process. It is of interest to know if it is possible to fine-tune the coordination environments of $L_nM–X$ so that their reactions with allenes preferentially give vinyl complexes.

Interesting reactions of allenes with $L_nM{=}CR_2$, $L_nM{=}O$, and $L_nM{=}NR$ have been documented. For these reactions, it is found that terminal carbon of an allene is usually attached to metal while the central carbon to the C, O, or N atom. New interesting results on the reactions of allenes with complexes with a MX multiple bond is expected.

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