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Review

Synthesis and reactivity of α,β-unsaturated alkylidene and cumulenylidene Group 8 half-sandwich complexes

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Contents

Abstract

The present review reports on the chemistry and catalytic applications of Group 8 half-sandwich complexes containing non-heteroatom stabilized α,β-unsaturated alkylidene and cumulenylidene groups. These include bis-carbenes $[ML_n]=C(R^1)-C(R^2)=C(R^3)-C(R^4)$, mono- and polyhapto alkenyl-alkylidenes $[ML_n]=C(R^1)–C(R^2)=CR^3(R^4)$, as well as substituted vinylidene $[ML_n]=C=CR^1(R^2)$ and allenylidene $[ML_n]=C=C=CR^1(R^2)$ complexes (R^1 and/or R^2 = unsaturated hydrocarbon substituent). Synthetic methodologies and stoichiometric reactions as well as the involvement of these species in a series of catalytic transformations are presented. Important recent developments in catalytic studies reveal the role of bis-carbene and alkenyl–vinylidene species as intermediate active species in C–C coupling reactions of alkynes.

Keywords: Alkylidene complexes; Vinylidene complexes; Allenylidene complexes; Cumulenylidene complexes; Carbene complexes; Iron, Ruthenium and osmium complexes; Half-sandwich complexes

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1. Introduction

The search of synthetic and catalytic applications of classical transition-metal carbene complexes (Fischer and Schrock type) constitutes a continuous challenge in modern organic synthesis [1a,b]. Among the most promising alternatives the chemistry of electrophilic carbene [MLn]=$CR^1(R^2)$ and cumulenylidene [MLn]=$C(=C)_n$=$CR^1(R^2)$ complexes has recently disclosed new synthetic approaches including both stoichiometric and catalytic processes. A number of former reviews [1c–h] and specific surveys [2] illustrate the state-of-the-art of this field including seminal applications in catalytic processes. The rapid development of this chemistry probably raised from the presence in the carbon chain of both electrophilic and nucleophilic sites which provide an unusual versatility towards a wide range of reactivity approaches.

A particular class of derivatives are those in which the carbene chain also contains other type of unsaturated functional groups (R^1 and/or R^2 non-aromatic unsaturated hydrocarbon chain) which potentially can increase the scope of the reactive sites. Although some of these derivatives have been known for years, its chemistry has recently attracted special attention owing to the catalytic activity mainly in RCM and ROMP of olefins and in a number of processes involving alkynes. The present reviews will focus on the chemistry of Group 8 half-sandwich carbene complexes in which the alkylidene (**A**) or the vinylidene (**B**) and allenylidene (**C**) groups bear an unsaturated hydrocarbon chain as a substituent (heteroatom stabilised carbenes are excluded) (see Plate 1). Only mononuclear complexes containing terminal carbene groups will be reviewed. Special attention will be devoted to the role of some of theses species in catalytic processes.

2. α, β-Unsaturated alkylidene complexes

In accordance with the type of co-ordination mode of the carbene moiety the following complexes can be envisaged [3,4]:

2.1. Monohapto alkylidenes

It is well-known that alkenyl metal derivatives [M]–CH=CR_2 are prone to undergo typical electrophilic additions to give alkylidene derivatives $[M]^+$=CHC(E)R_2. Following this synthetic methodology, and starting from (η^5-indenyl)-ruthenium(II) derivatives containing unsaturated alkenyl groups, we have synthesized via protonation with HBF_4 in diethyl ether a series of cationic alkylidenes of the type (Scheme 1): (i) η^1-α,β-alkenyl-alkylidenes **1**–**2** formed through the addition of the proton at C_δ of the alkenyl moiety [5a,b], and (ii) the η^1-alkynyl-alkylidene **3** generated via addition of the proton at C_β atom of the alkenyl group [5c,d]. This procedure constitutes an alternative synthetic route for unsaturated alkylidene five-coordinate Grubbs catalysts [3a].

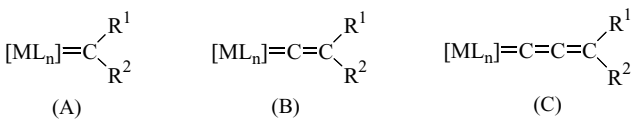
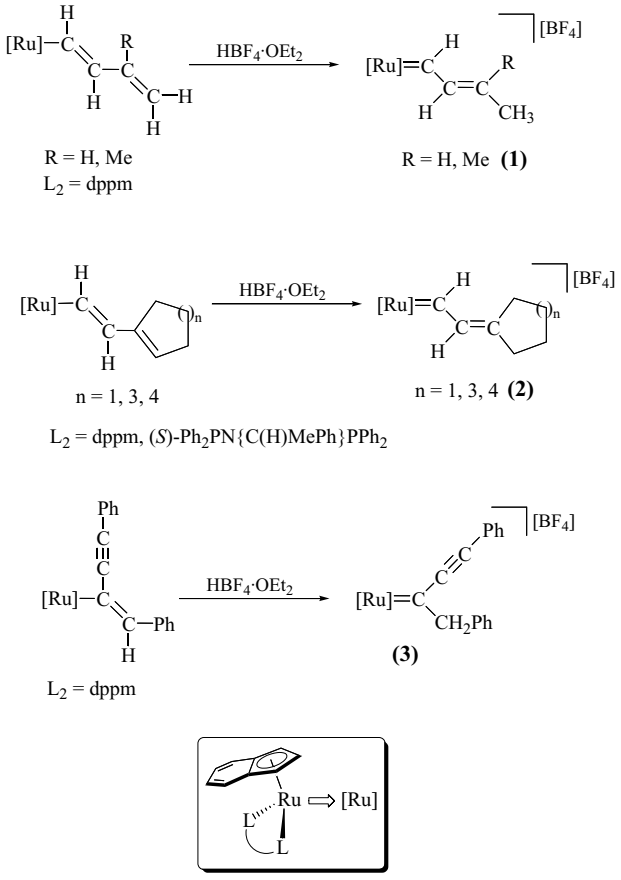


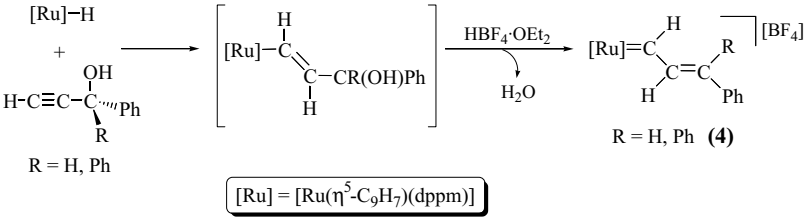
Plate 1.



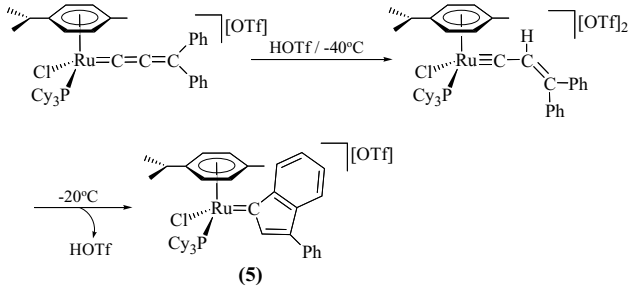
Scheme 1.

Analogous alkenyl-alkylidene complexes **4** are obtained via one-pot synthesis by the reaction of [RuH(η^5-C_9H_7)(dppm)] (dppm = bis(diphenylphosphino)methane) with HC≡CR(OH)Ph (R = H, Ph) in refluxing toluene followed by the addition of a stoichiometric amount of HBF_4·Et_2O (Scheme 2) [5a,e,f].

A series of five-coordinate 16-electron ruthenium(II) 3-phenyl-1-indenylidene complexes [$RuCl_2(PCy_3)$(L)(indenylidene)] (L= PCy_3, PPh_3, imidazolylidene) have been described. The presence of the α,β-alkenyl-alkylidene group has been now confirmed by X-ray diffraction studies [3d]. These unsaturated alkylidene derivatives are spontaneously formed from the intramolecular rearrangement of an intermediate allenylidene moiety. Dixneuf and co-workers [6] have recently reported the formation of an analogous 18-electron η^6-*p*-cymene derivative (**5**) by protonation of



Scheme 2.



Scheme 3.

a solution of the corresponding allenylidene complex at −40 °C. The reaction proceeds through an intermediate carbyne derivative which gives the indenylidene after 30 min at −20 °C (Scheme 3). Complex **5** decomposes at room temperature and all attempts to isolate it failed. However, it has proven to be an outstanding catalyst in RCM and ROMP processes (see Section 5.1).

Cyclization reactions between the C_β=C_γ or the C_α=C_β double bond of allenylidene ligands with unsaturated organic substrates have been reported to afford also unsaturated alkylidenes **6** and **7** (see Fig. 1) which are proposed as transient species. Thus, the reaction of [Ru(=C=C=CPh$_2$)(η^5-C$_5$H$_5$)(CO)(P^{i}Pr$_3$)][BF$_4$] and dicylohexylcarbodiimide CyN=C=NCy, which lead to an unprecedented iminium azetidinylidenemethyl complex, is rationalized to proceed through a [2+2] cycloaddition process and subsequent formation of the intermediate alkylidene **6** [7a]. Similarly, the η^1-cyclobutenyl species **7** has been proposed as an intermediate in the cycloaddition between the allenylidene complex [Os(=C=C=CPh$_2$)(η^5-C$_5$H$_5$)Cl(P^{i}Pr$_3$)] and MeO$_2$CC≡CCO$_2$Me [7b] (see also Scheme 42). The doubly α,β-unsaturated oxygen-containing cyclic carbene **8** has been isolated and characterized from the reaction of [Ru(=C=C=CPh$_2$)(η^5-C$_5$H$_5$)(CO)(P^{i}Pr$_3$)][BF$_4$] with ethyl diazoacetate (see Fig. 1) [7c].

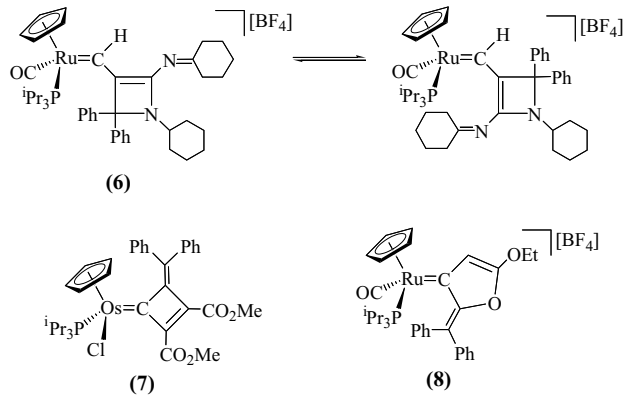


Fig. 1. Unsaturated heterocyclic monohapto alkylidenes.

2.2. Polyhapto alkylidenes

The presence of both an unsaturated chain as substituent of the alkylidene moiety and potential free co-ordination sites in the metal fragment, enable the formation of a series of complexes in which the unsaturated chain is attached to the metal center. The following types of these polyhapto coordination modes are known: η^1:η^3-allyl-carbenes (I), η^1:η^2-butadienyl-carbenes (II) and η^1:η^2-allenyl carbenes (III) (Fig. 2). A number of alkenyl-carbenes have been also proposed as intermediate species in catalytic processes (see Section 5.1; Schemes 51–53).

The first example of an allyl-carbene derivative [Ru{η^1:η^3-CPh-C(Ph)C(Ph)CH(Ph)}(η^5-C$_5$H$_5$)] (**9**) was synthesized (85% yield) by Green and co-workers [8] from the reaction of the cationic η^4-bonded tetraphenylcyclobutadiene complex [Ru(η^5-C$_5$H$_5$)(NCMe)(η^4-C$_4$Ph$_4$)][BF$_4$] with K[BH^{s}Bu$_3$] through a formal nucleophilic addition of H$^-$ and ring-opening of the η^4-cyclobutadiene ring (Scheme 4) [8]. The X-ray crystal structure determination shows an open η^1:η^3-butadienylidene chain to which the CpRu moiety is formally attached through a Ru=C carbene bond and a η^3-allyl system. From the structural X-ray crystallographic data three resonance structures can be proposed (Fig. 3). An analogous substituted allyl-carbene complex [Ru{η^1:η^3-CPh-C(Ph)C(Ph)C(CHO)(Ph)}(η^5-C$_5$H$_5$)] is formed starting from [Ru(η^5-C$_5$H$_5$)(CO)(η^4-C$_4$Ph$_4$)][BF$_4$] (Scheme 4). These allyl-carbenes are prone to react with PPh$_3$ and P(OMe)$_3$ at room temperature affording the η^1:η^2-butadienyl and η^1:η^2-acyl-butadienyl derivatives **10** and **11** (Scheme 4), respectively, resulting from

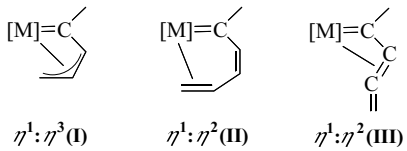
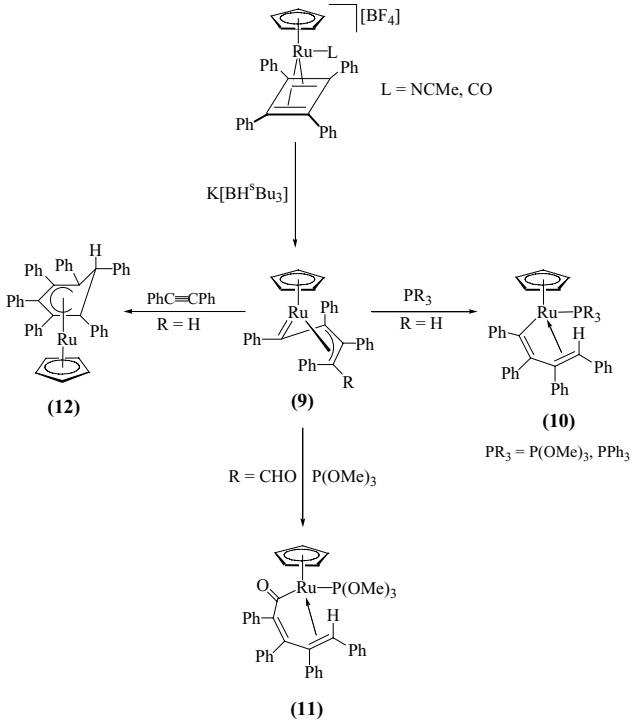


Fig. 2. Coordination modes of unsaturated alkylidenes.



Scheme 4.

the co-ordination of the $2e^-$ ligands L at the ruthenium center. Similarly, the aryldiazenide cationic complex $[Ru\{\eta^1{:}\eta^2\text{-}CPh{=}C(Ph){-}C(Ph){=}CH(Ph)\}(\eta^5\text{-}C_5H_5)(p\text{-}NO_2C_6H_4N_2)][BF_4]$ is formed from the reaction of the $\eta^1{:}\eta^3$-allyl-carbene with the diazonium derivative $[p\text{-}NO_2C_6H_4N_2][BF_4]$. This behavior is assessed in the reaction

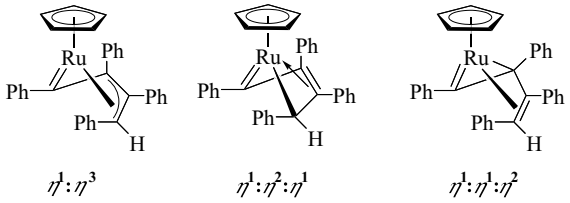
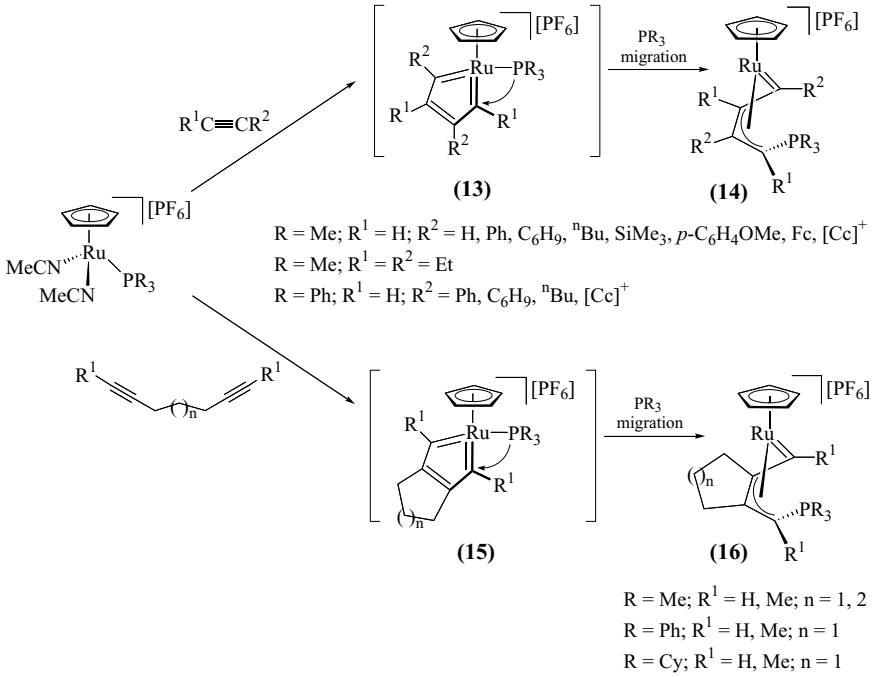


Fig. 3. Resonance structures of allyl-carbenes.

with diphenylacetylene which leads to the formation of the sandwich complex $[Ru(\eta^5\text{-}endo\text{-}C_6Ph_6H)(\eta^5\text{-}C_5H_5)]$ (**12**) via co-ordination of the alkyne to ruthenium in **9** and subsequent C–C coupling with the η^3-butadienyl group (Scheme 4). In contrast, the protonation of the allyl-carbene **9** leads to decomposition although the diene complex $[Ru\{\eta^4\text{-}(E,Z)\text{-}CH(Ph){=}C(Ph)C(Ph){=}CH(Ph)\}(\eta^5\text{-}C_5H_5)\{P(OMe)_3\}][BF_4]$ is formed after the electrophilic addition of proton in the presence of $P(OMe)_3$ [9].

Some years later, Kirchner and co-workers have developed an alternative synthetic route of $\eta^1{:}\eta^3$-allyl-carbenes **14** and **16** starting from the ready accessible labile complexes $[Ru(\eta^5\text{-}C_5H_5)(PR_3)(NCMe)_2][PF_6]$ which react with a wide range of alkynes, including terminal $HC{\equiv}CR^1$ and internal $R^1C{\equiv}CR^2$ alkynes and diynes $R^1C{\equiv}CCH_2(CH_2)_nCH_2C{\equiv}CR^1$ ($n = 1, 2$) (Scheme 5). The reactions generally proceed rapidly at room temperature and the allyl-carbenes are obtained in good yields [10]. Structural parameters obtained from X-ray diffraction studies in several of these complexes confirm both the alkylidene carbon double bond to the ruthenium atom and the presence of a η^3-allyl system. The four carbon atoms of



Scheme 5.

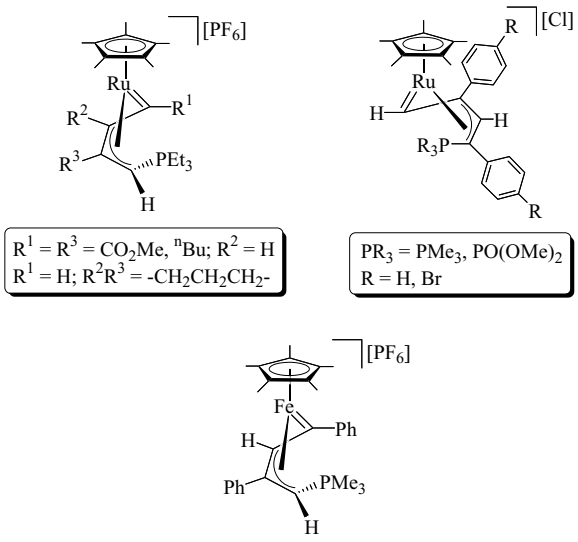
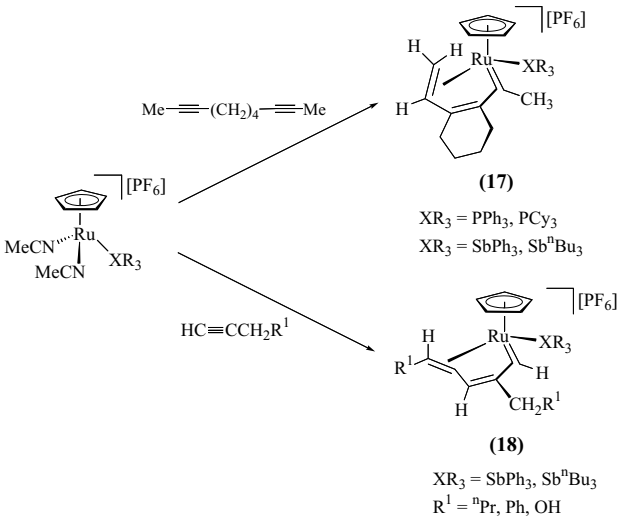


Fig. 4. Cp*-ruthenium complexes containing allyl-carbene groups.



Scheme 6.

the allyl-carbene chain are nearly in a plane. The formation of these carbene complexes most probably proceeds via ruthenacyclopentatriene (bis-carbene) intermediates **13** and **15** generated from the oxidative head-to-tail coupling of the alkynes (see below) which undergo a subsequent intramolecular migration of the phosphine to one of the electrophilic carbene carbon atoms. The remarkable electrophilicity of the α-carbon atom in these carbenes promotes the ready rearrangement. Analogous (η^5-C_5Me_5)Ru and (η^5-C_5Me_5)Fe allyl-carbenes have been also prepared (Fig. 4) [11,12].

Competitive processes leading to the formation of η^1:η^2-butadienyl-carbene complexes instead of the expected η^1:η^3-allyl-carbenes can be operative. These processes are the result of a preferred 1,2-hydrogen shift pathway versus ligand migration (A in Fig. 5) which are favored due to the presence of either: (i) a too bulky and/or nucleophilic poor co-ligand (SbR_3= $SbPh_3$, Sb^nBu_3; PR_3= PCy_3, PPh_3) or (ii) an alkyne with a α-alkyl substituent [10c,d,13]. The reactions of [Ru(η^5-C_5H_5)(XR_3)$(NCMe)_2$][PF_6] with 2,8-decadiyne and HC≡CCH_2R^1 (R^1 = ^{n}Pr, Ph, OH) illustrate the formation of η^1:η^2-butadienyl carbenes (**17** and **18**) (Scheme 6) [10c,13]. For HC≡CCH_2R^1 (R^1 = ^{n}Pr, Ph, OH) the butadienyl-carbene group in **18** rearranges to give η^3-allyl-acyl (**19**) and η^3-allyl-vinyl (**20**) complexes (Scheme 7) [13c]. It is interesting to note that a remarkable change in the reactivity has also been observed starting from the related complexes

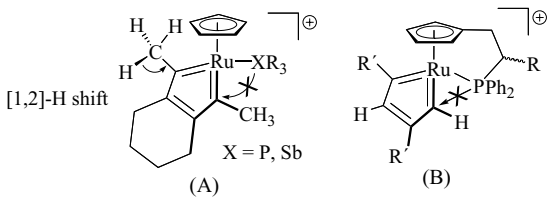
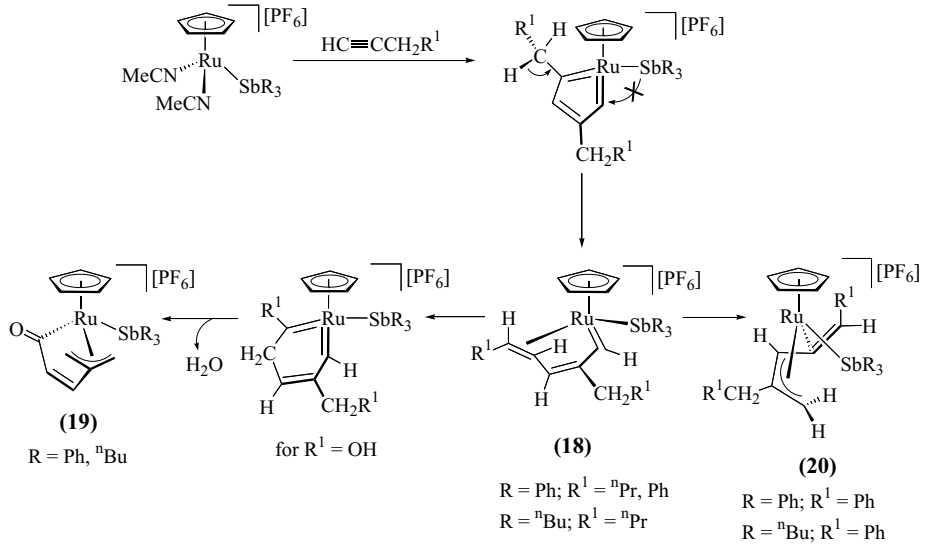


Fig. 5. Stability of bis-carbene groups vs [1,2]-H shift or phosphine migration.

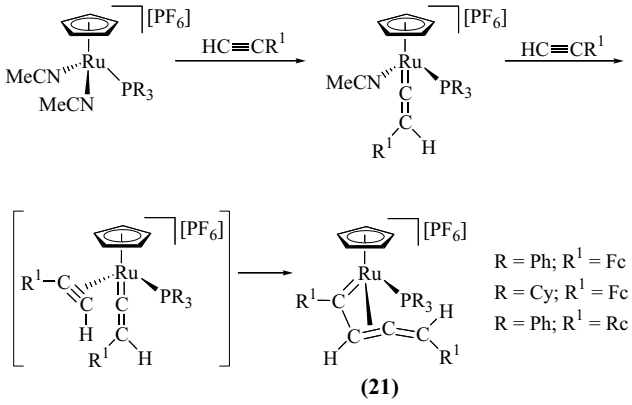
[Ru{η^5-$C_5H_4CH_2CH(R)$-κ^1-*P*-PPh_2}$(NCMe)_2$][PF_6], containing a phosphine ligand tethered onto the Cp ring. Thus, in contrast to the above mentioned phosphine migration, the metallacyclopentatriene intermediates **B** (Fig. 5) undergo the coordination of a third alkyne molecule resulting in an unusual C–C coupling process to give the cycloaddition products [Ru{η^5-$C_5H_4CH_2CH(R)PPh_2$-κ^1-*C*-CH-(η^4-$C_5R'_3H_2$)}][PF_6] [10d]. A series of theoretical studies rationalizing the mechanisms of the competitive processes have been also performed [10c,d,13c].

In contrast, the reaction of [Ru(η^5-C_5H_5)(PR_3)$(NCMe)_2$][PF_6] with the terminal alkynes ethynylferrocene (HC≡CFc) and ethynylruthenocene (HC≡CRc) proceeds in a completely different way affording η^1:η^2-allenyl-carbene complexes **21** (Scheme 8) [10b,c]. The proposed mechanism involves the intermediate formation of a vinylidene complex followed by the co-ordination of a second alkyne molecule to give an η^2-alkyne-vinylidene species [Ru{=C=(H)R^1}(η^5-C_5H_5)(η^2-HC≡CR^1)(PR_3)]$^+$. The subsequent alkyne insertion into the Ru=C bond gives the final product **21**. The observed π-conjugation of the allenyl-carbene unit with one of the Cp π systems in the ferrocenyl and ruthenocenyl moieties likely favors the C–C coupling through the efficient stabilization of the positive charge. When HC≡$CSiMe_3$ is used only the formation of vinylidene complexes [Ru{=C=C(H)$SiMe_3$}(η^5-C_5H_5)(NCMe)(PR_3)]$^+$ (R = Ph, Cy) is observed [10c].

In a similar way as shown by the reactivity of the parent allyl-carbene complexes **9**, the analogous allyl-carbenes **14** and **16** are acting as pseudo 16-electron species also reacting with nucleophiles (PPh_3) and electrophiles (H^+) to give η^1:η^2-butadienyl (**22**) and η^4-diene (**23**) complexes, respectively (Scheme 9). The first reaction involves a 1,4-hydrogen shift and the resulting diene from the protonation with CF_3COOH(D) is consistent with the presence a nucleophilic carbene carbon atom [10a].

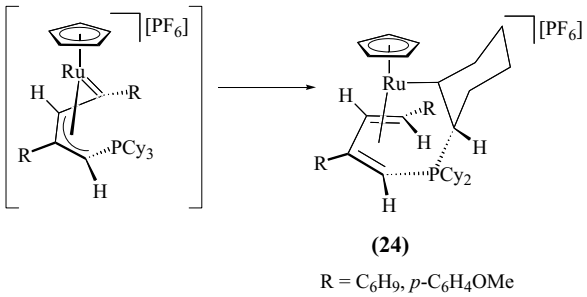


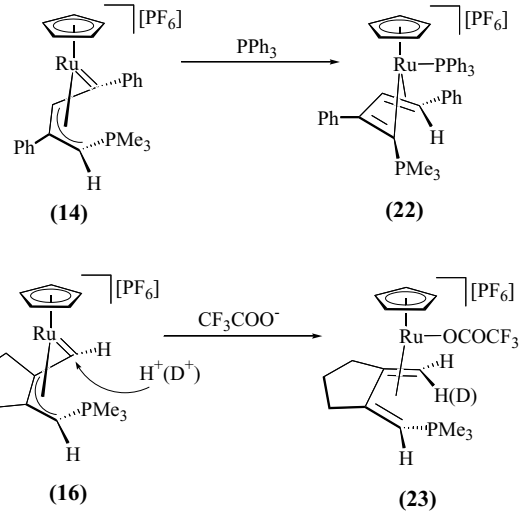
Scheme 7.



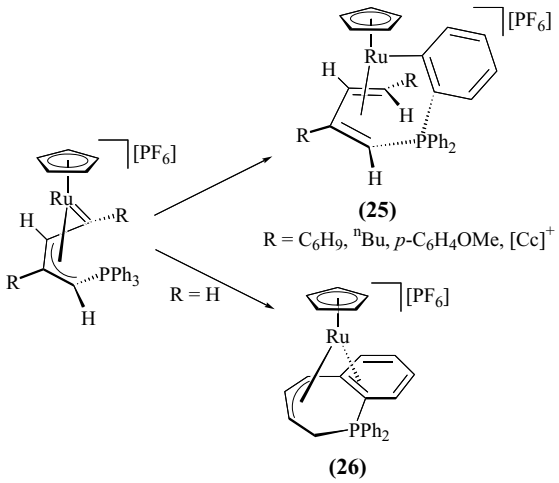
Scheme 8.

These allyl-carbenes are not only able to add nucleophiles to the metal center but are also capable to dehydrogenate aryl and alkyl groups, at room temperature, in the bulky tertiary phosphine ligands PCy_3 and PPh_3 through a C–H bond activation to give novel η^4-butadiene complexes **24** and **25**, respectively, or the unusual allyl complex **26** (Scheme 10) [11a].

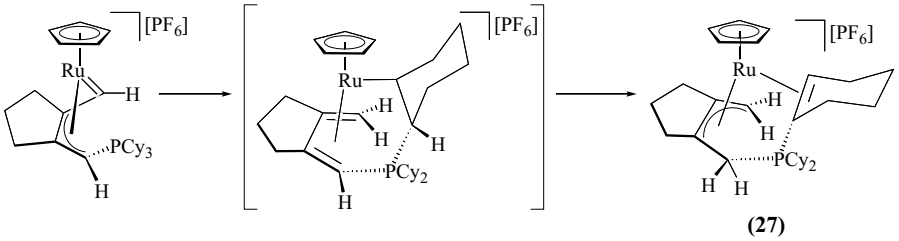




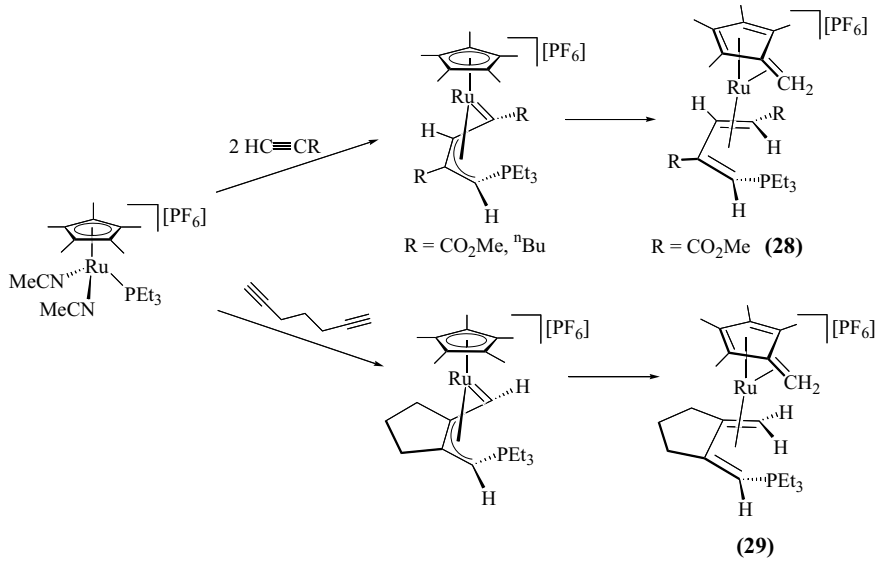
Scheme 9.



Scheme 10.



Scheme 11.



Scheme 12.

An analogous η^3:η^2-allyl-cyclohexenyl complex (**27**) is formed from the corresponding η^1:η^3-allyl-carbene after an eventual hydrogen β-elimination of the resulting cyclohexyl substituent of the phosphine and hydrogen transfer to the allyl chain of the carbene (Scheme 11) [11a].

An unusual methyl C-H bond activation of the Cp* ring to give tetramethylfulvene-type complexes **28** and **29** occurs in the corresponding Cp*-allyl-carbenes (Scheme 12) [11a].

2.3. α,β-Unsaturated bis-carbenes

The first complex [Ru($C_4Ph_2H_2$)Br(η^5-C_5H_5)] was discovered by Singleton et al. in 1986 [14a]. This metalacycle bis-carbene (metalacyclopentatriene) derivative was prepared by reaction of [Ru(η^5-C_5H_5)Br(COD)] with phenylacetylene via a head to head oxidative coupling of two molecules of the alkyne. Since then a variety of analogous half-sandwich ruthenium complexes have been prepared through a similar methodology including [Ru($C_4Ph_2H_2$)Cl(η^5-C_5Me_5)] (**30a**) [14b-d], [Ru{C_4(*p*-$C_6H_4Br)_2H_2$}Cl(η^5-C_5Me_5)] (**30b**) [11b], [Ru($C_4Fc_2H_2$)Br(η^5-C_5H_5)] (**30c**) [14e] and [Ru(bis-carbene)Cl(η^5-C_5Me_5)] (**30d**) [14f] (Fig. 6). In general, the formation of these derivatives proceeds in THF, benzene or CH_2Cl_2 at 0–20 °C in a few hours. A longer time (4 days) is used to form the bis-carbene **30d** (51% yield) from an 1,6-diyne bearing phenyl terminal groups. These bis-carbenes have been fully characterized including NMR spectroscopy and X-ray crystallography [14a,c–g]. The main structural features are: (i) the typical low field carbon resonance in the $^{13}C\{^1H\}$ NMR spectra of the carbenic carbon atoms (δ ca. 245–270 ppm); (ii) the relatively short Ru-C distances (ca. 1.94–1.99 Å) indicative of a partial double-bond character; and (iii) the almost identical C–C bond lengths of the

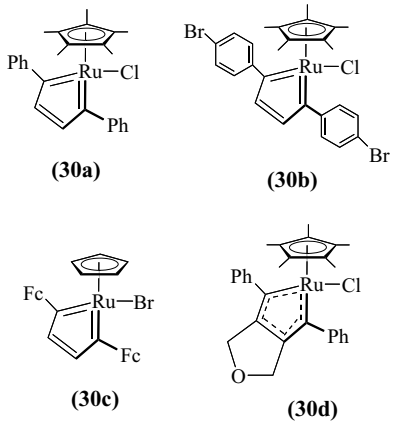


Fig. 6. Isolated bis-carbene ruthenium complexes.

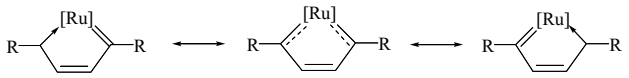
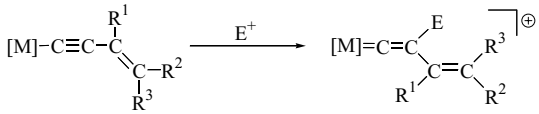


Fig. 7. Resonance forms of the bis-carbene group.



Scheme 14.

ruthenacycle. These facts indicate that the metalacyclopentatriene has a highly delocalized structure which can be described as the contribution of two resonance forms (Fig. 7). The electronic structure and the geometrical features of the model bis-carbene [Ru(η^5-C_5H_5)Cl(C_4H_4)] have been studied theoretically [14f,15].

A number of unsaturated bis-carbene complexes have been also proposed as intermediates either in stoichiometric or catalytic processes. As it was mentioned above (Schemes 5–7 and Fig. 5), Kirchner et al. have proposed a series of cationic ruthencyclopentatrienes as key intermediates in the formation of η^1:η^3-allyl and η^1:η^2-butadienyl carbenes. Although no intermediate has been isolated, the reactivity and NMR data are in accord with the transient formation of bis-carbene species formed by oxidative coupling of two molecules of the alkyne in the presence of [Ru(η^5-C_5H_5)(PR_3)($NCMe)_2$][PF_6].

As it will be discussed below (Section 5.2) some half-sandwich ruthenium(II) bis-carbene complexes are active catalytic species in the cyclotrimerization of alkynes and other C–C coupling reactions.

3. α, β-Unsaturated vinylidene complexes

3.1. Alkenyl–vinylidene complexes

3.1.1. Synthesis

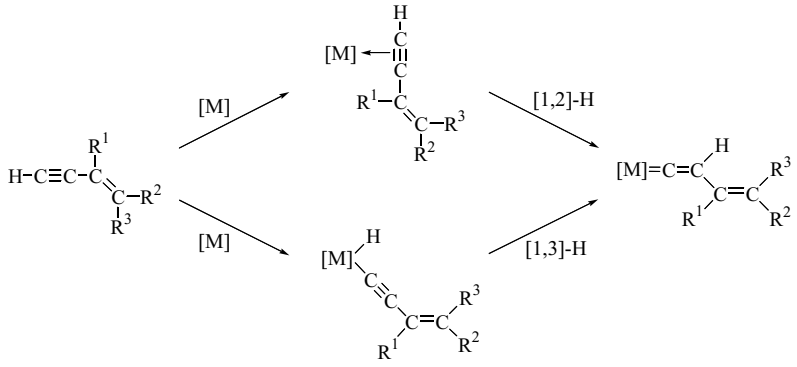
Alkenyl–vinylidene complexes of general formula [M]=C=C(R^1)C(R^2)=CR^3(R^4) are the most popular and simple class of α,β-unsaturated vinylidene derivatives [1,2]. Although several synthetic approaches have been described in the bibliography, the most general methods are the following:

(A) The direct activation of terminal 1,3-enynes HC≡CC(R^1)=CR^2(R^3) by a coordinatively unsaturated transition-metal complex via the generation of unstable η^2-1,3-enyne or hydride-enynyl intermediates which tautomerize into the thermodynamically more stable alkenyl–vinylidene isomers (Scheme 13).

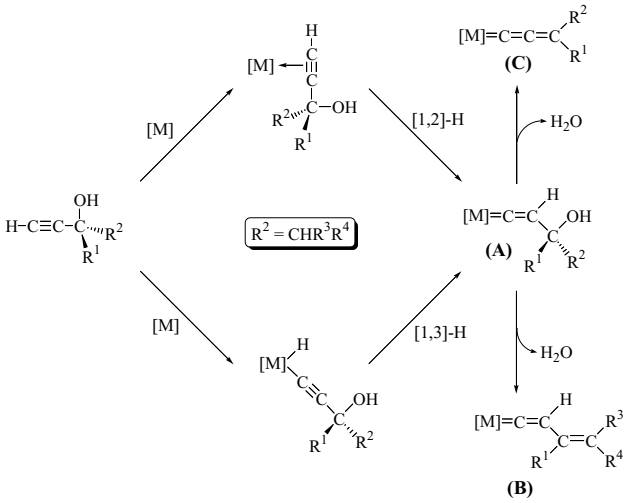
(B) The regioselective addition of electrophiles (i.e. H^+ or Me^+) to the nucleophilic C_β atom of neutral σ-enynyl derivatives [M]-C≡CC(R^1)=CR^2(R^3) (Scheme 14). We note that methods A and B are classical in the chemistry of vinylidenes [1,2].

(C) The activation of propargylic alcohols containing hydrogen atoms at the carbon atom adjacent to the one bearing the OH group by a coordinatively unsaturated complex. Although dehydration of the hydroxyvinylidene intermediates (A) can take two different reaction pathways, leading either to alkenyl–vinylidene (B) or allenylidene (C) derivatives (Scheme 15), in most cases it affords vinylidenes **B** regioselectively [1,2]. A rationalization of this general behaviour has been provided on the basis of theoretical calculations using the models [Ru{=C=C(H)CH=CH_2}(η^5-C_5H_5)($PH_3)_2$]$^+$ and [Ru{=C=C=C(H)CH_3}(η^5-C_5H_5)($PH_3)_2$]$^+$, which disclose that the alkenyl–vinylidene tautomer is ca. 2.1 kcal/mol more stable than the allenylidene [16]. Nevertheless, it should be noted that the fate of dehydration reaction strongly depends on the nature of the metal auxiliary as well as the propargylic alcohol substituents pointing out the limitations of this synthetic methodology [1,2]. As an example, electrophilic metallic fragments such as [RuCl(η^6-arene)(PR_3)]$^+$ usually lead to the formation of allenylidenes [2c].

Only half-sandwich alkenyl–vinylidene ruthenium(II) and osmium(II) complexes have been reported to date



Scheme 13.



Scheme 15.

[17], the activation of propargylic alcohols (Scheme 15) being probably the most used method for its preparation. This synthetic methodology, used for the first time by J.P. Selegue in 1991 [18a], has been successfully applied in the selective synthesis of the cationic species **31** and **32** starting from the corresponding chloride complex via initial chloride abstraction with NH_4PF_6, $NaPF_6$, $NaBPh_4$ or $AgBF_4$ (Scheme 16) [18]. Taking advantage of the tendency shown by $[OsCl(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]$ to release a triisopropylphosphine ligand, Esteruelas and co-workers have also reported that the treatment of this compound with 1-ethynyl-1-cyclohexanol and 2-methyl-3-butyn-2-ol, in pentane at room temperature, leads to the stable π-alkyne complexes $[Os\{\eta^2\text{-}HC{\equiv}CCR_2(OH)\}Cl(\eta^5\text{-}C_5H_5)(P^iPr_3)]$ (CR_2 = cyclohexanediyl, CMe_2), which selectively

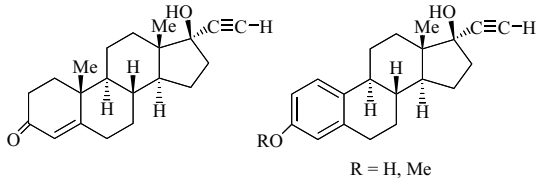
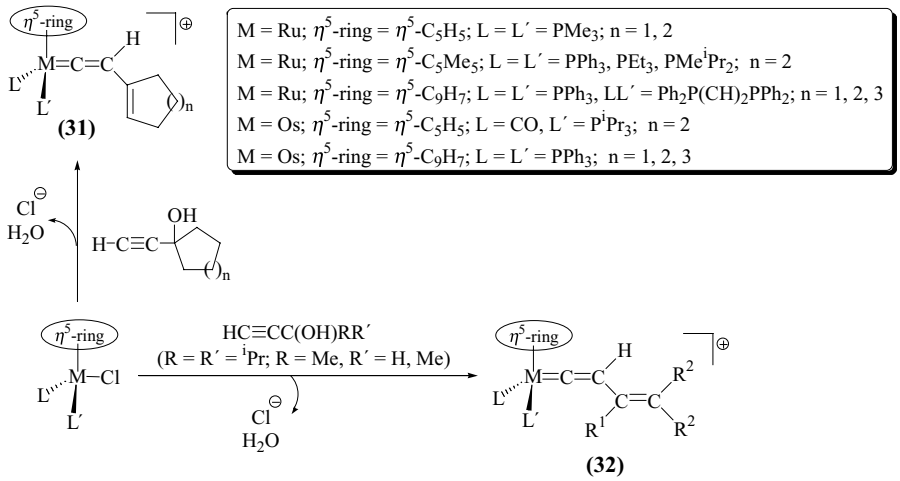


Fig. 8. Biologically active propargylic alcohols.

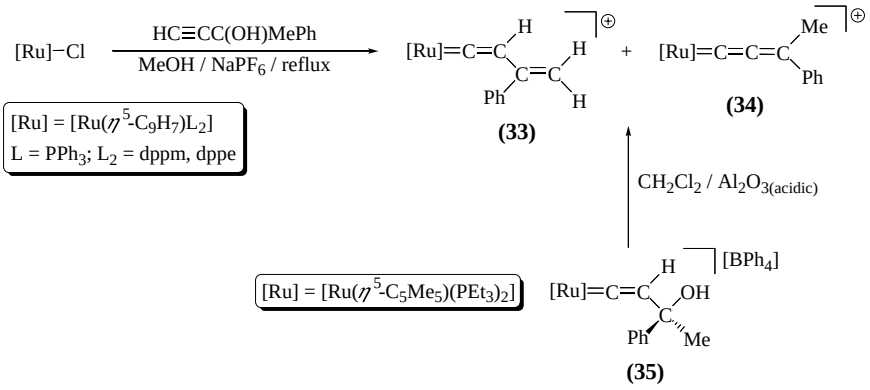
evolve to the corresponding neutral alkenyl–vinylidene derivatives $[Os\{=C=C(H)R\}Cl(\eta^5\text{-}C_5H_5)(P^iPr_3)]$ (R = 1-cyclohexenyl, $C(Me)=CH_2$) in toluene at 85 °C [19].

Mixtures of the alkenyl–vinylidene **33** and allenylidene **34** tautomers (ca. 1:1 ratio) have been obtained by reacting complexes $[RuCl(\eta^5\text{-}C_9H_7)L_2]$ (L = PPh_3, L_2 = dppe, dppm) with HC≡CC(OH)MePh in methanol and in the presence of $NaPF_6$ (Scheme 17) [20]. Similar results have been observed in the activation of the biologically active propargylic alcohols ethisterone, 17α-ethynylestradiol (R = H) and mestranol (R = Me) by $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (see Fig. 8) [16,21]. Puerta and co-workers have also described that the spontaneous dehydration of the 3-hydroxyvinylidene complex **35** in methanol generates cleanly the allenylidene species **34**. However, when a CH_2Cl_2 solution of **35** is passed through a column of acidic alumina a mixture of the allenylidene/alkenyl–vinylidene isomers (**34**/**33**) is obtained [18f].

The activation of terminal 1,3-enynes has been also applied for the preparation of half-sandwich alkenyl–vinylidene ruthenium and osmium derivatives. Thus, the neutral tris(pyrazolyl)borate-ruthenium(II) complexes **36** and **37** have been prepared by treatment of $[RuCl\{HB(pz)_3\}(DMF)(PPh_3)]$ (DMF = dimethylformamide) and $[RuCl\{HB(pz)_3\}(\kappa^2\text{-}P,O\text{-}Ph_2PCH_2CH_2OMe)]$ with 1-ethynyl-cyclohexene,



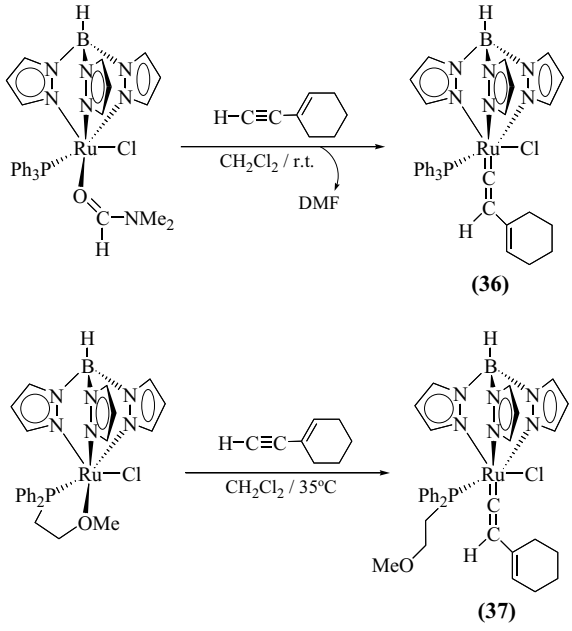
Scheme 16.



Scheme 17.

respectively (see Scheme 18) [22]. Complex [Os{=C=C(H)C(Me)=CH_2}Cl(η^5-C_5H_5)(P^iPr_3)] can be also prepared starting from [OsCl(η^5-C_5H_5)(P^iPr_3)$_2$] and the corresponding 1,3-enyne HC≡CC(Me)=CH_2 via P^iPr_3 dissociation [19].

Protonation of neutral σ-alkynyl derivatives [M]–C≡C–R is a well-known route to the corresponding cationic vinylidene complexes $[M]^+$=C=C(H)R [1,2]. In agreement, addition of HBF_4 to the σ-enynyl complex [Ru(C≡CC_6H_9)(η^5-C_5H_5)(PPh_3)$_2$] (C_6H_9 = 1-cyclohexenyl) affords the cationic alkenyl–vinylidene [Ru{=C=C(H)C_6H_9}(η^5-C_5H_5)(PPh_3)$_2$][BF_4] [23]. Similarly, protonation of [Ru{C≡CC(PPh_3)=CH_2}(η^5-C_5H_5)(PPh_3)$_2$][PF_6] generates the dicationic species [Ru{=C=C(H)C(PPh_3)=CH_2}(η^5-C_5H_5)(PPh_3)$_2$][PF_6]$_2$ [24]. In our laboratory, we have developed an efficient and straightforward procedure for the preparation of σ-enynyl and σ-polyenynyl complexes **39** starting from the readily available (η^5-indenyl)-ruthenium(II)-phosphonioalkynyl derivatives **38**, via Wittig-type reactions



Scheme 18.

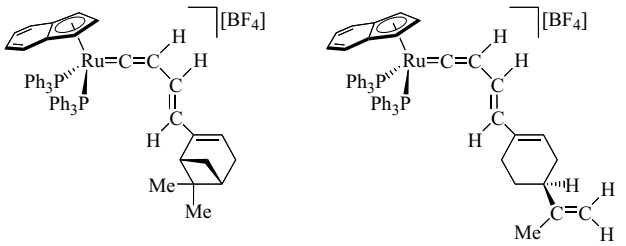


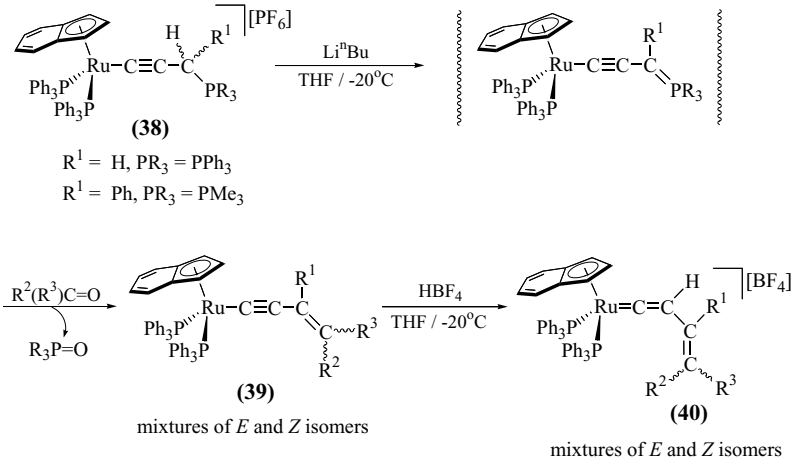
Fig. 9. Optically active alkenyl-vinylidene ruthenium(II) complexes.

with carbonyl compounds (Scheme 19) [25]. As expected, protonation of these polyunsaturated alkynyl derivatives (**39**) affords the corresponding alkenyl–vinylidene and polyalkenylvinylidene complexes **40** (Scheme 19) [25]. Optically active alkenyl–vinylidenes have been also obtained (as the thermodynamically more stable *E* isomers) using this methodology starting from the commercially available chiral aldehydes (1*R*)-(−)-myrtenal and (*S*)-(−)-perillaldehyde (see Fig. 9) [26].

The disubstituted alkenyl–vinylidene ruthenium(II) complexes **42** derived from the hormonal steroids ethisterone, 17α-ethynylestradiol and mestranol (Fig. 8) have been prepared by methylation of the corresponding σ-enynyl species **41** (see Scheme 20) [16].[1]

Lin and co-workers [27] have found that the cationic alkenyl–vinylidene derivatives **43** are easily formed, in dichloromethane at room temperature, by reaction of the corresponding neutral σ-alkynyl complexes [Ru(C≡CPh)(η^5-C_5H_5)LL′] (L = PPh_3, L′ = CN^tBu; LL′ = dppe) with Cl(Ph)C=$C(CN)_2$ (α-chlorobenzylidenemalononitrile), via electrophilic addition of the vinylic unit to the C_β atom of the phenylacetylide ligand. Similarly, treatment of complex [Ru(C≡CPh)(η^5-C_5H_5){P($OMe)_3$}(PPh_3)] with Cl(Ph)C=$C(CN)_2$ results in the formation of the neutral

[1] We have also reported that the treatment of [Ru(C≡CC_6H_9)(η^5-C_9H_7)(PPh_3)$_2$] (C_6H_9 = 1-cyclohexenyl) with $MeOSO_2CF_3$ in diethyl ether leads to the precipitation of the cationic vinylidene [Ru{=C=C(Me)C_6H_9}(η^5-C_9H_7)(PPh_3)$_2$][CF_3SO_3] which was characterized by X-ray diffraction. See ref. [18b,18e].



Scheme 19.

alkenyl–vinylidene **44** in which an Arbuzov-like dealkylation of the phosphite ligand has also occurred (Scheme 21) [27].

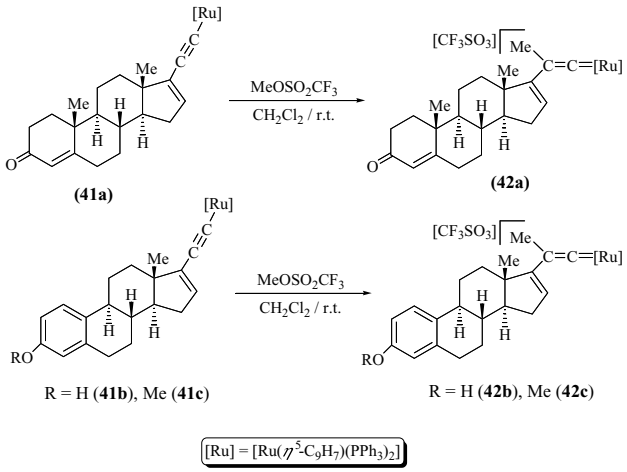
The synthesis and X-ray crystal structure analysis of the alkenyl–vinylidene complex **46** has been described by Selegue (Scheme 22) [28]. This compound was obtained by reaction of the neutral keto-alkynyl complex $[Ru\{C{\equiv}CC(=O)CHMe_2\}(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ with two equivalents of trifluoroacetic anhydride, via acylation of the intermediate α-enynyl trifluoroacetate ester **45** (characterized by X-ray diffraction) by a trifluoroacetyl group.

Puerta and co-workers [29] have reported that the treatment of the cationic vinylidene complex $[Ru\{=C=C(H)CO_2Me\}\{HB(pz)_3\}(PEt_3)_2][BPh_4]$ with $HC{\equiv}CCO_2Me$ generates the alkenyl–vinylidene derivative **48** stereoselectively (*E* isomer) (Scheme 23) [29]. This C–C coupling reaction has been interpreted in terms of a [2+2] cycloaddition of the terminal alkyne to the $C_\alpha{=}C_\beta$ of the vinylidene ligand to yield a cyclobutenylidene intermediate (**47**), followed by a concerted ring-opening.

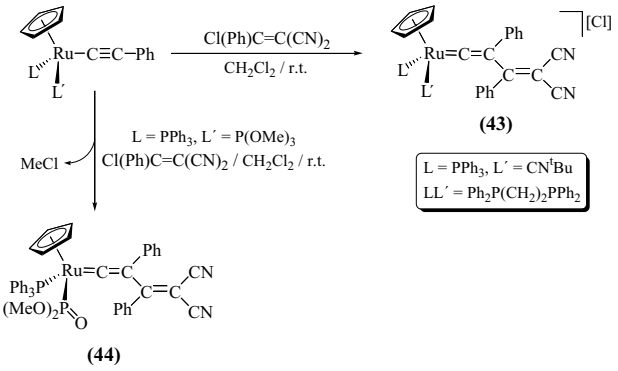
The zwitterionic alkenyl–vinylidene complex **50** is also known [30]. It has been prepared by addition of tetracyanoquinodimethane (TCNQ) to the neutral cyclopropenyl complex **49** (Scheme 24).

3.1.2. Reactivity

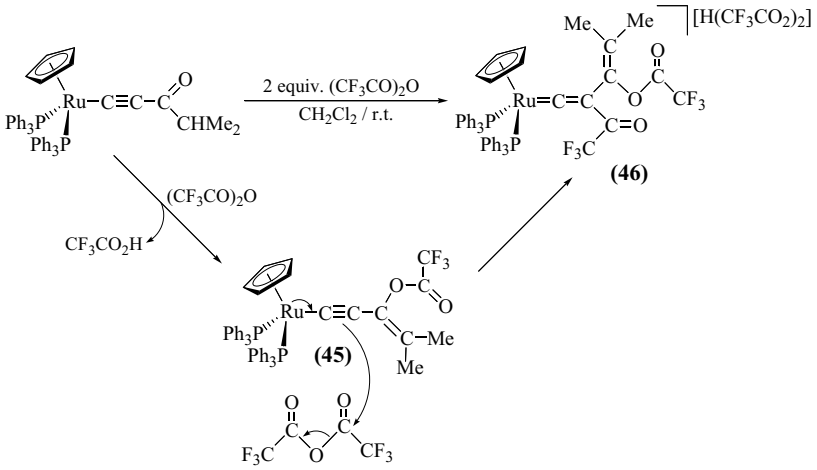
Deprotonation of the acidic of vinylidene proton in cationic transition-metal vinylidene complexes $[M]^+{=}C{=}C(H)R$ is a classical synthetic route to neutral σ-alkynyl derivatives [M]–C≡C–R [1,2]. In agreement, treatment of the monosubstituted alkenyl–vinylidene ruthenium(II) and osmium(II) complexes of the type **31** and **32** (see Scheme 16) with NaOMe, KO^tBu or Al_2O_3 leads to the high yield formation of the corresponding σ-enynyl species $[M(C{\equiv}CR)(\eta^5\text{-ring})LL']$ (R = 1-cycloalkenyl) and $[M\{C{\equiv}CC(R^1){=}CR^2R^2\}(\eta^5\text{-ring})LL']$, respectively



Scheme 20.



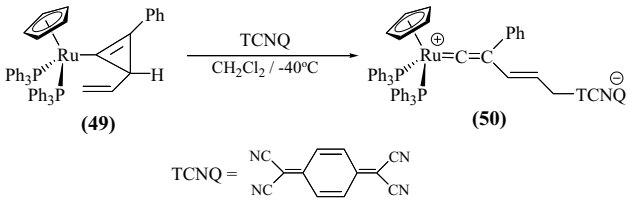
Scheme 21.



Scheme 22.

[18ac,e,20]. We note that in most cases these deprotonation reactions were found to be reversible [18b,e,20].

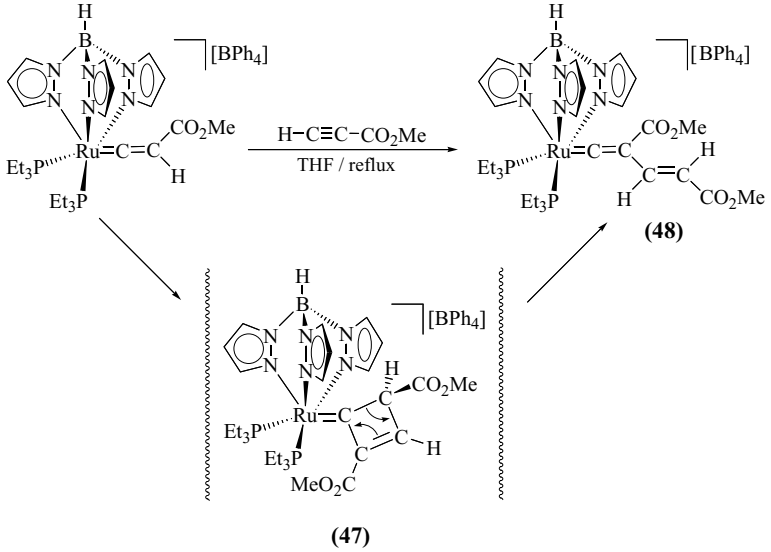
One of the most significant reactions of transition-metal vinylidene complexes [M]=C=CR^{1}R^2 is the nucleophilic attack of alcohols at the electrophilic C_α atom to afford Fischer-type alkoxy-carbene derivatives [M]=C(OR^3)–C(H)R^{1}R^2 [1,2]. It is now well-established that the ability of the vinylidene unit to undergo these nucleophilic attacks is dependent on the electronic and steric nature of the ancillary ligands on the metal atom, being clearly favoured when sterically undemanding and/or π-acceptor ligands are present [1,2]. This is clearly exemplified by the electrophilic complexes [RuCl$_2$(η^6-arene)(PR$_3$)] which usually react with terminal alkynes in alcoholic media leading to the formation alkoxy-carbenes [1,2c]. In accordance with this, Nelson and co-workers have found that complex **51** reacts with 1-ethynyl-1-cyclohexanol, in a mixture CH_2Cl_2/MeOH and in the presence of $NaPF_6$, to afford



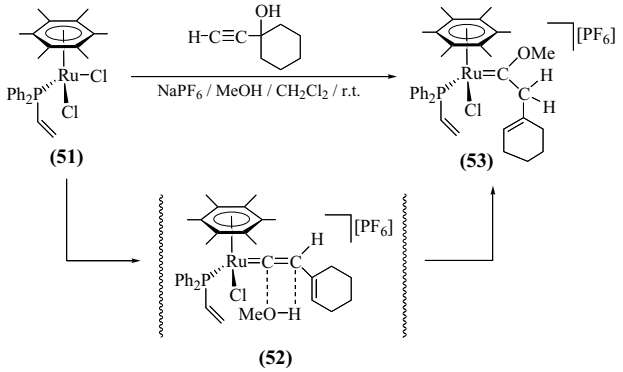
Scheme 24.

the methoxy-carbene complex **53**, via nucleophilic addition of methanol on the corresponding alkenyl–vinylidene intermediate **52** (Scheme 25) [31].

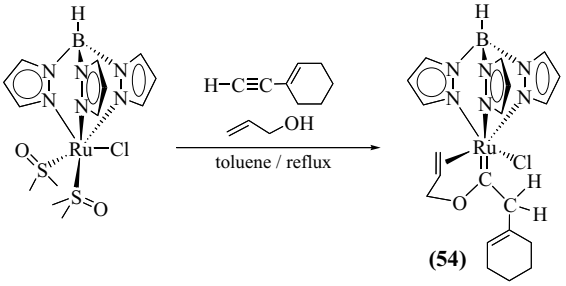
Similarly, the neutral allyloxy-carbene complex **54** has been obtained by treatment of [RuCl{HB(pz)$_3$}(DMSO)$_2$] (DMSO = dimethyl sulfoxide) with an excess of 1-ethynylcyclohexene and allyl alcohol in refluxing toluene (Scheme 26) [32].



Scheme 23.

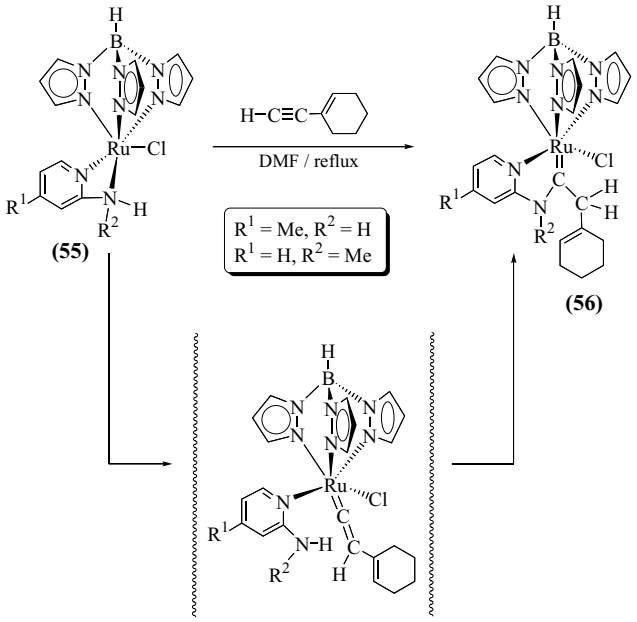


Scheme 25.



Scheme 26.

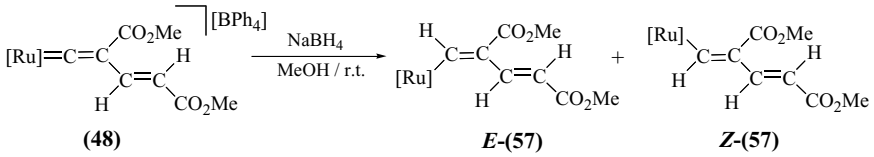
By analogy with the above-mentioned reactions, the addition of primary or secondary amines to a vinylidene complex generates the corresponding amino-carbene derivative [M]=C{N(R^3)R^4}–C(H)R^1R^2 [1,2]. In this context, Kirchner and co-workers have recently described the activation of 1-ethynyl-cyclohexene by the tris(pyrazolyl)borate-ruthenium(II) complexes **55** containing the hemilabile ligands 2-(methylamino)pyridine and 2-amino-4-picoline [33]. As expected, intramolecular addition of the N–H bond of the amine groups to the C_α=C_β double bond of the corresponding alkenyl–vinylidene intermediates takes place, yielding cyclic amino-carbenes **56** (Scheme 27).



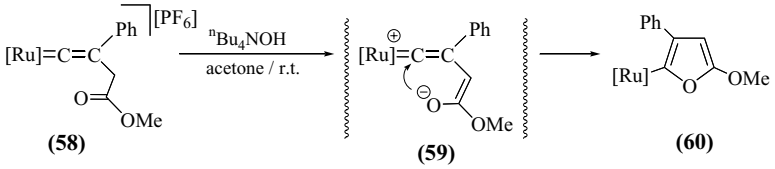
Scheme 27.

The electrophilic character of the C_α atom of cationic vinylidene complexes allows also the addition of anionic nucleophiles at this carbon yielding neutral alkenyl species [M]-C(Nu)=CR_2 [1,2]. In agreement with this, Puerta and co-workers [29] have found that complex **48** regioselectively reacts with $NaBH_4$ to afford the neutral butadienyl derivative **57**, which was isolated as a mixture of *E* and *Z* isomers (Scheme 28).

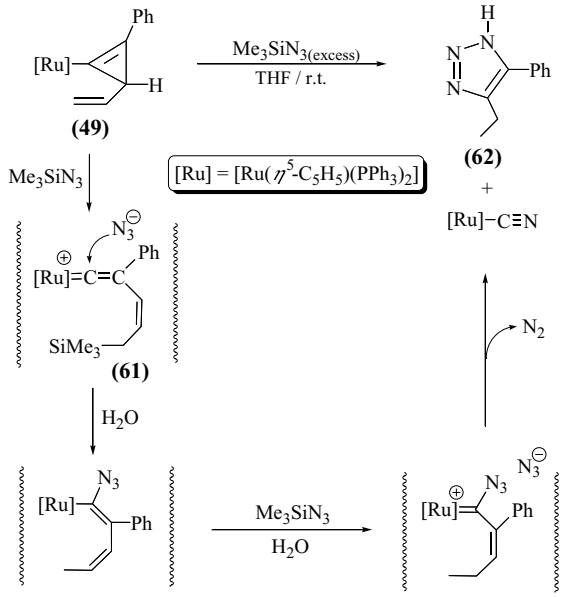
Deprotonation of the disubstituted cationic vinylidene derivative **58**, with $^nBu_4NOH$ in acetone at r.t., results in the cyclization of the organic chain, yielding a neutral furan complex (**60**) via intramolecular nucleophilic addition



Scheme 28.



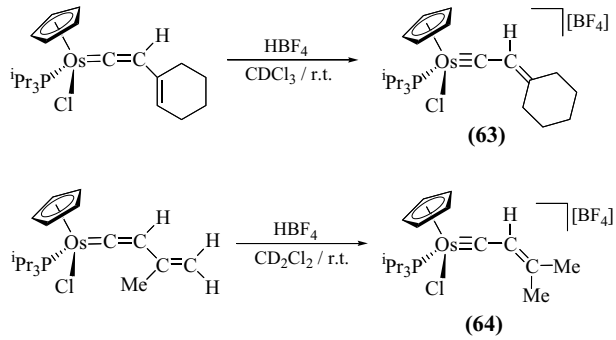
Scheme 29.



Scheme 30.

of the alcoholate anion at the C_α atom in the intermediate zwitterionic alkenyl–vinylidene **59** (Scheme 29) [30,34].

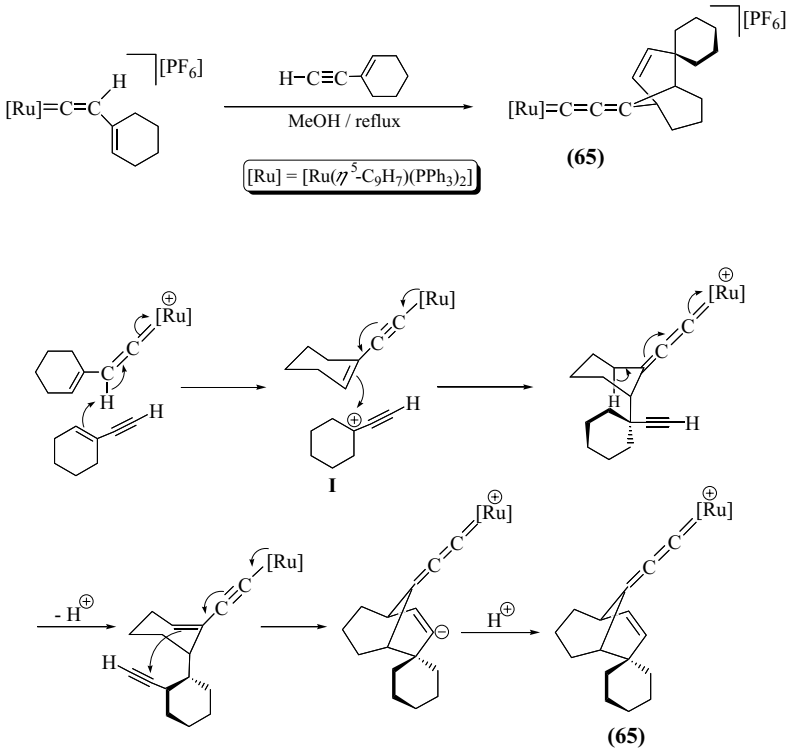
The nucleophilic addition of the azide anion at the C_α on the intermediate alkenyl–vinylidene complex **61** has been also proposed by Lin and co-workers [35] as a key step in the formation of the cyanide complex $[Ru(C{\equiv}N)(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ and 4-ethyl-5-phenyl-1*H*-[1,2,3]triazole (**62**) from the reaction of the neutral alkenyl-cyclopropenyl ruthenium(II) derivative **49** with Me_3SiN_3 (Scheme 30).



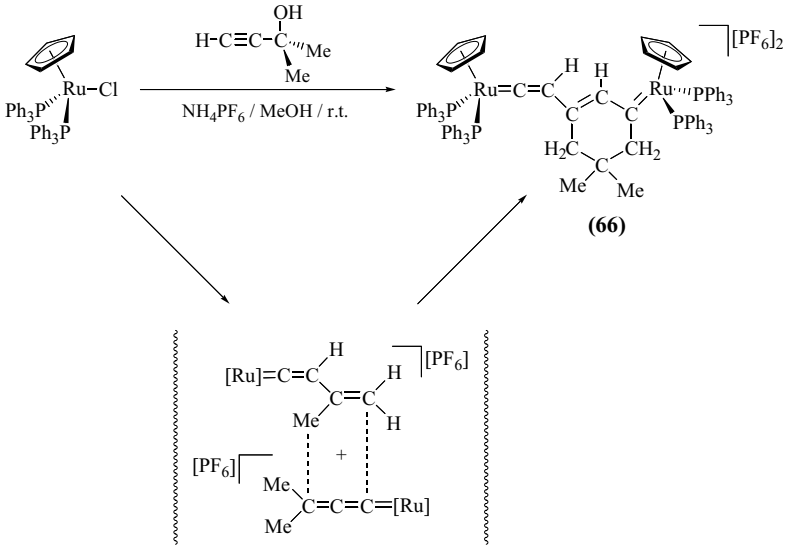
Scheme 31.

Electrophilic additions at C_β of vinylidene complexes $[M{=}C{=}CR_2]$ to afford carbyne species $[M{\equiv}CC(E)R_2]$ are well-documented [1,2]. In this context, Esteruelas and co-workers [19] have found that the protonation of the neutral alkenyl–vinylidene complexes $[Os\{{=}C{=}C(H)R\}Cl(\eta^5\text{-}C_5H_5)(P^iPr_3)]$ (R = 1-cyclohexenyl, $C(Me){=}CH_2$) yields the cationic alkenyl-carbyne derivatives **63** and **64**, respectively, as the result of the selective proton addition at C_δ of the unsaturated chain (Scheme 31).

The involvement of alkenyl–vinylidene complexes in C–C coupling reactions has been also reported. Thus, we have reported the synthesis of the unprecedented



Scheme 32.



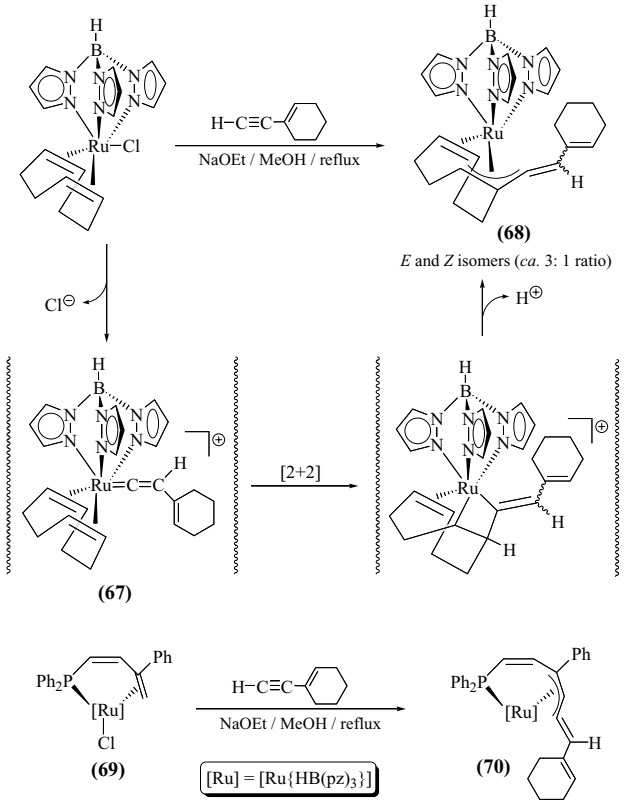
Scheme 33.

indenyl-ruthenium(II) allenylidene complex **65**, which contains the spiro(bicyclo[3.3.1]non-2-en-9-ylidene-4-cyclohexane) moiety $C_{13}H_{20}$, as the result of the coupling between the alkenyl–vinylidene derivative [Ru{=C=C(H)C_6H_9}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (C_6H_9 = 1-cyclohexenyl) and 1-ethynyl-cyclohexene (Scheme 32) [18b,36]. The first step in the formation of this complex involves the transfer of the acidic vinylidene proton from [Ru{=C=C(H)C_6H_9}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] to the C=C double bond of the 1,3-enyne which generates the neutral σ-enynyl derivative [Ru(C≡CC_6H_9)(η^5-C_9H_7)(PPh_3)$_2$] and the transient carbocation species I.

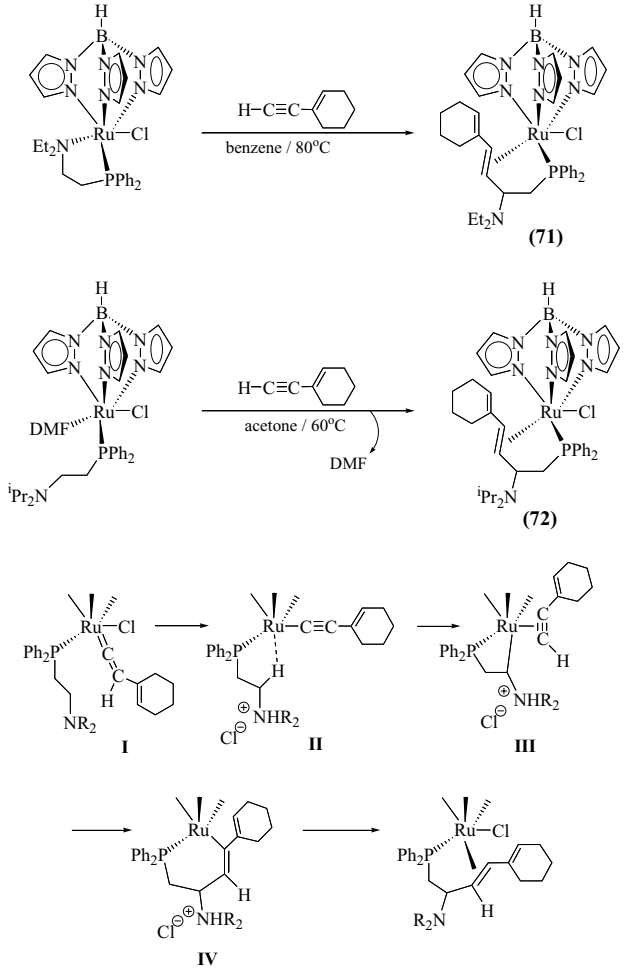
The reaction of [RuCl(η^5-C_5H_5)(PPh_3)$_2$] with 2-methyl-3-butyn-2-ol, in methanol and in the presence of NH_4PF_6, has been reported to yield the binuclear alkenyl–vinylidene-alkylidene complex **66** (Scheme 33) [37]. The suggested reaction pathway for the formation of this compound involves the coupling of the mononuclear alkenyl–vinylidene derivative [Ru{=C=C(H)C(Me)=CH_2}(η^5-C_5H_5)(PPh_3)$_2$][PF_6] and its allenylidene tautomer [Ru(=C=C=CMe_2)(η^5-C_5H_5)(PPh_3)$_2$][PF_6], both generated in situ by the spontaneous dehydration of an intermediate hydroxyvinylidene complex. The related compounds [{Ru{HB(pz)$_3$}(dippe)}$_2$(μ-$C_{10}H_{12}$)][PF_6]$_2$ (dippe = ^{i}Pr$_2$PCH$_2$CH$_2$P^{i}Pr$_2$) and [{Os(η^5-C_5H_5)(PPh_3)$_2$}$_2$(μ-$C_{10}H_{12}$)][PF_6]$_2$ have been also prepared in a similar way [38].

Treatment of [RuCl{HB(pz)$_3$}(COD)] (COD = 1,5-cyclooctadiene) with 1-ethynyl-cyclohexene, in refluxing MeOH and in the presence of NaOEt, has been reported to generate the unusual η^3-butadienyl-ruthenium(II) complex **68** via a formal [2+2] cycloaddition between one of the C=C double bonds of the COD ligand and the Ru=C$_\alpha$ unit in the cationic alkenyl–vinylidene intermediate **67** (Scheme 34) [39]. We note that this coupling process is not restricted to the COD ligand. Thus, through a similar [2+2] cycloaddition, complex **69** was found to react with 1-ethynyl-cyclohexene to give the corresponding η^3-butadienyl species **70** (Scheme 34) [39].

Kirchner and co-workers have also reported that tris(pyrazolyl)borate ruthenium(II) complexes containing hemilabile phosphinoamine ligands react with 1-ethynyl-cyclohexene to yield the corresponding coupling products **71**–**72** (Scheme 35) [40]. This C–C coupling process in-

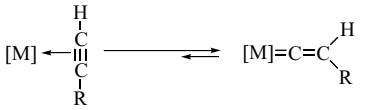


Scheme 34.



Scheme 35.

volves the initial formation of neutral alkenyl–vinylidene intermediates [Ru{=C=C(H)C_6H_9}Cl{HB(pz)$_3$}(κ^1-*P*-$Ph_2PCH_2CH_2NR_2$)] I, which undergo amine-promoted elimination of HCl yielding the σ-enynyl complex II. The agostic interaction in II leads to hydrogen migration by means of a σ-bond metathesis pathway to give the four-membered phospharuthenacycle III. Subsequent regioselective migratory insertion of the π-coordinated 1,3-enyne into the Ru-C bond of the phosphametallacyclobutane ring affords the alkenyl complex IV, which on protonation, yields the final product.



Scheme 36.

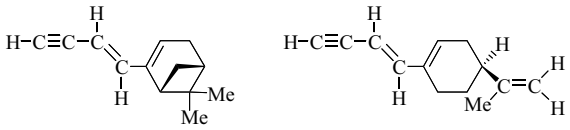
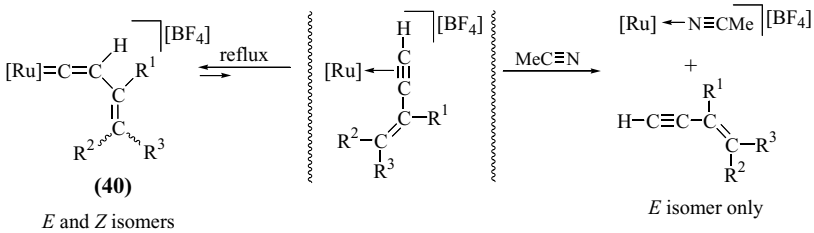


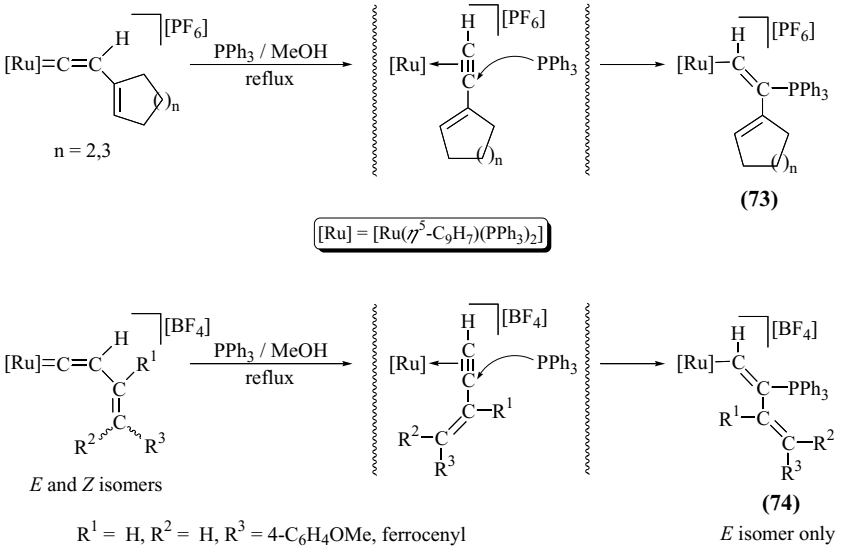
Fig. 10. Optically active 1,3-enynes.

Although the conversion of η^2-alkyne complexes into its η^1-vinylidene tautomers is a thermodynamically favoured process [1,2], the reverse transformation (Scheme 36) can in some cases be accomplished. For example, the presence of a coordinating solvent gives rise to the decoordination of the alkyne through an exchange process [25c,41].

Tautomerizations of monosubstituted alkenyl–vinylidene complexes into the corresponding η^2-1,3-enyne species have been also reported. Thus, in our laboratory we have found that the (η^5-indenyl)-ruthenium(II) derivatives **40** are able to undergo demetalation reactions by heating in acetonitrile, affording stereoselectively (*E* isomer) the corresponding terminal 1,3-enynes HC≡CC(R^1)=CR^2R^3 and the nitrile complex [Ru(NCMe)(η^5-C_9H_7)(PPh_3)$_2$][BF_4] (Scheme 37) [25c]. As commented previously, complexes **40** can be easily generated through Wittig-type reactions (see Scheme 19). The overall process depicted in Schemes 19 and 37 represents an appealing approach for the synthesis of terminal (*E*)-1,3-enynes from carbonyl compounds and propargylic alcohols. The practical utility of this synthetic route has been exemplified in the stereoselective preparation of optically active enynes derived from the chiral aldehydes (1*R*)-(−)-myrtenal and (*S*)-(−)-perillaldehyde (Fig. 10) [26]. Kirchner and co-workers have also described that the treatment of the neutral tris(pyrazolyl)borate derivative [Ru{=C=C(H)C_6H_9}Cl{HB(pz)$_3$}(PPh_3)] (C_6H_9 = 1-cyclohexenyl) (**36**) with a large variety of ligands L, in



Scheme 37.



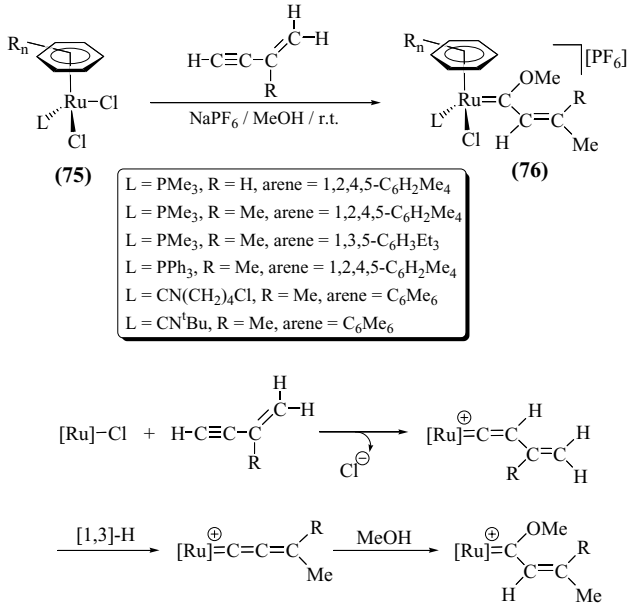
Scheme 38.

benzene at r.t., results in the quantitative formation of complexes [RuCl{HB(pz)$_3$}(PPh$_3$)L] (L = PMe$_3$, PPh$_3$, CO, py, MeCN) and free 1-ethynyl-cyclohexene HC≡CC$_6$H$_9$, via initial tautomerization of the η^1-alkenyl–vinylidene group to the η^2-coordinated 1,3-enyne and subsequent exchange with L [22a].

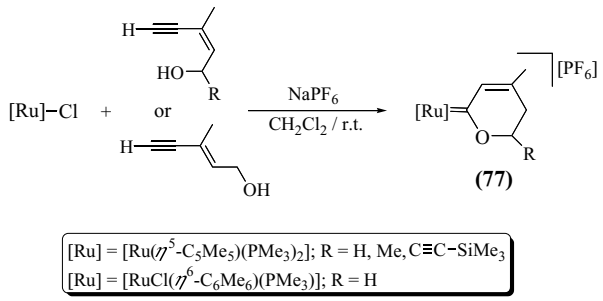
The formation of transient η^2-1,3-enyne species from alkenyl–vinylidenes [Ru{=C=C(H)C(R^1)=CR^{2}R^3}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]$^+$ has been clearly confirmed in the reaction of these complexes with triphenylphosphine in refluxing methanol which yields the alkenyl-phosphonio derivatives **73**–**74**, via nucleophilic addition of PPh$_3$ to the π-coordinated enyne (Scheme 38) [18e,41]. Theoretical calculations seem to indicate that the less electron density at the metal center the more tendency of η^1-vinylidene ligands to rearrange to η^2-alkyne ligands [22a,41]. In agreement with this, the more electrophilic ruthenium(II) complexes [RuX(η^5-1,2,3-C$_9$H$_4$R$_3$)(CO)(PR$_3$)$_2$] (R = Me, PR$_3$ = PPh$_3$, X = Br; R = H, PR$_3$ = P^{i}Pr$_3$, X = I) react with 1-ethynyl-1-cyclooctanol, in dichloromethane at r.t. and in the presence of AgBF$_4$, to afford equilibrium mixtures of the corresponding alkenyl–vinylidene and π-bonded enyne complexes [41]. The addition of PPh$_3$ to these reaction mixtures favours the displacement of the equilibrium leading to the selective formation of the corresponding alkenyl-phosphonio derivatives [Ru{C(H)=C(PPh$_3$)R}(η^5-1,2,3-C$_9$H$_4$R$_3$)(CO)(PR$_3$)$_2$][BF$_4$] (R = 1-cyclooctenyl) [41].

Formal exchange of the alkenyl–vinylidene moiety in complex [Ru{=C=C(H)C$_6$H$_9$}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (C$_6$H$_9$ = 1-cyclohexenyl) by an allenylidene group has been also observed when it was treated with an excess of 1,1-diphenyl-2-propyn-1-ol or 9-ethynyl-9-fluorenol in refluxing methanol, which generates the allenylidene derivatives [Ru{=C=C=CR$_2$}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (R = Ph, R$_2$ = 2,2′-biphenyldiyl) and free 1-ethynyl-cyclohexene [36].

The isomerization of monosubstituted alkenyl–vinylidene complexes [M]=C=C(H)C(R^1)=CR^{2}R^3 into their allenylidene tautomers [M]=C=C=C(R^1)C(H)R^{2}R^3, via a formal 1,3-hydrogen shift, has also been in some cases observed. As a clear example, M.C. Puerta and co-workers have recently reported that the alkenyl–vinylidene derivative [Ru{=C=C(H)C(Ph)=CH$_2$}(η^5-C$_5$Me$_5$)(PEt$_3$)$_2$][BPh$_4$] spontaneously isomerizes in solution, at r.t., into the thermodynamically more stable allenylidene [Ru{=C=C=C(Ph)Me}(η^5-C$_5$Me$_5$)(PEt$_3$)$_2$][BPh$_4$] [18f]. A related iso-



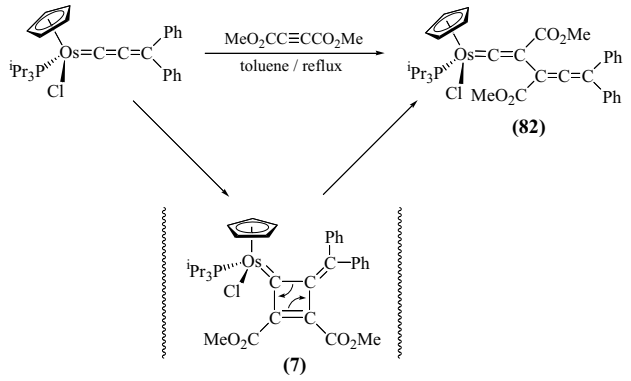
Scheme 39.



Scheme 40.

merization has been also proposed by Dixneuf in the activation of 1,3-enynes HC≡CC(R)=CH$_2$ (R = H, Me) by (η^6-arene)-ruthenium(II) complexes **75** which leads to the formation of Fischer-type alkenyl-carbene species **76** via nucleophilic addition of methanol at the electrophilic C$_\alpha$ atom of the corresponding allenylidene intermediates (Scheme 39) [42]. The intramolecular version of this reaction, i.e. the activation of terminal enynols HC≡CC(Me)=C(H)CH(R)OH to afford 2-oxacyclohex-5-en-1-ylidene ruthenium complexes **77**, has been also reported (Scheme 40) [43].

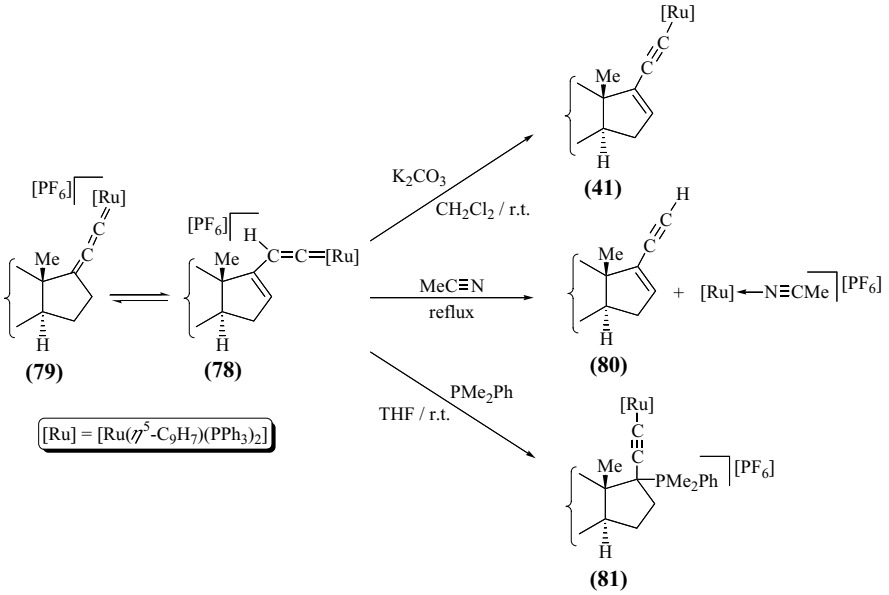
As commented previously, we have recently reported that the activation of the biologycally active propargylic alcohols ethisterone, 17α-ethynylestradiol and mestranol by the indenyl-ruthenium(II) complex [RuCl(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] affords mixtures containing the corresponding alkenyl–vinylidene **78** and allenylidene **79** isomers (Scheme 41) [16]. Moreover, we have also shown that in solution both tautomers are in equilibrium which can be selectively displaced by means of the typical reactivity of each of these species [16]. Thus (see Scheme 41), (i) σ-enynyl complexes **41** are selectively obtained via deprotonation of the alkenyl–vinylidene tautomers by treatment of the equilibrium mixtures with a base; (ii) terminal 1,3-enynes **80** are formed, through a η^1-vinylidene-η^2-alkyne tautomerization, after heating under reflux the equilibrium mixtures in acetonitrile; (iii) phosphonio-alkynyl complexes **81** are selectively generated via nucleophilic addition of PMe$_2$Ph to the electrophilic C$_\gamma$ atom of the cumulenic chain in the allenylidene tautomers [1,2].



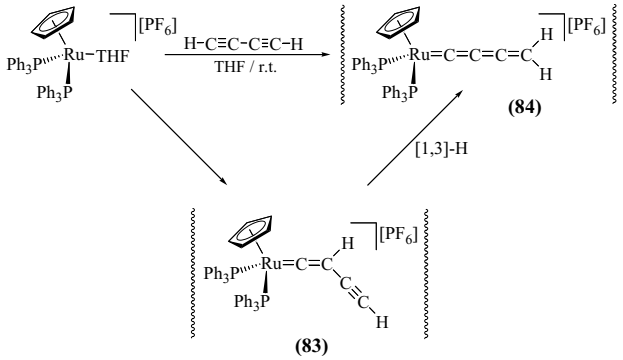
Scheme 42.

3.2. Other α,β-unsaturated vinylidene complexes

The allenyl-vinylidene osmium(II) complex **82** has been synthesized by treatment of the neutral allenylidene derivative [Os{=C=C=CPh$_2$}Cl(η^5-C$_5$H$_5$)(P^{i}Pr$_3$)] with dimethyl acetylenedicarboxylate. The formal insertion of the alkyne into the C$_\alpha$=C$_\beta$ double bond of the allenylidene chain has been rationalized as a stepwise cycloaddition to form an η^1-cyclobutenyl intermediate **7**, which readily undergoes a ring-opening process to form the allenyl-vinylidene product (Scheme 42) [7b].



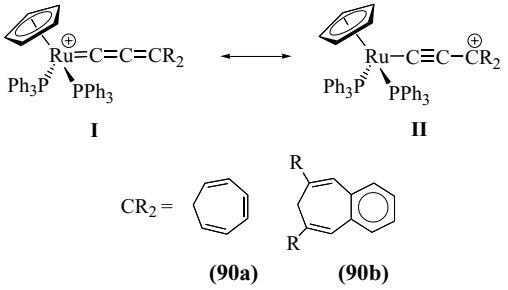
Scheme 41.



Scheme 43.

Although no stable half-sandwich alkynyl-vinylidene complexes [M]=C=C(R^1)C≡CR^2 of Group 8 metals are known [44], the occurrence of these species has been in some cases suggested. Thus, M.I. Bruce and co-workers have found that treatment of [Ru(η^5-C_5H_5)(PPh_3)$_2$(THF)][PF_6] with buta-1,3-diyne affords the highly reactive butatrienylidene complex **84** which cannot be isolated but trapped instead by addition of large variety of nucleophiles at the electrophilic C_γ (i.e. the addition of $NHPh_2$ yields [Ru{=C=C=C(NPh_2)CH_3}(η^5-C_5H_5)(PPh_3)$_2$][PF_6]) [24,45]. The formation of this butatrienylidene derivative can be explained through the initial formation of the alkynyl-vinylidene intermediate **83** which then further rearranges via a 1,3-H shift (Scheme 43). Similarly, the reaction of the iron(II) complex [FeCl(η^5-C_5Me_5)(dppe)] with trimethylsilyl-1,3-butadiyne, in methanol and in the presence of $NaBPh_4$, generates the allenylidene derivative [Fe{=C=C=C(OMe)Me}(η^5-C_5Me_5)(dppe)][BPh_4] via addition of a methanol molecule to the butatrienylidene intermediate [Fe(=C=C=C=CH_2)(η^5-C_5Me_5)(dppe)][BPh_4] [46].

The formation of transient alkynyl-vinylidene intermediates **85** has been also proposed by Dixneuf and co-workers in the course of their studies directed to the preparation of penta-1,2,3,4-tetraenylidene ruthenium(II) complexes **86** (see Scheme 44) by activation of diynes HC≡CC≡CCR_2(OX) (X = H, $SiMe_3$) with complexes [$RuCl_2$(η^6-arene)(PR_3)] [47]. Such cumulenes **86** are in general extremely unstable species and behave as highly reactive electrophiles leading to a large variety of organometallic compounds of the type **87** or **88**, depending on the electronic and steric properties of the metallic unit. Neutral diynyl complexes **89** could be also isolated via deprotonation of intermediates **85** [48].



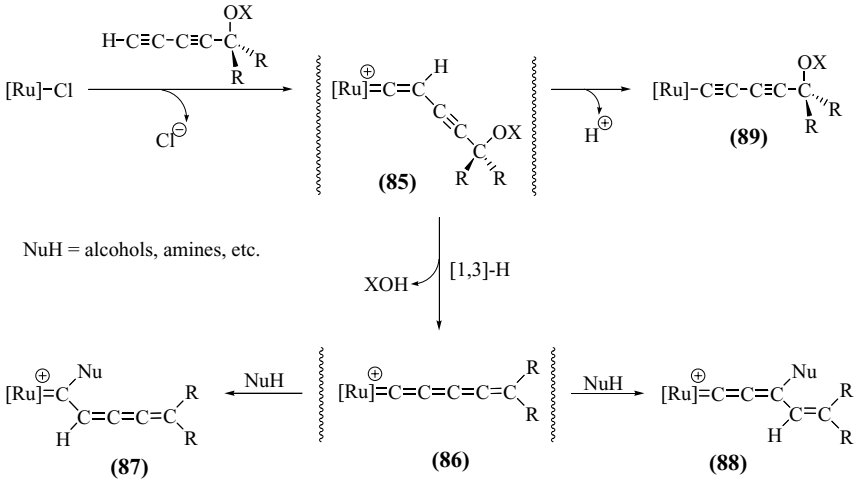
Scheme 45.

4. α, β-Unsaturated allenylidene complexes

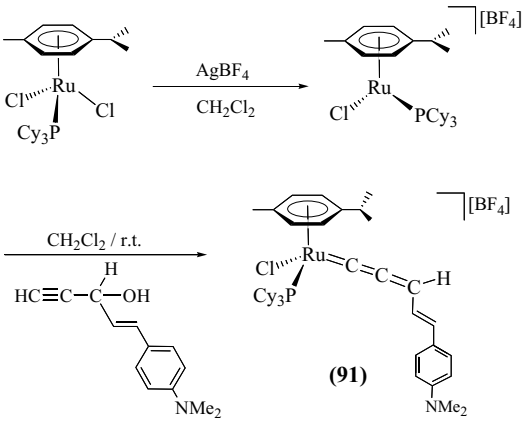
Only a few examples are known (no higher half-sandwich α,β-unsaturated metallacumulenes have been described to date) and they are prepared as follows:

4.1. By activation of alkynols

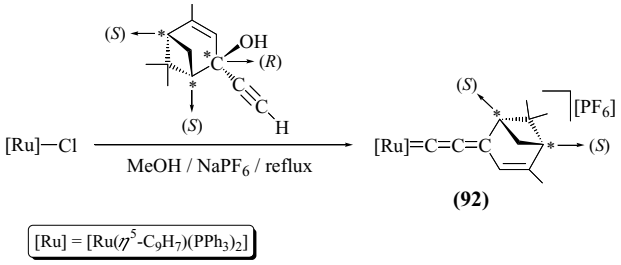
Following the Selegue's methodology for the synthesis of transition-metal allenylidene complexes (see Scheme 15) [49], the reaction of [$RuCl(\eta^5$-$C_5H_5)(PPh_3)_2$] with the corresponding 1-alkyn-3-ol in the presence of NH_4PF_6 gives the unsaturated allenylidenes **90a**,**b** (Scheme 45) [50]. These complexes are best described as allenylidene rather than



Scheme 44.



Scheme 46.

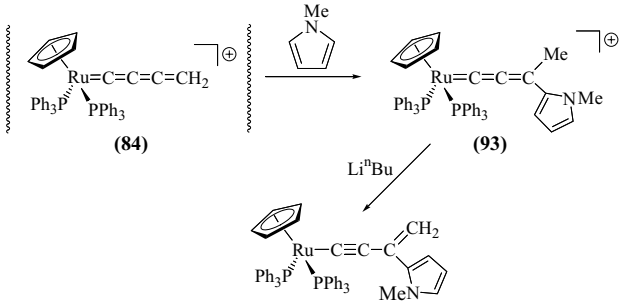


Scheme 47.

alkynyl complexes although there is a substantial contribution of the resonance form II.

Dixneuf has recently prepared the α,β-unsaturated allenylidene **91** by reaction of $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PCy_3)]$, 1-(*p*-dimethylaminostyryl)propynol and $AgBF_4$, in CH_2Cl_2 (Scheme 46) [51].

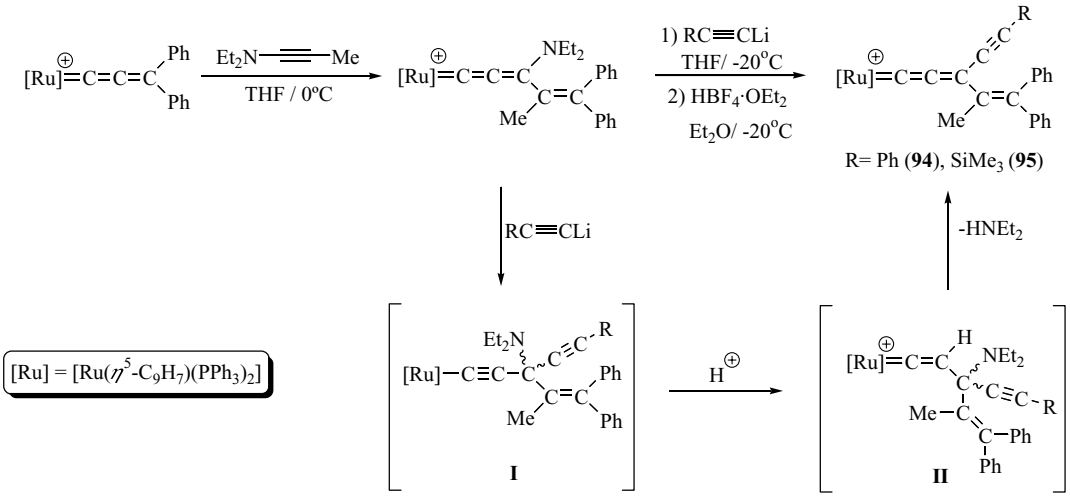
The chiral allenylidene complex $[Ru\{=C=C=C(C_9H_{14})\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ ($C(C_9H_{14})$ = (1*S*,5*S*)-4,6,6-trimethyl-bicyclo[3,1,1]hept-3-en-2-ylidene) (**92**) has been synthesized by reaction of $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ with the corresponding propargylic alcohol, in refluxing methanol and in the presence of $NaPF_6$ (Scheme 47) [52].



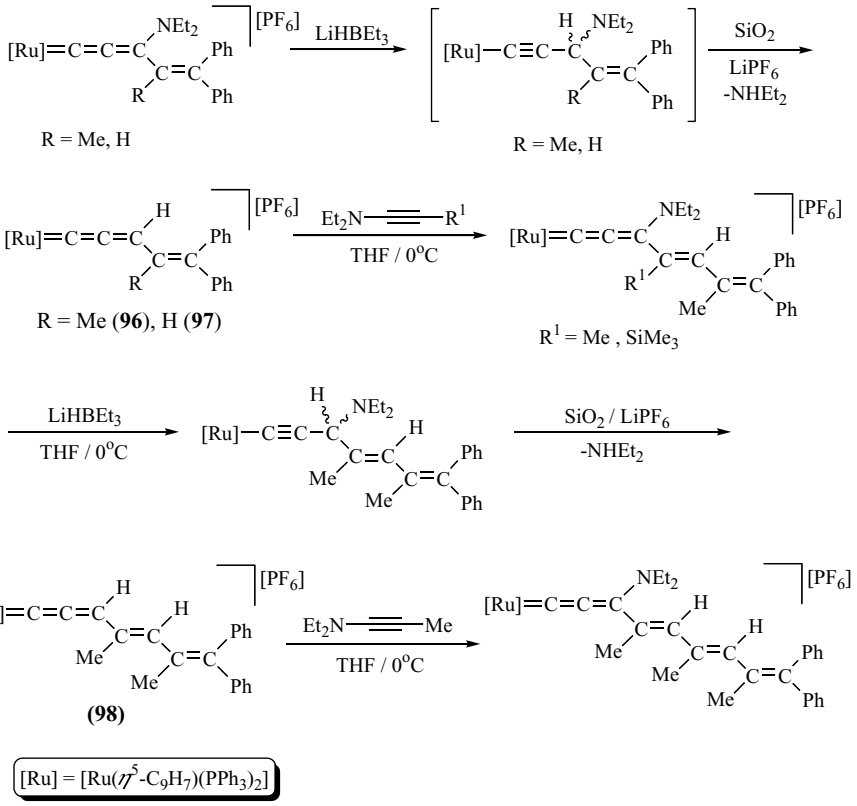
Scheme 48.

4.2. By nucleophilic additions to highly reactive $[Ru]^+=C(=C)_2=CR^1R^2$ species

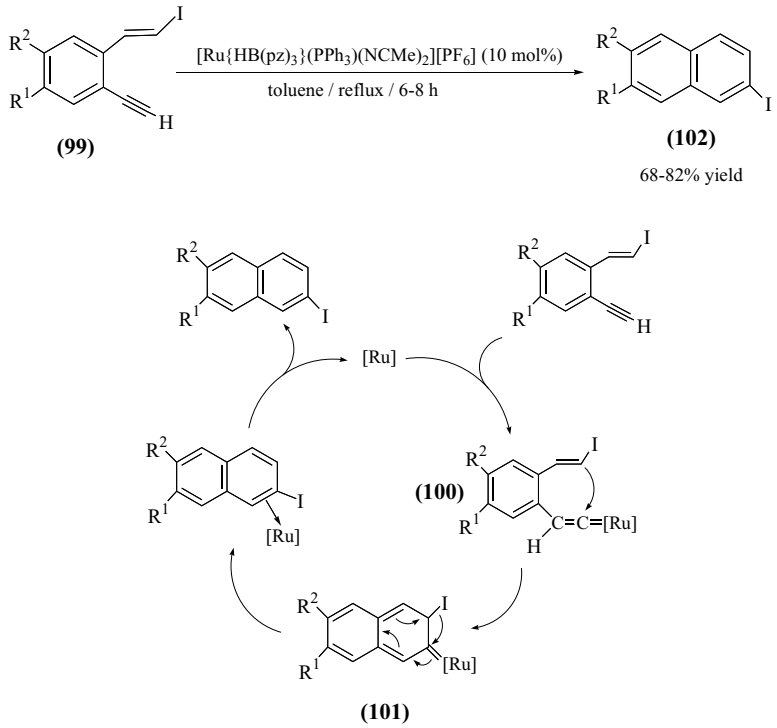
Mononuclear ruthenium complexes containing butatrienylidene ligands $[Ru]^+=C(=C)_2=CR^1R^2$ have usually been reported as highly reactive intermediates in a number of reactions [1g], and nucleophilic additions at the odd-numbered carbon atoms can be expected. Thus, the reaction of $[Ru(\eta^5\text{-}C_5H_5)(THF)(PPh_3)_2][X]$ (X^- = PF_6^-, BF_4^-), prepared from $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ and AgX, with buta-1,3-diyne in the presence of *N*-methylpyrrole affords the alkenyl-allenylidene **93**, via the corresponding butatrienylidene complex **84**. The deprotonation of the methyl group with butyllithium allows to access the functionalised σ-alkynyl complex $[Ru\{C\equiv CC(C_4H_3NMe\text{-}2)=CH_2\}(\eta^5\text{-}C_5H_5)(PPh_3)_2]$. This deprotonation is reversible and complex **93** regenerates by treatment of the σ-alkynyl derivative with water [24] (Scheme 48).



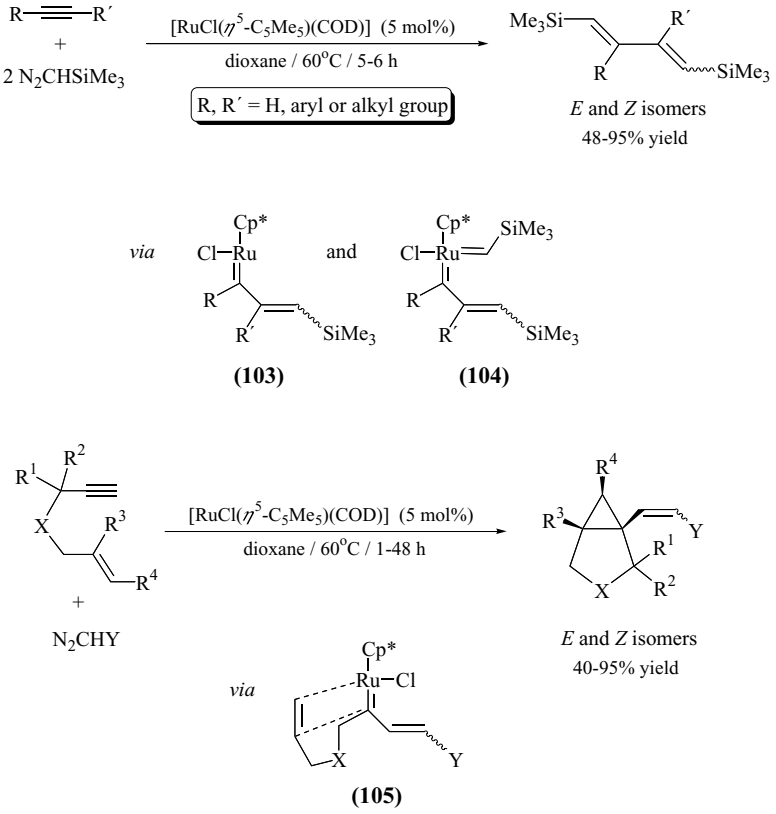
Scheme 49.



Scheme 50.



Scheme 51.



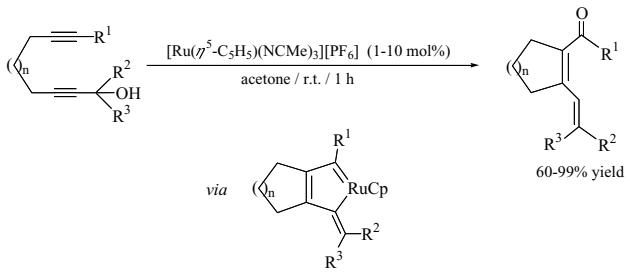
Scheme 52.

4.3. By nucleophilic addition of acetylides and hydride to amino-allenylidene complexes

Although a number of ruthenium amino-allenylidene complexes are known, their reactivity has not been explored yet, in spite of the presence of a functional group [53].[2] The reaction of complex [Ru(=C=C=CNEt$_2${C(Me)=CPh$_2$})(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (obtained by reaction of allenylidene complex [Ru(=C=C=CPh$_2$)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] [20] and MeC≡CNEt$_2$) with LiC≡CR (R = Ph, SiMe$_3$) followed by addition of HBF$_4$ led to the formation of the α,β-unsaturated allenylidene complexes **94** and **95** (Scheme 49) [54]. This transformation involves the addition of lithium acetylide to the C$_\gamma$ of the unsaturated chain to produce the unstable alkynyl intermediate I, which then undergoes protonation to the vinylidene derivative II and spontaneous loss of diethylamine.

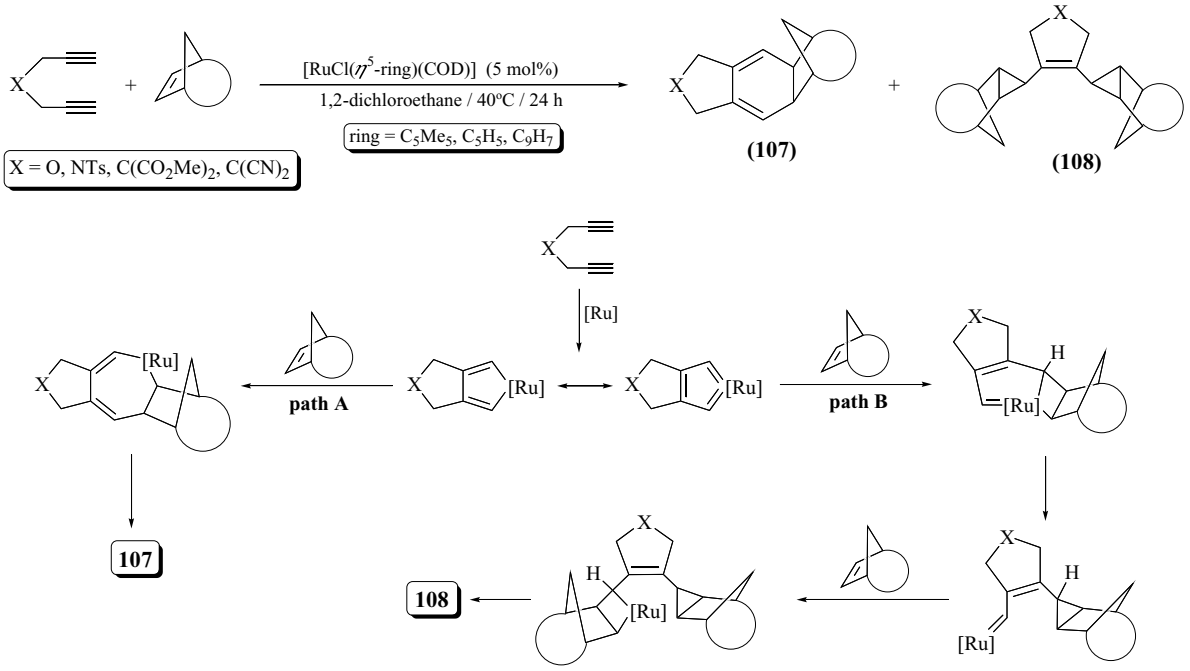
Monosubstituted unsaturated allenylidene complexes **96** and **97** can be obtained in two steps, via addition of LiBHEt$_3$ to the amino-allenylidene complexes followed by treatment of the alkynyl complex intermediate on a short silica gel column (Scheme 50). The insertion of ynamine in **96** generates the expected butadienyl(amino)allenylidene complex. These sequential processes constitute an efficient synthetic methodology for building up higher-unsaturated-allenylidene chains. In this way, the secondary butadienyl-allenylidene complex **98** is prepared by reaction of the corresponding aminoallenylidene species with LiHBEt$_3$ and SiO$_2$ treatment. The insertion of ynamine MeC≡CNEt$_2$ in **98** generates the hexatrienyl(amino)allenylidene complex shown in Scheme 50. These reactions proceed in a regio- and stereoselective manner, a sole isomer being detected in all cases [53].

Group 8 dinuclear cationic complexes containing unsaturated allenylidene bridges are also known [55].



Scheme 53.

[2] Other half-sandwich alkoxy- or amino-alkenyl-allenylidene complexes (of the type **88**; Scheme 44) have been described. See refs. [47b-47d].



Scheme 54.

5. Catalysis

5.1. α,β-Unsaturated alkylidenes

Despite the ruthenium five-coordinate complex [Ru(=CHCH=CPh_2)Cl_2(PCy_3)$_2$] is one of the first catalysts reported in ring closing metathesis of olefins (RCM) [56], only one example using related half-sandwich derivatives has been reported to date, namely the indenylidene (η^6-arene)-ruthenium(II) complex **5** (see Scheme 3) [6].[3] Low loadings of **5**, prepared in situ from the corresponding allenylidene precursor, features a high activity for ring-opening metathesis polymerization (ROMP) of cyclooctene and cyclopentene under mild conditions as well as for RCM or acyclic diene metathesis (ADMET) reactions. Both rate and spectroscopic studies support that an intramolecular rearrangement of the allenylidene ligand into an indenylidene is a key step in the catalytic RCM reactions [57]. The catalytic activity of complex **5** seems higher than that of analogous neutral five-coordinate complexes [58].

A number of α,β-unsaturated alkylidenes have also been proposed as intermediate species in catalytic processes:

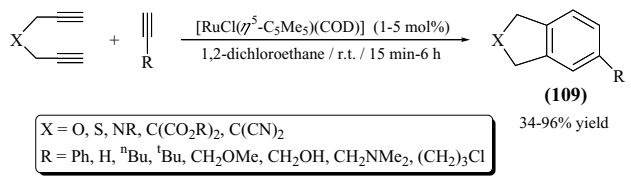
(i) The naphtylidenes **101**, formed via electrocyclization of vinylidenes **100**, involved in the aromatization of enynes **99** to give naphtalene derivatives **102** (Scheme 51) [59].

(ii) The alkenyl-alkylidenes **103**–**105** [60] generated in the addition of diazomethanes to: (a) alkynes, leading to the regioselective synthesis of buta-1,3-dienes; and (b) enynes, giving alkenylbicyclo[3.1.0]hexane derivatives (Scheme 52).

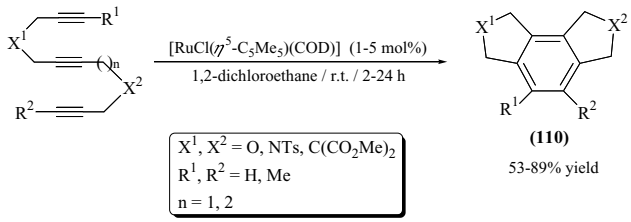
(iii) The cyclic carbene **106** involved in the intramolecular cycloisomerization of alkynes and propargylic alcohols using the cationic complex [Ru(η^5-C_5H_5)(NCMe)$_3$][PF_6] as catalyst precursor (Scheme 53) [61].

5.2. α,β-Unsaturated bis-carbenes (ruthenacyclopentatrienes)

Although the catalytic activity of the isolated bis-carbene complexes **30a**,**d** (see Fig. 6) has been experimentally proven in a number of transformations (see below), the

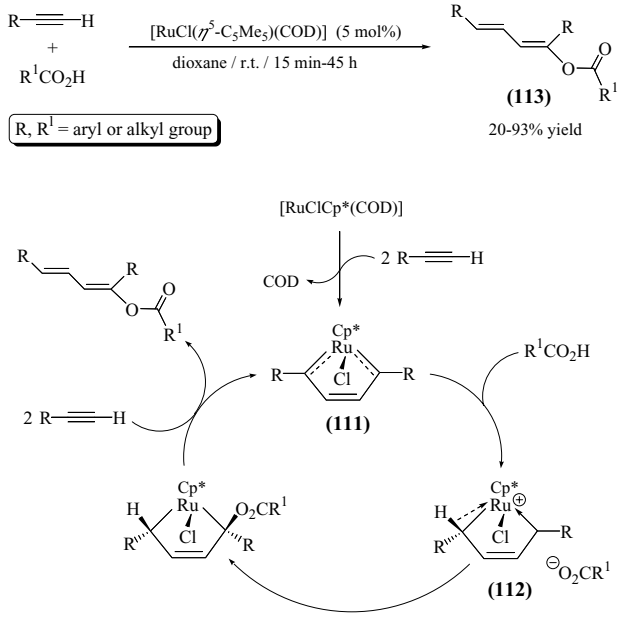


Scheme 55.

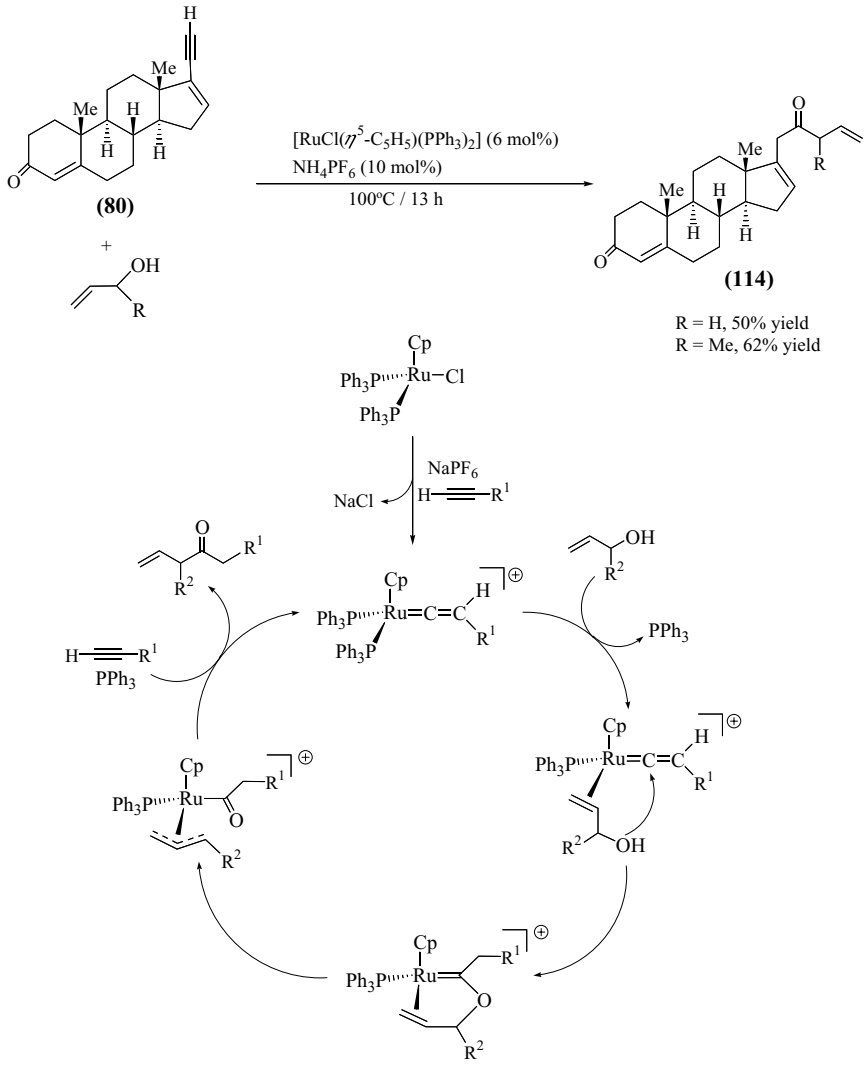


Scheme 56.

[3] (η^5-Indenyl)-ruthenium(II) vinyl-alkylidenes **1**–**2** (see Scheme 1) show no catalytic activity in RCM and ROMP reactions. See ref. [5b].



Scheme 57.



Scheme 58.

formation of these species in the first step of a series of catalytic cyclotrimerization of alkynes to give substituted arenes under mild conditions is well documented [14f,15b,62]. Complexes **30a**,**d** are formed in situ generally from [RuCl(η^5-C_5Me_5)(COD)], although analogous precatalysts such as [RuCl(η^5-C_5H_5)(COD)] and [RuCl(η^5-C_9H_7)(COD)] have also been eventually used [62]. The labile cationic complex [Ru(η^5-C_5H_5)(NCMe)$_3$][PF_6] has also been used as precursor although the formation of stable and inert sandwich complexes of the type [Ru(η^5-C_5H_5)(η^6-arene)][PF_6] deactivate the catalyst [15b]. Analogous iron(II)-sandwich derivatives have been also isolated by V. Guerchais and co-workers starting from [Fe(η^5-C_5Me_5)(NCMe)$_3$][PF_6] [12].

Besides these catalytic cyclotrimerizations of alkynes, the following processes have been recently reported:

(i) Tandem cycloaddition of 1,6-heptadiynes with bicyclic alkenes, such as bicyclo[3.2.1]heptenones and norbornene derivatives, affording the 1:2 adducts

between the diynes and two molecules of the bicycloalkenes (**108**) together with common [2+2+2] cyclotrimerization products (**107**). A general reaction along with the proposed mechanism is shown in Scheme 54 [62]. It is noteworthy that the selectivity of the tandem cyclopropanation adducts was increased in the order of the precatalyst [RuCl(η^5-C_9H_7)(COD)] > [RuCl(η^5-C_5H_5)(COD)] > [RuCl(η^5-C_5Me_5)(COD)]. Normal [2+2+2] cyclotrimerization between 1,6-heptadiynes and alkenes are achieved in the case of cyclic and linear alkenes containing heteroatoms at the allylic position.

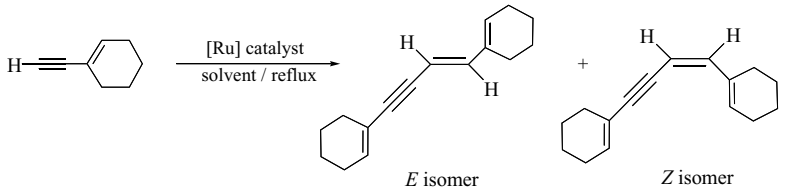
(ii) Cycloaddition of α,ω-diynes with terminal mono-alkynes to give bicyclic benzene derivatives **109** in good yields [14f]. A wide variety of diynes and monoynes containing functional groups such as esters, ketones, nitriles, amine-alcohols, etc. can be used. Illustrative examples of regioselective processes are shown in Scheme 55. Other type of analogous [2+2+2] cycloadditions of 1,6-diynes with alkenes, nitriles, isocyanates, isothiocyanates and tricarbonyl compounds have been also reported [62,63].

(iii) Completely intramolecular alkyne [2+2+2] cyclotrimerization of triynes to give tricyclic aromatic compounds fused with 5 to 7-membered rings (**110**) (Scheme 56) [14g,h].

(iv) Stereoselective synthesis of disubstituted 1,3-dienes (**113**) via coupling of two molecules of alkynes and one molecule of carboxylic acid (Scheme 57) [14d]. Reactivity studies and theoretical calculations are consistent with the intermediate formation of a mixed Fischer-Schrock type bis-carbene species **111**. In fact, it has been shown that the bis-carbene complex [Ru($C_4H_2Ph_2$)Cl(η^5-C_5Me_5)] catalyzes the reaction. On the basis of theoretical studies a catalytic cycle has been proposed suggesting that a chelating mixed C(1) alkyl, C(4) carbene ligand is formed via direct protonation at the C(1) carbene atom of the bis-carbene **111** rather than at the ruthenium site (**112**). This system is stabilized by a very weak agostic H–C(1) bond interaction.

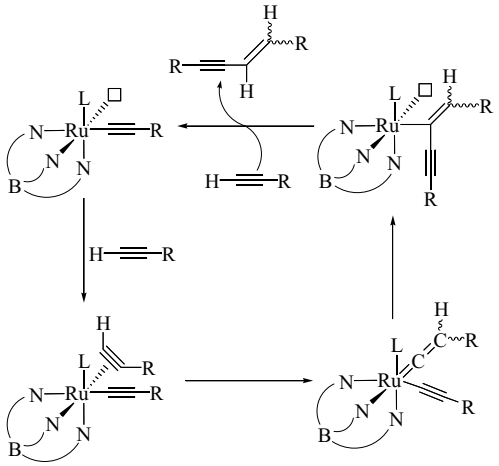
5.3. α,β-Unsaturated vinylidenes

Although the use of half-sandwich alkenyl–vinylidene Group 8 complexes as catalysts has not been reported to date [1,2], the involvement of such species as reactive intermediates in some catalytic transformations has been in some



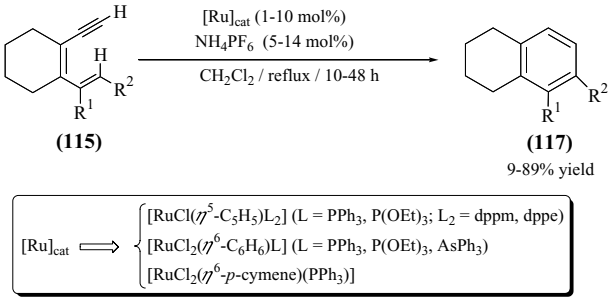
[RuH{HB(pz)$_3$}(PPh$_3$)$_2$] (2 mol%)
Solvent = toluene
Time = 20 h
Yield = 86%
E/Z ratio = 5.6:1

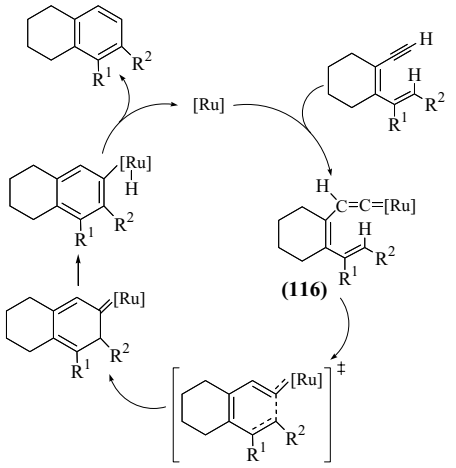
[RuCl{HB(pz)$_3$}(κ^2-*P,O*-$Ph_2PCH_2CH_2OMe$)] (5 mol%)
Solvent = benzene
Time = 40 h
Yield = 89%
E/Z ratio = 2.7:1



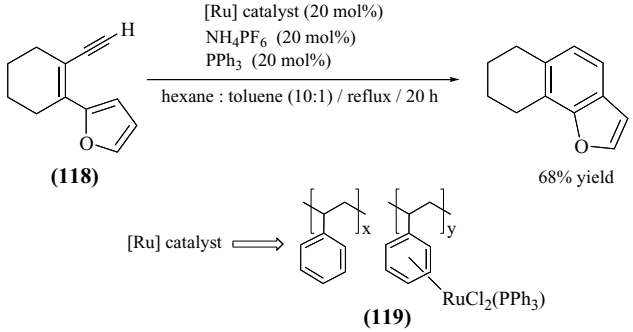
L = PPh$_3$, κ^1-*P*-$Ph_2PCH_2CH_2OMe$
R = 1-cyclohexenyl

Scheme 59.





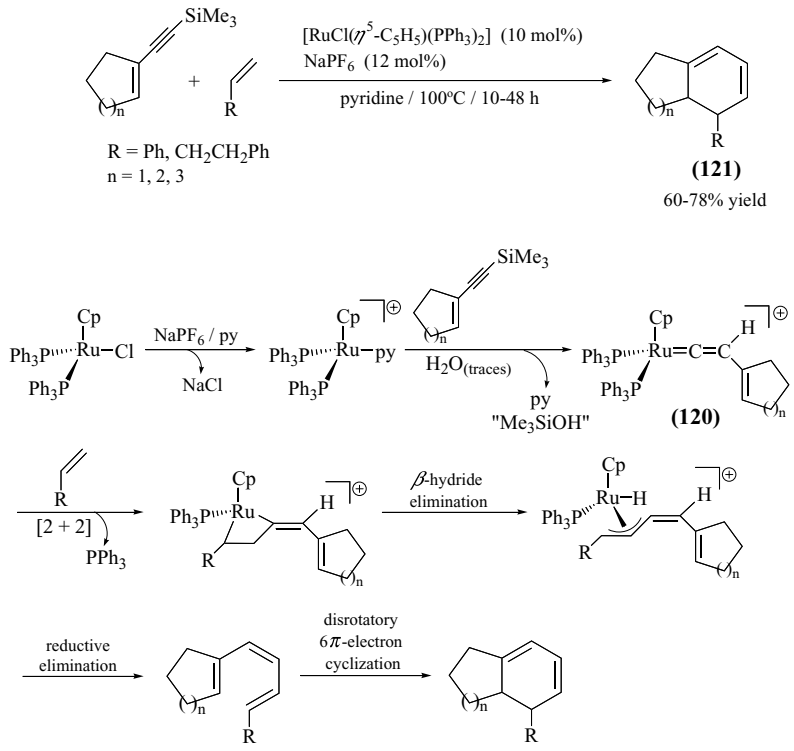
Scheme 60.



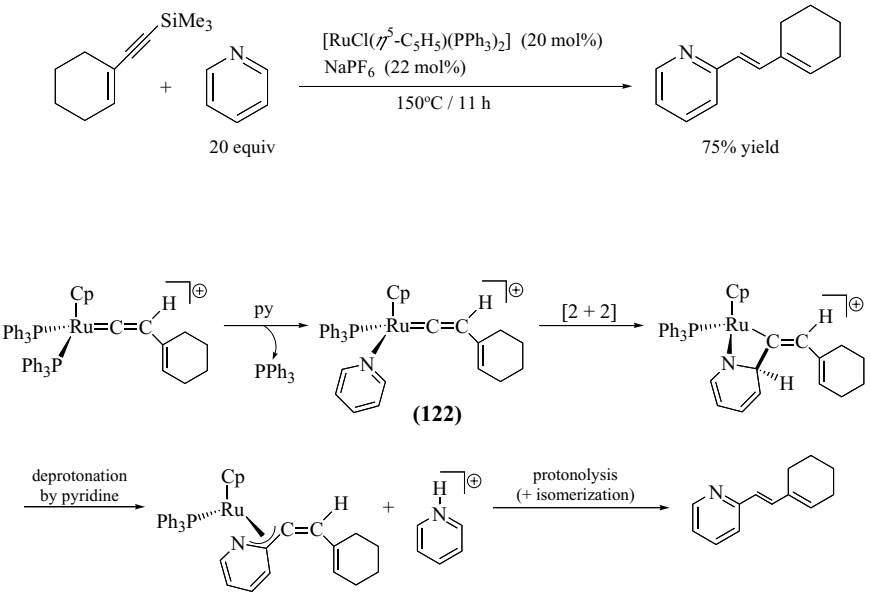
Scheme 61.

cases proposed. Thus, Trost and co-workers have described that the ruthenium(II) complex [RuCl(η^5-C_5H_5)(PPh_3)$_2$] catalyzes the addition of allylic alcohols to the terminal 1,3-enyne **80** to yield β,γ-unsaturated ketones **114**, via initial formation of an alkenyl–vinylidene intermediate (Scheme 58) [64].

The hydrotris(1-pyrazolyl)borate complexes [RuH{HB(pz)$_3$}(PPh_3)$_2$] [65] and [RuCl{HB(pz)$_3$}(κ^2-*P,O*-$Ph_2PCH_2CH_2OMe$)] [22b] have been tested as catalysts in the dimerization of 1-ethynylcyclohexene into (*E*)- and (*Z*)-1,4-di(1-cyclohexenyl)but-3-en-1-yne (Scheme 59). The proposed mechanism for this transformation involves the initial formation of unsaturated σ-enynyl species [Ru(C≡CR){HB(pz)$_3$}L] (R = 1-cyclohexenyl; L = PPh_3, κ^1-*P*-$Ph_2PCH_2CH_2OMe$) which react with a second alkyne molecule,



Scheme 62.

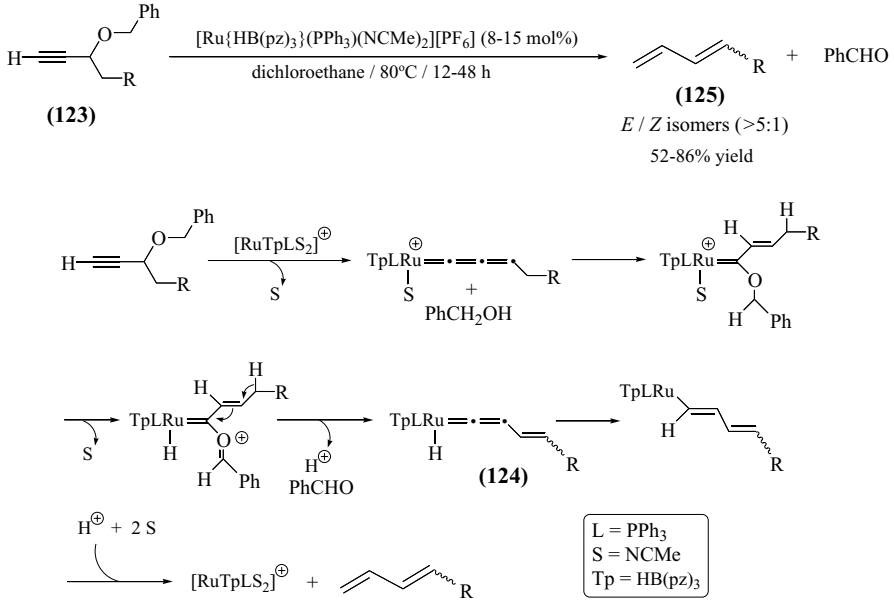


Scheme 63.

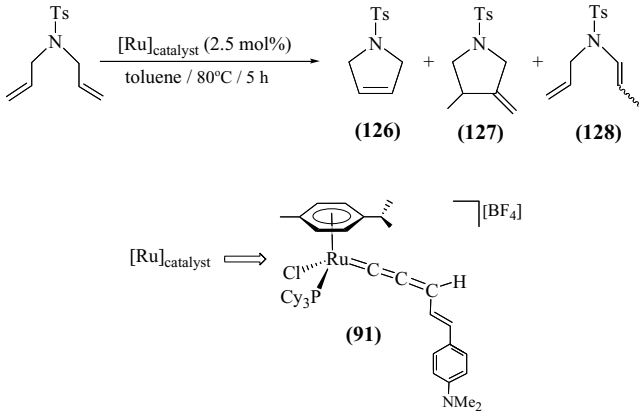
via alkenyl–vinylidene formation, and subsequent C–C coupling. The best results, in terms of both activity and *E*/*Z* selectivity, have been obtained using the hydride complex $[RuH\{HB(pz)_3\}(PPh_3)_2]$ as catalyst precursor (Scheme 59).

Several half-sandwich ruthenium(II) complexes, i.e. $[RuCl(\eta^5\text{-}C_5H_5)L_2]$ (L = PPh_3, $P(OEt)_3$; L_2 = dppm, dppe), $[RuCl_2(\eta^6\text{-}C_6H_6)L]$ (L = PPh_3, $P(OEt)_3$, $AsPh_3$) and $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PPh_3)]$, have proved to be active pre-catalysts in the cyclization of dienylalkynes **115** into substituted arenes **117** (Scheme 60) [66a]. The first step in the catalytic cycle involves the formation of a dienyl-vinylidene species **116** which undergoes an intramolecular electrocyclization followed by aromatization of the resulting carbene intermediate. In accord with this mechanism, in which the key step is the nucleophilic addition of the olefin to the electrophilic α-carbon of the vinylidene group, the less electron-rich complexes $[RuCl_2(\eta^6\text{-}C_6H_6)(PPh_3)]$ and $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PPh_3)]$ lead to the best catalytic performances. The catalytic cyclization of the dienylalkyne **118** with a polymer-supported (η^6-arene)-ruthenium(II) complex (**119**) has been also reported (Scheme 61) [66b].

Murakami and co-workers have described a domino reaction in which six-membered ring dienes **121** are



Scheme 64.



Scheme 65.

formed in a regio- and stereoselective manner from silyl-protected enynes and alkenes through the mediation of [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (Scheme 62) [67]. Formation of dienes **121** is explained assuming the initial formation of the corresponding alkenyl–vinylidene ruthenium complex **120** from the protected enyne, via protiodesylilation due to the presence of water in the reaction medium, and subsequent formal insertion of the vinylidene unit into an olefinic C–H bond.

Complex [RuCl(η^5-C_5H_5)(PPh_3)$_2$] catalyzes also the direct alkenylation of pyridine with (cyclohexenylethyn-1-yl) trimethylsilane (Scheme 63) [68]. In this case, the alkenyl–vinylidene ruthenium intermediate **122** regio- and stereoselectively inserts the vinylidene group into the C_α–H bond of the pyridine core.

The involvement of alkenyl–vinylidene species **124** in the transformation of 3-benzyl but-1-ynyl ethers **123** into 1,3-dienes **125** and benzaldehyde catalyzed by the cationic hydrotris(1-pyrazolyl)borate complex [Ru{HB(pz)$_3$}(PPh_3)($NCMe)_2$][PF_6] has been also reported (Scheme 64) [69].

5.4. α,β-Unsaturated allenylidenes

Despite the well-known ability of Ru(II)-allenylidenes to act as efficient pre-catalysts in olefin metathesis [70], only the alkenyl-allenylidene complex **91** has been checked as pre-catalyst in the RCM of *N*,*N*-diallyltosyl amide. Thus, it affords the expected dihydropyrrole **126** (60% yield) along with the methylenecyclopentane **127** (36% yield) and the dienes **128** (traces); the latter products resulting from the cycloisomerization and simple isomerization of one of the C=C bond of the substrate, respectively (Scheme 65) [51]. We note that, under similar reaction conditions, the diphenylallenylidene derivative [Ru(=C=C=CPh_2)Cl(η^6-*p*-cymene)(PCy_3)][BF_4] catalyzes in preference the isomerization processes rather than the RCM of the diene (**126**/**127**/**128** yields = 31/43/16%), pointing out the effect of the allenylidene substituent on the selectivity of the reaction.

6. Conclusions

The advent of ruthenium alkylidene catalysts for alkene metathesis within the last few years has promoted the generation of a large variety of catalytic processes involving transformations of other simple molecules. The high catalytic activity of these species, associated with the tolerance towards many polar functional groups, has led to search potential alternatives. To this regard the discovery of methodologies for the synthesis of novel α,β-unsaturated alkylidenes and analogous ruthenium complexes, as well as the generalization of the stoichiometric studies, has increased the availability of catalysts and/or appropriate precursors. The above reactions illustrate the state of the art of a wide group of Group 8 half-sandwich complexes containing non-heteroatom stabilized carbene groups. In particular, synthesis and reactivity studies of alkylidene [ML*n*]=CR^1R^2, vinylidene [ML*n*]=C=CR^1R^2 and allenylidene [ML*n*]=C=C=CR^1R^2 complexes (R^1 and/or R^2 unsaturated hydrocarbon chain) are described. Besides the general electrophilic nature of the carbenic carbon atom, it is striking to note that the presence of highly unsaturated moieties provides a versatile reactivity. This is mainly based on the availability of both electrophilic and nucleophilic sites along the carbon chain. To this respect it is shown that these complexes are prone to add a wide number of electrophiles and nucleophiles as well as dipolar substrates which generates a series of cycloaddition processes. Despite the well-known variety of stoichiometric reactions the involvement of these species in catalytic processes are much scarcer. However, the recent achievements by using the bis-carbene complexes in a series of C–C couplings of alkynes and enynes to give high value chemicals with atom economy are specially challenging. Moreover, it has been also recently discovered the role of other α,β-unsaturated carbenes as active intermediate species. All of this allows to foresee a very promising field of research in the close coming years.

Acknowledgements

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