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Ruthenium and osmium vinylidene complexes and some related compounds☆

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☆ Dedicated to Professor Helmut Werner, University of Würzburg, on his 60th birthday in appreciation of his dedication and important contributions to this field.

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Abstract

A review of the large number of studies completed during the current decade on the chemistry of ruthenium and osmium vinylidene complexes is presented. Interest in these studies arises not only from the reactivity modes and structural properties, but also because vinylidene species play an important role in the selective catalytic transformation of terminal alkynes (polymerization, C–C bond formation in the condensation of alkynes with other substrates, etc.). Attention is mainly focused on the mononuclear compounds, studying their preparative methods where coordinatively unsaturated species and good donor ligands are often involved. Recent methods of synthesis from polyhydrides are also summarized. Metal alkynyl derivatives are closely related to vinylidene complexes, both being common precursors to, and reaction products of vinylidene complexes. Subsequently, 1-alkyne and π-alkyne to vinylidene rearrangements on these metal centers are studied. The transformations from vinyl 14 electron to hydride-vinylidene 16 electron species and from hydride–vinylidene to ethylidyne species, etc. are also considered.

Keywords: Vinylidene complexes; Polymerization; Ruthenium

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1. Introduction

During the last decade, the chemistry of transition metal complexes containing unsaturated carbenes such as: C=CRR′ (vinylidenes), :C=C=RR′ (allenylidenes) and: C=C=C=CRR′ (butatrienylidenes) as ligands has attracted a great deal of attention because of their occurrence as key intermediates in the stoichiometric and catalytic transformation of organic molecules. One of the most interesting properties of these complexes is that they promote C–R bond formation reactions. In this regard there are reports on the coupling between vinylidene and acetylide ligands and other examples of coupling between vinylidene and other ligands. Other processes such as dimerization of alkynes, condensation of alkynes with allylic complexes or carboxylic acids and in general olefin methathesis are also important. Many of these reactions use d^6 metal (Ru, Os) as an electron-rich metal center in such intermediate active carbenes.

A large number of vinylidene complexes with cyclopentadienyl, arene rings or hydride-tris-pirazolylborate and mono, bi or polydentate phosphines as supporting ligands are well known. However, few of them are reported with phosphite ($P(OR)_3$, $PPh(OR)_2$) ligands, although it may be expected that the steric and electronic properties of these ligands would reveal some new properties of these vinylidene and related derivatives.

Many of the catalytic or synthetic reactions leading to the alkyne dimerization or polymerization are stereoselective and, in addition, the proposed mechanisms generally involve unsaturated alkynyl–ruthenium species. Consequently, they are reactive toward the activation of small molecules like CO, H_2, CO_2, etc.

On the other hand, vinylidene compounds are often used to generate new carbenes and carbynes. The activation of diynes by ruthenium complexes to produce cumulenes is also a process that goes through the formation of vinylidene intermediates.

The importance of vinylidenes in chemistry has become evident and it is now opportune to summarize progress that has been achieved during the 1990s, after the excellent reviews by Bruce and Antonova [1].

2. Preparation methods

The vinylidene metal complexes can be obtained by means of the activation of terminal alkynes with 16-electron species as a preliminary stage towards the synthesis of metal carbene derivatives [2]. The formation of these coordinatively unsaturated species from a suitable precursor complex are produced by somewhat different ways: (a) the dissociation of an halide ligand, generally in alcohols or dichloromethane, favored by the precipitation of an insoluble salt of the cationic vinylidene complex; (b) the dissociation of a monodentate phosphine ligand, normally in thf, benzene or toluene; (c) the dissociation of a solvent molecule coordinated to the metal center; (d) the partial dissociation of hemilabile ligands able to decrease their coordination over the metal center producing a vacant coordination site. In many cases, the stability of such 16 electron species is increased by the presence of ligands like η^5-C_5H_5, η^5-C_5Me_5, Tp, arenes, etc., which make the metal center more electron rich and more reactive towards 1-alkynes; and (e) the reaction of alkynes with some hydride complexes which are a source of 14 electron fragments, constitutes a new way for the synthesis of carbene and/or vinylidene complexes. In some cases, the carbyne metal complexes are good starting materials to prepare vinylidene complexes.

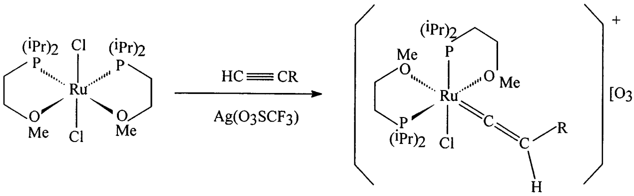
This classification should not be considered rigid and some procedures could be adequately included in more than one of the above methods. There are more cationic than neutral vinylidene complexes described in the literature, although in recent years interest in the neutral vinylidene complexes has increased, especially because of their role as intermediates in many C–C coupling reactions. For these reasons methods to prepare cationic and neutral vinylidene complexes will be summarized. With the same starting material and alkyne it is sometimes possible to obtain different neutral or cationic vinylidene complexes by varying the reaction conditions particularly the solvent.

Dixneuf and co-workers have shown [2] that HC≡CR activation by means of *cis*-$[RuCl_2(Ph_2PCH_2PPh_2)_2]$ in dichloromethane produces the cationic *trans*-$[(Ph_2PCH_2PPh_2)_2(Cl)Ru^+{=}C{=}CHR]$ even starting with acetylene (R = H) or propargylic alcohol to obtain the corresponding $Ru^+{=}C{=}CH$ or $Ru^+{=}C{=}CH(CH_2OH)$. The same authors have reported [3] a variety of vinylidene–ruthenium complexes [*trans*-$Ru({=}C{=}CHR(Cl)(Ph_2PCH_2CH_2PPh_2)_2][PF_6]$ (R = H, ^{n}Bu, Ph, *p*-PhOMe, *p*-$PhNO_2$) obtained by the reaction of $[RuCl_2(Ph_2CH_2CH_2PPh_2)_2]$ with terminal alkynes and $NaPF_6$ in dichloromethane.

Similarly, vinylidene complexes $[Ru(Me_3tacn)(PMe_3)(O_2CCF_3)({=}C{=}CHR)][PF6]$, (R = Ph or *p*-tolyl; Me_3tacn = the tertiary amine 1,4,7-trimethyl-1,4,7-triazacyclononane) can be obtained by reaction of Ru^{II} complexes $[Ru(Me_3tacn)(PMe_3)_2(O_2CCF_3)][PF_6]$ with 1-alkynes in 1,2-dichloroethane under reflux [4].

Some authors have been interested in the synthesis and reactivity of transition metal complexes containing phosphino-ethers, -amines and -esters as ligands.

At room temperature (r.t.) and in the absence of UV light the compound $[RuCl_2(\kappa^2\text{-}(P,O)\text{-}{}^iPr_2PCH_2CH_2OMe)_2]$ is rather inert towards alk-1-ynes. However, in the presence of silver triflate $Ag(O_3SCF_3)$ this species smoothly reacts with $HC{\equiv}CR$ (R = H, Ph, $p\text{-}C_6H_4Me$ or $m\text{-}C_6H_4C{\equiv}CH$) to give the triflates of the cationic vinylideneruthenium(II) complexes [5].



Convenient starting points for these studies are the 16-electron complexes $[(\eta^5\text{-}C_5Me_5)Ru(PR_3)Cl]$ (R = Cy, ^{i}Pr) and the labile cluster $[(\eta^5\text{-}C_5Me_5)Ru(\mu_3\text{-}Cl)]_4$, which serve as synthetic equivalents for the 14-electron fragment $[(\eta^5\text{-}C_5Me_5)RuCl]$. The reaction chemistry of these starting materials with alkynes was studied by Tilley [6] and they are summarized in Bruce's review [1a].

Actually, some ruthenium(II) complexes have been shown easily to yield vinylidene complexes $Ru^+{=}C{=}CHR$ by displacement of an halide in the presence of both a noncoordinating anion and a terminal alkyne, from $[RuCl(L_2)(\eta^5\text{-}C_5H_5)]$ $\{L_2 = (PPh_3)_2$ [7], $(PMe_3)_2$ [8], $(PMe_2Ph)_2$ [9], or L_2 = diphosphines like $\kappa^2(P,P)\text{-}Ph_2P(CH_2)_2PPh_2$ [7] or chiral diphosphine [10], $RuCl_2(\kappa^2(P,O)\text{-}{}^iPr_2PCH_2CH_2OMe)_2$ [11], $RuCl_2(\kappa^2(P,O)\text{-}{}^iPr_2PCH_2CO_2Me)_2$ [11], and $RuCl_2(\kappa^2(P,P)\text{-}Ph_2P(CH_2)_nPPh_2)_2$ ($n = 1$ [12], $n = 2$ [13])$\}$.

The comparative study of these reactions suggests that only electron rich ruthenium(II) complexes allow the isolation of ruthenium vinylidene complexes. The study of $RuCl_2(dppm)_2$ [12] and $RuCl_2(dppe)_2$ [13] derivatives in the activation of terminal alkynes and propargyl alcohol derivatives suggests that, beside the necessary electron richness of the ruthenium(II) atom, the bulkiness of the ligands was a determining factor for the stabilization of vinylidene or allenylidene ruthenium intermediates. To check this hypothesis, Dixneuf et al. have studied the influence of a combination of very bulky and electron-releasing ligands on the ruthenium site. Thus, they reported [14] that complex $(C_5Me_5)(PMe_2Ph)_2RuCl$ in methanol reacts with phenylacetylene and trimethylsilylacetylene in the presence of $(NH_4)PF_6$ to afford vinylidene complexes $[(C_5Me_5)(PMe_2Ph)_2Ru{=}C{=}CHR]PF_6$ (R = Ph, H).

In the same way, Sato and coworkers [15] have reported the reaction of $[(\eta^5\text{-}C_5Me_5)(PPh_3)_2RuCl]$ with $HC{\equiv}CSiMe_3$ in the presence of $(NH_4)(PF_6)$ to afford the cationic Ru(II) terminal vinylidene complex $[(\eta^5\text{-}C_5Me_5)(PPh_3)_2Ru({=}C{=}CH_2)][PF_6]$ in 73% yield. According to Wong's methodology these terminal vinylidene complexes were doubly deprotonated with ^{t}BuLi to generate the corresponding reactive lithioacetylide complex, which was trapped with Me_3SiCl and MeI to give $[(\eta^5\text{-}C_5Me_5)(PPh_3)_2Ru(C{\equiv}CSiMe_3)]$ and $[(\eta^5\text{-}C_5Me_5)(PPh_3)_2Ru\text{-}$

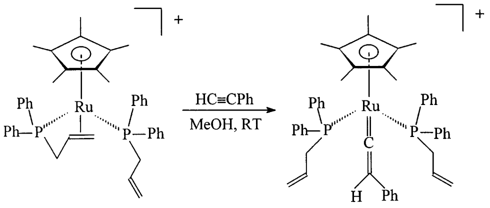
(C≡CMe)], respectively. The desilylation forming the terminal vinylidene complex is explained by the significant susceptibility of the C(sp^2)–Si bond towards moisture described for a Re(I) complex by Bianchini et al. [16]. A similar observation was reported in the preparation of Fe(II) [17] and Ru(II) [7,8] complexes.

We have prepared [18] several η^5-C_5H_5 or η^5-C_5Me_5 Ru vinylidene complexes containing the bulky 1,2-bis(diisopropylphosphino)ethane (dippe) as ligand [18,19]. In these cases [(η^5-C_5R_5)Ru(dippe)Cl] (R = H or Me) reacts in MeOH at r.t. with different 1-alkynes in the presence of sodium tetraphenylborate yielding the corresponding cationic vinylidene complexes. Even in the case of (trimethylsilyl)acetylene the Ru(II) (trimethylsilyl)vinylidene complex was isolated without desilylation. Analogous reactions have been tried using acetylene and then the corresponding cationic vinylidenes [(η^5-C_5R_5)Ru(dippe)(=C=CH_2)][BPh_4] have been obtained.

Similarly, but using a silver salt to abstract the halogenide ligand, treatment of [(η^5-C_5Me_5)Os(CO)(PPh_3)I] with $AgBF_4$ followed by addition of terminal alkynes, the stable cationic vinylidene complexes [(η^5-C_5Me_5)Os(CO)(PPh_3)(=C=CHR)][BF_4] (R = Ph, Bu^t) were obtained [20].

Complexes containing hemilabile *P–O* or *P–N* ligands are able to facilitate the stoichiometric and catalytic transformations of organic molecules such as acetylene to vinylidene tautomerization [5,11a,21]. In this way Kirchner et al. [22] studied the synthesis and reactivity of several cyclopentadienyl and pentamethyl–cyclopentadienyl ruthenium compounds containing these hemilabile ligands. The chloride abstraction from [Ru(η^5-C_5Me_5)(κ^2(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$)Cl] with $TlCF_3SO_3$ leads to [Ru(η^5-C_5Me_5)(κ^2(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$)(κ^1-OSO_2CF_3)] where $(CF_3SO_3)^-$ is directly bound to the metal center. Both complexes are excellent precursors for the synthesis of cationic vinylidene complexes. The reaction of [Ru(η^5-C_5Me_5)(κ^2(*P*,*N*)–$Ph_2PCH_2CH_2NMe_2$)Cl] with HC≡CPh in the presence of $TlCF_3SO_3$ in CH_2Cl_2 yields the cationic vinylidene complex [Ru(η^5-C_5Me_5)(κ^2(*P*,*N*)–$Ph_2PCH_2CH_2NMe_2$) (=C=CHPh)]$^+$ in high yield as an air-stable red solid. Similar treatment of [Ru(η^5-C_5Me_5)(κ^2(*P*,*N*)-$Ph_2PCH_2CH_2NMe_2$)(κ^1-OSO_2CF_3)] with one equivalent of HC≡CPh in CH_2Cl_2 also affords the cationic vinylidene complex in essentially quantitative yield.

The investigations of Nelson and co-workers [23] with alkenyl phosphines as hybrid hemilabile ligands, resulted in the synthesis of compound [η^5-(C_5Me_5)Ru(η^3-DPVP)(η^1-DPVP)][PF_6] (DPVP = diphenylvinylphosphine), which reacts in MeOH with HC≡CPh to give the cationic vinylidene complex [(η^5-C_5Me_5)Ru(η^1-DPVP)$_2${=C=C(H)Ph}][PF_6]. Similarly, the hemilabile properties of the novel η^3-ADPP ligand are illustrated by reactions of compound [(η^5-C_5Me_5)Ru-(η^3-ADPP)(η^1-ADPP)][PF_6] with HC≡CPh or HC≡CCH_2OH to form compound [(η^5-C_5Me_5)Ru(η^1-ADPP)$_2$(=C=C(H)Ph)][PF_6] and unstable compound [(η^5-C_5Me_5)Ru([η^3-ADPP)(η^1-ADPP)$_2$(=C=C(H)(CH_2OH))][PF_6], respectively [24].

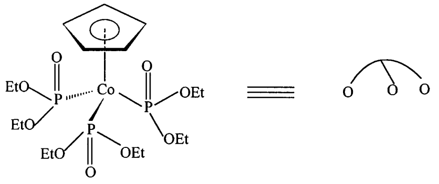


The tris(pyrazolyl)borate anion (Tp = $[HB(pz)_3]^-$) was introduced by Trofimenko [25] as a ligand in transition metal complexes and it has been extensively used for more than 20 years in organoruthenium chemistry. This ligand is often compared with C_5H_5 and C_5Me_5 due to the same formal charge and number of electrons available for donation to the metal center, all these ligands are considered as six-electron donors. Notwithstanding, differences in size and electronic properties are obvious. A wide range of complexes can be derived readily from $[(C_5R_5)RuCl(P_2)]$ (R = H, Me; P_2 = two monodentate phosphines or one bidentate phosphine) and terminal acetylenes [26], but until last year, such a rich chemistry was virtually unknown for ruthenium complexes containing the Tp ligand.

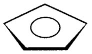
In recent work, we have shown that the complex [TpRuCl(dippe)] exhibits chemical reactivity towards small molecules similar in many aspects to that of the related half-sandwich derivatives $[(\eta^5\text{-}C_5H_5)RuCl(dippe)]$ and $[(\eta^5\text{-}C_5Me_5)RuCl(dippe)]$ [27]. Following our studies on the reactivity of these half-sandwich ruthenium complexes toward alkynes, we became interested in carrying a parallel study on the formally homologous TpRu system. Thus, we have shown that [TpRuCl(dippe)] reacts with terminal alkynes in MeOH in the presence of $NaBPh_4$ yielding vinylidene complexes $[TpRu{=}C{=}CHR(dippe)][BPh_4]$ [28]. When R = COOMe, the vinylidene derivative reacts further with MeOH furnishing the corresponding methoxy–carbene complex $[TpRu{=}C(OMe)CH_2COOMe(dippe)][BPh_4]$. The X-ray crystal structure of this compound was determined.

In the same way, chloride abstraction from two starting compounds [RuTp(tmeda)Cl] (tmeda = $Me_2NCH_2CH_2NMe_2$) and $[RuTp(py)_2Cl]$ (py = pyridine) using $NaBPh_4$, NH_4PF_6 or $TlCF_3SO_3$ in a weakly coordinating solvent allows the easy reaction with HC≡CPh yielding the corresponding cationic vinylidene complexes $[RuTp(tmeda)({=}C{=}CHPh)]^+$ and $[RuTp(py)({=}C{=}CHPh)]^+$ [29]. The reaction begins with the formation of the solvent adduct. In fact, when [RuTp(tmeda)Cl] is treated with $NaBPh_4$ in acetone, the cationic complex $[RuTp(tmeda)(\eta^1\text{-acetone})][BPh_4]$ was isolated and characterized. An analogous intermediate for the bis(pyridine) complex was not isolated.

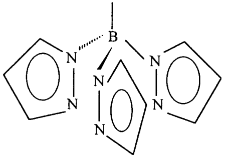
On the other hand, the anionic cobalt(III)-based oxygen tripod ligand L_{OEt} (I, $CpCo\{PO\text{–}(OEt)_2\}_3$), first introduced by Klaüi, has been employed as an oxygen donor analog for Cp (II, cyclopentadienyl) and Tp (III, hydrotris(pyrazol-yl)borate) [30], and as a model for the facially disposed triaqua moiety [31].



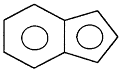
I



II

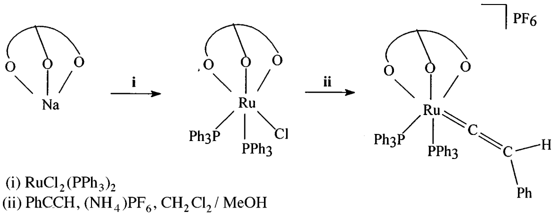


III



IV

The reaction of [Ru(PPh_3)$_2$$Cl_2$] with Na$L_{OEt}$ (L_{Oet}=CpCo{PO–$(OEt)_2$}$_3$) in thf afforded [L_{OEt}Ru(PPh_3)$_2$Cl] [32], isolated as air-stable orange crystals. This last complex reacts with $NaBPh_4$ or $(NH_4)PF_6$ in MeOH/thf resulting in yellow solutions of the cation [(L_{OEt})Ru(PPh_3)$_2$(MeOH)]$^+$ from which hygroscopic solids were isolated. If this reaction is made in CH_2Cl_2/MeOH in the presence of PhC≡CH and $(NH_4)PF_6$, the corresponding cationic vinylidene complex is obtained.

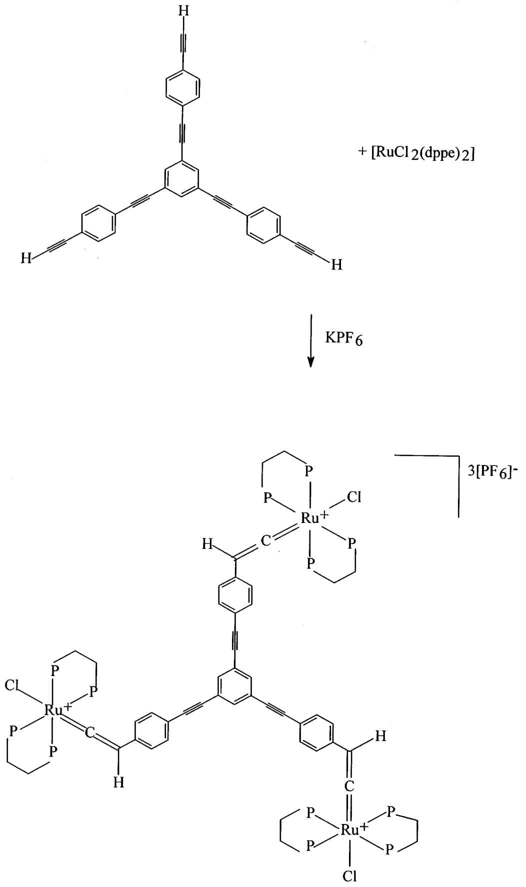


(i) $RuCl_2(PPh_3)_2$
(ii) PhCCH, $(NH_4)PF_6$, CH_2Cl_2 / MeOH

In recent years the potential utility of unsaturated carbenes for chemical transformation has been studied. In this regard, the possibility of enhancing the reactivity of carbene complexes by using (indenyl)–ruthenium moieties [Ru(η^5-C_9H_7)] as metal auxiliaries is particularly interesting [33]. Thus, Gimeno et al. [34] studied the reaction of [RuCl(η^5-C_9H_7)L_2] ($L_2 = 2$ PPh_3, 1,2-bis(diphenylphosphino)ethane (dppe) or 1,2-bis(diphenylphosphino)methane (dppm)) with $(NH_4)PF_6$ and HC≡C$SiMe_3$ in refluxing dichloromethane, giving the cationic unsubstituted vinylidene complexes [Ru(=C=CH_2)(η^5-C_9H_7)L_2]$^+$. The analogous reaction in refluxing methanol or ethanol with HC≡C$SiMe_3$ or HC≡CPh, yields the alkoxycarbene derivatives.

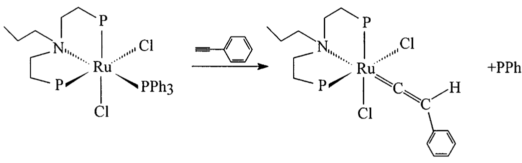
In general, the coordination of an acetylide anion to a transition metal center transfers the nucleophility from the Cα to the Cβ carbon atom. In this context, the addition of electrophiles to the Cβ of σ-alkynyl complexes [M]–C≡CR has been described as the most versatile entry into vinylidene complexes for a wide variety of systems. Fragment [M] can be [Ru(η^5-C_5R_5)L_2] (R = H, Me), [Ru(η^5-C_9H_7)L_2], [Ru{HB$(pz)_3$}L_2] (2 L = two monodentate phosphines or one diphosphine). Accordingly, the treatment of a group of acetylide-ruthenium indenyl complexes [Ru]–C≡CR (R = H, Ph, Bu^t, ^{n}Pr) with an excess of HBF_4·OEt_2 leads to the formation of the monosubstituted cationic vinylidene complexes [Ru{=C=C(H)R}(η^5-C_9H_7)L_2]$^+$ ($L_2 = 2PPh_3$) [34].

The activation of the tripodal polyyne 1,3,5-(HC≡CC_6H_4C≡C)$_3$$C_6H_3$ containing three terminal C≡CH functionalities was successfully attempted with the bulky 16-electron species [RuCl$(dppe)_2$][PF_6], generated in situ from [$RuCl_2$$(dppe)_2$] in the presence of KPF_6 at r.t., yielding a novel tris(vinylideneruthenium(II)) complex [35].



As indicated above, until recently most vinylidene complexes known were cationic. Usually they were obtained from a chloro complex precursor by ready dissociation of the halide, especially in polar solvents such as methanol. The studies carried out with complexes containing hemilabile ligands have shown that neutral vinylidene complexes could be formed by replacement of donor atoms more weakly attached to the ruthenium than chloride.

Bianchini et al. [36] reported that the complex *mer,trans*-[(PNP)Ru(Cl)$_2$(PPh$_3$)] (PNP = $CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$) reacts with phenylacetylene or *p*-tolylacetylene to give *fac,cis*-[(PNP)Ru(Cl)$_2$(=C=CHR)] (R = Ph or *p*-tolyl) in a mixture thf/EtOH (1:2 V:V).



In this way Jia et al. [37] studied the reaction of the coordinatively unsaturated complex [RuCl(PPh$_3$)(PCP)] (PCP = 2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$), a cyclometalated tridentate ligand with terminal acetylenes HC≡CPh. To their surprise, these reactions did not lead to the expected vinylidene but an unusual coupling product probably formed through an intermediate vinylidene complex.

The characteristic feature of phosphino-ethers, -amines and -esters is that they behave as hemilabile chelating units and even under mild conditions are able to create a free coordination site to which a reactive substrate can be added. When this substrate is a terminal alkyne it is possible to prepare a variety of neutral vinylidenemetal compounds with ruthenium(II) [11] and osmium(II) [38]. The dichloro-(dihydrido)osmium(IV) and dichloroosmium(II) compounds which contain the hemilabile chelating phosphino-ester ^{i}Pr$_2$PCH$_2$CO$_2$Me as ligand, both react with phenylacetylene to give the vinylideneosmium(II) derivative [OsCl$_2$-(=C=CHPh){κ^1(*P*)-^{i}Pr$_2$PCH$_2$CO$_2$Me}{κ^2-(*P*,*O*)-^{i}Pr$_2$PCH$_2$C(=O)OMe}] [38a]. However, the similar starting material [OsCl$_2$H$_2$(P^{i}Pr$_3$){κ^1(*P*)-^{i}Pr$_2$PCH$_2$CH$_2$NMe$_2$}] containing ^{i}Pr$_2$PCH$_2$CH$_2$NMe$_2$, reacts with phenylacetylene in refluxing benzene to lead the neutral vinylidene [OsCl$_2$(=C=CHPh)(P^{i}Pr$_3$){κ^2-(*P*,*N*)-^{i}Pr$_2$PCH$_2$CH$_2$-NMe$_2$}] for which the structure was determined by X-ray single crystal analysis [38b].

In the same way, Kirchner et al. [39] reported the preparation of the complex Ru{κ^2-(*P*,*N*)-Ph$_2$PCH$_2$CH$_2$NMe$_2$}$_2$Cl$_2$ in which the hemilabile nature of the Ph$_2$PCH$_2$CH$_2$NMe$_2$ ligand is revealed by the reaction with HC≡CPh in toluene at 80°C affording the neutral vinylidene complex [Ru(=C=CHPh)(Cl)$_2$. {κ^1(*P*)–Ph$_2$PCH$_2$CH$_2$NMe$_2$}{κ^2-(*P*,*N*)–Ph$_2$PCH$_2$CH$_2$NMe$_2$}]. On the contrary, halide abstraction from complex [RuCl$_2${κ^2-(*P*,*N*)–Ph$_2$PCH$_2$CH$_2$NMe$_2$}$_2$] in CH$_2$Cl$_2$ with NaBPh$_4$ affords the five-coordinate cationic complex [RuCl{κ^2-(*P*,*N*)–Ph$_2$PCH$_2$CH$_2$NMe$_2$}$_2$]$^+$, which reacts with HC≡CR (R = Ph, SiMe$_3$, ^{n}Bu) yielding the corresponding cationic *cis* (R = Ph) or *trans*-chlorovinylidene complex (R = SiMe$_3$ or ^{n}Bu), respectively.

The facile cleavage of one Ru–O bond in bis(ether–phosphine)ruthenium(II) complexes [Cl$_2$Ru(P$\frown$O)$_2$] (P$\frown$O represents the chelating bidentate ligands Ph$_2$PCH$_2$CH$_2$OCH$_3$, Ph$_2$PCH$_2$C$_4$H$_7$O$_2$ or Cy$_2$PCH$_2$CH$_2$OCH$_3$) allows reaction with HC≡CPh to give the neutral vinylidene complexes [Cl$_2$Ru(=C=CHPh)-(κ^1(*P*)–P–O)(P$\frown$O)] in which one hemilabile ligand is κ^1-coordinated [40]. The ease of Ru–O bond rupture depends on the O basicity, the donor strength of the phosphine, and the coordination abilities of incoming substrates.

The neutral vinylidene complex [(η^5-C$_5$H$_5$)RuCl(=C=CHCO$_2$Me)(PPh$_3$)] was obtained by stepwise treatment of the allyl complex [(η^5-C$_5$H$_5$)Ru(η^3-C$_3$H$_5$)(PPh$_3$)] with HC≡CCO$_2$Me and HCl in toluene/benzene [41].

Replacement of C$_5$H$_5$ by the bulky electron-releasing C$_5$Me$_5$ ligand makes the metal center more electron rich and the corresponding complexes more reactive towards 1-alkynes. The ruthenium–vinylidene complex [(η^5-C$_5$Me$_5$)Ru-(PPh$_3$)(Cl)(=C=CHPh)] was readily prepared following a literature procedure [42] from the ligand substitution reaction of [(η^5-C$_5$Me$_5$)Ru(PPh$_3$)$_2$Cl] [43] with PhC≡CH and a subsequent acetylene-to-vinylidene tautomerization reaction. Thus, treatment of [(η^5-C_5Me_5)Ru(PPh_3)$_2$Cl] with an excess of PhC≡CH in thf at 60°C for 12 h produced the vinylidene complex in a very good yield. The structure of [(η^5-C_5Me_5)Ru(PPh_3)(Cl)(=C=CHPh)] [44] was fully characterized by spectroscopic methods and X-ray crystal analysis. Very recently Bruce et al. [45] described the preparation of this neutral chlorovinylidene complex and other analogs using the reaction between the same starting material and HC≡CR (R = Bu^t, $SiMe_3$, Me) in refluxing benzene.

In developing the chemistry of the tris(pyrazolyl)borate (Tp) ligand, Kirchner [46] has recently described that the stirring of a thf solution of RuTp(PPh_3)$_2$Cl in the presence of HC≡CR for 36 h afforded dark-red crystals of the neutral vinylidene RuTp(PPh_3)(Cl)(=C=CHR) which is a good catalytic precursor for the dimerization of those 1-alkynes. The same authors [47] have recently shown that [Ru{HB(pz)$_3$}(PPh_3)Cl(dmf)] (pz = pyrazolyl, dmf = dimethylformamide) is a very useful precursor for the easy production of a variety of complexes of the type [Ru{HB(pz)$_3$}(PPh_3)Cl(=C=CHR)] (R = Ph, ^{n}Bu or $SiMe_3$) by displacement of the dmf by the vinylidene ligands. The method fails, however, when bulkier phosphines such as P(C_6H_{11})$_3$ or P^iPr_3 are used instead of PPh_3. The reason is that the corresponding complex [Ru{HB(pz)$_3$}{P(C_6H_{11})$_3$}Cl(dmf)] is extremely air-sensitive and, in addition, dmf is highly labilized obviously due both to the greater steric demand as well as the higher basicity of P(C_6H_{11})$_3$ relative to PPh_3. When [Ru{HB(pz)$_3$}{P(C_6H_{11})$_3$}Cl(dmf)] was obtained in situ and in the presence of an alcohol (MeOH or EtOH), the novel complexes [Ru{HB(pz)$_3$}{P(C_6H_{11})$_3$}Cl(OCH_2R)] (R = H or Me) were formed. These last complexes appear to be useful precursors for the vinylidene complexes [Ru{HB(pz)$_3$}{P(C_6H_{11})$_3$}Cl(=C=CHR)] (R = Ph, CO_2Et, $SiMe_3$, ^{n}Bu) [48]. In addition, on treatment of [Ru{HB(pz)$_3$}(PPh_3)Cl(=C=CHR)] with an excess of HC≡CR′ (R′ = $SiMe_3$, ^{n}Bu, Bu^t, CO_2Et or C_6H_9) the neutral vinylidene complexes [Ru{HB(pz)$_3$}(PPh_3)Cl(=C=CHR′)] were reversibly formed [47].

In relation to this, the treatment of [RuTp(κ^2(*P*,*N*)–$Ph_2PCH_2CH_2NMe_2$)Cl] in methanol with terminal alcetylenes HC≡CR (R = Ph, CH_2Ph, COOEt) led to simple chloride substitution giving the cationic vinylidene [RuTp(κ^2(*P*,*N*)–$Ph_2PCH_2CH_2NMe_2$)(=C=CHR)]$^+$ [49]. However, from this last starting material in refluxing toluene an unusual coupling reaction takes place with an excess of HC≡CR, to afford after 7 h, the novel complex [RuTpCl(κ^3(*P*,*C*,*C*)–Ph2PCH=CHC(R)=CH_2)] in high yields [50]. This is an insertion reaction of acetylene featuring C–H activation of the –(CH_2)$_2$– group with concomitant C–N bond cleavage. The difference in reactivity between the methanol and toluene solution may be sought in terms of the stabilization of the chloride anion in a polar solvent.

While the subject of transformation of a terminal alkyne into its vinylidene isomer promoted by a metal center has been widely addressed, the role that polyhydrides play in this transformation has scarcely been investigated.

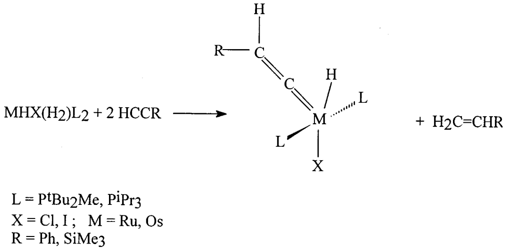
In this sense, it was recently found that the reaction of [OsH_2Cl_2(P^iPr_3)$_2$] with terminal alkynes HC≡CR leads to carbyne hydrido complexes [$OsHCl_2$(≡CCH_2R)(P^iPr_3)$_2$] [51]. To explain the unexpected formation of the carbyne ligand, the

$[Os(=C=CHR)(\eta^2\text{-}H_2)]$ species was postulated as an intermediate which then gives the isolated product by intramolecular hydrogen transfer.

On the other hand, Werner et al. [52] studied the reaction of $[RuH_2Cl_2(P^iPr_3)_2]$ with PhC≡CH in CH_2Cl_2 at 25°C to give a mixture of $[RuCl_2(=C=CHPh)(P^iPr_3)_2]$ (90% yield) and $[RuCl_2(=CHCH_2Ph)(P^iPr_3)_2]$ (10% yield).

In relation to this, $[RuHCl(H_2)L_2](L = P^iPr_3$ or $PCy_3)$ reacts with ethyne or phenylacetylene in the absence of the phosphonium chlorhydrate yielding the hydrido vinylidene complexes $[RuHCl(=C=CHR)L_2]$ (R = H, Ph) [53].

Caulton et al. [54] recently found that the complexes $RuHX(H_2)L_2$ (X = Cl, I; $L = P^tBu_2Me$) and OsH_3ClL_2 ($L = P^iPr_3$) react (time of mixing) with terminal alkynes in a 1:2 stoichiometry to give MHX $(=C=HR)L_2$. With PhC≡CD the ruthenium complex leads to $RuDX(=C=CHPh)L_2$ as the only isotopomer. This result is understood in terms of an insertion of the alkyne in the Ru–H bond to make a vinyl, followed by an α-hydrogen migration, giving the hydrido-vinylidene. The reaction is calculated to be exotermic from starting compounds to intermediates and products with no large activation energy along path: noticeably, the transformation of the 14 e^- vinylspecies to 16 e^- hydrido/vinylidene complex occurs with almost no activation energy.



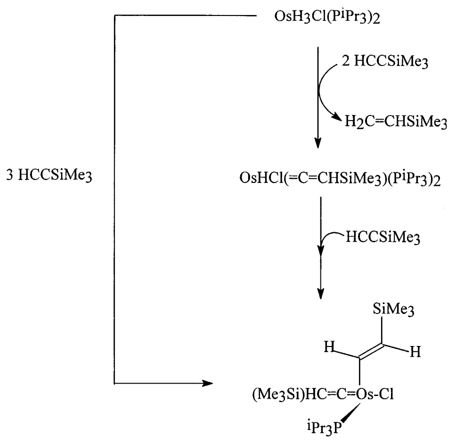
The initial loss of 2H from RuH_3XL_2, which is already unsaturated, represents a conceptual advance by providing a 14-electron equivalent, '$RuHXL_2$', for reacting with substrate.

$$\text{`RuH'} + HCCPh \rightarrow \underset{\textstyle A}{H_2RuRuCC{\equiv}CPh} \rightarrow HRu{=}C{=}CHPh$$

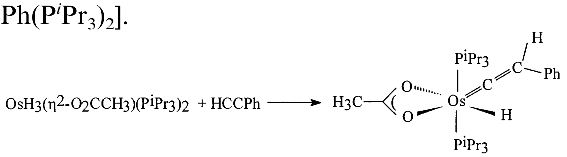
In contrast, Esteruelas et al. [55] found that the reaction of $[OsDCl(CO)(P^iPr_3)_2]$ with HC≡CCy gives a mixture of $[OsHCl(=C=CDCy)(CO)(P^iPr_3)_2]$ and $[OsDCl(=C=CHCy)(CO)(P^iPr_3)_2]$, implicating an intermediate analogous to A.

Similarly, combining $[OsH_3Cl(P^iPr_3)_2]$ and Me_3SiCCH at −80°C in toluene-d_8 shows no intermediates but forms $[OsHCl[CCH(SiMe_3)](P^iPr_3)_2]$.

In addition, trimethylsilylacetylene inserts in the Os–H bond of $[OsHCl(=C=CHSiMe_3)(P^iPr_3)_2]$ giving the vinyl–vinylidene complex $[OsCl\{(E)\text{-}CH=CHSiMe_3\}(=C=CHSiMe_3)(P^iPr_3)_2]$. Alternatively, this compound can be prepared by reaction of $[OsH_3Cl(P^iPr_3)_2]$ with $HC{\equiv}CSiMe_3$ in molar ratio 1:3 [56].

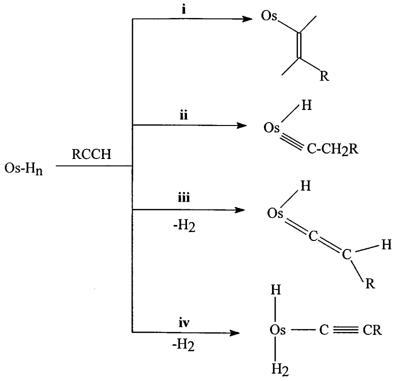


Esteruelas [57] showed that the complex $[OsH_3(\eta^2\text{-}O_2CCH_3)(P^iPr_3)_2]$, prepared by reaction of $[OsH_2Cl_2(P^iPr_3)_2]$ and $K(O_2CCH_3)$ in MeOH, reacts with PhC_2H in toluene at r.t. to give, after 5 h the hydride–vinylidene compound $[OsH(\eta^2\text{-}O_2CCH_3)(=C=CHPh(P^iPr_3)_2]$.



Bianchini et al. [58] then observed, that the complex $[(PP_3)OsH(N_2)][BPh_4]$ ($PP_3 = P(CH_2CH_2Ph_2)_3$) catalyzes the dimerization of terminal alkynes to disubstituted but-3-en-1-ynes. Interestingly, at 0°C, this complex reacts with a stoichiometric amount of (trimethylsilyl)acetylene to give a mixture of the cationic compounds $[(PP_3)OsH(=C=CHSiMe_3)][BPh_4]$ and (*E*)-$[(PP_3)Os\{\eta^3\text{-}(SiMe_3)C_3=CH\text{-}(SiMe_3)\}]$-$[BPh_4]$.

The reactions of osmium hydride complexes with terminal alkynes allow the preparation of specific organometallic compounds, if the nature and number of hydride ligands and the electronic properties of the starting complexes are appropriately selected [59–62].



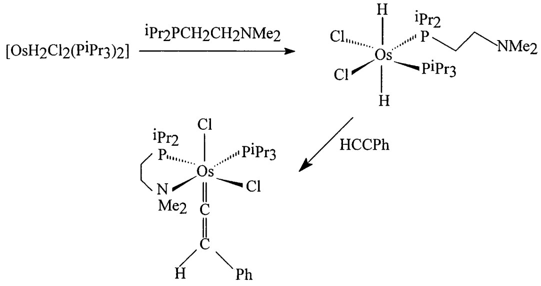
(i) $OsHCl(CO)(P^iPr_3)_2$; (ii) $OsH_2Cl_2(P^iPr_3)_2$;
(iii) $OsH_3(\eta^2\text{-}O_2C{=}CH_3)(P^iPr_3)_2$; (iv) $OsH_4(CO)(P^iPr_3)_2$

In addition, the relation between the species summarized in the above scheme are well known:

$$\underset{\text{carbyne}}{M{\equiv}C{-}CH_2R} \xrightarrow{-H^+} \underset{\text{vinylidene}}{M{=}C{=}CHR} \xrightarrow{-H^+} \underset{\text{alkynyl}}{M{-}C{\equiv}CR}$$

In the same way [63], the complex [OsHCl(CO)(P^{i}Pr$_3$)$_2$] reacts with cyclohexylacetylene to give [OsHCl(=C=CHCy)(CO)(P^{i}Pr$_3$)$_2$], which evolves in solution to [OsCl{(*E*)–CH=CHCy}(CO)(P^{i}Pr$_3$)$_2$]. The reaction of [OsDCl(CO)(P^{i}Pr$_3$)$_2$] with cyclohexylacetylene leads to a mixture of [OsDCl(=C=CHCy)(CO)(P^{i}Pr$_3$)$_2$] and [OsHCl(=C=CDCy)(CO)(P^{i}Pr$_3$)$_2$] in ca. 1:1 molar ratio, indicating that the formation of the vinylidene complex involves a 1,3-hydrogen shift via an alkynyl intermediate.

The reaction of [OsH$_2$Cl$_2$(P^{i}Pr$_3$)$_2$] with the hemilabile phosphine ^{i}Pr$_2$PCH$_2$CH$_2$NMe$_2$ gives the dichloro–dihydrido osmium(IV) complex which reacts with HC≡CPh yielding a vinylidene osmium(II) compound [38b].



Very recently it has been proven that [Os(η^5-C$_5$H$_5$)(Cl)(P^{i}Pr$_3$)$_2$] is obtained by treatment of a toluene solution of OsH$_2$Cl$_2$(P^{i}Pr$_3$)$_2$ with cyclopentadienylthallium in a 1:1 molar ratio for 2 h, and is a very good starting material to prepare carbene complexes. The compound [Os(η^5-C$_5$H$_5$)(Cl)(P^{i}Pr$_3$)$_2$] shows a tendency to release a triisopropylphosphine ligand and, in agreement with that, reacts towards alkynols to lead the π-alkyne which evolves to the corresponding alkynylvinylidene derivatives by loss of a water molecule in toluene at 85°C [64].

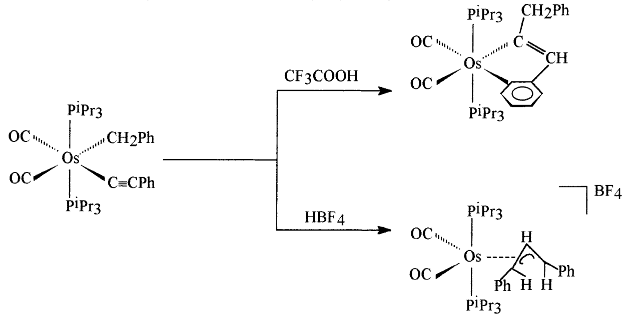
The behaviour of [Os(η^5-C$_5$H$_5$)(Cl)(P^{i}Pr$_3$)$_2$] towards 1-ethynyl-1-cyclohexanol and 2-methyl-3-butyn-2-ol agrees well with that previously observed for the carbonyl complex Os(η^5-C$_5$H$_5$)Cl(CO)(P^{i}Pr$_3$), which reacts with 1-ethynyl-1-cyclohexanol in the presence of AgBF$_4$ to give [Os(η^5-C$_5$H$_5$){=C=CH–C=CH(CH$_2$)$_3$CH$_2$}(CO)(P^{i}Pr$_3$)][BF$_4$] [65]. The formation of these alkenylvinylidene compounds most probably involves hydroxyvinylidene intermediates which spontaneously dehydrate. The dehydration of hydroxyvinylidenes, containing hydrogen atoms adjacent to the hydroxy group, can occur in two different directions to afford either alkenylvinylidene or allenylidene derivatives, mainly, depending on the electronic properties of the metallic center. Thus, Dixneuf has observed that in the presence of NH$_4$PF$_6$/MeOH, the reactions of [RuCl$_2$(η^6-C$_6$H$_6$)(PMe$_3$)] with 1,1-dimethyl-2-propyn-1-ol and 1-ethy-nyl-1-cyclohexanol lead to α,β-unsaturated methoxycarbene compounds, via allenylidene intermediates [66]. In the same sense, Esteruelas recently reported that the solvato complex [Ru(η^5-C$_5$H$_5$){η^1-OC(CH$_3$)$_2$}(CO)(P^{i}Pr$_3$)][BF$_4$] reacts with 1-ethynyl-1-cyclohexanol to give the hydroxycarbene complex $[Ru(\eta^5\text{-}C_5H_5)\{C(OH)CH{=}\overline{C(CH_2)_4CH_2}\}(CO)(P^iPr_3)]$ $[BF_4]$ [67].

In contrast to these systems, the electron-rich fragment $[Ru(\eta^5\text{-}C_5H_5)(PMe_3)_2]^+$ [68] preferentially affords alkenylvinylidene derivatives. The formation of $[Os(\eta^5\text{-}C_5H_5)\{{=}C{=}CH\text{–}\overline{C{=}CH(CH_2)_3CH_2}\}(CO)(P^iPr_3)][BF_4]$ and $[Os(\eta^5\text{-}C_5H_5)Cl\ \{{=}C{=}CH\text{–}C(CH_3){=}CH_2\}(P^iPr_3)]$ from $[Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2]$ is in agreement with the strong base character of the $[Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)]$ moiety, which could be a consequence of both the high basicity of the phosphine and the large π-donor power of the chlorine. Furthermore, osmium shows an intrinsically higher basicity than ruthenium [69].

The π-alkyne complexes $[Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HCC\text{–}\overline{C(OH)(CH_2)_4CH_2}\}(P^iPr_3)]$ and $[Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HCC\text{–}C(OH)(CH_3)_2\}(P^iPr_3)]$ were isolated as brown solids. Complex $[Os(\eta^5\text{-}C_5H_5)Cl\{{=}C{=}CH\text{–}C(CH_3){=}CH_2\}(P^iPr_3)]$ can also be prepared by reaction of $[Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2]$ with 2-methyl-1-buten-3-yne at r.t., in this case the π-alkyne intermediate was not detected but it was detected in the case of phenylacetylene. The above mentioned observations suggest that for 2-methyl-1-buten-3-yne and phenylacetylene the isomerization π-alkyne-vinylidene is faster than the substitution of the phosphine by the alkyne. However, for the alkynols, the replacement of the phosphine is favored. This could be a result of the presence of an OH group on the alkyne ligand, which should increase the stability of the π-alkyne intermediate.

Similarly, the reaction of $[Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2]$ with $HC{\equiv}CPh$ in pentane leads to the neutral vinylidene complex [63] also via the π-alkyne intermediate, but no spectroscopic evidence was found of the participation of a hydrido(alkynyl), related to those reported by us [18,19].

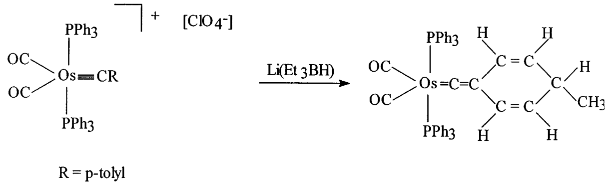
Although the protonation of alkyne complexes is a general method to obtain vinylidene complexes, this method does not always produce a stable vinylidene complex. In this sense [63], in methanol under reflux and in the presence of cat-alytic amounts of trifluoroacetic acid, the alkynyl benzyl complex $[Os(CH_2Ph)(C{\equiv}CPh)(CO)_2(P^iPr_3)_2]$ isomerizes into the osmaindene derivative $[\overline{Os\{C(CH_2Ph){=}CHC_6H_4}\}(CO)_2(P^iPr_3)_2]$. However, when the same starting alkynyl complex reacts with HBF_4 this leads to a mixture of the aforementioned osmaindene complex and the π-allyl complex $[Os\{\eta^3\text{-}CH(Ph)(CHCHPh)\}(CO)_2\text{-}(P^iPr_3)_2][BF_4]$, which results from the addition of the proton from the acid and the C–C coupling of the benzyl and the alkynyl ligands.



On the basis of isotope labeling experiments, the mechanism of such a transformation is discussed.

The deprotonation of carbyne complexes can also be used in some cases for the synthesis of vinylidene complexes. Thus, Esteruelas et al. [70] have shown that the treatment of the hydrido–carbyne complex with stronger bases that the Cβ carbon atom of a vinylidene group may afford five-coordinate hydrido–vinylidene complexes $[OsHCl(=C=CHR)(P^iPr_3)_2]$. The treatment at r.t. of a tetrahydrofuran solution of the hydrido–carbyne complex $[OsHCl(\equiv CCH_2Ph)(P^iPr_3)_2]$ with sodium methoxide in a 1:1 molar ratio for 15 min gives, after solvent removal, a sticky residue. Pentane extraction of the residue and filtration to remove NaCl affords a green solution, from which the five-coordinate hydrido–vinylidene complex $[OsHCl(=C=CHPh)(P^iPr_3)_2]$ was isolated as a green solid in 82% yield. The starting carbyne complex was previously obtained by reaction of Meyer's compounds $[OsH_2Cl_2(P^iPr_3)_2]$ with terminal alkynes $HC\equiv CR$.

Previously, an unusual neutral vinylidene complex was prepared from hydride addition to the aromatic ring of the tolyl–carbyne ligand in a cationic osmium carbyne complex [71], The cationic osmium carbyne complex $[Os(CR)(CO)_2(PPh_3)_2]^+$ (R = *p*-tolyl) reacts with $Li(Et_3BH)$ with hydride addition to the *para*-position of the aromatic ring of the carbyne ligand giving an unusual vinylidene complex characterized by NMR spectroscopy and X-ray single crystal structure determination.



3. Structure and bonding

3.1. Main features in the spectral characterization of vinylidenes

The IR spectra of vinylidene complexes contain a medium to strong band ranging between 1650 and 1600 cm^{-1} which is typical for the stretching frequencies of the C=C group.

In the NMR spectra, the quaternary α-carbon atoms of the M=C=C (M = Ru, Os) moiety in the vinylidene complexes resonate at much lower field ($350 \leq \delta \leq 390$ ppm) than the β-carbon atoms (ca. 90–100 ppm) [1a]. The large deshielding of the vinylidene Cα carbon resonance, which is a consequence of its electron-deficient character, was interpreted by Czech et al. [72] as being due to changes in the paramegnetic contribution, σ_p, to the nuclear shielding. However, in most of the osmium vinylidene complexes the chemical shift for the Cα carbon atom is observed even below 300 (280–300 ppm) [38a,55,57,64,73]. The Cβ chemical shift in vinylidene complexes containing hemilabile amino-phosphine or ether-phosphine ligands lies in the range 110–120 ppm. [5,21,39].

On the other hand, the ^{1}H spectra of vinylidene complexes show signals between 2 and 5 ppm corresponding to the H bonded to C_β. It is significant that this proton in the complexes *trans*-[Ru(C=CHR)(dppe)$_2$(Cl)][PF$_6$] [3] is clearly at high field (2.15–3.5 ppm) compared with other ruthenium vinylidene derivatives with the same R group. On the other hand, with R = Ph, δ(Ru=C=C*H*) = 5.66 ppm in [Ru(C=CHPh)(η^6-C$_6$Me$_6$)(PMe$_3$)(Cl)][PF$_6$] [74], 5.42 ppm in [Ru(C=CHPh)(η^5-C$_5$Me$_5$)(PMe$_2$Ph)$_2$][PF$_6$] [14], or 5.22 ppm in [Ru(C=CHPh)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] [34]. This high-field shift is likely due to the presence of four phenyl groups neighbouring the vinylidene ligand as found in the analogous [Ru(C=CHPh)-(dppm)$_2$(Cl)][PF$_6$] (δ = 3.05 ppm) [12b]. In the case of the tris-(vinylidene) complex recently reported by Dixneuf [35] this signal appears at 3.75 ppm (br. s, 3H, 3 × Ru=C=C*H*).

A similar effect can be observed in neutral vinylidene complexes *fac*,*cis*-(PNP)RuCl$_2${C=CH(R)}(R = Ph, *p*-tolyl) and *mer*,*trans*-(PNP)RuCl$_2${C=CH(R)}. The vinylidene hydrogens in the *mer*,*trans* compound are shifted upfield by ca. 1.6 ppm compared to those in the *fac*,*cis* isomers, probably because of the larger shielding effect provided by the phenyl rings of the mutually PPh$_2$ groups [36b].

3.2. Crystal structure and bonding

Until the beginning of this decade few crystal structures of ruthenium and osmium (or even any transition metal) vinylidene complexes had been reported [1a]. Indeed, the primary metal vinylidene fragment M=C=CH$_2$ still remained uncharacterized. However, in a few years the number of predominant ruthenium and osmium vinylidene complex structures has increased four or five times. The first structural characterization of a complex containing the M=C=CH$_2$ moiety was reported for [Ru(C=CH$_2$)(PMe$_2$Ph)$_2$(η^5-C$_5$H$_5$)][BF$_4$] by Lomprey and Selegue [9]. There are still only a few structurally characterized M=C=CH$_2$ complexes.

The bond lengths and angles of most of the hitherto known mononuclear vinylidene complexes of ruthenium and osmium are listed in Table 1.

For comparison the theoretically optimized structure of [Ru(C=CH$_2$)HCl(PH$_3$)$_2$] considering C_s symmetry is also included [54]. The M=C=C linkage is essentially linear in all cases, the measured angle ranging from 180 to 161°.

In Bruce's review [1a] on the organometallic chemistry of vinylidene and related unsaturated carbenes it is noted that the metal–carbon bond length in mononuclear vinylidene complexes is consistent with a bond order of about 2 and the C=C bond corresponds to an order between 2 and 3, as predicted by theory.

A short M=C bond distance is likely to result from the electron-releasing capability of the [LM] moiety toward the electron-withdrawing vinylidene ligand. This M=C bond distance and other characteristics of the vinylidene ligand are very similar for ruthenium and osmium complexes (see Table 1). A theoretical study of the vinylidene complex revealed localization of electron density on $C\beta$ (HOMO) or the M=C double bond and electron deficiency at $C\alpha$ [88,89]. Thus, the M=C double

Table 1
Structures of mononuclear ruthenium and osmium vinylidene complexes [a]

Compound	M=C	=C=C	M=C=C	Ref.
[Ru(C=CH$_2$)(PMe$_2$Ph)$_2$(η^5-C$_5$H$_5$)][BF$_4$]	1.843(10)	1.287(13)	174.1(8)	[9]
[Ru(C=CMePh)(PPh$_3$)$_2$(η^5-C$_5$H$_5$)]I	1.86(1)	1.29(2)	173	[75]
[Ru(C=CPhI)(PPh$_3$)$_2$(η^5-C$_5$H$_5$)][I$_3$]	1.839(7)	1.31(1)	171.0(7)	[76]
[Ru{C=CBr(*p*-C$_6$H$_4$Br)}(PPh$_3$)$_2$(η^5-C$_5$H$_5$)][Br$_3$]	1.85(1)	1.31(2)	169.4(14)	[76]
[Ru{C=CPh(3,4-N$_2$C$_6$H$_3$Me$_2$)}(PPh$_3$)$_2$(η^5-C$_5$H$_5$)][BF$_4$]	1.823(9)	1.34(1)	169.9(7)	[77]
[Ru{C=CPh(C$_7$H$_7$)}(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(η^5-C$_5$H$_5$)][PF$_6$]	1.848(9)	1.32(1)	174.9(6)	[77a,78]
[Ru(C=CHPh)(Ph$_2$PCHMeCH$_2$PPh$_2$)(η^5-C$_5$H$_5$)][PF$_6$]	1.84(1)	1.25(1)	175(1)	[79]
[Ru(C=CHMe)(PMe$_3$)$_2$(η^5-C$_5$H$_5$)][PF$_6$]	1.845(7)	1.313(1)	180(2)	[80]
[Ru{C=CHC=CHCH$_2$(CH$_2$)$_2$CH$_2$}(PMe$_3$)$_2$(η^5-C$_5$H$_5$)][PF$_6$]	1.843(7)	1.30(1)	178.2	[68c]
[Ru(C=CHPh)(PPh$_3$)$_2${(η^5-C$_5$H$_5$)Co{P(O)(OEt)$_2$}$_3$}][PF$_6$]	1.80(2)		173(1)	[32]
[Ru(C=CH$_2$)(PPh$_3$)$_2$(η^5-C$_5$Me$_5$)][PF$_6$]	1.843(5)	1.297(8)	172.2(5)	[15]
[Ru(C=CHCO$_2$Me)(^{i}Pr$_2$PCH$_2$CH$_2$P^{i}Pr$_2$)(η^5-C$_5$Me$_5$)][BPh$_4$]	1.807(9)	1.32(1)	170.5(8)	[19]
[Ru(C=CH$_2$)HCl(PH$_3$)$_2$] calc. DFT/B3LYP	1.820	1.317	174.8	[54]
[Ru(C=CHPh)(PMe$_2$Ph)$_2$(η^5-C$_5$Me$_5$)][PF$_6$]	1.76(1)	1.34(2)	174(1)	[14]
[Ru(C=CHCH(Me)OMe)(PMe$_2$Ph)$_2$(η^5-C$_5$Me$_5$)][PF$_6$]	1.854(8)	1.29(1)	174.6(7)	[14]
[Ru(C=CHPh){κ^2(*P*,*N*)-Ph$_2$PCH$_2$CH$_2$NMe$_2$}(η^5-C$_5$Me$_5$)]-[CF$_3$SO$_3$]	1.81(2)	1.33(2)	173(1)	[22]
[Ru(C=CMe$_2$)(PPh$_3$)$_2$(η^5-C$_9$H$_7$)][CF$_3$SO$_3$]·1/2CH$_2$Cl$_2$	1.839(7)	1.30(1)	173.7(6)	[34]
[Ru{C=C(Me)C=CCHCH$_2$(CH$_2$)$_2$CH$_2$}(PPh$_3$)$_2$(η^5-C$_9$H$_7$)]-[CF$_3$SO$_3$]	1.838(5)	1.299(6)	176.2(4)	[81]
[Ru(C=CH$_2$)(Ph$_2$PCH$_2$PPh$_2$)$_2$Cl][PF$_6$]	1.882(8)	1.22(1)	178.3(8)	[12b]
[Ru(C=CHPh){HB(pz)$_3$}{κ^2(*P*,*N*)-Ph$_2$PCH$_2$CH$_2$NMe$_2$}]-[CF$_3$SO$_3$]·CH$_2$Cl$_2$	1.821(5)	1.287(2)	169.6(4)	[49]
[Ru(C=CHPh){HB(pz)$_3$}(Me$_2$NCH$_2$CH$_2$NMe$_2$)][BPh$_4$]-·CH$_2$Cl$_2$	1.820(5)	1.305(6)	173.5(4)	[82]
[Ru(C=CHPh){κ^2(*P*,*O*)-^{i}Pr$_2$PCH$_2$CH$_2$OMe}$_2$Cl][O$_3$SCF$_3$]	1.790(3)	1.313(5)	170.9(3)	[5]
[Ru(C=CMePh){P(OEt$_3$)}$_4$(C≡CPh)][CF$_3$SO$_3$]	1.898(7)	1.323(11)	174.9(7)	[83]
[Ru{C=CPhCH(CN)C(CN)$_2$(C$_6$H$_4$)C(CN)$_2$}(PPh$_3$)$_2$-(η^5-C$_5$H$_5$)] zwitterionic	1.811(10)	1.328(14)	173.7(8)	[84]
[Ru(C=CHPhC(SH) = NPh){P(O)(OMe)$_2$}(PPh$_3$)(η^5-C$_5$H$_5$)]	1.799(6)	1.336(8)	175.2(5)	[85]
[Ru(C=CHPh)Cl(PPh$_3$)(η^5-C$_5$Me$_5$)]	1.817(3)	1.315(4)	175.3(3)	[44]
[Ru(C=CHPh)Cl(PPh$_3$)(η^5-C$_5$Me$_5$)]	1.80(1)	1.29(2)	176(1)	[45]
[Ru(C=CH(SiMe$_3$))Cl(PPh$_3$)(η^5-C$_5$Me$_5$)] two independent molecules are described	1.83(1)	1.31(2)	176(1)	[45]
	1.85(2)	1.29(2)	173(1)	
[Ru(C=CHPh)Cl(PPh$_3$)(η^5-C$_5$Me$_5$)]	1.80(1)	1.40(2)	176(1)	[86]
[Ru(C=CHPh){HB(pz)$_3$}Cl(PPh$_3$)]	1.801(4)	1.315(6)	177.2(3)	[46]
[Ru(C=CH^{t}Bu)(Br)$_2$(PPh$_3$)$_2$]	1.768(17)	1.36(3)	161(2)	[87]
[Ru(C=CHPh){κ^2(*P*,*O*)-^{i}Pr$_2$PCH$_2$CH$_2$OMe}$_2$(Cl)$_2$]	1.749(1)	1.34(1)	176.6(7)	[11a]
[Ru(C=CHPh){κ^2(*P*,*O*)-Ph$_2$PCH$_2$CH$_2$OMe}-{κ^1(*P*)-Ph$_2$PCH$_2$CH$_2$OMe}Cl$_2$]	1.815(2)	1.319(3)	178.6(14)	[21]
[Ru(C=CHPh){κ^2(*P*,*O*)-Cy$_2$PCH$_2$CH$_2$OMe}-{κ^1(*P*)-Cy$_2$PCH$_2$CH$_2$OMe}Cl$_2$]	1.780(3)	1.326	178.0(2)	[21]
[Os(C=CH^{t}Bu)(CO)(PPh$_3$)(η^5-C$_5$Me$_5$)][BF$_4$]	1.879(6)	1.28(1)	175.0(5)	[20]
[Os(C=CHPh){κ^2(*P*,*N*)-^{i}Pr$_2$PCH$_2$CH$_2$NMe$_2$}Cl$_2$(P^{i}Pr$_3$)]	1.82(1)	1.31(2)	177(1)	[38b]
[Os(C=CCH=CHC(Me)HCH=CH)(CO)$_2$(PPh$_3$)$_2$]	1.90(1)	1.33(1)	169(3)	[71]

[a] Bond lengths (Å) and angles (°) with E.S.D. values in parentheses.

bond and the Cβ atom are more susceptible to electrophilic attack whereas the Cα carbon atom is prone to nucleophilic attack [51,59]. Hence the reactions of such compounds containing electron-rich metals with electrophiles lead to formation of carbene complexes [90].

A very short C=C distance in the vinylidene fragment has been interpreted in terms of a partial sp character of the Cβ carbon [2]. A carbon–carbon double bond of the vinylidene ligand of 1.337(9) Å [85] is considered typical for a C(sp^2)–C(sp) allene bond [91].

Particular attention has been given to the orientation of the vinylidene ligand in relation to the basal plane in the complex. Although the plane of the vinylidene is predicted to be perpendicular to the molecular plane in complexes of the type $M(CCR_2)(L)_2(\eta^5\text{-}C_5H_5)$ [92] the barrier to rotation is computed to be only ca. 15 kJ mol^{-1}, so that this preference is often overridden by steric effects.

In $[(\eta^5\text{-}C_5H_5)Ru(PR_3)_2(=C=CR^1R^2)]^+$ cations, the vinylidene plane is usually orthogonal to the plane bisecting the P(1)–Ru–P(2) angle [26b]. In $[Ru(C=CHCH(Me)OMe)(PMe_2Ph)_2(\eta^5\text{-}C_5Me_5)]^+$ [14] the ruthenium–vinylidene plane makes an angle of 73.1(4)° with the plane bisecting the P(1)–Ru–P(2) plane. This distortion can be explained by the relatively weak rotation barrier around a (vinylidene)–Cα =Ru bond in these complexes, the influence of steric factors like the interaction of the OMe group with the C_5Me_5 methyl groups.

The structure of the model $[Ru(C=CH_2)HCl(PH_3)_2]$ was optimized in C_s symmetry with ab initio DFT/B3LYP using the Gaussian 94 package [54]. A distorted trigonal bipyramid with apical phosphines and inequivalent angles within the Y-shaped equatorial plane was obtained, with H–Ru–Cl = 128.7° and H–Ru–C = 84°. This Y structure is, thus, typical of d^6 ML_5 species with one π-donor ligand. In this case a π-acceptor ligand is also present and the square pyramidal geometry could be favored but the preference for a Y structure originates from neutral vinylidene which is a potent π acceptor in the CH_2 plane and a weak π donor in the orthogonal plane. The donating property of π_{cc} does not favor a *trans* relationship of Ru–Cl and vinylidene since this maximizes the overlap between the occupied orbitals of the metal (d) and the two ligands (π_{cc} and p_{Cl}). The rotation of CH_2 by 90° costs 4.6 kcal mol^{-1} in the absence of any steric effect.

Significant deviations of the angles from the ideal sp^2 hybridization at the Cβ carbon atom in $[Ru(C=CMe_2)(PPh_3)_2(\eta^5\text{-}C_9H_7)]^+$ have been observed [34]. The vinylidene ligand also deviates significantly from planarity. The indenyl group is η^5-bonded to ruthenium with a distance between the metal atom and the centroid of the five-membered ring C* of 1.97(9) Å. The preferred conformation of the indenyl ligand is such that the benzo ring is oriented *trans* to the vinylidene group. CA (conformational angle) is defined as the dihedral angle between the plane C** (centroid of the benzo ring), C*; Ru and the plane C*, Ru, Cα (of the vinylidene ligand). According to Extended Hückel Molecular Orbital calculations the '*trans*' orientation (CA = 0°) is energetically more favored than the '*cis*' orientation (CA = 180°) by 7 kcal mol^{-1}. Based on the distortion parameters and Ru–indenyl distances determined by X-ray diffraction the calculations showed that minimum energies are obtained for CA not exactly equal to 0° (the chain Ru=C=C of the vinylidene group lying out of the C**, C*, Ru plane). The LUMO is a π-antibonding combination between the p_z orbital of Cα of the vinylidene group (30% of the contribution) and a hybrid orbital (25%) involving $d_{x^2-y^2}$, d_{z^2} and d_{xz}. The HOMO is a combination of the orbitals p_y of Cβ (20%), p_y of Cα (5%), d_{xy} (37%) and one p_z orbital of the five-membered ring of the indenyl group (3%). The low barrier (ca. 3 kcal mol^{-1}) between the different conformers of the complex for the values of CA = ± 10.7° allows the chemical equivalence of the phosphorus atoms in solution, as shown by $^{31}P\{^1H\}$NMR spectra at r.t.

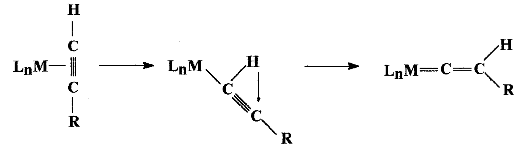
A similar study has been carried out on the complex $[Ru\{C{=}C(Me)\text{-}C{=}CCHCH_2(CH_2)_2CH_2\}(PPh_3)_2(\eta^5\text{-}C_9H_7)]^+$ [93]. Although the indenyl group is η^5-bonded to ruthenium this structure shows moderate distortions of the five-carbon ring from planarity, which is similar to those shown by analogous vinylidene derivatives. The moderate distortion toward a η^3 binding mode in the solid state appear to be maintained in solution, according to the $^{13}C\{^1H\}$ NMR spectra. As also observed in other indenyl vinylidene complexes the preferred conformation of the indenyl ligand is such that the benzo ring is oriented *trans* to the vinylidene group.

From the molecular orbital studies the different stabilities of the vinylidene and acetylene complexes are due to changes in both the σ and π-bonding interactions. The nature of the bonding between a metal center and the vinylidene ligand can not be understood adequately without distinguishing two types of π interactions, viz. d_{xz} (metal)-π (vinylidene) and d_{yz} (metal)-*p*(vinylidene) back bonding, where the latter turns out to be essential to the stability of the vinylidene complex. If this contribution is small, reconversion of a vinylidene complex into an η^2-alkyne complex can be accomplished. This is effected in either of two ways: (a) destabilization of the d_{yz} orbital by the presence of halide in *cis* position, and (b) weak π donor strength of the metal fragment by using strong π-acceptor (or weak π-donor) coligands [47]. The coligands have a dramatic effect on the vinylidene complex stability. Thus, the binding tendency of the $[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)]^+$ or $[Ru\{HB(pz)_3\}(Me_2NCH_2CH_2NMe_2)]^+$ fragments to a sixth ligand was found to increase in the order phosphines ≈ amines < CO ≤ vinylidene [49]. However, the presence of chloride in a basal position of the fragment $[Ru\{HB(pz)_3\}Cl(PPh_3)]$ reverses the stability order according to dmf < PPh_3 ≈ vinylidene < CO with the consequence that vinylidene becomes easily replaceable by acetylenes or even phosphines. The chloride produces a destabilization of the d_{yz}(Ru)–*p*(vinylidene) interaction with a subsequent increase in the C=C bond length due to an unusual effect of back bonding [47].

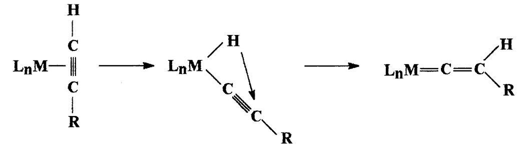
4. Isomerization of alkyne to vinylidene complexes

The formation of vinylidene from free acetylene is strongly endothermic and is observed only under special conditions [94,95]. However, the transformation occurs in the coordination sphere of transition metal complexes and many of these stabilize vinylidene moieties [1a,96]. This phenomenon may be relevant to a number of transition metal catalyzed reactions of alkynes. There are a few theoretical analyses to study this isomerization on [Mn(η^5-C_5H_5)$(CO)_2$(HC≡CH)] [97], [$RuCl_2(PH_3)_2$(HC≡CH)] [87], or [$RhCl(PH_3)_2$(HC≡CH)] [98] systems.

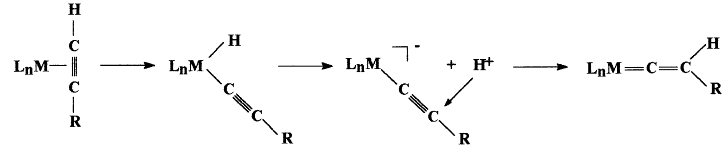
It was initially suggested that oxidative addition of the alkyne to give a hydrido–alkynyl metal complex could be a feasible pathway for the formation of the corresponding vinylidene complex, via a concerted 1,3-hydrogen shift of the hydride from the metal to the β-carbon atom of the alkynyl ligand [99]. Extended Hückel calculations on the d^6 metal complex [Mn(η^5-C_5H_5)$(CO)_2$(η^2-HC≡CH)] [97] showed that the concerted 1,3-hydrogen shift in the intermediate hydrido–alkynyl complex [(η^5-C_5H_5)Mn(H)$(CO)_2$(C≡CH)] would have a very high activation energy, and a direct 1,2-hydrogen shift in the former complex seems more plausible.



1,2-hydrogen migration



1,3-hydrogen migration



Dissociative pathway

The process from a hydrido alkynyl to a vinylidene complex can be intramolecular as the 1,3-hydrogen migration above showed or can involve a dissociative two-step process: elimination/addition. The first step consists of the dissociation of proton and the second is the protonation of the alkynyl resulting intermediate.

Bullock [8] reported the first organometallic system [(C_5H_5)$(PMe_3)_2$RuCl] able to produce the conversion of a free alkyne through isolable η^2-alkyne and metal vinylidene complex, and then back into the free alkyne. The possibility of an alkynyl–hydride complex intermediate was discussed in this case and would be consistent with the relatively low entropy of activation. However, the 18 e^- cationic complexes would be less likely to facilitate the intramolecular oxidative addition required to convert an η^2-alkyne complex into an alkynyl–hydride compared to the neutral and electronically unsaturated complexes of Rh and Ir studied by Werner [100].

Lomprey and Selegue [9] have structurally characterized the alkyne and vinylidene isomers of $[Ru(C_2H_2)(PMe_2Ph)_2(Cp)][BF_4]$. The structures determined by X-ray diffraction are very similar, differing significantly only in the bonding mode of the C_2H_2 ligand. In the π-alkyne complex the η^2-ethyne ligand is symmetrically bound to Ru, with Ru–C distances of 2.20(2) and 2.21(2) Å and a C(1)–C(2) distance of 1.22(2) Å. While the vinylidene ligand is bound to Ru with an Ru–C distance of 1.84(1) Å, a C(1)–C(2) distance of 1.29(1) Å and a Ru–C(1)–C(2) angle of 174.1(8)°.

The behaviour of an acetylene molecule in the coordination sphere of transition metals has been probed by the reactions of $RuX_2(PPh_3)_3$ ($X = Cl$, Br) with *tert*-butylacetylene to give vinylidene complexes of the formula $RuX_2(PPh_3)_2(C{=}CHBu^t)$ [87]. Spectroscopic data have indicated that the initial product of this reaction is a mixture of two complexes each of which has a vinylidene unit and nonequivalent *cis*-bis(phosphine) ligands. In solution, these kinetic products gradually isomerize to the final *trans*–bis(phosphine) complex. The potential surface for the transformation of coordinated acetylene to vinylidene was calculated by the ab initio molecular orbital method. The primary process was concluded to be a slippage of the η^2-CC coordinated alkyne to the η^2-CH coordinated complex via a transition state with an η^1-acetylene and a side-on acetylene. The η^2-CH complex undergoes 1,2-hydrogen migration within the acetylene unit, whose transition state is the highest point of the whole process, giving finally the themodynamically metastable vinylidene complex with a *cis*-bis-(phosphine). The isomeric vinylidene ruthenium(II) complex with *trans*-bis(phosphine) has been calculated to be the final product and thermodynamically most stable form of this reaction system.

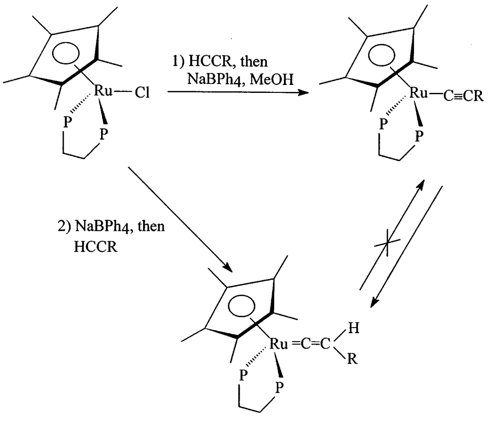
Bianchini et al. [58] observed that the 16-electron fragment $[(PP3)OsH]^+$ ($PP_3 = P(CH_2CH_2P)_3$) is capable of promoting the terminal alkyne to vinylidene tautomerism.

In their study of the transformation of coordinated acetylene to vinylidene Wakasutki et al. [87] performing ab initio orbital molecular calculations on the C_2H_2 unit with the $Ru(PH_3)Cl_2$ moiety found six possible complexes and two transition states containing different coordination forms of C_2H_2 to the metal. The final thermodynamically most stable product was calculated to be the isomeric vinylidene complex $[Ru(C{=}CH_2)Cl_2(PH_3)_2]$ with two phosphines in apical positions and an equatorial plane containing both chloride and the vinylidene ligands. The process consists again as described above in the transformation from the η^2-CC coordinated alkyne to the η^2-CH coordinated complex. This complex undergoes 1,2-hydrogen migration within the acetylene unit, whose transition state is the highest point of the whole process, giving finally the thermodynamically metastable vinylidene complex with a *cis*-bis(phosphine).

The formation of a hydrido–vinylidene osmium complex via a 1,3-hydrogen shift was reported by Esteruelas et al. [55]. $[OsHCl(CO)(P^iPr_3)_2]$ reacts with cyclohexylacetylene to give $[OsHCl({=}C{=}HCy)(CO)(P^iPr_3)_2]$, which in solution rearranges to the vinyl derivative $[OsCl\{(E)\text{-}CH{=}CHCy\}(CO)(P^iPr_3)_2]$. The reaction of $[OsDCl(CO)(P^iPr_3)_2]$ with cyclohexylacetylene leads to a mixture of [Os-

DCl(=C=CHCy)(CO)(P^{i}Pr$_3$)$_2$] and [OsHCl(=C=CDCy)(CO)(P^{i}Pr$_3$)$_2$] in a ca. 1:1 molar ratio, indicating that the formation of the hydrido vinylidene complex involves a 1,3-hydrogen shift via an alkynyl intermediate. This is proposed to be a dihydrogen alkynyl instead of an alkynyl dihydride species. These results have now been explained by Kaulton and Eisenstein [56], as we consider later.

We reported that the product of the reaction of [Cp*RuCl(dippe)] (Cp* = C_5Me_5 with 1-alkynes and $NaBPh_4$ in MeOH is sensitive to the order in which the reagents are added [18].



R = CO_2Me, $SiMe_3$, Ph

If the starting material in MeOH is treated with the alkyne and then with $NaBPh_4$ the corresponding vinylidene complexes are obtained. However, if $NaBPh_4$ is added first, followed by the alkyne, then the corresponding metastable hydrido alkynyl derivatives precipitate from the reaction mixture.

In this way the complex [(η^5-C_5Me_5)RuCl(dippe)] (dippe = 1,2-*bis*(diisopropylphosphino)ethane) reacts with 1-alkynes in MeOH in the presence of $NaBPh_4$, yielding the metastable hydrido-alkynyl derivatives [(η^5-C_5Me_5)Ru(H)(C≡CR)(dippe)][BPh_4] (R = COOMe, Ph or $SiMe_3$), intermediates in the formation of the corresponding vinylidene complexes, to which these compounds rearrange both in solution and in the solid state [19]. The structures of the two related isomers were determined by X-ray diffraction analysis with R = COOMe. In Fig. 1 the complex cation [Ru(H)(C≡CCOOMe)(η^5-C_5Me_5)(dippe)]$^+$ is shown.

The resulting vinylidene cation [Ru(C=CHCOOMe)(η^5-C_5Me_5)(dippe)]$^+$ after rearrangement is represented in Fig. 2.

Kinetic studies have shown that the mechanism for this isomerization process seems to be dissociative and that it is inhibited in solution by strong acids. The isomerization by a concerted mechanism would not be affected by the addition of acid. In contrast with this, no hydrido-alkynyl complex was observed in the course of the reaction of 1-alkynes with [(η^5-C_5H_5)RuCl(dippe)]. Instead, the π-alkyne complexes [(η^5-C_5H_5)Ru(η^2-HC≡CR)(dippe)]$^+$ were detected and isolated in some cases. In comparison, with the (η^5-C_5Me_5)Ru system, only the η^2-alkyne was

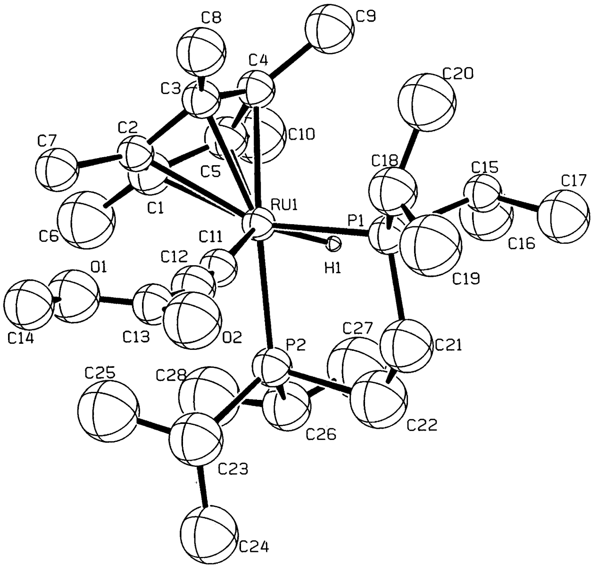


Fig. 1. Structure of the metastable cation $[Ru(H)(C\equiv CCOOMe)(\eta^5\text{-}C_5Me_5)(dippe)]^+$ isolated as tetraphenylborate salt before its rearrangement to vinylidene in a representation adapted from [19]. Hydrogen atoms except H(1) are omitted for clarity.

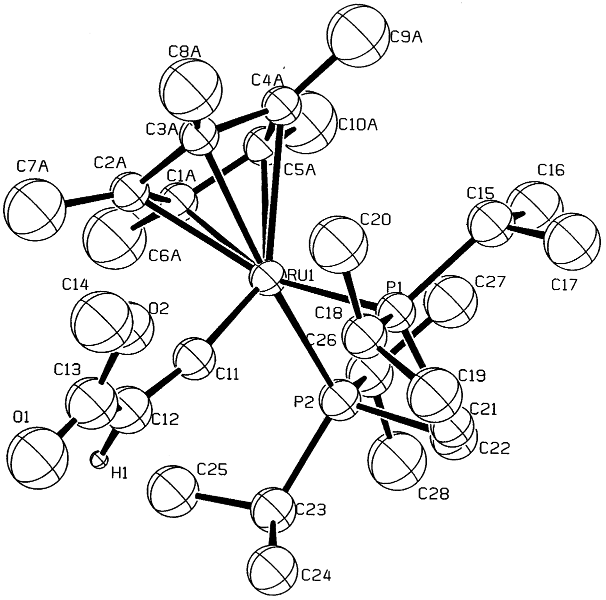


Fig. 2. Structure of the cation $[Ru(=C=CHCOOMe))(\eta^5\text{-}C_5Me_5)(dippe)]^+$ obtained as a tetraphenylborate salt after rearrangement from the corresponding hydrido–alkynyl complex in a representation adapted from [19]. Hydrogen atoms except H(1) are omitted for clarity.

observed in the case of R = H (acetylene) and this seems to be in equilibrium with the corresponding hydrido-alkynyl complex $[(\eta^5\text{-}C_5Me_5)RuH(C{\equiv}CH)(dippe)]^+$, which isomerizes to $[(\eta^5\text{-}C_5Me_5)Ru({=}C{=}CH_2)(dippe)]^+$.

A new route to vinylidenes from ruthenium polyhydrides was reported by Caulton et al. [54]. The reaction of the terminal acetylenes $RC{\equiv}CH$ (R = Ph and $SiMe_3$) with RuH_3XL_2 (X = Cl, I; L = PBu^t_2Me) in a 2:1 stoichiometry leads immediately to vinylidene complexes $RuHX(CCHR)L_2$ with release of $RHC{=}CH_2$. The second equivalent of alkyne serves as a hydrogen acceptor to give the corresponding alkene. No intermediate was detected for this reaction, even at low temperature, or for the analogous reaction of $OsH_3Cl(P^iPr_3)_2$. Since using $PhC{\equiv}CD$ forms only the isotopomer $RuDI(CCHPh)L_2$ and $PhHC{=}CHD$, excluding both 1,2- and 1,3-hydrogen migration, the authors proposed a mechanism in which at an early stage there is the addition of Ru–H across the C≡C bond. A mechanistic study has recently been reported [56]. The process seems to proceed via an insertion of the alkyne into the Ru–H bond leading to a vinyl, which by means of an α-hydrogen migration leads to the final hydrido/vinylidene product. By ab initio (B3LYP) calculations the proposed path starting with insertion into the Ru–H bond is in this case more favorable than a 1,2-migration within the coordinated alkyne ligand. Although Ru and Os have a similar energetic ability to form the hydrido/vinylidene product, the nature of the intermediates on the path may be different in agreement with recent observations for Ru and Os.

5. Reactivity

In agreement with theoretical calculations of structure and chemical bonding, it is convenient to distinguish between, (a) the interaction with nucleophilic agents, in this case the attack mainly takes place at Cα and (b) the interaction with electrophilic agents (at Cβ) in this case the reaction it is also strongly dependent on the partial charge at the carbon atom.

Most of the reactions of vinylidene complexes are stereospecific and they occur with retention of the metal center configuration.

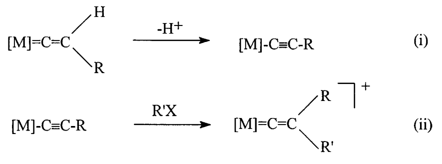
The nucleophilic agents most used are hydrydes, alcohols and water which lead to vinyl, alkoxycarbene and acyl complexes, respectively.

The most common reaction with electrophilic reagents is protonation which generally produces carbyne complexes.

Recent reports on the ruthenium–vinylidene complexes [1a,9,74] suggest that the acetylide species can be generated from the reaction of ruthenium–vinylidene complexes with a base. Some examples of these reactions follow.

5.1. Deprotonation reactions

A general reaction of the vinylidene complexes is deprotonation which leads to the corresponding σ-alkynyls (i). This process is usually reversible in the sense that the addition of an electrophilic agent at the alkynyl Cβ in a metallic acetylide produces the vinylidene complex (ii).

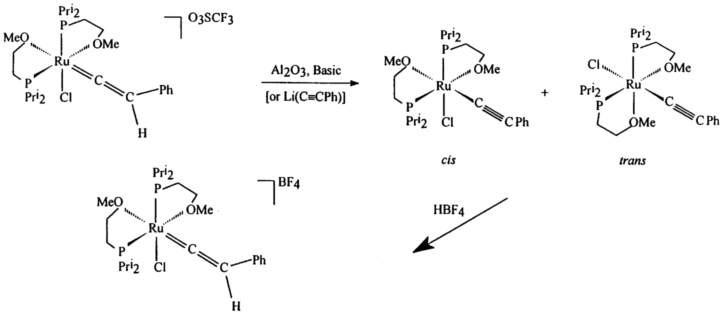


(R' = H or electrophilic group)

The complexes *trans*-$[(Ph_2PCH_2PPh_2)_2(Cl)Ru{=}C{=}CHR]^+$ (where R = H (a), Me (b), Bu^t (c)) are stable in MeOH, especially the primary vinylidene (a), probably because of the protection of the Cβ atom by both the electron rich $[Ru(dppm)_2Cl]$ moiety and the steric hindrance of four phenyl groups. This exceptional stability allowed its single crystal X-ray structure analysis. The short $(RuC_2H_2)C{=}C$ bond length of (a) and the chemical shifts of =CHR groups suggested that these vinylidene complexes are strongly acid. Accordingly, these complexes (a), (b) and (c) can be deprotonated either with $NaBH_4$ in tetrahydrofuran or by treatment with $KOCMe_3$ in CH_2Cl_2, however the best results were obtained by reaction of the vinylidene complexes with DBU (1,8-diaza-bicyclo[5,4,0]undec-7-ene) in dichloromethane which gave the yellow *trans*-chloro acetylide complexes [2].

Nucleophilic attack at the α-carbon of vinylidene complexes to give heteroatom-stabilized carbene species is well established and can be affected by the steric and electronic properties of the spectator ligands [101]. Complexes $[Ru(Me_3tacn)(PMe_3)(O_2CCF_3)\{C{=}CHR\}][PF_6]$ (Me_3tacn = the tertiary amine 1,4,7-trimethyl-1,4,7-triazacyclononane; R = Ph and *p*-tolyl) [4] are stable in refluxing methanol, while only deprotonation of the vinylidene ligand is observed upon reaction with primary and secondary amines, the σ-acetylide complex is formed. This is in contrast to the report by Bianchini that primary and secondary amines react with ruthenium vinylidene derivatives to give amino-carbene and isocyanide complexes [36a,102]. Che [4] proposes that the vinylidene complexes $[Ru(Me_3tacn)(PMe_3)(O_2CCF_3)\{C{=}CHR\}][PF_6]$ are resistant to nucleophilic addition as a result of electronic rather than steric factors: the auxiliary ligands in the present system do not appear to impart steric hindrance, while the high π-basicity of the $[Ru(Me_3tacn)]$ fragment is expected to lower the electrophilicity of the α carbon atom. Thus, the reaction of $[Ru(Me_3tacn)(PMe_3)(O_2CCF_3)\{C{=}CHR\}][PF_6]$ with PMe_3 in methanolic KOH solution gives the corresponding σ-acetylide complexes $[Ru(Me_3tacn)(PMe_3)_2(C{\equiv}CR)][PF_6]$. The vinylidene derivative is first deprotonated by KOH to give the σ-acetylide intermediate; substitution of the CF_3CO_2 ligand by PMe_3 then proceeds to give $[Ru(Me_3tacn)(PMe_3)_2(C{\equiv}CR)][PF_6]$. In the same way, treatment of those vinylidene complexes with KOH followed by $RC{\equiv}CH$ in refluxing methanol allows the C–C coupling reaction to give the η^3-butenynyl complexes $[Ru(Me_3tacn)(PMe_3)\{\eta^3\text{-}RC_3{=}CH(R)\}][PF_6]$.

On the other hand, the octahedral cationic vinylidene complexes *cis*-$[RuCl({=}C{=}CHR)\{\kappa^2\text{-}(P,O)\text{-}{}^iPr_2PCH_2CH_2OMe\}_2][O_3SCF_3]$ (R = Ph, C_6H_4Me-p or $C_6H_4C{\equiv}CH$-*m*) produces with basic Al_2O_3 by deprotonation, a mixture of two isomers *cis* or *trans* chloro-alkynyl [5].



If a solution of these two isomers in thf is treated with $HBF_4 \cdot OEt_2$ immediately the color changes from yellow to orange and after partial removal of the solvent an orange solid can be isolated. This corresponds to the cationic vinylidene as its tetrafluoroborate salt.

Gimeno et al. [81] published the synthesis of enynylruthenium derivatives through deprotonation reactions to the cationic vinylidene derivatives, using an excess of Al_2O_3 in dichloromethane at r.t. These deprotonations are reversible, since the addition of one equivalent of $HBF_4 \cdot Et_2O$ in diethyl ether at r.t. to the enynyl complexes gives selectively the parent vinylvinylidene derivatives.

In other cases, the deprotonation of cationic vinylidene complexes such as $[Ru(=C=CH_2)(\eta^5\text{-}C_9H_7)L_2]^+$ [34] with potassium *tert*-butoxide yields the neutral σ-alkynyl complexes $[Ru(C{\equiv}CH)(\eta^5\text{-}C_9H_7)L_2]$ ($L_2 = 2\ PPh_3$ or dppe).

A coordinatively unsaturated acetylide species [103] $(C_5Me_5)Ru(PPh_3)(C{\equiv}CPh)$ was generated in situ from the reaction of ruthenium–vinylidene complex $(C_5Me_5)Ru(Cl)(PPh_3)(=C=CHPh)$ with Et_3N. This species was found to react readily with a variety of small molecules, such as CO, H_2, PhC≡CPh and CO_2. In some of these last cases the reaction is better using a strong base such as LiOMe.

On the other hand, the deprotonation of $[L_{OEt}Ru(PPh_3)_2(=C=CHPh)][PF6]$ (L_{OEt}=CpCo{PO–$(OEt)_2\}_3$) with NaOH in thf/MeOH led to isolation of the σ-acetylide complex $[L_{OEt}Ru(PPh_3)_2(C{\equiv}CPh)]$ [32].

Bianchini et al. [36b] described the reaction of the vinylidene complexes *fac,cis*-$(PNP)RuCl_2\{=C=CH(R)\}$ [PNP=$CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$, R = Ph or *p*-tolyl] with an excess of LiC≡CPh converting them to the σ-alkynyl-η^3-enynyl complexes *anti,mer*-$(PNP)Ru(C{\equiv}CR)\{\eta^3\text{-}PhC_3{=}CH(Ph)\}$. The results reported in this paper confirm that alkynyl(vinylidene)ruthenium(II) complexes are key intermediates to C–C coupling reactions involving 1-alkynes and show that subtle factors, such as the bonding mode of an ancillary ligand, can tip the balance in favor of the formation of either enynyl or dienynyl complexes (dimerization and trimerization of 1-alkynes, respectively).

In similar fashion, the terminal vinylidene $[(\eta^5\text{-}C_5Me_5)(PPh_3)_2\ Ru(=C=CH_2)][PF_6]$ was doubly deprotonated with ^{t}BuLi to generate the reactive lithioacetylide complex $[(\eta^5\text{-}C_5Me_5)(PPh_3)_2Ru(C{\equiv}CLi)]$, which was trapped with Me_3SiCl and MeI to give $[(\eta^5\text{-}C_5Me_5)(PPh_3)_2\ Ru(C{\equiv}CSiMe_3)]$ and $[(\eta^5\text{-}C_5Me_5)(PPh_3)_2\ Ru(C{\equiv}CMe)]$, respectively [15].

The deprotonation reaction of vinylidene complexes into their corresponding acetylides can also be made using a variety of basic reagents such as $NaBH_4$ in thf or DBU (1,8-diazabicyclo[5,4,0]undec-7-ene) in dichloromethane. Thus, $[(\eta^5\text{-}C_5Me_5)(PMe_2Ph)_2\ Ru({=}C{=}CHR)][PF_6]$ (R = Ph, CH_2OMe, CHMeOMe) can easily be deprotonated into their corresponding acetylide complexes by a variety of basic reagents such as alumina, sodium methoxide, and DBV. However, potassium carbonate offers the best compromise for the ease of separation and yields [14].

Acetylide–vinylidene ruthenium(II) complexes $[Ru(C{\equiv}CR)\{{=}C{=}CHR\}P_4]^+$ (P = phosphite $P(OR)_3$) can be deprotonated by NEt_3, BH_4^- or even by Br^- or Cl^- yielding $[Ru(C{\equiv}CR)_2P_4]$ species [83].

5.2. Reactions with dioxygen

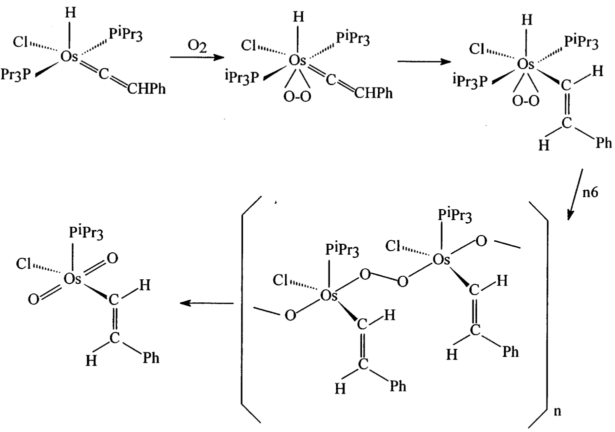
Introduction of dioxygen into a 1,2-dichloroethane solution of $[Ru(Me_3tacn)(PMe_3)(O_2CCF_3)\{C{=}CH(R)\}][PF_6]$ (Me_3tacn = the tertiary amine 1,4,7-trimethyl-1,4,7-triazacyclononane; R = Ph, *p*-tolyl) affords $[Ru(Me_3tacn)\text{-}(CO)(PMe_3)(O_2CCF_3)]^+$ and benzaldehyde [4]. Oxidative cleavage of vinylidene ligands have previously been reported [104]. Yang et al. [105] found that the incorporation of an electron-withdrawing group (e.g. NO_2, Cl) into the *para* position of the phenyl ring in these vinylidene leads to longer reaction times. The stability of the vinylidene complexes towards oxidation therefore increases as the electron density at the C=C bond decreases.

In analogous fashion, the octahedral *fac,cis*-$(PNP)RuCl_2(CO)$, [PNP= $CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$], complex was obtained by treatment of the vinylidenes *fac,cis*-$(PNP)RuCl_2\{C{=}CH(R)\}$(R = Ph; *p*-tolyl) with molecular oxygen and *mer,trans*-$(PNP)RuCl_2(CO)$, starting from vinylidenes *mer,trans*- $(PNP)RuCl_2\{C{=}CH(R)\}$ (R = Ph; *p*-tolyl) [36b]. In these cases, GC-MS analysis of the reaction mixture showed the formation of benzaldehyde (or *p*-tolylaldehyde).

Dixneuf et al. [14] showed that complex $[(\eta^5\text{-}C_5Me_5)(PMe_2Ph)_2\ Ru{=}C{=}CHPh][PF_6]$ is slowly oxidized in solution in the presence of air to give mixtures of the vinylidene and the carbonyl $[(\eta^5\text{-}C_5Me_5)\ Ru(CO)\ (PMe_2Ph)_2][PF_6]$ complexes.

In an attempt to obtain the primary allenylidene complex $[(\eta^5\text{-}C_5Me_5)Ru({=}C{=}C{=}CH_2)(dippe)][BPh_4]$ by dehydration of the hydroxyvinylidene $[(\eta^5\text{-}C_5Me_5)Ru({=}C{=}CHCH_2OH)(dippe)][BPh_4]$ using P_2O_5, the previously reported carbonyl complex $[(\eta^5\text{-}C_5Me_5)Ru(CO)(dippe)][BPh_4]$ [106] was obtained and its crystal structure determined [107]. P_2O_5 seems to act as an oxidant of hydroxyvinylidene. Atmospheric oxygen may also perform this oxidation, but more slowly, several days being necessary for complete oxidation. There are some other reports of the formation of the carbonyl complexes by aerial oxidation of vinylidene species [104c]. Actually crystallization of the vinylidene complex in non-deoxygenated chloroform afforded monocrystals containing both vinylidene and carbonyl complexes and allowed their structural study. This has been interpreted in terms of a cycloaddition reaction between molecular oxygen and the vinylidene ligand [26b], which results in the oxidative cleavage of the C=C bond and affords the corresponding carbonyl complex and an organic acid. In our case, the fate of the organic fragment of the hydroxyvinylidene ligand resulting from the oxidative cleavage is unknown.

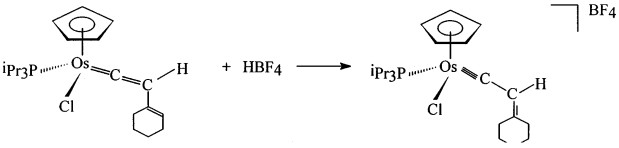
Esteruelas et al. studied the reactivity of the unusual five-coordinate hydrido–vinylidene complex $OsHCl(C{=}CHPh)(P^iPr_3)_2$. In the solid state and in solution this complex is stable if kept under argon. However, at r.t. under air, it is capable of activating the oxygen–oxygen double bond of molecular oxygen from the air to give the dioxo-styryl compound $OsCl\{(E)\text{-}CH{=}CHPh\}(O_2)(P^iPr_3)_2$, characterized by X-ray diffraction analysis. It has been previously proposed [73] that the formation of oxocompounds involves the participation of μ-peroxo intermediates which, in this case, could be formed according to the following scheme.



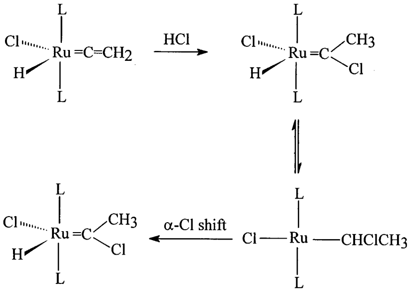
The hydrido–vinylidene complex could coordinate dioxygen to afford the peroxo–vinylidene complex. The insertion of the Cα carbon atom of the vinylidene ligand (of peroxo–Os–vinylidene) into the osmium–hydrido bond could afford unsaturated peroxo–styryl species. The coupling of several units of these last species by one oxygen atom of the peroxo ligand could give a polymer, which finally should lead to the resultant product.

5.3. Reactions with acids

Esteruelas et al. [64] reported the preparation of alkenylcarbyne–osmium complexes in addition to the synthesis and characterization of simple carbyne derivatives. For instance, the addition of a stoichiometric amount of $HBF_4{\cdot}OEt_2$ to the alkenyl–vinylidene or vinylidene complexes yields carbyne complexes.



Recently Werner and coworkers [53,108] showed that hydrogen chloride initially attacks the C=C double bond of the vinylidene ligand in the complex [RuHCl(=C=CH$_2$)(PCy$_3$)$_2$]. From the resulting intermediate [RuHCl(=CCl-CH$_3$)(PCy$_3$)$_2$], the 14-electron species [RuCl(CHClCH$_3$)(PCy$_3$)$_2$] is formed by carbene insertion into the Ru–H bond. Such α-chloroalkyl compounds were also proposed by Grubbs et al. [109] as intermediates in the recently described synthesis of [RuCl$_2$(=CHCH$_2$R)(PCy$_3$)$_2$] (R = H, Me) from [RuHCl(H$_2$)(PCy$_3$)$_2$] and vinyl chlorides RCH=CHCl, and the results are in agreement with the above mechanism. On the other hand, the similar 14-electron species 'RuHClL$_2$' (L = PBu$^t_2$Me) was described by Caulton et al. [110]. A relatively weak acid [HPCy$_3$]Cl is sufficient as a source of HCl, because the first step of the reaction is a nucleophilic attack of the chloride at the α-C atom of the vinylidene ligand. Even MgCl$_2$/H$_2$O can be used as a chloride source. In relation with these results RuCl$_3$, PR$_3$, 1-alkynes, magnesium, hydrogen and water are ingredients of an efficient one-pot synthesis of ruthenium carbenes.



5.4. Reaction with nucleophiles

The electron deficiency at the α-carbon atom of the vinylidenes is well known [88]. Accordingly, the most significant reaction of vinylidene complexes is nucleophilic attack at the Cα carbon atom.

Unsubstituted vinylidene complexes [Ru{=C=CH$_2$)}(η^5-(C$_9$H$_7$)L$_2$][BF$_4$] (L$_2$ = 2 PPh$_3$, dppe) react with methanol or ethanol to give the alkoxycarbene derivatives [Ru{=C(OR)Me}(η^5-(C$_9$H$_7$)L$_2$]$^+$ (R = Me, Et) with good yield [34].

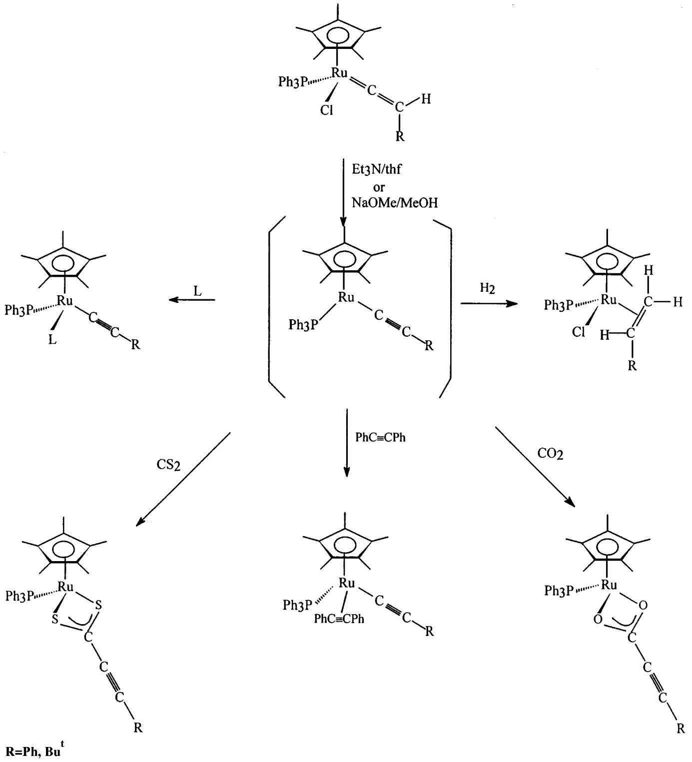
The influence of the substituents on the ability of the vinylidene group to undergo nucleophilic addition at the Cα atom is clearly shown by the behaviour of the monosubstituted vinylidene complexes; thus [Ru{=C=C(H)Ph)}(η^5-(C$_9$H$_7$)L$_2$][BF$_4$] compounds (L$_2$ = 2PPh$_3$, dppe) are unreactive towards methanol or ethanol. The influence of the small-bite chelating dppm ligand is also evident, since the analogous complex containing dppm reacts quickly with methanol to give the corresponding methoxycarbene complex, although the reaction with ethanol requires a longer reaction time. The aminocarbene derivative [Ru{=C(NH$_2$)Me}(η^5-(C$_9$H$_7$)(dppm)][PF$_6$] is obtained by reaction of [RuCl(η^5-(C$_9$H$_7$)(dppm)] with HC ≡ CSiMe$_3$ and (NH$_4$)PF$_6$. A similar procedure involving in situ generation of NH$_3$ from NH$_4$PF$_6$ and NEt^{i}Pr$_2$ has been reported in the case of [Ru{=C(NH$_2$)CH$_2$(CH$_2$)$_2$CH$_2$Cl}(η^5-(C$_5$H$_5$)(dppe)]$^+$ [26b].

Gimeno et al. [81] showed the unexpected formation of alkenyl–phosphonio complexes (*E*)–$[Ru\{C(H)=C(PPh_3)R\}(\eta^5\text{-}(C_9H_7)(PPh_3)_2][PF_6]$ (R = 1-cyclohexenyl, 1-cycloheptenyl) through nucleophilic addition of triphenylphosphine on vinylvinylidene derivatives $[Ru\{=C=C(H)\overline{C=CHCH_2(CH_2)_nC}H_2\}(\eta^5\text{-}(C_9H_7)(PPh_3)_2]$-[PF6] ($n = 2$, 3).

In the study of Ru(II)-mediated reactions of phenylacetylene with primary amines to give ruthenium(II) isonitrile complexes Bianchini et al. [102] showed that the reaction is initiated by 1-alkyne to vinylidene tautomerization at the ruthenium center, followed by attack of the primary amine on the vinylidene ligand to give Ru(II) aminocarbenes of the formula *fac*,*cis*-$[(PNP)RuCl_2\{=C(NHR)(CH_2Ph)\}]$-$[PNP=CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2]$. The latter compound thermally converts to the corresponding isonitrile complexes *fac*,*cis*-$[(PNP)RuCl_2(CNR)]$, while toluene is eliminated via C–C cleavage ($R=CH_2CH_2CH_3$, *cyclo*-C_6H_{11}, (*R*)-(+)-CH(Me)(Ph), (*R*)-(−)-CH(Me)(Et), (*S*)-(−)-CH(Me)(1-naphthyl)).

All data suggest that CO is a weaker σ donor and/or π acceptor than =C=CHR. Accordingly, the vinylidene moiety can not be replaced by nucleophiles like CO or MeCN from the cationic complex $[Ru\{HB(pz)_3\}(Ph_2PCH_2CH_2NMe_2)$-$(=C=CHPh)]^+$ [49]. It is thus surprising that the vinylidene fragment in $[Ru\{HB(pz)_3Cl(PPh_3)(=C=CHR)\}]$ (R = Ph, $SiMe_3$, ^{n}Bu, Bu^t, CO_2Et or C_6H_9) is labile, being easily replaced by nucleophiles like PMe_3, PPh_3, MeCN, pyridine or CO [47]. Most remarkably, complex $[Ru\{HB(pz)_3\}Cl(PPh_3)(=C=CHPh)]$ also reacts easily with terminal acetylenes HC≡CR′ (R′ = $SiMe_3$, ^{n}Bu, ^{t}Bu, CO_2Et, or C_6H_9) to afford reversibly the respective vinylidene complexes $[Ru\{HB(pz)_3\}Cl(PPh_3)$-$(=C=CHR')]$. Although no product other than vinylidene complexes could be detected by NMR spectroscopy, it is likely that these are in equilibrium with their respective η^2-coordinated acetylene complexes. The authors demonstrated that the presence of chloride in the basal position of the fragment $Ru\{HB(pz)_3\}Cl(PPh_3)$, reverses the stability order according to dmf < PPh_3 ≈ vinylidene < CO, with the consequence that vinylidene becomes easily replaceable by acetylenes or even phosphines [47]. The vinylidene moiety in the complex $[Ru(^iPr_2PCH_2$-$CH_2OMe)_2Cl(=C=CHPh)]^+$ is also replaceable by CO under different conditions giving the monocarbonyl $[RuCl(CO)(\kappa^2\text{-}(P,O)\text{-}^iPr_2PCH_2CH_2NMe)_2]^+$ and/or a mixture of this complex and *trans*,*trans*,*trans*-$[RuCl_2(CO)_2(\kappa\text{-}(P)\text{-}^iPr_2PCH_2CH_2$-$NMe)_2]^+$ [5]. Other reactions with phosphite ligands unusually result in displacement of the vinylidene and formation of $[RuCl\{P(OR)_3\}_2(\eta^5\text{-} C_5Me_5)]$ from $[Ru(\eta^5\text{-}C_5Me_5)Cl(PPh_3)(=C=CHPh]$ [111]. These reactions contrast with those of the cationic C_5H_5 analogues, which are generally resistant to ligand exchange.

The unsaturated ruthenium–acetylide complex $[Ru(\eta^5\text{-}C_5Me_5)(PPh_3)(C\equiv CPh)]$ was cleanly generated 'in situ' from the reaction of ruthenium–vinylidene complex $[Ru(\eta^5\text{-}C_5Me_5)(PPh_3)Cl(=C=CHPh)]$ with Et_3N in thf. The spectral data of the new species were consistent with the solvent-coordinated form of the acetylide complex, but several attempts to isolate the complex were not successful as it decomposed during evaporation of the solvent [44].



R=Ph, Bu^t
L=PPh_3, $P(OMe)_3$, $AsPh_3$, CO, dppe-P, dppm-P, C_2H_4, S_2, O_2, PhC≡CPh

Bruce et al. found similar results [45]. The treatment of neutral vinylidene complexes [Ru(η^5-C_5Me_5)(PPh_3)Cl(=C=CHR)] (R = Ph, ^{t}Bu) with 2 e^- donor ligands (L) in the presence of base (NaOMe) readily afforded the corresponding acetylides [Ru(η^5-C_5Me_5)(PPh_3)L(C≡CR)] (R = Ph; L = PPh_3, CO, O_2 or dppm-P; R = Bu^t; L = PPh_3, CO, C_2H_4, dppe-P, dppa-P, S_2, $P(OMe)_3$ or $AsPh_3$). The similar reaction between [Ru(η^5-C_5Me_5)(PPh_3)Cl(=C=CHBu^t)] and CS_2 yields the alkyne dithiolate complex [Ru(η^5-C_5Me_5)(PPh_3)Cl(S_2CC≡CBu^t)] which is analogous to the previously described [Ru(η^5-C_5H_5)(PPh_3)Cl(S_2CC≡CPh)] [112,113]. This reaction may proceed by initial coordination of CS_2 in the η^2-mode, followed by migration of the alkynyl group to the central carbon atom. An alternative mechanism, involving cycloaddition, ring opening and rearrangement requires cleavage of the C–R bond, for which little precedent exists.

The reactivity of hydrido-vinylidenes [MHX(=C=CHR)L_2] towards nucleophiles have been studied by Eisenstein and Caulton [54,56]. Addition of nucleophiles (CO, CNMe) to the complexes [MHX(=C=CHR)L_2] induces migration of the hydride back to the α-carbon atom of the vinylidene yielding vinyl derivatives. [OsHCl(=C=CHSiMe_3)(P^iPr_3)$_2$] reacts with nucleophiles (L = CO, CNMe) in the time of mixing to give [Os{(*E*)-CH=CHSiMe_3}Cl(L)$_2$(P^iPr_3)$_2$]. [RuHI(=C=CHSiMe_3)-(PBu^t_2Me)$_2$] reacts with excess MeNC, giving [Ru{(*E*)-CH=CHSiMe_3}-(MeNC)$_3$(PBu^t_2Me)$_2$]I that has *trans* phosphines and *mer*-MeNC ligands. Addition of NaBAr$'_4$ (Ar$'$ = 3,5-bis-trifluoromethylphenyl) to a solution of [Ru{(*E*)-

$CH{=}CHSiMe_3\}(MeNC)_3(PBu^t_2Me)_2]I$ leaves the NMR signature of the cation unchanged proving that the iodide is not coordinated.

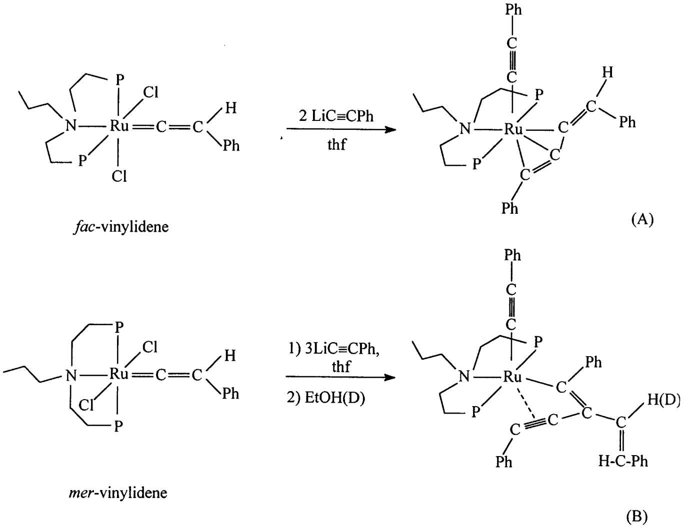
On the other hand, $[OsHCl({=}C{=}CHCy)(CO)(P^iPr_3)_2]$ rearranges to $[Os\{(E)\text{-}CH{=}CHCy\}Cl(CO)(P^iPr_3)_2]$ in solution after 3 days [55]. This reaction probably goes via a similar mechanism, upon coordination of one nucleophile, and is greatly accelerated by the presence of an excess of nucleophile. These reactions formally reverse the formation of the vinylidene from a vinyl intermediate.

6. C–C coupling reactions

These reactions are perhaps among the most important reactions of vinylidene complexes because they are very versatile processes and have great utility in stoichiometric or catalytic reactions towards organic synthesis.

Dimerization to butenynyl complexes or, more rarely, to butatrienyl isomers, apparently occurs at iron, ruthenium and osmium by C–C bond formation between alkynyl and vinylidene ligands. Progress has been made in elucidation of the mechanism of the C–C bond-forming step, but little is known about the factors governing the formation of either butenynyl or butatrienyl ligands. Subtle factors, such as the bonding mode of the ancillary ligand, in addition to their electronics and steric properties, can tip the balance in favor of the formation of either enynyl or dienynyl complexes.

The neutral vinylidene complexes *fac*-*cis*-$[(PNP)RuCl_2({=}C{=}CHR)]$ $[PNP{=}CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$, R = Ph or *p*-tolyl] react with an excess of $LiC{\equiv}CPh$ converting them to the σ-alkynyl-η^3-enynyl complexes *anti*,*mer*-$[(PNP)Ru(C{\equiv}CPh)\{\eta^3\text{-}PhC_3{=}CH(Ph)\}]$ and *anti*,*mer*-$[(PNP)Ru(C{\equiv}CPh)\{\eta^3\text{-}PhC_3{=}CH(p\text{-tolyl})\}]$, respectively. Conversely, treatment of the *mer*,*trans*-vinylidene isomers with an excess of $LiC{\equiv}CPh$, followed by addition of a primary alcohol, gives exclusively the σ-alkynyl-η-dienynyl complexes *mer*-$[(PNP)Ru(C{\equiv}CPh)\{\eta\text{-}PhC{=}C\text{–}C{=}CPh)(CH{=}CH(R)\}]$.



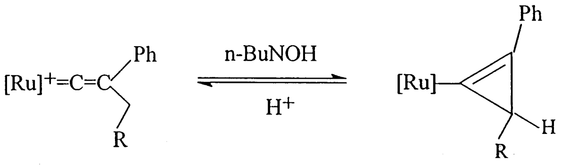
In both compounds the coordination geometry around the Ru atom approximates an octahedron with three positions taken by a *mer* PNP ligand and one position taken by a phenylethynyl group. The coordination sphere around the metal center is completed by an η^3-1,4-diphenylbut-3-en-1-ynyl ligand in (A) and by a 1-phenyl-3-(phenylethynyl)-4-phenylbuta-1(*E*),3(*Z*)-dien-4-yl ligand in (B). The latter ligand essentially uses the C_1 atom to bind the metal, although a weak bonding interaction may also be envisaged with the alkynyl substituent in the 3-position. This influence of the bonding mode of PNP ligand on the different reactivity of the *fac*- and *mer*-complexes is discussed using multimolecular NMR spectroscopy, deuterium-labeling experiments, independent reactions with isolated compounds and X-ray structure determination of some of them [36b].

Analogously, alkyne-coupling reactions in ruthenium–vinylidene and σ-acetylide complexes containing 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3tacn) have been described by Che et al. [4]. Reaction of the vinylidene $[Ru(Me_3\text{-tacn})(PMe_3)(O_2CCF_3)\{=C=CHR\}][PF_6]$ (R = Ph and *p*-tolyl) with PMe_3 in methanolic KOH solution gives the corresponding σ-acetylide complexes. These vinylidene complexes react with RC≡CH and KOH in methanol to give the η^3-butenynyl species $[Ru(Me_3tacn)(PMe_3)\{\eta^3\text{-}RC_3{=}CHR\}][PF_6]$. In addition, treatment of $[Ru(Me_3\text{-tacn})(PMe_3)(O_2CCF_3)\{=C=CHPh\}]^+$ with *p*-tolyl-C≡CH and KOH in methanol gives a mixture of both the η^3-butenynyl species (one of them containing Ph and the other one with *p*-tolyl) in a 1:1 ratio. In fact, the KOH serves to deprotonate the vinylidene ligand, which probably with *p*-tolylacetylene in the presence of KOH yields the (η^2-*p*-tolyl-C≡CH)(σ-C≡CPh) intermediate. Rearrangement of the *p*-tolyl-C≡CH results in formation of the (vinylidene)(σ-acetylide) intermediate and subsequent 1,2-migratory insertion of the acetylide gives the final η^3-butenynyl compound.

From a thermodynamic viewpoint, the strong basicity at the β-carbon of the actylide moiety and the high acidity of the vinylidene proton will favor the proton migration, and this is further facilitated by the electron-donating nature of the $[Ru(Me_3tacn)]$ fragment. It seems probable that the isomerization is not kinetically favored in aprotic solvents, while in this system the proton transfer/isomerization can be assisted by the methanol solvent. Moreover, the C–C coupling vinylidene–acetylide is slower than the rate of proton transfer because of the weak *trans* effect of the Me_3tacn ligand.

It has recently been shown [114] that migratory insertion of vinylidene ligands into metal–alkyl, metal aryl and metal–vinyl bonds provides a novel route to (η^3-allyl) and (η^3-butadienyl) rhodium complexes. It is possible to do similar reactions using chloro-half-sandwich–ruthenium complexes. Thus, the vinylideneruthenium complex $[(C_5H_5)RuCl(=C=CHCO_2Me)(PPh_3)]$ reacts with $Sn(CH{=}CH_2)_n$ in the presence of CuCl to give (2-4-η)-butadienyl compound $[(C_5H_5)Ru(\eta^3\text{-}CH_2CHC{=}CHCO_2Me)]$ [41]. For the description of the bonding mode of the butadienyl unit to the metal, probably more than one resonance formula should be considered. However, the carbene type is the most consistent with the NMR spectral data. With regard to the mechanism of formation of the η^3-allyl-type compound, it is possible that a nucleophilic substitution of the chloro ligand initially takes place and a vinylmetal intermediate is generated. This could rearrange by migratory insertion of the vinylidene unit into the Ru–C=CH_2 bond to give the final product. An alternative pathway leading to the η^3-butanedienyl complex, namely the addition of the vinyl nucleophile to the α-carbon atom of the vinylidene ligand followed by elimination of chloride with concomitant η^1 to η^3 rearrangement, could also be considered but seems less likely. Since the chlorovinylidene compounds do not react with $Sn(CH{=}CH_2)_4$ in the absence of CuCl, this electrophilic substrate seems to play a crucial role in the formation of the final product. Although it is possible that CuCl adds to the Ru=C of the vinylidene unit, Werner thinks [115] that CuCl interacts with the ruthenium-bonded chloride and thus supports the substitution process. Lewis et al. [116] showed that mono- and polynuclear alkynylruthenium complexes are accessible from the corresponding chlorometal precursors and $SnMe_3$-substituted alkynes and diynes, but only in the presence of CuI.

The localization of electron density on Cβ (HOMO) or the M=C double bond and electron deficiency at Cα is well known in the study of vinylidene complexes. On the other hand, the addition of acetylenic alcohols $HC{\equiv}C(CH_2)_nOH$ to $CpRuL_2Cl$ affords cyclic carbene complexes. The reaction proceeds via initial formation of the vinylidene complexes, followed by an intramolecular attack of the terminal alcohol function on Cα [101,117]. A study of the reaction of alcohols with Ru vinylidene complexes has shown that the electron-withdrawing groups on the acetylide unit or on the metal facilitate nucleophilic attack at Cα. Lin et al. [84] believed that electron-withdrawing functionality, such as the CN group, at Cγ might play a role in enhancing the acidity of its neighbouring proton. Thus, an intramolecular cycloaddition leading to the formation of the cyclopropenyl complex may be affected by a base.



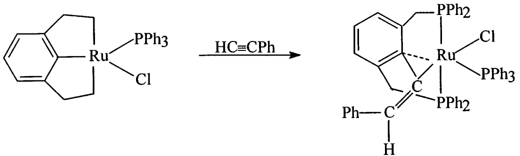
R = CN, C_6H_5, CH=CH_2, CH=CMe_2

[Ru] fragment is $RuCp(PPh_3)_2$

The facile preparation of neutral Ru cyclopropenyl complexes has been achieved by deprotonation of a CH or CH_2 unit at Cγ of the cationic vinylidene complexes in acetone. The deprotonation of vinylidene complexes consisting of an ester group yields the five-membered furan moiety as the thermodynamic product. Protonation of both the cyclization products, yielding back the vinylidene complexes, shows the nucleophilic nature of the antecedent Cγ carbon of the vinylidene ligand.

Another interesting example of metal-assisted C–C bond formation between vinylidene and aryl ligand is the reaction of $[RuCl(PPh_3)(PCP)]$ (PCP = 2,6-

$(Ph_2PCH_2)_2C_6H_3$, a cyclometalated tridentate ligand) [37] with terminal acetylenes HC≡CPh and HC≡CC(OH)RR′ leading to an unusual coupling product, but not the expected vinylidene or allenylidene complexes.

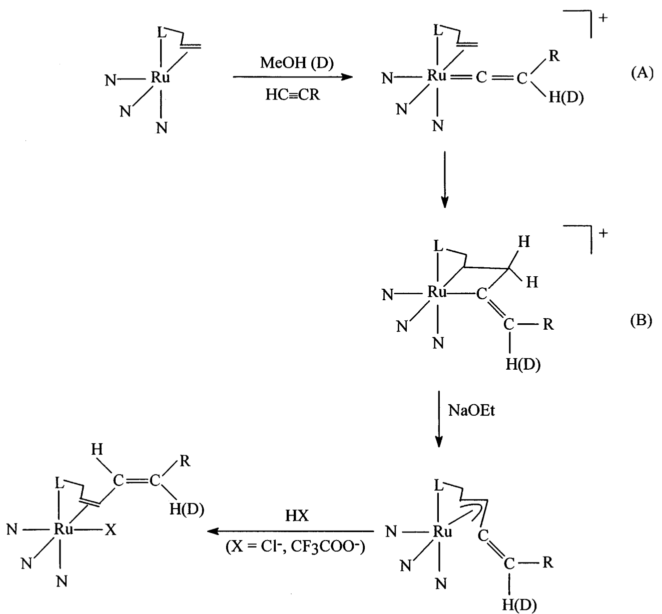


$RuCl(PPh_3)(\eta^4$- $PhCH{=}C$-2,6-$(PPh_2)_2C_6H_3)$

Formation of the coupling products can be explained as below. The coordinatively unsaturated complex $[RuCl(PPh_3)(PCP)]$ reacts with PhC≡CH initially to give the *trans*-chloro-η^2-acetylene complex, which then rearranges to form the *trans*-chloro-vinylidene complex. Migratory insertion of the aryl group of the PCP ligand at the α-carbon atom of the vinylidene ligand would produce the final product. Only starting and final products were observed when the reaction was monitored by $^{31}P\{^1H\}$ NMR at low temperature. Apparently, the coupling reaction is too fast to observe the vinylidene intermediate.

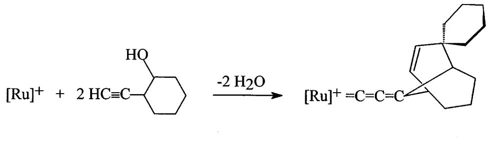
Precedence for C–C bond formation between vinylidene and aryl ligands comes from a recent report about rhodium complexes [114]. However, the C–C bond formation reaction cited above is unexpected, especially in view of the fact that C–C bond cleavage processes [118] were observed in the reactions of related bis(phosphine)ligands with rhodium complexes.

Another example of C–C bond formation within a vinylidene complex is the cycloaddition of alkynes and olefins to the M=C bond giving, respectively, metallacyclobutene and metallacyclobutane intermediates, which then polymerize through ring opening [119]. Although the underlying process is characteristic of early transition metals, Kirchner et al. [120] recently showed a facile C–C coupling reaction between olefins and terminal acetylenes proceeding via a metallacyclobutane intermediate finally converting into either η^3-butadienyl or η^2-butadiene complexes. Thus, treatment of [RuTp(COD)Cl] (Tp = hydro*tris*(pyrazolyl)borate; COD = 1,5-cyclooctadiene) with terminal acetylenes HCCR (R = Ph, C_6H_9, ferrocenyl, CH_2Ph, ^{n}Bu) in MeOH in the presence of NaOEt at 65°C for 24 h, afforded the η^3-butadienyl complexes. This process is not restricted to COD complexes. For instance, in similar fashion $[RuTp(\eta^3$-(P,C,C)–$Ph_2PCH{=}CH(Ph){=}CH_2)Cl]$ reacts with HCCR to give the η^3-butadienyl complex. The mechanism involves for the first step, the formation of the cationic vinylidene complex (A) via a 1,2 hydrogen shift. Subsequently, the metallacyclobutane complex (B) is formed via a cycloaddition, followed by deprotonation of one of the β-hydrogen atoms of (B) yielding the stable η^3-butadienyl complex. The butadienyl fragment is nucleophilic at C-3 and is capable of reactivity with electrophiles such as H^+ and I_2 to give the 1,3-diene unit.



(A) and (B) are intermediate species

An unprecedented coupling process has been reported by Gimeno [121] studying the ability of the indenyl fragment $[Ru(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ to stabilize cumulene systems. Thus, a formal addition of two molecules of alkynols via a metal-promoted double dehydration of 1-ethynyl-1-cyclohexanol, yielded the unprecedented allenylidene complex which contains the bicyclic [3.3.1] non-2-en-9-ylidene moiety.

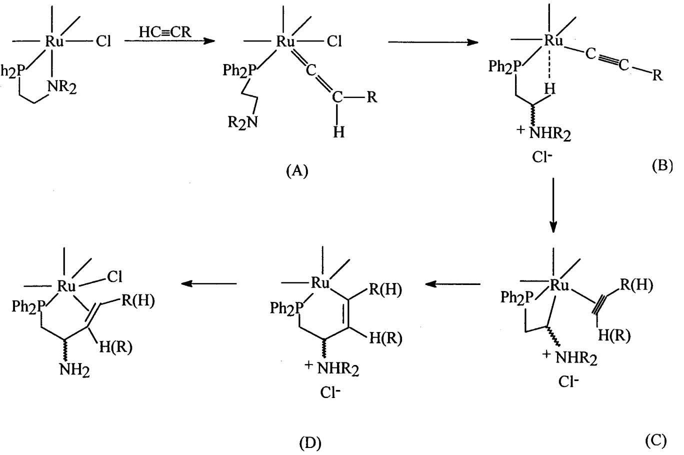


$[Ru] = [Ru(PPh_3)_2(\eta^5\text{-}C_9H_7)]$

The authors of this work propose a mechanism which begins with the formation of a cationic alkenyl-vinylidene and then alkenyl–acetylide after dehydration, but the key step is the attack of this alkenyl–acetylide intermediate on the carbocation simultaneously generated from the starting materials under the reaction conditions.

Coordinatively unsaturated alkynyl complexes, obtained through HCl elimination of vinylidene complexes, are capable of initiating selective coupling of alkanes and terminal acetylenes in the coordination sphere of Ru(II) [46,122]. In addition, as indicated above, phosphino-amine ligands are in fact hemilabile promoting the formation of vinylidene complexes. Consequently, the facile γ-C–H bond activation in phosphino-amine ligands has been shown resulting in regio and stereoselective C–C coupling with terminal acetylenes [39,123].

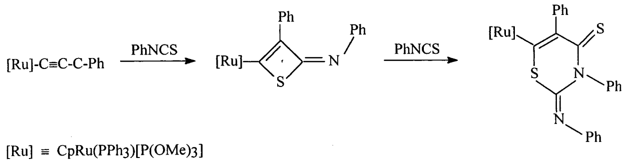
Tris(pyrazolyl)borate ruthenium complexes containing the phosphino-amine ligands $Ph_2PCH_2CH_2NEt_2$ and $Ph_2PCH_2CH_2N^iPr_2$ are found to react with terminal acetylenes yielding regio- and diastereoselective complexes of the types $[\mathrm{RuTp(Cl)}(\kappa^3\text{-}(P,C,C)\text{–}\mathrm{Ph_2PCH_2C(NEt_2)C(R){=}CH_2})]$, $[\mathrm{RuTp(Cl)}(\kappa^3\text{-}(P,C,C)\text{-}\mathrm{Ph_2PCH_2C(NEt_2)CH{=}CHR})]$, $[\mathrm{RuTp(Cl)}(\kappa^3\text{-}(P,C,C)\text{-}\mathrm{Ph_2PCH_2C(N^{\mathit{i}}Pr_2)C(R){=}CH_2})]$, and $[\mathrm{RuTp(Cl)}(\kappa^3\text{-}(P,C,C)\text{-}\mathrm{Ph_2PCH_2C(N^{\mathit{i}}Pr_2)CH{=}CHR})]$. A reasonable mechanism could involve several intermediates summarized as follows [124].



After the initial Ru–N bond cleavage, the vinylidene intermediate is formed (A). Subsequent HCl elimination is favored by the presence of the dialkylamino group giving the coordinatively unsaturated alkynyl complex (B). It is conceivable that the γ-C–H bond of the phosphino-amine ligand is weakened by an agostic interaction to give the phospharuthenacycle and η^2-acetylene (C). At this point, the substituent on the alkyne contributes to the regioselectivity of the C–C coupling process. Subsequent migratory insertion of the acetylene molecule into the Ru–C bond of the phosphametallacyclobutane ring affords the vinyl complex (D) which, on protonation, yields the final product. When the starting complex contains $\mathrm{Ph_2CH_2CH_2NMe_2}$ as the ligand, the C–C coupling involves C–N bond cleavage and elimination of $\mathrm{HNMe_2}$ leading to dehydrogenation of the $\text{–}\mathrm{CH_2CH_2}\text{–}$ chain, and yielding $[\mathrm{RuTp(Cl)}(\kappa^3\text{-}(P,C,C)\text{–}\mathrm{Ph_2CH{=}CHC(R){=}CH_2})]$ as final product. Although the present C–H activation is particularly assisted by the intramolecular mode with favorable stereochemical conditions brought about by the anchoring phosphine group, an extension to the intermolecular mode is conceivable [124].

The Pauson–Khand method [125] is well known to afford functionalized cyclopentane derivatives from the reaction of alkenes with alkynes in the presence of dicobalt octacarbonyl. In this way, Gimeno et al. recently reported [126] several selective reactions of functionalized ruthenium(II)-σ-alkynyl complexes with dicobalt octacarbonyl and tetracobalt dodecarbonyl. In addition, dicobalt adduct complexes $[\mathrm{Ru}\{\mathrm{C{\equiv}CCPh_2}(\mu_2\text{-}\eta^2\text{-}\mathrm{C{\equiv}CH})\mathrm{Co_2(CO)_6}\}(\eta^5\text{-}\mathrm{C_7H_9})(\mathrm{PPh_3})_2]$ and $[\mathrm{Ru}\{\mathrm{C{\equiv}CCCH{=}CH}(\mu_2\text{-}\eta^2\text{-}\mathrm{C{\equiv}CPh})\mathrm{Co_2(CO)_6}\}(\eta^5\text{-}\mathrm{C_7H_9})(\mathrm{PPh_3})_2]$ (*E*,*Z*) undergo Pauson–Khand cyclization processes with strained cyclic alkenes (norbornadiene and norbornene) to afford regioselectively the tricyclic cyclopentenone derivatives. On the other hand, protonation of the above dicobalt adduct complexes with $HBF_4{\cdot}Et_2O$ yields the corresponding cationic vinylidene derivatives.

Other coupling processes in which vinylidene complexes are involved are the reactions of ruthenium acetylides complexes with isothiocyanate or isocyanate yielding a series of addition products [85]. Complex $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)\{P(OMe)_3\}(C{\equiv}CPh)]$ adds one RNCS molecule to the acetylide ligand via a [2 + 2] cycloaddition giving a four-membered ring product and the neutral vinylidene phosphonate complex, which results from an Arbuzov-like dealkylation reaction possibly after addition of PhN=C=S. Addition of a second RNCS molecule generated a complex with a heterocyclic six-membered ring.



For the acetylide complex with a bidentate dppe (1,2-bis(diphenylphosphino)ethane) ligand a third addition led to an organic trimerization product and regenerated the acetylide complex.

As we have summarized, the C–C coupling processes involving vinylidene complexes are stoichiometric or catalytic and their inclusion would be appropriate either in this or in the following section.

7. Some catalytic processes in which vinylidene complexes are implicated

Reports on the reactivity of transition metal vinylidene and acetylide complexes demonstrate a close relationship between these organometallic interactions. Their interconversions are important in the dimerization of alkynes and condensation of alkynes with allylic alcohols or carboxylic acids. The transition metal-mediated dimerization of terminal alkynes is of considerable current interest because it can lead to a wide variety of organic enyne and oligoacetylene products that are useful synthetic precursors for organic conducting polymers and other carbon-rich allotropes [127]. An overview of the literature concerning catalytic dimerization of terminal alkynes has been published by Trost et al. [127e]. On the other hand, a very recent review about ruthenium-catalyzed reactions for organic synthesis [128] contains a part on C–C bond formation through several ways, one of them corresponds to reactions via ruthenium vinylidene complexes.

In this section some catalytic cycles involving vinylidene and/or acetylide ruthenium and osmium are summarized.

While the formation of 1,3-disubstituted enynes from the head-to-tail dimerization of alkynes [129] and of 1,4-disubtituted enynes [46] and cumulenes [87] from the head-to-head dimerization have been reported, the factors influencing different dimeric product formations have not been clearly understood.

In this way, Yi et al. showed [122b] that the ruthenium hydride complexes $[(C_5Me_5)Ru(L)(H)_3]$ ($L = PPh_3$, PCy_3, PMe_3) are versatile catalysts for the dimerization reaction of terminal alkynes $RC{\equiv}CH$ ($R = Ph$, ^tBu, $SiMe_3$, CH_2Ph, C_4H_9) to produce *cis* and *trans*-1,4-disubstituted enynes $RCH{=}CHC{\equiv}CR$ and 1,3-disubstituted enynes $CH_2{=}C(R)C{\equiv}CR$, and even cumulenes $PhCH_2CH{=}C{=}C{=}CHCH_2Ph$. The selective product formation was achieved by modulating both the catalyst and the alkyne substrate. The proposed mechanism involves a coordinatively unsaturated ruthenium–acetylide and also a ruthenium–acetylide–vinylidene species.

Recently, the same authors [103] reported the coordinatively unsaturated ruthenium–acetylide-mediated catalytic dimerization of terminal alkynes and the formation of a new (η^3-butadienyl)–ruthenium complex. Thus, the in situ generated species $[(C_5Me_5)Ru(PPh_3)(C{\equiv}CPh)]$ from reaction of the vinylidene complex $[(C_5Me_5)Ru(PPh_3)Cl({=}C{=}CHPh)]$ with a base, catalyzes the dimerization of 1-alkynes $HC{\equiv}CR$ ($R = Ph$, CO_2Me). If $R = Ph$, *trans*-$PhCH{=}CHC{\equiv}CPh$ and *cis*-$PhCH{=}CHC{\equiv}CPh$ in 4:1 proportion are obtained. This dimeric product ratio was complementary to the previously reported dimerization of $PhC{\equiv}CH$ by the ruthenium–hydride complex $[(C_5Me_5)Ru(PPh_3)H_3]$ which produced a 35:65 mixture of *trans*:*cis* isomers [122b]. When $R = CO_2Me$ the reaction produced exclusively the linear dimer *trans*-$MeO_2C{-}CH{=}CHC{\equiv}CCO_2Me$. A metal-mediated homocoupling reaction of $HC{\equiv}CCO_2Me$ is well-known to preferentially give the cyclotrimerization products [130], and this is the first example of metal-catalyzed linear dimerization of $HC{\equiv}CCO_2Me$.

Kirchner et al. [39] have been examining ruthenium complexes with hemilabile ligands for their efficiency in stoichiometrically and catalytically operating processes. The catalytic coupling of phenylacetylene was studied by these authors. Reactions of the complex $[Ru(\kappa^2\text{-}(P,N)\text{-}Ph_2PCH_2CH_2NMe_2)_2(Cl)_2]$ or the neutral vinylidene complex $[Ru(\kappa^2\text{-}(P,N)\text{–}Ph_2PCH_2CH_2NMe_2)(\kappa^1\text{-}(P)\text{–}Ph_2PCH_2CH_2NMe_2)(Cl)_2({=}C{=}CHPh)]$ with a 50-fold excess of $HC{\equiv}CPh$ in toluene at reflux for 20 h results in an isomeric mixture of *Z*- and *E*-butenynes in a 9:1 ratio in 70% isolated yield. Conversion with unchanged product distribution decreases with temperature and the reaction ceases below 90°C. Other terminal alkynes $HC{\equiv}CR$ ($R = {}^nBu$, ^tBu, CH_2OH, $SiMe_3$) gave no dimerization reaction under the conditions mentioned above. Mechanistically, it seems likely that the catalytic dimerization is initiated by a neutral vinylidene complex (or a possible isomer thereof) by HCl elimination to afford a 16 electron alkynyl catalyst. Such elimination might be facilitated owing to the basic NMe_2 group. In fact, neutral vinylidene complexes undergo 1,3-HCl eliminations upon treatment with base to give 16 electron intermediates which were trapped in the presence of potential ligands as CO, pyridine or CH_3CN [122c]. The occurrence of such intermediates has also been identified in the coupling reaction catalyzed by $[Ru(Tp)(PPh_3)_2Cl]$ (Tp = hydro*tris*(pyrazolyl)borate) and $[Ru(\eta^5\text{-}C_5Me_5)(PR_3)H_3]$ ($R = Ph$, Me, Cy) [46,122b].

Other coupling C–C processes were studied [131] using the electron rich half-sandwich complex $[Ru(\eta^5\text{-}C_5Me_5)(tmeda)Cl]$ (*tmeda* = tetramethylethylene diamine). This complex reacts readily with terminal acetylenes $HC{\equiv}CR$ with the reaction products strongly varying with the substituent R (Ph, $SiMe_3$, ^nBu, and

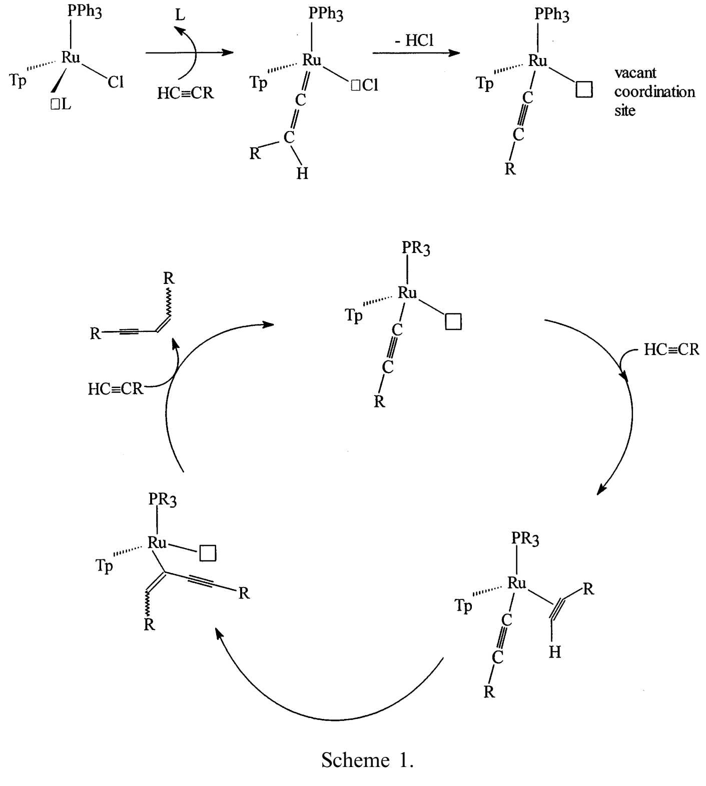
CO_2Et). Thus, with R = Ph, *tmeda* is liberated and the mononuclear ruthenacyclopentatriene complex $[Ru(\eta^5\text{-}C_5Me_5)(\sigma,\sigma^1\text{-}C_4Ph_4H_2)]$ is formed via tail-to-tail dimerization of the acetylene. When the 1-alkyne is HC≡$CSiMe_3$, the cyclobutadiene complex $[Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_4H_2(1,2\text{-}SiMe_3)_2)Cl]$ is formed. When R = ^{n}Bu and CO_2Et, the binuclear complexes $[(\eta^5\text{-}C_5Me_5)RuCl_2(\eta^2{:}\eta^4\text{-}\mu_2\text{-}C_4H_2(1,3\text{-}^nBu)_2)Ru(\eta^5\text{-}C_5Me_5)]$ and $[(\eta^5\text{-}C_5Me_5)RuCl_2(\eta^2{:}\eta^4\text{-}\mu_2\text{-}C_4H_2(1,3\text{-}CO_2Et)_2)Ru(\eta^5\text{-}C_5Me_5)]$ are obtained in high yields. In order to establish the factors that control the reactivity of the catalyst and consequently the selectivity of the C–C coupling process, the coupling of HC≡CPh with several related complexes was studied [122a]. The complex $[RuTp(PPh_3)_2Cl]$ catalyzes the coupling of terminal alkynes to give butenynes [46]. The catalytic cycle is initiated by loss of a PPh_3 ligand and formation of the coordinatively unsaturated species $[RuTp(PPh_3)Cl]$. Upon adding HC≡CPh, the neutral vinylidene complex $[RuTp(PPh_3)(Cl)({=}C{=}CHPh)]$ is formed as an intermediate; no other intermediates could be detected in addition to the reaction products in the further course of the reaction. The use of this isolated neutral vinylidene complex in an independent reaction catalyzes the coupling of HC≡CPh in a fashion nearly identical to the $[RuTp(PPh_3)_2Cl]$. A possible reaction scheme could involve the coordinatively unsaturated alkyne complex $[RuTp(PPh_3)(C{\equiv}CPh)]$ formed by the liberation of HCl (from the neutral vinylidene), a proposal in accordance with other investigations [16b,36b,122c,132]. The catalytically active species is a metal alkynyl complex generated by the intervention of a strongly basic ligand such as hydride and alkyl groups. In order to establish the role of ligated base in the present reactions [RuTp(py)Cl] and $[RuTp(PPh_3)_2H]$ [122a] bearing the basic coligands py and H^- as catalyst precursors for the dimerization of HC≡CPh were also tested. The first steps were the release of py and PPh_3 from the complex, respectively. The catalytic species should be the same alkynyl complex as that arising from $[TpRu(PPh_3)_2Cl]$, but the hydrido complex produced $[RuTp(PPh_3)_2]$ presumably arrived at by the usual insertion of the alkyne into the Ru–H bond giving a vinyl intermediate.

Other complexes [RuTp(L)(L′)Cl] (L,L′ = P, N, O donors) have been tested as possible catalysts for homocoupling ruthenium catalysis of terminal alkynes and the results are summarized in Ref. [122a]. It is noteworthy that complex [RuTp(dppe)Cl] (dppe = 1,2-bis(diphenylphosphino)ethane), for instance, does not show any catalytic activity, but the analogous complex featuring the hemilabile ligand $Ph_2PCH_2CH_2NMe_2$ (pn) exhibits some reactivity although modest. $[Ru(\eta^5\text{-}C_5Me_5)(pn)Cl]$ has catalytic activity towards the catalytic dimerization of HC≡CR (R = Ph), but shows no selectivity yielding a 1:1 mixture of the *E* and *Z* isomers. However, in the case of R = CO_2Et, cyclotrimerization was exclusively observed affording a 1:1 mixture of 1,2,4- and 1,3,5-benzene-tricarbyoxylicacid esters in 96% yield [100a]. In the case of $[Ru(pn)_2Cl_2]$ the selectivity of the reaction is reversed giving predominantly the head-to-head dimer (*Z*)-1,4-diphenyl-1-buten-3-yne with about 70% conversion. The poor reactivity of most of these complexes can be attributed to the lack of substitutive reactivity. Whereas ligands forming weak metal–ligand bond (weak bases such PPh_3, py) and/or sterically demanding ligands (e.g. PPh_3, PCy_3) facilitate the formation of a 16 electron intermediate, π acceptor ligands such as CO suppress ligand dissociation. Furthermore, the presence of bulky and/or hemilabile ligands promotes the subsequent formation of vinylidene complexes.

In these systems, the catalytically active species seems to be the alkynyl complex produced from the vinylidene after liberation of HCl. A second alkyne molecule is readily added to the alkynyl intermediate followed by a selectivity determining C–C coupling step (Scheme 1).

Accordingly, the C_4 unsaturated product is eventually liberated from an intermediate σ-organyl metal species by σ-bond metathesis with an additional alkyne molecule [133].

The majority of all hitherto known catalytic dimerizations of alkynes to C_4 units are migratory insertions of acetylenes into σ metal–carbon bonds proceeding, for instance, via alkynyl–vinylidene or alkynyl–vinyl coupling (Bianchini's mechanism) [16b,36b,132]. Thus, a Ru(II) bis(alkynyl) complex catalyzes the regio and stereoselective dimerization of phenylacetylene to (*Z*)-diphenylbut-3-en-1-yne. Several observations are consistent with a catalytic cycle involving protonation of a σ-phenylethynyl ligand by external HC≡CPh, followed by C–C bond formation between *cis* σ-alkynyl and vinylidene groups. The ruthenium bis (alkynyl) catalyst

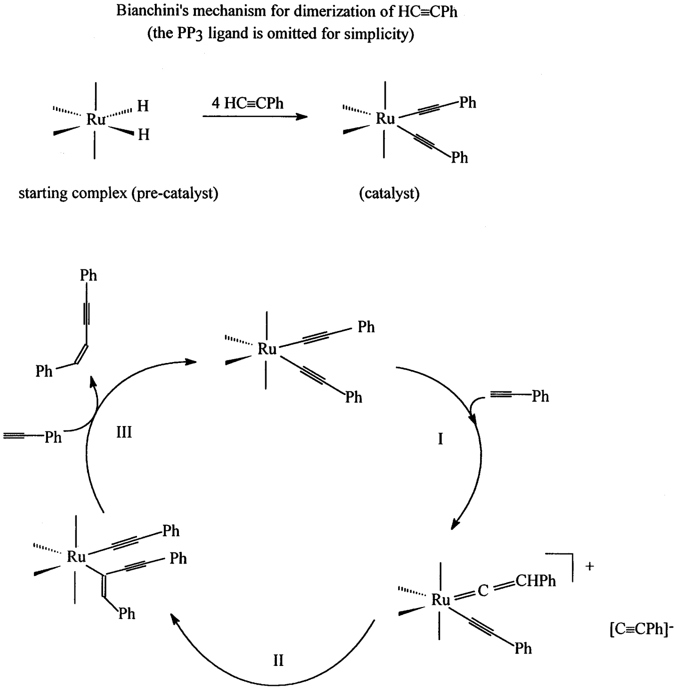


Scheme 1.

is formed from a dihydride precursor $[(PP_3)RuH_2]$ $(PP_3 = P(CH_2CH_2PPh_2)_3)$ [134] which consumes four equivalents of HCCPh and comprises a number of reaction steps all of them occurring at the same metal–ligand fragment.

In the case of late transition metals, enynyl intermediates could be occasionally isolated giving predominantly (*Z*) head-to-head coupling products [4,135]. Another mechanism appears to operate in the case of early transition metals, lanthanides, and actinides, where preferentially (*E*) head-to-head and head-to-tail dimers together with trimeric and even oligomeric coupling products are obtained (Scheme 2).

The stereo- and regioselectivity of the dimerization should vary with the substituent of the alkyne [36b,122b,127e,136a]. Studies on the catalytic dimerization of HCCPh have shown that terminal alkynes which are able to form a conjugated system with the intermediate vinylidene or vinyl complexes appear to yield exclusively 1,4-enynes (*E* and/or *Z*), suggesting the operation of Bianchini's mechanism. Whether an *E* or *Z* isomer is formed depends on the ligand environment of the ruthenium complex as well as on the size of the substituent of the alkyne. For smaller alkynes, the insertion of another alkyne is often faster than the elimination of enynes; thus, also trimeric [22] or even oligomeric products are generated. In another case, when acetynene to vinylidene isomerization seems sluggish [122b,136a,137], the direct insertion of η^2-alkynes into the Ru-alkynyl σ-bond



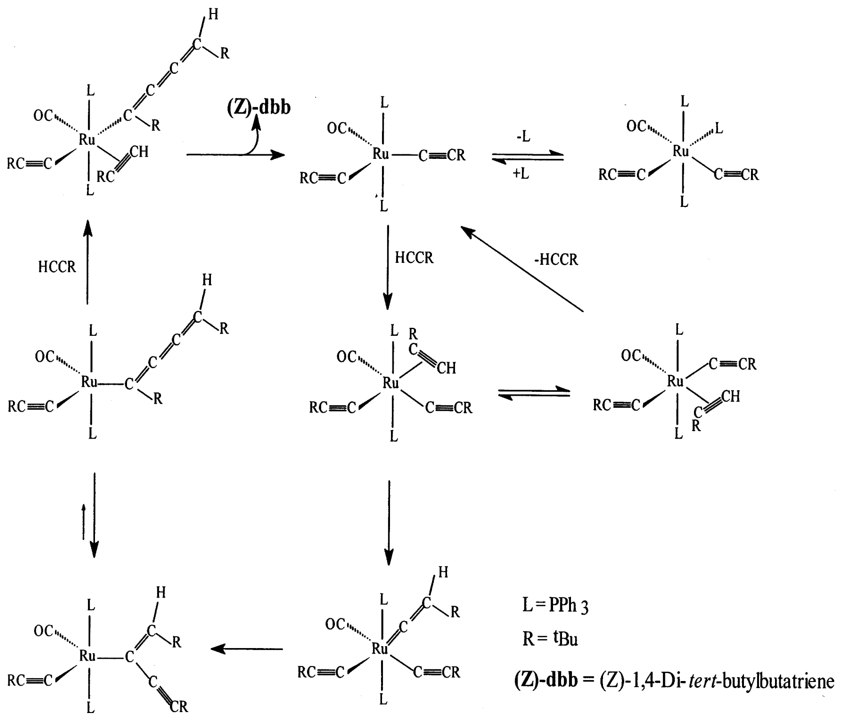
Scheme 2.

produces preferentially 1,3-enynes in a fashion similar to the early transition metal-catalyzed dimerizations of alkynes.

A completely different type of dimerization, the regio- and stereocontrolled dimerization of *tert*-butylacetylene to (*Z*)-1,4-di-*tert*-butylbutatriene (abbreviated (*Z*)-dbb) by ruthenium catalysis has been studied by Wakatsuki et al. [136a]. The catalysts were $RuH_2(CO)(PPh_3)_3$ or Ru(cod)(cot) (cod = 1,5-cyclooctadiene, cot = cyclooctatriene), and the reaction sequence in the catalytic cycle was elucidated by a series of model reactions: formation of the bis-(alkynyl)complex, isomerization of the η^2-alkyne to the vinylidene ligand, migration of the alkynyl to the vinylidene carbon, and finally, rearrangement of the butenynyl moiety to the butatrienyl form. While some of these elemental reaction steps have precedents, the present system is unique in that all of these reactions are linked to form a catalytic cycle (Scheme 3).

Very recently the first anti-Markovnikov hydration of terminal alkynes through a vinylidene intermediate complex and formation of aldehydes catalyzed by a ruthenium(II) phosphane mixture has been reported by Wakatsuki et al. [136b].

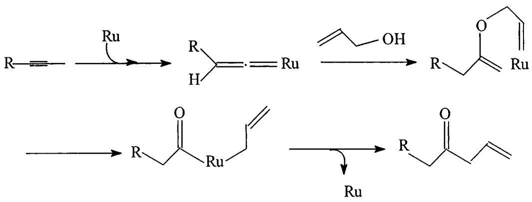
Concerning 1-alkyne dimerization processes in which a vinylidene complex can be implicated, Esteruelas et al. [57] found the hydridovinylidene complex $[OsH(\eta^2\text{-}O_2CCH_3)(=C=CHPh)(P^iPr_3)_2]$ to be an active catalyst (or catalyst precursor) for the dimerization of phenylacetylene to give a mixture of *trans*- and *cis*-PhC≡CH=CHPh. This accords from a mechanistic point of view with the formation



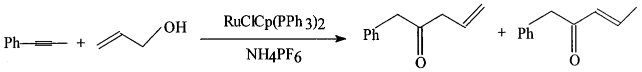
Scheme 3.

of an alkynyl–vinyl or alkynyl–vinylidene intermediate, even the intramolecular coupling of both ligands to lead to M(η^3-RC_3CHR) species in agreement with Bianchini's mechanism. Concerning the oligo- and polymerization processes of terminal alkynes, a prerequisite for such a catalyst is the availability of two vacant coordination sites such as [RuTp(COD)Cl] (COD = 1,5-cyclooctadiene) and [RuTp$(py)_2$Cl] [138]. This catalysis presumably proceeds via a metathesis mechanism. The stereochemistry of the transition state of the coupling reaction determines the primary structure of the polymer [139]. If bulky substituents (Ph) are involved, a *trans* dominated polymer backbone is generated which is more difficult to degrade. In this case, longer polymer chains are obtained. Small substituents (Bu, CO_2Et), give rise to polymers of a *cis* dominated structure which can be readily degraded, and therefore, short oligomers are obtained. The high temperature needed for the activation of the catalyst can also favor the breaking of the oligomeric chain.

Other catalytic reactions of ruthenium complexes have been studied. Trost et al. [140] studied the carbon–carbon bond forming reactions by condensation processes in which the product is the sum of the two reactants and consider that such condensation reactions involving vinylidene metal complexes as reactive intermediates can readily happen under the conditions of a catalytic cycle. Thus, reconstitutive condensation of acetylenes and allyl alcohols takes place via the formation of an allyloxy carbene complex, subsequent metalla-Claisen rearrangement and reductive elimination of ruthenium.



These authors have reported that a combination of $RuClCp(PPh_3)_2$ and NH_4PF_6 catalyzes the reaction of terminal alkynes with allyl alcohols to afford the corresponding β,γ-unsaturated ketones [141].

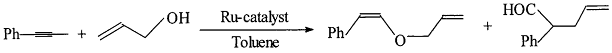


When propargylic alcohol is employed as an alkyne the corresponding allenylidene ruthenium intermediate is formed. Intramolecular nucleophilic attack of a hydroxy group to the allenylidene moiety affords the vinylidene complex, which undergoes similar reconstitutive addition.

β,γ-unsaturated ketones bearing cyclic ether skeletons can be directly prepared by the reaction of hydroxy propargyl alcohol with allyl alcohol [142].

The coupling of phenylacetylene with benzoic acid in toluene with catalyst (5%) yields vinyl ester up to essentially quantitative yield depending on the catalyst used.

The neutral complexes [Ru{HB(pz)}$_3$(COD)Cl], [Ru{HB(pz)}$_3$(tmeda)Cl], [Ru{HB(pz)}$_3$(py)$_2$Cl] and some cationic Ru–Tp complexes have all been tested as catalysts. These complexes lead to selective addition of benzoic acid to the terminal carbon atom of the phenylacetylene giving a mixture of vinyl ester isomers. In relation to that, the coupling of phenylacetylene with allyl alcohol in refluxing toluene (2% catalyst) yields a mixture of the *cis* allyl vinyl ether and aldehyde.



Under these reaction conditions, the aldehyde appears to be formed from the thermally unstable *trans* isomer via a Claisen rearrangement. Both products were obtained in a 1:1 ratio. This reaction does not occur in the absence of the ruthenium catalyst [138]. Considering the final products, this appears to be the first time that C–O coupling between acetylenes and allyl alcohols catalyzed by ruthenium complexes has been reported. The mechanism of this reaction can only be speculated upon at present. It seems likely, however, that a vinylidene complex is a reactive intermediate in this catalytic process.

8. Concluding remarks

This review summarizes the recent progress in research on ruthenium and osmium vinylidene chemistry, which is a very active field with a growing number of reports. The preparative methods, structural characterization and chemical reactivity are considered, particularly in relation with C–C coupling processes and the use of these compounds as catalysts for organic synthesis. Some mechanistic features in the formation of vinylidene complexes are not yet well systematized in relation with the nature of the coligands, substituent groups, solvent influence, etc. However, there is a lot of work in progress and development in the future will extend the number and type of processes in which vinylidene complexes are involved.

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