Recent Developments in the Reactivity of Allenylidene and Cumulenylidene Complexes

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Dedicated to Prof. Dr. José Barluenga on the occasion of his 60th birthday

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Allenylidene and higher cumulenylidene complexes [M]=C(=C)$_n$=CR^{1}R^2 (n = 1, 2, 3) have continuously gained significance in the context of transition metal carbene chemistry. Important developments which have been disclosed during the last two years are reviewed. These include a variety of stoichiometric and catalytic reactions of allenylidene complexes and their utility in organic synthesis. The related chemistry of butatrienylidene (n = 2) and pentatetraenylidene (n = 3) complexes as well as theoretical studies are also reviewed.

I. Introduction

The chemistry of transition metal carbene complexes has reached such a state of development so as to allow its wide use as one of the most powerful tools in modern organic synthesis.[1] Allenylidene (propadienylidene) complexes [ML$_n$]=C=C=CR^{1}R^2, which belong to the series of unsaturated carbene derivatives [ML$_n$]=C(=C)$_n$=CR^{1}R^2 ($n > 0$; cumulenylidene complexes), have received increasing interest during the last few years. Although the utility of these carbene complexes is still not comparable to that of the classical Fischer-type, both experimental and theoretical studies have been the subject of special attention.

The continuous growth of this chemistry stems mainly from:

a) The presence of an unsaturated carbon chain. Similar to the analogous polyinyl derivatives [ML$_n$]−(C≡C)$_n$−R, cumulenylidenes are potentially useful as precursors of molecular wires or polymers related to polyacetylene of interest in the field of novel materials with opto-electronic properties.[2]

b) The search for novel carbene complexes bearing unsaturated carbon moieties and/or other types of functional groups which can provide multifaceted reactive sites of interest in organic synthesis.

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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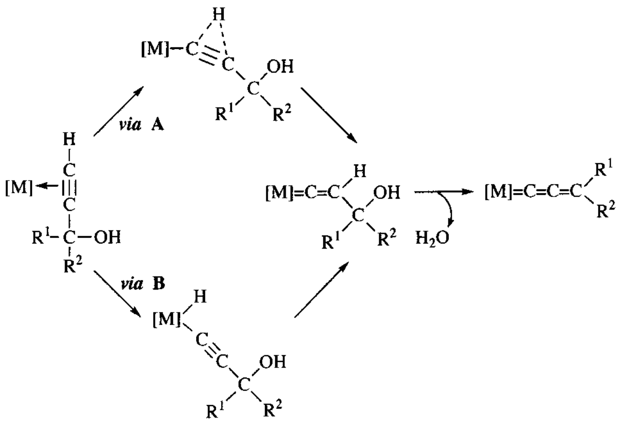
c) The recent discovery of the catalytic activity of allenylidene ruthenium(II) complexes in ring-closing metathesis (RCM) of olefins. These are more accessible catalysts than the classical Schrock-type and Grubbs' alkylidene derivatives.[3]

d) The synthetic accessibility of the cumulenylidene complexes $[ML_n]{=}C({=}C)_n{=}CR^1R^2$ with higher unsaturation (n = 2, 3) which have also provided further reactivity patterns, albeit in a limited number.

The chemistry of allenylidene complexes and related species have been the subject of two general reviews[4a][4b] which cover the literature up to June 1998 including other specific surveys on rhodium, iridium[4c] and ruthenium complexes.[4d−4f] Brief accounts of the particular aspects of dinuclear and cluster species containing bridging allenylidene moieties have also appeared.[4g−4i] Since the discovery of the first allenylidene complexes $[M\{{=}C{=}C{=}CPh(NEt_2)\}(CO)_5]$ (M = Cr, W)[5a] and $[Mn({=}C{=}C{=}C\mathit{t}Bu_2)(\eta^5\text{-}C_5H_5)(CO)_2]$[5b] in 1976 several synthetic approaches have been reported.[4a,4b] Those with the greatest use follow essentially the strategy first used by Selegue for the preparation of $[Ru({=}C{=}C{=}CPh_2)(\eta^5\text{-}C_5H_5)(PMe_3)_2][PF_6]$ which is based on the spontaneous dehydration of the hydroxyvinylidene species formed, either via **A** or via **B** (see Scheme 1), after the coordination of 2-propyn-1-ols at the metal center.[6]



Scheme 1. Mechanism of the isomerization of 2-propyn-1-ols into allenylidene ligands

Large series of mono- and dinuclear derivatives containing half-sandwich (**A**) as well as octahedral (**B**) or square-planar (**C**) electron-rich metal fragments of Groups 6, 7, 8, and 9 have now been isolated (see Figure 1).[7] They are obtained in generally good yields as stable solids and have been fully characterized through the usual spectroscopic and/or diffractometric techniques. Octahedral Group 6 metal carbonyl derivatives $[M({=}C{=}C{=}CR^1R^2)(CO)_5]$ are generally thermally unstable and the stabilization of the carbene moiety requires the presence of electron-releasing substituents ($R^1 = R^2 = p\text{-}NR'_2C_6H_4$, $p\text{-}OR'C_6H_4$, etc.). Furthermore, a short number of dinuclear and cluster complexes containing bridging allenylidene groups $[(M_nL_m)(\mu\text{-}\eta^x{=}C{=}C{=}CR^1R^2)_y]$ are also known.[4] More recently, cumulenylidene complexes of the type: (*i*) buta-1,2,3-trienylidenes $[ML_n]{=}C({=}C)_2{=}CR^1R^2$ with $[ML_n]$ = *trans*-$[RuClL_2]^+$ [L_2 = bis(diphenylphosphanyl)methane (DPPM), bis(diethylphosphanyl)methane (DEPM), 1,2-bis(diphenylphosphanyl)ethane (DPPE)}, $[Ru(\eta^5\text{-}C_5H_5)L_2]^+$ {L = PPh_3, $P(OMe)_3$], $[Fe(\eta^5\text{-}C_5Me_5)L_2]^+$ [L_2 = DPPE, 1,2-bis(diisopropylphosphanyl)ethane (DIPPE)], and (*ii*) penta-1,2,3,4-tetraenylidenes$[ML_n]{=}C({=}C)_3{=}CR^1R^2$ with $[ML_n]$ = *trans*-$[RuCl(DPPE)_2]^+$, *trans*-$[RhCl(P\mathit{i}Pr_3)_2]$, *trans*-$[IrCl(P\mathit{i}Pr_3)_2]$, $[Cr(CO)_5]$, $[W(CO)_5]$ have also been described, the latter being prepared through the intermediate formation of $[M\{{=}C({=}C)_5{=}CR^1R^2\}(CO)_5]$ (M = Cr, W).[4b]

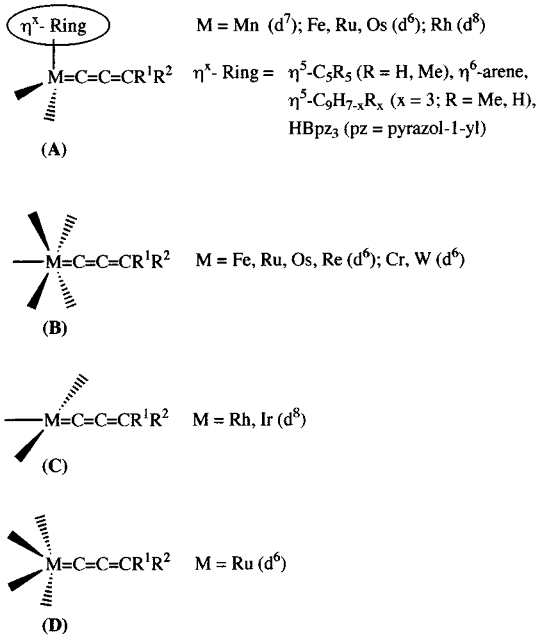


Figure 1. Stereochemistry of mononuclear allenylidenes

Although the first reactivity studies of allenylidene and higher cumulenylidene derivatives emerged simultaneously to their synthesis, their chemistry has grown rapidly and important developments have been disclosed after the period covered in the above-mentioned reviews. The present review will focus mainly on the reactivity studies of allenylidene complexes including stoichiometric and catalytic processes. Special attention will be devoted to the regioselective nucleophilic additions and the utility of these species in organic synthesis. It is worth mentioning the first coordinatively unsaturated Group 8 allenylidene complexes **D** (see Figure 1), some of them showing catalytic activity in RCM (ring-closing metathesis) of olefins.[8] Furthermore, recent advances in theoretical studies which shed light on the chemical behavior as well as a short account of novel structural and spectroscopic properties will be also discussed. Recent developments in the chemistry of related cumulenylidene complexes are also mentioned. This review covers the literature up to May 2000.

II. Structural and Spectroscopic Properties

II.1 X-ray Diffraction Studies

Structural parameters of novel allenylidene complexes studied by X-ray diffraction confirm the previously known features of the metal−allenylidene bonding. Thus, metal−carbon, $C_\alpha-C_\beta$, and $C_\beta-C_\gamma$ bond lengths are in accordance with the well-known description of the bonding as a resonance of metal−carbene and metal−alkynyl mesomers, the latter being the dominant contribution to the observed structures (zwitterionic species $[M]^--C{\equiv}C-C^+R^1R^2$ for neutral allenylidene complexes):

$$[M]^+{=}C{=}C{=}CR^1R^2 \rightleftarrows [M]-C{\equiv}C-C^+R^1R^2$$

The first coordinatively unsaturated 16-electron allenylideneruthenium complexes, namely $[RuCl_2(=C=C=CPh_2)(PCy_3)_2]$ and $[RuCl_2(=C=C=CPh_2)(PCy_3)(IMes)]$ [IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene], have now been described.[8] The crystal structures show that the allenylidene moiety is located at the apex and the ruthenium atom at the bottom of a square pyramid. The most relevant structural feature in both structures is the almost equal bond lengths $Ru-C_\alpha$ (ca. 1.79 Å) which are in the usual range found in other 16-electron carbeneruthenium complexes (1.76−1.84 Å).[9] These values contrast with the larger bond lengths shown by cationic 18-electron species $[Ru]^+{=}C{=}C{=}CR^1R^2$ (see below) indicating that the metal−allenylidene bond is stronger for the former complexes. This structural property is related to the lower catalytic activity of these complexes relative to that observed in the cationic 18-electron (arene)ruthenium complexes in ring-closing metathesis (RCM) reactions (see below). The bond lengths along the allenylidene chain are in the usual range for ruthenium complexes (see below). The allenylidene chain in $[RuCl_2(=C=C=CPh_2)(PCy_3)_2]$ shows an unusual bending [$C_\alpha-C_\beta-C_\gamma = 167.20(18)°$] which is attributed to a C−H interaction with hydrogen atoms of the PCy_3 ligands.

The rest of the structures reported show $M-C_\alpha$ bond lengths in the 1.858(7)−1.943(8) Å range and $C_\alpha-C_\beta$ in the 1.221(9)−1.267(3) Å range, which compare well with those found previously (1.84−1.94 and 1.24−1.27 Å, respectively).[4a,4b] The allenylidene chain also shows the expected slightly bent linear arrangement (ca. 170−176°).[4a,4b] It should be noted that the *trans*-$[Ru(C{\equiv}CPh)(=C=C=CPh_2)(DPPE)_2][PF_6]$ complex shows bond lengths $Ru-C_\alpha$ [2.11(1) Å] and $C_\alpha-C_\beta$ [1.14(2) Å], unusually larger and shorter, respectively, than those found in analogous mononuclear ruthenium(II) complexes.[10]

Other X-ray crystal-structure determinations include:

A) Mononuclear Derivatives

a) Cationic complexes: (*i*) hexacoordinated ruthenium(II) complexes $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_5Me_5)(PEt_3)_2][BF_4]$,[11] $[Ru\{=C=C=C(Me)(C_4H_3NMe\text{-}2)\}(\eta^5\text{-}C_5H_5)(PPh_3)_2][PF_6]$,[12] $[RuCl(=C=C=CPh_2)(\eta^6\text{-}p\text{-cymene})(IMes)][PF_6]$,[13] $[Ru(=C=C=CPh_2)(\eta^5\text{-TRIPOD})][PF_6]$ (TRIPOD = $CH_3C(CH_2\text{-}\eta^5\text{-}C_5H_4)(CH_2\text{-}\eta^1\text{-}PPh_2)_2$),[14] $[Ru(=C=C=CPh_2)\{HB(pz)_3\}(PPh_3)_2][PF_6]$ (pz = pyrazol-1-yl)[15] and $[RuCl(=C=C=CPh_2)(PPh_3)\{\kappa^3\text{-}N,N,N\text{-}(S,S)\text{-}i\text{Pr-PYBOX}\}][PF_6]$ {(*S,S*)-*i*Pr-PYBOX = 2,6-bis[4′-(*S*)-isopropyloxazolin-2′-yl]pyridine},[16] and (*ii*) the tetra-coordinated rhodium(I) complex *trans*-$[Rh(=C=C=CPh_2)(O=CMe_2)(PiPr_3)_2][PF_6]$.[17]

b) Neutral octahedral ruthenium(II) *fac,cis*-$[RuCl_2(=C=C=CPh_2)(PNP)]$ {PNP= $MeCH_2CH_2N(CH_2CH_2PPh_2)_2$},[18] $[RuCl_2(=C=C=CPh_2)(CO)(SbiPr_3)_2]$[19] and square-planar iridium(I) *trans*-$[IrF(=C=C=CPh_2)(PiPr_3)_2]$[20] complexes.

B) Polynuclear Derivatives

a) Dinuclear cationic complexes of three types (Figure 2): (*i*) the osmium(II) derivative $[(\eta^5\text{-}C_5H_5)(PPh_3)_2Os\{=C=C=C(H)-C{\equiv}C-Os(\eta^5\text{-}C_5H_5)(PPh_3)_2\}][BF_4]$ (**A**);[21] (*ii*) the mixed-valence ruthenium(II)−ruthenium(III) complex $[Ru(=C=C=Rc)(\eta^5\text{-}C_5H_5)(DPPE)][BF_4]_2$ [Rc = $(\mu^2\text{-}\eta^6{:}\eta^5\text{-}C_5Me_4)Ru(\eta^5\text{-}C_5H_5)$] containing a half-sandwich ruthenium(III) fragment bonded to a (cyclopentadienylidene)ethylidene group which acts as the bridging chain to the $(\eta^5\text{-}C_5H_5)Ru$ moiety (**B**).[22] Another example of this type is the dimetallic iron(II)−chromium(0) complex $[(CO)_2(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}\eta^1{:}\eta^7\text{-}C_2C_7H_6)Cr(CO)_3][BF_4]$ (**C**) although structural parameters of the $Fe-C_\alpha-C_\beta-C_\gamma$ chain indicate that the bridging moiety can be better described as a substituted tropylium alkynyl group;[23] and (*iii*) the bis(allenylidene)dirhodium(I) complex $\{[(PiPr_3)_2\{Ph(o\text{-Tol})C=C=C=\}Rh]_2(\mu\text{-}1,3\text{-}N_3)\}^+$ (**D**) in which the two allenylidene groups, both rhodium atoms and the bridging azide ligand form an unusual eleven-membered chain.[24]

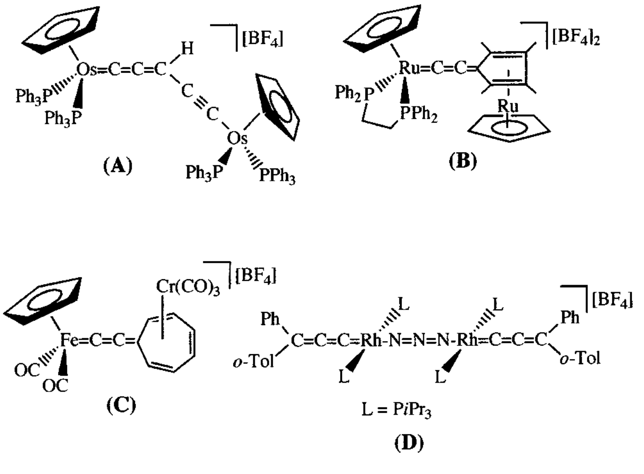


Figure 2. Some structures of dinuclear allenylidene complexes

b) Bridging cumulenylidene complexes (Figure 3): (*i*) The polynuclear complex $[Re(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)(CCC)Os_3(CO)_9(\mu\text{-}OMe)]$ (**A**) showing a bridging moiety Re=C=C−C in which the terminal carbon atom is bonded to the three osmium atoms and the center carbon atom binds to the osmium atom that is not methoxide-bridged. The ReCCC chain is highly distorted;[25] (*ii*) bridging butatrienylidene pentanuclear ruthenium complexes [Ru$_5$(μ_5-CCCCH$_2$)(μ_3-SMe)(μ-SMe)(μ-PPh$_2$)$_2$(CO)$_{10}$] (**B**) and [Ru$_5$(μ_5-CCCCH$_2$)(μ-SMe)$_2$(μ-PPh$_2$)$_2$(CO)$_{11}$] (**C**) in which the cumulenylidene ligand is attached to the cluster by three of its four carbon atoms;[26] (*iii*) trinuclear ruthenium clusters containing bridging μ_3-allenylidene ligands of the type **D**.[27] The X-ray crystal structures of a series of analogous derivatives containing Ru$_3$ and Ru$_3$Au cores have been also reported;[27] (*iv*) the Fe,Co mixed metal cluster of composition [(η^5-C$_5$Me$_5$)Fe$_2$Co$_4$(μ-C$_4$H)(CO)$_{17}$] (**E**) which consists of two triangular Fe$_2$Co and Co$_3$ cluster fragments linked by a C$_4$H bridge.[28] This moiety acts as a bridging allenylidene interacting with the Fe$_2$Co fragment as a μ_3-η^1(Fe):η^1(Fe):η^2(Co) ligand.

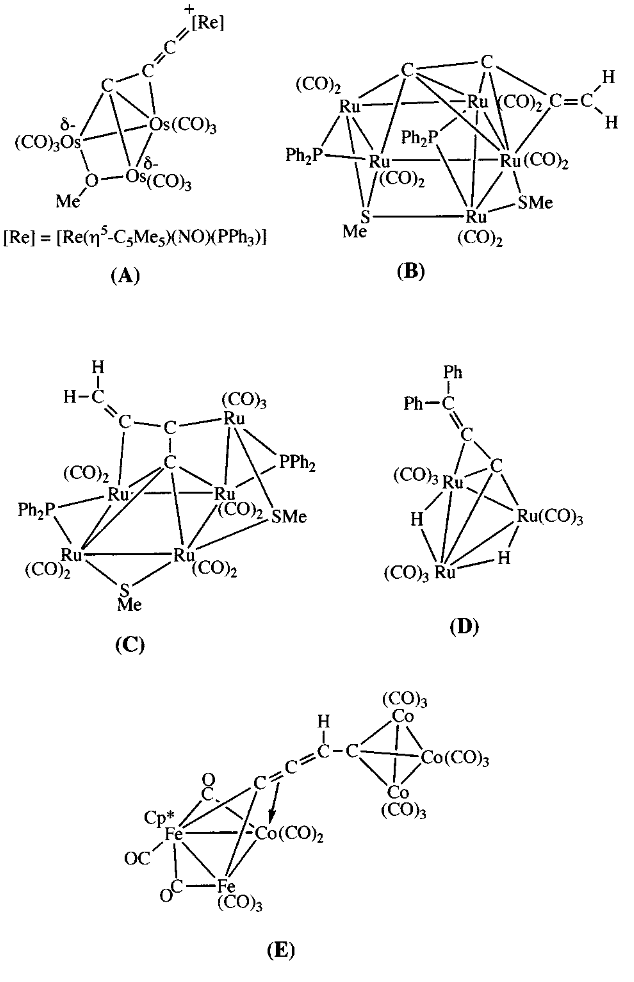


Figure 3. Some structures of polynuclear cumulenylidene complexes

Furthermore, the structures of the dinuclear complexes [(DMPE)$_2$IMn=C=C=C=C=MnI(DMPE)$_2$][BPh$_4$] [DMPE = 1,2-bis(dimethylphosphanyl)ethane],[29a] [(η^5-C$_5$Me$_5$)(DIPPE)Fe=C=C=C=C=Fe(DIPPE)(η^5-C$_5$Me$_5$)][PF$_6$]$_3$[29b] and [(η^5-C$_5$Me$_5$)(NO)(PPh$_3$)Re=C=C=C=Mn(CO)$_2$(η^5-C$_5$H$_5$)][BF$_4$][30] have also been determined by X-ray diffraction. They consist of a linear arrangement of the bridging cumulenylidene ligand with almost equal C=C distances (ca. 1.27−1.33 Å).

II.2 Spectroscopic Properties

II.2.1 IR and ^{13}C NMR

The infrared spectra of novel allenylidene complexes show the characteristic ν(C=C=C) strong absorption in the 1870−1971 cm^{-1} region. A lower frequency is observed (1803−1825 cm^{-1}) for the dinuclear Ru^{III}−Ru^{II} complexes [Ru(=C=C=Rc)(η^5-C$_5$H$_5$)L^{1}L^2][BF$_4$]$_2$ [Rc = (μ^2-η^6:η^5-C$_5$Me$_4$)Ru(η^5-C$_5$H$_5$); L^1 = L^2 = PPh$_3$, L^{1}L^2 = DPPE] which seems to indicate that the unsaturated chain is intermediate between that of a vinylidene and an allenylidene moiety.[22] C$_\alpha$ chemical shifts and coupling constants *J*(CP) in the ^{13}C NMR spectra have been widely reported and generally used as one of the most relevant data to support the existence of the metal−carbene bond. As expected, typical low field signals are found in the range $\delta \approx 255-320$. The following features deserve to be mentioned: a) although the resonance for the dinuclear iron(II) complex [(η^5-C$_5$H$_5$)(PPh$_3$)$_2$Fe{=C=C=CH−C≡C−Fe(PPh$_3$)$_2$(η^5-C$_5$H$_5$)}][BF$_4$] appears as usual ($\delta_{C\alpha}$ = 223.3), an high field chemical shift is shown by the corresponding resonance in the analogous osmium derivative ($\delta_{C\alpha}$ = 196.2);[21] b) a significant shielding effect on the C$_\alpha$ nucleus is observed in allenylidenes containing donor groups of the type *trans*-[RuX{=C=C=CR^{1}R^2}(DPPE)$_2$][PF$_6$], i.e. X = Cl; R^1 = H; R^2 = *p*-NMe$_2$C$_6$H$_4$ ($\delta_{C\alpha}$ = 265.7) vs. X = Cl; R^1 = H; R^2 = Ph ($\delta_{C\alpha}$ = 321.07), X = Cl; R^1 = R^2 = *p*-OMeC$_6$H$_4$ ($\delta_{C\alpha}$ = 288.4) vs. X = Cl; R^1 = R^2 = Ph ($\delta_{C\alpha}$ = 308.58), and R^1 = H; R^2 = CH=CH(*p*-NO$_2$C$_6$H$_4$) ($\delta_{C\alpha}$ = 322.77);[10] c) although the order $\delta_{C\alpha} > \delta_{C\beta} > \delta_{C\gamma}$ is usually found for most of the allenylidene complexes, an inversion of the sequence of the chemical shifts has been reported in several cases, i.e. *trans*-[IrX(P*i*Pr$_3$)$_2$] (X = OH, OPh, F; $\delta_{C\alpha}$ = 202.7−205.8, $\delta_{C\beta}$ = 252.8−273.9).[20]

II.2.2 Mössbauer Spectroscopy

^{57}Fe Mössbauer spectroscopic studies have been performed for mono- and dinuclear iron−allenylidene complexes by Lapinte et al.[31] The spectrum of the complex [Fe{=C=C=C(OMe)Me}(η^5-C$_5$Me$_5$)(DPPE)][BPh$_4$] displays a quadrupole doublet at δ = 0.160 mm s^{-1} with a quadrupole splitting of ΔE_Q= 1.451 mm s^{-1}. These parameters are well-differentiated from those of analogous complexes containing iron−carbon single bonds with the conclusion that by using this spectroscopic technique, it is possible to identify the metal−carbon bonding order. The spectra of the bridging butatrienylidene complexes [(η^5-C$_5$Me$_5$)L^{1}L^{2}Fe{=C=C=C=C(H)Fe(η^5-C$_5$Me$_5$)(CO)$_2$}]-[BF$_4$] (L^{1}L^2 = DPPE, DIPPE) at 80 K show two quadrupole doublets δ = 0.161−0.257 and 0.029 mm s^{-1} (ΔE_Q= 1.973−1.264 and 1.974−1.778 mm s^{-1}, respectively) which are characteristic of iron dinuclear species with two different coordination environments around the metal atoms.[32] The doublet with the larger isomeric shift was assigned to the [(η^5-C$_5$Me$_5$)L^{1}L^{2}Fe] fragment. These values are consistent with a weak Fe=C π-bond which is in agreement with the electron delocalization along the cumulenylidene chains in which significant contributions of the mesomers $[Fe]-C^+=C=C=C(R)-[Fe]$ and $[Fe]-C{\equiv}C-C^+=C(R)-[Fe]$ are present.

III. Theoretical Studies

Since the early studies by Hoffman[33] using the half-sandwich complex $[Mn(=C=C=CH_2)(\eta^5\text{-}C_5H_5)(CO)_2]$ as a model, a series of theoretical calculations on allenylidene complexes involving several metallic fragments have now been reported. These studies, performed using the Extended Hückel Molecular Orbital (EHMO) methodology, generally confirm the initial results obtained on the electronic structure[33] and on the reactivity[34] which establish: (*i*) the most stable conformation of the allenylidene group $=C=C=CR^1R^2$ is that contained in the molecular plane, (*ii*) the allenylidene fragment is a σ-donor π-acceptor ligand with a dominant contribution to the bonding of the latter component, and (*iii*) the carbon atoms of the unsaturated chain are alternatively electron-poor and electron-rich, starting from the metal center. Hence, electrophilic centers are located at the C_α and C_γ atoms while the C_β atom is a nucleophilic site.

Table 1 collects quantitative data of the LUMO and HOMO distribution, as well as net charges at the carbon atoms of the allenylidene chain on a series of cationic ruthenium and osmium(II) as well as the neutral $[OsCl(=C=C=CH_2)(\eta^5\text{-}C_5H_5)(PH_3)]$ models. On the basis of these data, the following points deserve to be highlighted: (*i*) the LUMO distribution along the C_3 chain (20−28% C_α; 30−37% C_γ) is similar, regardless of the nature of the metal (Ru or Os) and the auxiliary ligands, (*ii*) total charge transfer from the metallic fragments $[OsCl(\eta^5\text{-}C_5H_5)(PH_3)]$ and $[Os(\eta^5\text{-}C_5H_5)(PH_3)_2]^+$ is similar and higher (ca. 57−60%) than that of $[Os(\eta^5\text{-}C_5H_5)(CO)(PH_3)]^+$, (*iii*) the fragment $[Ru(\eta^5\text{-}C_9H_7)(PH_3)_2]^+$ shows total charge-transfer values which are notably higher (ca. 69−86%) than those of $[Ru(\eta^5\text{-}C_9H_7)(CO)(PH_3)]^+$ and $[Ru(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4)(CO)(PH_3)]^+$, respectively.

These results allow the rationalization of the reactivity of these species which can be classified, depending on the type of addition, as electrophilic and nucleophilic allenylidenes. It is worth mentioning the versatile chemical behavior of $[Os(=C=C=CPh_2)(\eta^5\text{-}C_5H_5)(PiPr_3)_2][PF_6]$, which probably arises from the particular total charge-transfer value and its cationic character which is able to undergo both electrophilic and nucleophilic additions (see below).[38] As a general trend, it can be observed that the cationic complexes undergo orbitally controlled nucleophilic additions at either C_α and C_γ atoms, and that the regioselectivity depends on the steric and/or electronic properties of the ancillary ligands (see below).

EHMO calculations have also been performed for a bridging (allenylidene)dirhodium(I) complex, using $[Rh_2(\mu\text{-}OOCH)(\mu\text{-}\sigma,\sigma\text{-}C=C=CH_2)(CO)_2(PH_3)_2]^+$ as a model, showing that the allenylidene ligand also behaves as a good π-acceptor ligand, the highest negative charge being located at the C_α atom.[39] This charge is found to decrease towards the C_γ atom. Brief accounts of theoretical calculations on the dinuclear complexes $[(\eta^5\text{-}C_5H_5)(PH_3)_2Ru\{=C=C=C(H)-C{\equiv}C-Ru(PH_3)_2(\eta^5\text{-}C_5H_5)\}]^+$ [21] and $[(PH_3)_4IMn=C=C=C=C=MnI(PH_3)_4]$[29a] have also been reported. More recently,[40] density-functional calculations have been performed on the metallacumulenylidene complexes $[Cr\{(=C)_nH_2\}(CO)_5]$ (n = 2−9) showing, as for the above-mentioned examples, that the electrophilic and nucleophilic attacks are frontier orbital controlled. Dissociation energies have been calculated and found to be essentially independent of the chain length.

IV. Reactivity of Cationic Allenylidene Complexes

As shown in previous theoretical and experimental studies,[4a,4b] the reactivity of novel cationic transition-metal allenylidene derivatives is mainly governed by the electron-deficient character of the C_α and C_γ carbon atoms in the cumulene chain, which are therefore subject to nucleophilic attacks. The regioselectivity of the nucleophilic additions seems to be controlled by the electronic and steric properties both of the substituents on the unsaturated hydrocarbon chain and the ancillary ligands on the metal atom and the nucleophile used (see below). Additions of electrophiles at the nucleophilic C_β atom of neutral allenylidene derivatives are scarce,[4a−4b] the protonation of the diphenylallenylidene osmium(II) complex $[Os(=C=C=CPh_2)(\eta^5\text{-}C_5H_5)(PiPr_3)_2][PF_6]$ with HPF_6 to give the alkenylcarbyne $[Os\{{\equiv}C-C(H)=CPh_2\}(\eta^5\text{-}C_5H_5)(PiPr_3)_2][PF_6]_2$ being the only example of an electrophilic addition in a cationic complex reported to date.[38]

Table 1. LUMO and HOMO distribution and net charges of the allenylidene chain on half-sandwich Ru^{II} and Os^{II} complexes

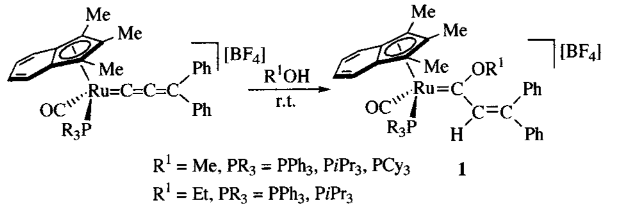
Model	HOMO (%)			LUMO (%)			Net charges			Ref.
	C_α	C_β	C_γ	C_α	C_β	C_γ	C_α	C_β	C_γ	
$[Ru(\eta^5\text{-}C_9H_7)(PH_3)_2]^+$	3	21	0	20	6	34	−0.352	−0.151	−0.048	[35]
$[Ru(\eta^5\text{-}C_9H_7)(CO)(PH_3)]^+$	4	21	0	24	4	37	−0.267	−0.118	0.033	[36a]
$[Ru(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4)(CO)(PH_3)]^+$	4[a]	21[a]	0[a]	23	4	36	−0.281	−0.118	0.023	[36b]
$[Ru(\eta^5\text{-}C_5H_5)(CO)(PH_3)]^+$	[b]	20	[b]	23	6	31	−0.36	−0.13	−0.05	[37]
$[OsCl(\eta^5\text{-}C_5H_5)(PH_3)]$	4	22	0	24	5	30	−0.46	−0.07	−0.17	[38]
$[Os(\eta^5\text{-}C_5H_5)(PH_3)_2]^+$	4	25	0	24	5	31	−0.41	−0.10	−0.15	[38]
$[Os(\eta^5\text{-}C_5H_5)(CO)(PH_3)]^+$	5	23	0	28	3	33	−0.33	−0.08	−0.09	[38]

[a] Next HOMO. − [b] $C_\alpha + C_\gamma$ = 6%.

IV.1 Additions of Neutral Nucleophiles

IV.1.1 Alcohols

One of the most remarkable reactions of cationic allenylidene complexes is the nucleophilic addition of alcohols to afford Fischer-type α,β-unsaturated alkoxycarbene derivatives of general formula $[M]^+{=}C(OR^1){-}C(H){=}CR^2R^3$.[4a–4b] The regioselectivity of the addition is in agreement with the formation of allenyl species $[M]{-}C(HO^+R^1){=}C{=}CR^2R^3$ as intermediates or transition states. This oxygen–C_α interaction labilizes the O–H bond, favoring the migration of the hydrogen atom to C_β. The ability of the allenylidene ligand to undergo these nucleophilic attacks is clearly dependent on the electronic and steric nature of the ancillary ligands on the metal atom.[4a–4b] This is nicely illustrated by the behavior of indenylruthenium(II)–allenylidene complexes. Thus, while the disubstituted derivatives $[Ru({=}C{=}C{=}CR^2R^3)(\eta^5\text{-}1,2,3\text{-}R^1_3C_9H_4)L^1L^2]^+$ (R^1 = H, $L^1 = L_2 = PPh_3$, L^1L^2 = DPPE, DPPM, $R^2 = R^3$ = Ph, $R^2R^3 = C_{12}H_8$; R^1 = Me, L^1L^2 = DPPM, $R^2 = R^3$ = Ph) are unreactive towards alcohols,[41,42] the diphenylallenylidene complexes $[Ru({=}C{=}C{=}CPh_2)(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4)(CO)(PR_3)]^+$ ($PR_3 = PPh_3$, $PiPr_3$, PCy_3) containing the less sterically demanding and more π-accepting CO/PR_3 combination react with methanol or ethanol to yield the alkenyl(alkoxy)carbene derivatives $[Ru\{{=}C(OR^1){-}C(H){=}CPh_2\}(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4)(CO)(PR_3)][BF_4]$ (**1**) (Scheme 2).[42,43] It should be noted that the diphenylallenylidenes $[RuCl({=}C{=}C{=}CPh_2)(\eta^6\text{-}p\text{-cymene})(PR_3)][PF_6]$ ($PR_3 = PCy_3$, $PiPr_3$, PPh_3), used recently by Dixneuf and co-workers as active catalysts for the RCM of olefins, are also unreactive towards alcohols.[44]



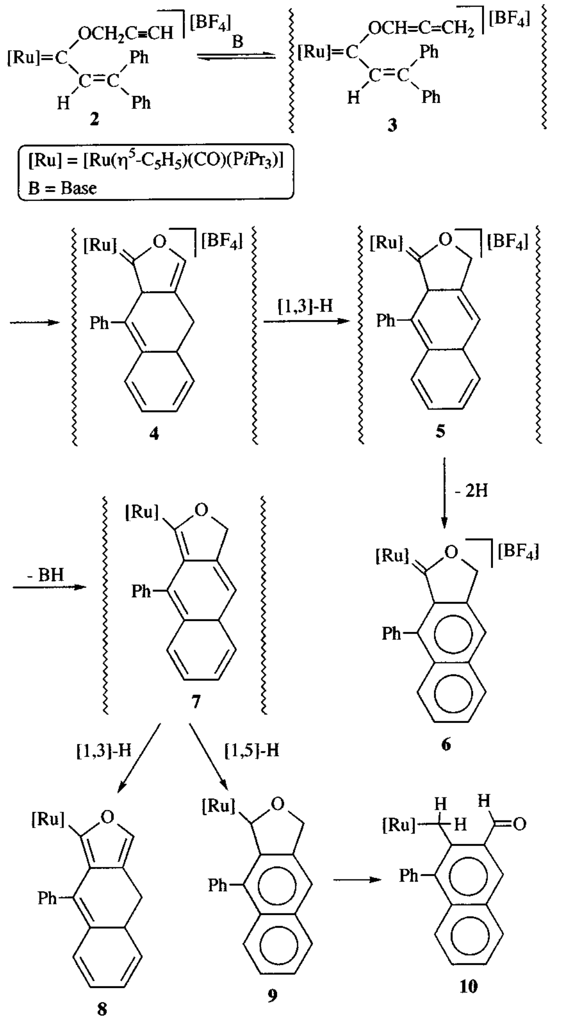
Scheme 2. Synthesis of (1,2,3-trimethylindenyl)ruthenium(II)–(alkenyl)(alkoxy)carbene complexes

There is also an influence of the allenylidene substituents in the reactivity of the corresponding complexes towards alcohols. This fact is clearly shown in the formation of the Fischer-type carbene complexes $[Ru\{{=}C(OMe){-}C(H){=}C(H)R\}(\eta^5\text{-}C_9H_7)L^1L^2][PF_6]$ (R = Ph, L^1L^2 = DPPE, DPPM; R = H, L^1L^2 = DPPM) which are readily obtained by the reaction of $[RuCl(\eta^5\text{-}C_9H_7)L^1L^2]$ with $HC{\equiv}CCH(OH)R$ and $NaPF_6$ in methanol by nucleophilic attack of the alcohol on the unstable allenylidene intermediates $[Ru\{{=}C{=}C{=}C(H)R\}(\eta^5\text{-}C_9H_7)L^1L^2][PF_6]$.[41] The related methoxycarbene derivatives $[Ru\{{=}C(OMe){-}C(H){=}CMe_2\}(\eta^6\text{-}C_6Me_6)(MDMPP\textit{P,O})][PF_6]$[MDMPP-*P,O* = P(2-*O*-6-MeOC$_6$H$_3$)Ph$_2$],[45] $[RuCl\{{=}C(OMe){-}C(H){=}CPh_2\}(PPh_3)\{\kappa^3\text{-}N,N,N(PYBOX)\}][PF_6]$ [PYBOX = 2,6-bis(dihydrooxazolin-2′-yl)pyridine],[16] and $[Re\{{=}C(OMe){-}C(H){=}C(H)Me\}(TRIPHOS)(CO)_2][CF_3SO_3]$ [TRIPHOS = 1,1,1-tris(diphenylphosphanylmethyl)ethane][46] have recently been obtained following this simple synthetic procedure. In addition, the methoxy(methoxyethyl)carbene complex $[Re\{{=}C(OMe)CH_2CH_2(OMe)\}(TRIPHOS)(CO)_2][CF_3SO_3]$ has been prepared by treatment of hydroxyvinylidene $[Re\{{=}C{=}C(H)CH_2(OH)\}(TRIPHOS)(CO)_2][CF_3SO_3]$ with methanol, through a concerted dehydration followed by a double addition of MeOH to the C_α and C_γ atoms of the transient allenylidene $[Re({=}C{=}C{=}CH_2)(TRIPHOS)(CO)_2][CF_3SO_3]$.[46]

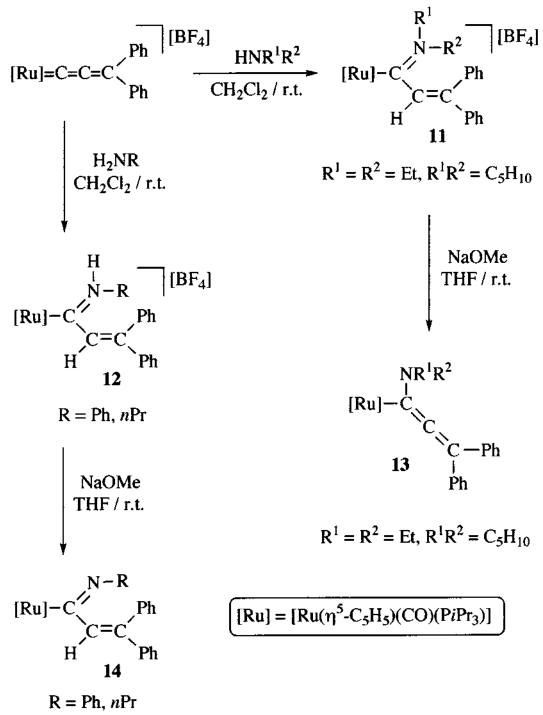
The reaction of $[Ru({=}C{=}C{=}CPh_2)(\eta^5\text{-}C_5H_5)(CO)(P\text{-}iPr_3)][BF_4]$ with propargyl alcohol is of particular interest. The addition gives the α,β-unsaturated (propargyloxy)carbene complex $[Ru\{{=}C(OCH_2C{\equiv}CH){-}C(H){=}CPh_2\}(\eta^5\text{-}C_5H_5)(CO)(PiPr_3)][BF_4]$ (**2**) which reacts with bases to afford a mixture of rare cycloaddition products including **6**, **8**, **9**, and **10** (Scheme 3),[47] the main components of the mixture being dependent on the nature of the base used. The following mechanism is proposed: (*i*) formation in the first step of the (allenyloxy)carbene intermediate **3** by a base-catalyzed isomerization of the propargylic unit into an allenic moiety, (*ii*) an intramolecular Diels–Alder reaction within complex **3** to give the unstable tricyclic alkoxycarbene **4** (the C_β–C_γ double bond and one of the phenyl groups of the alkenyl unit act as an inner-outer ring diene and the $C{=}CH_2$ fragment of the alkoxy group acts as a dienophile) and (*iii*) subsequent 1,3-hydrogen shift from the methylene group of the central ring to the OCH= carbon atom on **4** would give carbene intermediate **5** which by aromatization should yield the stable complex **6**. Formation of **8** and **9** has been explained by taking into account that a deprotonation process occurs on **5** to produce the tricyclic alkenyl derivative **7**, which could evolve both by a 1,3- or 1,5-hydrogen shift, respectively. Complex **10** seems to be the result of a concerted intramolecular proton-transfer reaction within the heterocycle of **9**.

IV.1.2 Amines

By analogy with the above-mentioned reactions, the addition of primary or secondary amines to a cationic allenylidene ligand should afford aminocarbene complexes $[M]^+{=}C(NR^1R^2){-}C(H){=}CR^3R^4$. In this context, Esteruelas and co-workers have recently described the reactivity of $[Ru({=}C{=}C{=}CPh_2)(\eta^5\text{-}C_5H_5)(CO)(PiPr_3)][BF_4]$ towards secondary and primary amines.[48] As expected, addition of the N–H bond of the amines to the C_α–C_β double bond of the allenylidene group takes place, yielding complexes **11** and **12** (Scheme 4). Nevertheless, structural studies as well as theoretical calculations seem to indicate that these complexes are better described as azoniabutadienyl species, where the contribution of the aminocarbene resonance form is not relevant. Once again, the regioselectivity of these nucleophilic attacks seems to be governed by the steric bulk of the ligands present at the metal center, since the cationic alkynyl derivative $[Ru\{C{\equiv}CCPh_2(NHMe_2)\}(\eta^5\text{-}C_5H_5)(PPh_3)_2][PF_6]$ was quantitatively obtained when



Scheme 3. Synthesis of polycyclic ruthenium(II) complexes starting from $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_5H_5)(CO)(PiPr_3)][BF_4]$



Scheme 4. Preparation of (azoniabutadienyl)-, (aminoallenyl)- and (azabutadienyl)Ru^{II} complexes

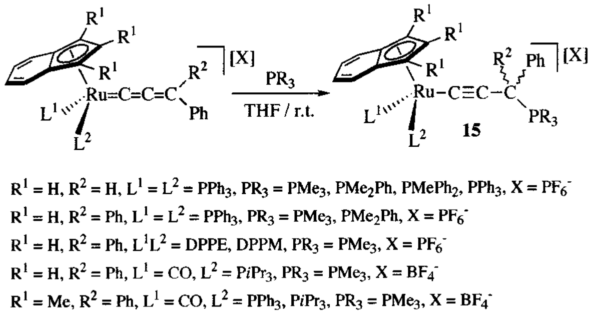
$[Ru(=C=C=CPh_2)(\eta^5\text{-}C_5H_5)(PPh_3)_2][PF_6]$ was dissolved in neat dimethylamine.[49] The marked difference in behavior between the tertiary and secondary azoniabutadienyl complexes **11** and **12** should be noted. Thus, while deprotonation of **11** takes place on the $CH=CPh_2$ group to yield aminoallenyl derivatives **13**, deprotonation of **12** occurs selectively at the nitrogen atom affording azabutadienyl complexes **14** (Scheme 4).[48]

The reactivity of the cationic Rh^I−diphenylallenylidene derivative *trans*-$[Rh(=C=C=CPh_2)(O=CMe_2)(PiPr_3)_2][PF_6]$ towards pyridine and ammonia has also been explored.[17] Surprisingly, in this case no addition of the amine on the allenylidene chain was observed, giving instead acetone substitution products i.e. *trans*-$[Rh(=C=C=CPh_2)(Py)(PiPr_3)_2][PF_6]$ and *trans*-$[Rh(=C=C=CPh_2)(NH_3)(PiPr_3)_2][PF_6]$. In addition, treatment of complexes *trans*-$[RuCl\{=C=C=C(OMe)CH_2Ph\}(DPPE)_2][PF_6]$[50] and $[Re\{=C=C=C(Me)Ph\}(TRIPHOS)(CO)_2][CF_3SO_3]$,[46] containing an acidic hydrogen atom at C_δ, with triethylamine exclusively yields neutral enynyl derivatives *trans*-$[RuCl\{C\equiv C-C(OMe)=C(H)Ph\}(DPPE)_2]$ and $[Re\{C\equiv C-C(Ph)=CH_2\}(TRIPHOS)(CO)_2]$, respectively, as the result of a deprotonation process.

IV.1.3 Phosphanes

a) Phosphonioalkynyl and -allenyl Complexes: The nucleophilic attack of phosphanes on allenylidene complexes is a well-documented reaction.[4a−4b] Thus, we have found that indenylruthenium(II)−allenylidene complexes $[Ru\{=C=C=C(R^2)Ph\}(\eta^5\text{-}1,2,3\text{-}R'_3C_9H_4)L^1L^2]^+$ (R^1 = H, R^2 = Ph, $L^1 = L^2 = PPh_3$, L^1L^2 = DPPE, DPPM, L^1 = CO, $L^2 = PiPr_3$; R^1 = H, R^2 = H, $L^1 = L^2 = PPh_3$; R^1 = Me, R^2 = Ph, L^1 = CO, $L^2 = PPh_3$, $PiPr_3$) undergo regioselective additions of tertiary phosphanes at the C_γ atom, affording cationic phosphonioalkynyl complexes **15** in excellent yields (Scheme 5).[43,51] The related phosphonioalkynyl derivatives $[Ru\{C\equiv CCR^1R^2(PPh_3)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ ($R^1 = R^2$ = H; CR^1R^2 = cyclopentyl, cyclohexyl) and $[Ru\{C\equiv CC(H)Ph(PPh_3)\}(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4(CO)(PPh_3)][BF_4]$ were obtained in a one-pot synthesis by reaction of halide complexes $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ and $[RuBr(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4)(CO)(PPh_3)]$ with the corresponding propargyl alcohol in the presence of $NaPF_6$ or $AgBF_4$ and a large excess of PPh_3.[43,52,53] These nucleophilic additions seem to be controlled not only by the steric properties of the metallic fragments but also both by the cone angle of the phosphane and the size of the allenylidene substituents. Thus, complexes $[Ru\{C\equiv CCPh_2(PMe_3)\}(\eta^5\text{-}C_9H_7)(DPPM)][PF_6]$ and $[Ru\{C\equiv CCPh_2(PMe_3)\}(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4)(CO)(PPh_3)][BF_4]$ slowly isomerize at room temperature to give the thermodynamically more stable phosphonioallenyl derivatives $[Ru\{C(PMe_3)=C=CPh_2\}(\eta^5\text{-}C_9H_7)(DPPM)][PF_6]$[51] and

$[Ru\{C(PMe_3){=}C{=}CPh_2\}(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4)(CO)(PPh_3)][BF_4]$,[43] respectively, while $[Ru\{C(PMe_2Ph){=}C{=}CPh_2\}(\eta^5\text{-}C_9H_7)(DPPM)][PF_6]$[51] and $[Ru\{C(PR_3){=}C{=}CPh_2\}(\eta^5\text{-}C_5H_5)(CO)(P\textit{i}Pr_3)][BF_4]$ (PR_3 = PPh_3, $PMePh_2$, $PHPh_2$)[54] were obtained regioselectively when allenylidenes $[Ru({=}C{=}C{=}CPh_2)(\eta^5\text{-}C_9H_7)(DPPM)][PF_6]$ and $[Ru({=}C{=}C{=}CPh_2)(\eta^5\text{-}C_5H_5)(CO)(P\textit{i}Pr_3)][BF_4]$ were treated with the appropriate phosphane. Related phosphanylalkynyl complexes $[Ru\{C{\equiv}CCR^1R^2(PEt_3)\}(\eta^5\text{-}C_5Me_5)(PEt_3)_2][BPh_4]$ (R^1 = R^2 = Me; CR^1R^2 = cyclohexyl) were recently synthesized in low yields, by the direct activation of $HC{\equiv}CC(OH)R^1R^2$ by $[RuCl(\eta^5\text{-}C_5Me_5)(PEt_3)_2]$ without an external source of PEt_3.[11] Apparently, phosphane dissociation occurs to some extent in solution, reacting with transient $[Ru({=}C{=}C{=}CR^1R^2)(\eta^5\text{-}C_5Me_5)(PEt_3)_2][BPh_4]$ species.

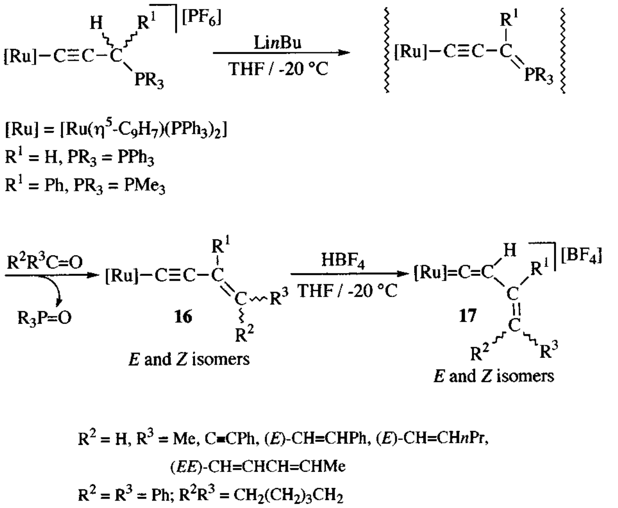


R^1 = H, R^2 = H, L^1 = L^2 = PPh_3, PR_3 = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, X = PF_6^-
R^1 = H, R^2 = Ph, L^1 = L^2 = PPh_3, PR_3 = PMe_3, PMe_2Ph, X = PF_6^-
R^1 = H, R^2 = Ph, L^1L^2 = DPPE, DPPM, PR_3 = PMe_3, X = PF_6^-
R^1 = H, R^2 = Ph, L^1 = CO, L^2 = $P\textit{i}Pr_3$, PR_3 = PMe_3, X = BF_4^-
R^1 = Me, R^2 = Ph, L^1 = CO, L^2 = PPh_3, $P\textit{i}Pr_3$, PR_3 = PMe_3, X = BF_4^-

Scheme 5. Synthesis of indenylruthenium(II)−phosphanylalkynyl complexes

b) Synthetic Utility of Phosphonioalkynyl Complexes: We have exploited the synthetic utility of the readily available indenylruthenium(II)−phosphonioalkynyl complexes $[Ru\{C{\equiv}CC(R^1)H(PR_3)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (R^1 = H, PR_3 = PPh_3; R = Ph, PR_3 = PMe_3) containing an acidic hydrogen atom at C_γ. These complexes are suitable precursors for the high-yield preparation of a wide series of neutral enynyl and polyenynyl complexes **16** (Scheme 6) by means of Wittig-type processes with carbonyl compounds.[55,56] When aldehydes are used, inseparable mixtures of the corresponding (*E*) and (*Z*) stereoisomers are obtained. The polyenynyl skeleton in complexes **16** should be an excellent pathway for electron delocalization between the electron-rich metal fragment $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ and terminal functional groups. We therefore carried out a series of Wittig reactions using unsaturated aldehydes and ketones bearing strong electron-accepting end groups (e.g. *p*-$NO_2C_6H_4$, *p*-CNC_6H_4) or efficient bridging groups (e.g. C≡N, pyridine), capable of coordinating metallic acceptor fragments [e.g. $Cr(CO)_5$, $W(CO)_5$]. As expected, the resulting donor−acceptor enynyl and polyenynyl complexes are of interest as materials with good second-order nonlinear optical (NLO) properties exhibiting high values of the molecular quadratic hyperpolarizability coefficient (β).[52]

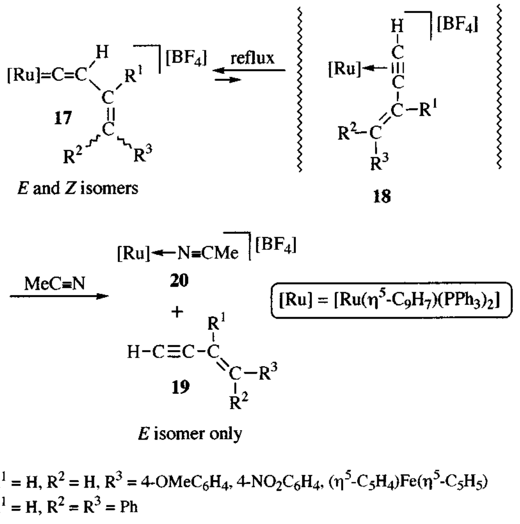
We have also shown that protonation of these polyunsaturated alkynyl derivatives proceeds regioselectively at the C_β atom of the alkynyl group affording unprecedented cationic vinylvinylidene and polyenylvinylidene species **17** (Scheme 6).[55,56] Vinylvinylidene complexes **17** are of interest in organic synthesis. Heating at reflux in acetonitrile stereoselectively generates the corresponding terminal (*E*)-1,3-enynes **19** and the cationic nitrile complex $[Ru(\eta^5\text{-}C_9H_7)(N{\equiv}CMe)(PPh_3)_2][BF_4]$ (**20**) (Scheme 7).[56] This reaction can be explained taking into account that vinylvinylidenes **17** are in equilibrium with their η^2-coordinated 1,3-enyne tautomers $[Ru\{\eta^2\text{-}HC{\equiv}CC(R^1){=}CR^2R^3\}(\eta^5\text{-}C_9H_7)(PH_3)_2][BF_4]$ (**18**). The rapid substitution of the labile coordinated enyne by the more basic acetonitrile ligand favors the displacement of the equilibrium to afford the final species **19** and **20**. Ab initio molecular orbital (MO) calculations on the model $[Ru({=}C{=}CH_2)(\eta^5\text{-}C_9H_7)(PH_3)_2]^+$ are consistent with the experimental results.



[Ru] = $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]$
R^1 = H, PR_3 = PPh_3
R^1 = Ph, PR_3 = PMe_3

R^2 = H, R^3 = Me, C≡CPh, (*E*)-CH=CHPh, (*E*)-CH=CH*n*Pr, (*EE*)-CH=CHCH=CHMe
R^2 = R^3 = Ph; R^2R^3 = $CH_2(CH_2)_3CH_2$

Scheme 6. Synthesis of indenylruthenium(II)−enynyl, −polyenynyl, −vinylvinylidene, and −polyenylvinylidene complexes



R^1 = H, R^2 = H, R^3 = 4-$OMeC_6H_4$, 4-$NO_2C_6H_4$, $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$
R^1 = H, R^2 = R^3 = Ph

Scheme 7. Synthesis of terminal (*E*)-1,3-enynes starting from indenylruthenium(II)−vinylvinylidene complexes

In summary, it was shown that indenylruthenium(II)−allenylidene complexes are useful precursors for the synthesis of functionalized terminal alkynes. Schemes 6 and 7 show a systematic synthetic approach which allows the isolation of free alkynes in good yields, recovering the metallic fragment quantitatively.

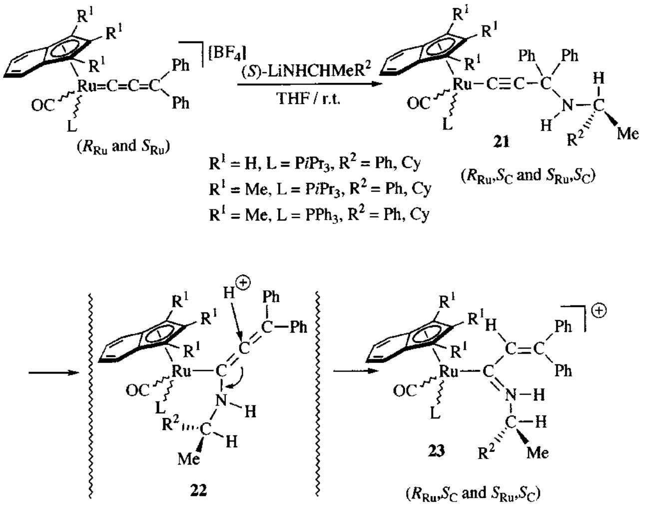
IV.2 Additions of Anionic Nucleophiles: Synthesis of Neutral Alkynyl Complexes $[M]-C{\equiv}C-C(Nu)R^1R^2$

IV.2.1 Heteroanions

In marked contrast to alcohols, alcoholates $[R^1O]^-$ add regioselectively at the C_γ atom of cationic allenylidene complexes to afford neutral alkynyl derivatives of general formula $[M]-C{\equiv}C-C(OR^1)R^2R^3$.[4a−4b] Complexes $[Ru\{C{\equiv}CC(OR)Ph_2\}(\eta^5\text{-}C_5H_5)L^1L^2]$ [$L^1 = L^2 = PPh_3$, R = Me; $L^1 = PPh_3$, $L^2 = PPh_2CH_2C(=O)t\text{Bu}$, R = Me, Et; L^1 = CO, $L^2 = PiPr_3$, R = Me],[49,54,57] $[Ru\{C{\equiv}CC(OMe)Ph_2\}(\eta^5\text{-}C_9H_7)L^1L^2]$ [$L^1 = L^2 = PPh_3$; L^1L^2 = DPPE, DPPM; L^1 = CO, $L^2 = PiPr_3$; $L^1 = PPh_3$, $L^2 = PPh_2CH_2C(=O)t\text{-Bu}$],[43,51,57] $[Ru\{C{\equiv}CC(OMe)Ph_2\}(\eta^{5-}1,2,3\text{-}Me_3C_9H_4)(CO)(PPh_3)]$,[42] $[Ru\{C{\equiv}CC(OMe)C_{13}H_{20}\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$,[58] $[Ru\{C{\equiv}CC(OMe)Ph_2\}\{HB(pz)_3\}(PPh_3)_2]$,[15] *trans*-$[Ru\{C{\equiv}CC(OMe)Ph_2\}(C{\equiv}CR)(DPPE)_2]$ (R = Ph, *p*-$OMeC_6H_4$)[10] and $[Os\{C{\equiv}CC(OMe)Ph_2\}(\eta^5\text{-}C_5H_5)(PiPr_3)_2]$[38] have recently been synthesized in high yields by treatment of the appropriate allenylidene complex with the corresponding sodium or potassium alkoxide. No isomerization of these alkynyl derivatives into alkoxyallenyl species $[M]-C(OR^1)=C=CR^2R^3$ has been reported. The inverse regioselectivity observed with these hard nucleophiles seems to be charge-controlled (see Table 1). In agreement with this, theoretical calculations carried out by Esteruelas and co-workers on the model complexes $[Ru\{C{\equiv}CC(OMe)H_2\}(\eta^5\text{-}C_5H_5)(CO)(PH_3)]$ and $[Ru\{C(OMe)=C=CH_2\}(\eta^5\text{-}C_5H_5)(CO)(PH_3)]$ indicate that the former is approximately 9.29 kcal/mol more stable than the latter.[54] Although neutral alkynyl derivatives usually react with electrophiles at the β-position to produce cationic vinylidene complexes,[4a] protonation of these methoxyalkynyl species regenerates the starting allenylidenes in almost quantitative yields.

The related alkynyl complexes $[Ru\{C{\equiv}CC(OH)Ph_2\}(\eta^5\text{-}C_5H_5)(CO)(PiPr_3)]$ and *trans*-$[Ru\{C{\equiv}CC(H)Ph_2\}(C{\equiv}CPh)(DPPE)_2]$ have also been regioselectively obtained by the reaction of $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_5H_5)(CO)(PiPr_3)][BF_4]$ and *trans*-$[Ru(C{\equiv}CPh)\{=C=C=CPh_2\}(DPPE)_2][PF_6]$ with KOH and $NaBH_4$, respectively.[10,54] The cationic (diphenylallenylidene)rhodium(I) derivative *trans*-$[Rh(=C=C=CPh_2)(O=CMe_2)(PiPr_3)_2][PF_6]$ also undergoes substitution of the labile acetone ligand when treated with sodium acetate or potassium hydroxide, yielding neutral allenylidenes *trans*-$[Rh(=C=C=CPh_2)\{\kappa^1(O)\text{-COOMe}\}(P\text{-}iPr_3)_2]$ and *trans*-$[Rh(=C=C=CPh_2)(OH)(PiPr_3)_2]$, respectively.[17]

In our laboratory we have explored the reactivity of indenylruthenium(II)−allenylidene compounds towards N-donor hard nucleophiles such as amides or azides and we have found that complexes $[Ru(=C=C=CPh_2)(\eta^5\text{-}1,2,3\text{-}R^1_3C_9H_4)(CO)L][BF_4]$ (R^1 = H, L = $PiPr_3$; R^1 = Me, L = PPh_3, $PiPr_3$) react with lithium (*S*)-α-methylbenzylamide or lithium (*S*)-1-cyclohexylethylamide to afford alkynyl derivatives **21** in a regioselective manner (Scheme 8).[43] These complexes were obtained as equimolecular mixtures of diastereoisomers. It should be noted that, in marked contrast to the above-mentioned methoxyalkynyl derivatives, complexes **21** are thermodynamically unstable and slowly generate azoniabutadienyl compounds **23** both in solution and in the solid state. Formation of **23** probably involves an initial migration of the amide group from the C_γ to C_α to yield allenyl complexes **22**, followed by protonation on the central carbon atom of the allenic moiety.

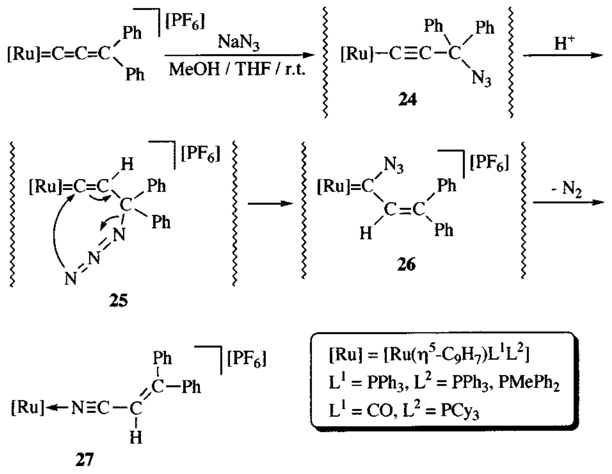


Scheme 8. Reactivity of indenylruthenium(II)−allenylidene complexes towards chiral amides

Treatment of indenyl complexes $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)L^1L^2][PF_6]$ ($L^1 = PPh_3$, $L^2 = PPh_3$, $PMePh_2$; L^1 = CO, $L^2 = PCy_3$) with sodium azide in methanol does not afford stable alkynyl species. Instead, the reaction gives the cationic nitrile complexes **27** (Scheme 9).[59] We propose that, although initially the expected alkynyl derivatives **24** are formed, they are readily protonated by the protic solvent (we note that no reaction was observed in the absence of methanol) to generate vinylidene intermediates **25**. Intramolecular attack of the terminal nitrogen atom of the azide group at the electrophilic C_α atom on vinylidenes **25**[4a] and subsequent rearrangement gives the α,β-unsaturated carbene complexes **26**. The reaction ends with the extrusion of N_2 and the migration of the metallic fragment to the nitrogen atom to give the observed products. Complexes **27** can be easily demetalated by treatment with a second equivalent of NaN_3 to yield free diphenylacrylonitrile and the azide complexes $[Ru(N_3)(\eta^5\text{-}C_9H_7)L^1L^2]$.

IV.2.2 Carbanions

Cationic allenylidene complexes can be used as suitable starting materials for carbon−carbon coupling reactions through the nucleophilic addition of carbanions to the unsaturated hydrocarbon chain. In this context we have reported that complexes $[Ru(=C=C=CR^1R^2)(\eta^5\text{-}C_9H_7)$-



Scheme 9. Reactivity of (indenyl)Ru^{II}−allenylidene complexes towards sodium azide

L^1L^2][PF_6] ($L^1 = L^2 = PPh_3$, $R^1 = R^2 = Ph$, $R^1R^2 = C_{13}H_{20}$; L^1L^2 = DPPE, $R^1 = R^2 = Ph$) regioselectively react with alkyllithium reagents or sodium cyanide under mild conditions to yield [Ru{$C{\equiv}CC(R^3)R^1R^2$}(η^5-C_9H_7)L^1L^2] ($L^1 = L^2 = PPh_3$, $R^1 = R^2 = Ph$, R^3 = Me, *n*Bu, C≡N; $L^1 = L^2 = PPh_3$, $R^1R^2 = C_{13}H_{20}$, R^3 = C≡N; L^1L^2 = DPPE, $R^1 = R^2 = Ph$, R^3 = Me, *n*Bu).[51,58,60] Related cyclopentadienyl complexes [Ru{$C{\equiv}CC(R)Ph_2$}(η^5-C_5H_5)(PPh_3)$_2$] (R = Me, C≡N, C_5H_5)[49] and [Os{$C{\equiv}CC(Me)Ph_2$}(η^5-C_5H_5)(P*i*Pr$_3$)$_2$][38] have recently been obtained using this synthetic methodology. Highly functionalized alkynyl complexes [Ru{$C{\equiv}CC(C{\equiv}CR^4)R^2R^3$}($\eta^5$-1,2,3-$R^1_3C_9H_4$)$L^1L^2$] ($R^1$ = H, $L^1 = L^2 = PPh_3$, $R^2 = R^3 = Ph$, R^4 = H, Ph, *n*Pr; R^1 = H, L^1L^2 = DPPE, $R^2 = R^3 = Ph$, R^4 = H, Ph, *n*Pr; R^1 = H, $L^1 = L^2 = PPh_3$, $R^2R^3 = C_{13}H_{20}$, R^4 = H; R^1 = H, L^1 = CO, L^2 = P*i*Pr$_3$, $R^2 = R^3 = Ph$, R^4 = H; R^1 = Me, L^1 = CO, $L^2 = PPh_3$, $R^2 = R^3 = Ph$, R^4 = Ph) have been prepared in our group using acetylides as nucleophiles.[42,43,51,56]

Some of these alkynyl species have proved to be of interest in both organometallic and organic synthesis. Using [Ru{$C{\equiv}CC(C{\equiv}CH)Ph_2$}($\eta^5$-$C_9H_7$)($PPh_3$)$_2$] as starting material, and taking advantage of the presence of a triple bond functionality at the end of the alkynyl chain, we carried out a series of Pauson-Khand cyclization reactions.[61] For instance, the unprecedented alkynyl and vinylidene derivatives **28** and **29** containing tricyclic cyclopentenone fragments (Figure 4) have been isolated from the strained cyclic alkenes norbornadiene and norbornene.

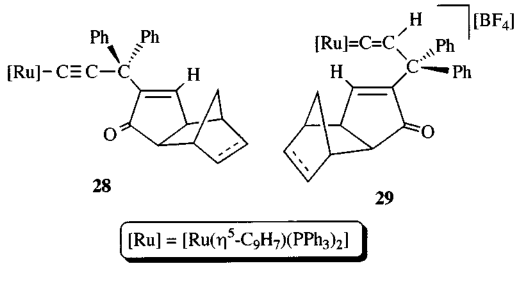
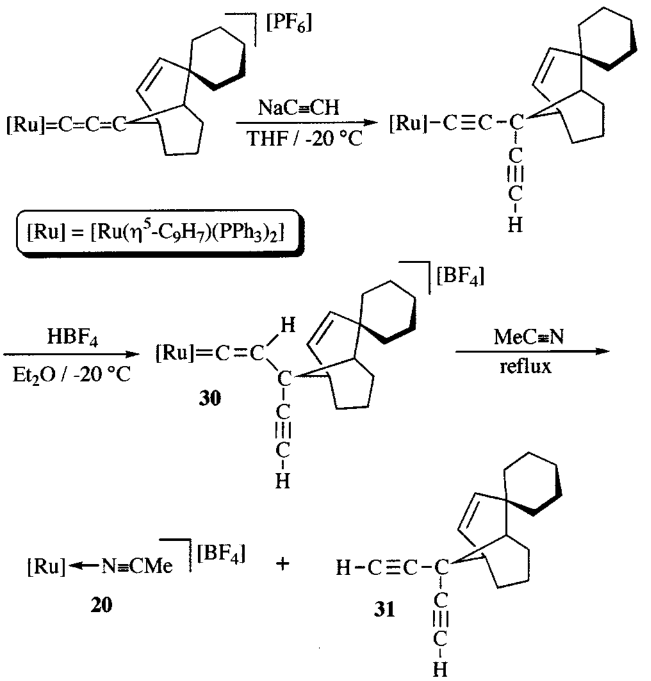


Figure 4. Structure of organometallic cyclopentenones

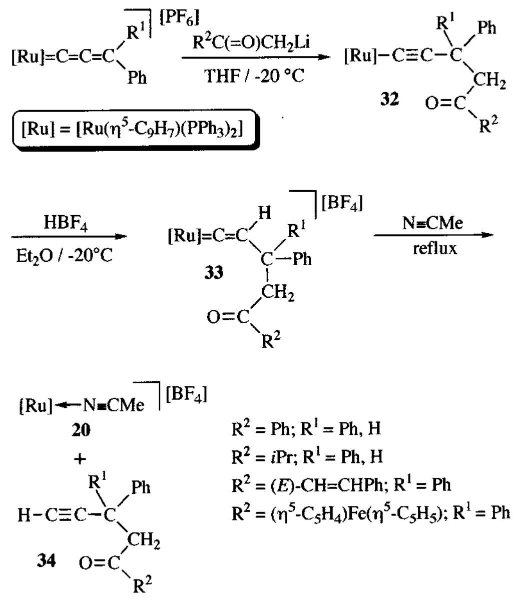
In addition, using the demetalation approach shown in Scheme 7, the unprecedented diyne $(HC{\equiv}C)_2CC_{13}H_{20}$ (**31**) can be easily prepared by demetalation of vinylidene [Ru{$=C=C(H)C(C{\equiv}CH)C_{13}H_{20}$}($\eta^5$-$C_9H_7$)($PPh_3$)$_2$][$BF_4$] (**30**) with acetonitrile (Scheme 10).[56]



Scheme 10. Demetalation of allenylidene complex [Ru{$=C=C=C(C_{13}H_{20})$}(η^5-C_9H_7) (PPh_3)$_2$][PF_6]

The utility of transition metal allenylidenes in organic synthesis is also demonstrated in the synthesis of terminal oxoalkynes $HC{\equiv}CC(R^1)Ph(CH_2COR^2)$ (**34**), starting from [Ru{$=C=C=C(R^1)Ph$}(η^5-C_9H_7)(PPh_3)$_2$][PF_6] (R^1 = H, Ph) and lithium enolates ($LiCH_2COR^2$) (Scheme 11).[62] The process is based on the regioselective nucleophilic attack of the enolate moiety at the C_γ atom of the cumulene chain to afford neutral oxo-functionalized alkynyl derivatives **32**. These derivatives are subsequently transformed into vinylidenes **33** and demetalated[62b] with MeC≡N as previously described. Regio- and diastereoselective nucleophilic additions of lithium enolates derived from the chiral ketones (−)-carvone and (+)-pulegone to [Ru($=C=C=CPh_2$)(η^5-C_9H_7)(PPh_3)$_2$][PF_6] allowed us to prepare chiral alkynyl complexes (*R*,*R*)**-35** and (*R*,*R*)**-36** (see Figure 5).[62a] We note that the related osmium(II)−oxoalkynyl complex [Os{$C{\equiv}CC(CH_2COMe)Ph_2$}($\eta^5$-$C_5H_5$)(P*i*Pr$_3$)$_2$] has recently been obtained by Esteruelas and co-workers.[38]

Chiral oxoalkynes **40** have been obtained by the same methodology from the optically active allenylidene **37** (Scheme 12).[59] The initial formation of alkynyl derivatives **38**, which involves the generation of a new stereogenic center at C_γ, is diastereoselective since only one diastereoisomer is detected by NMR spectroscopy. The configuration of this new chiral carbon atom in both alkynyl (**38**), vinylidene (**39**), or free alkyne (**40**) derivatives is presently unknown.



Scheme 11. Synthesis of terminal oxoalkynes from alkynylruthenium(II) complexes

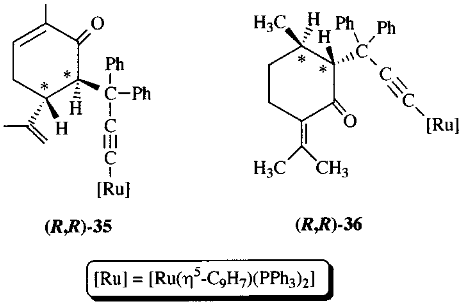
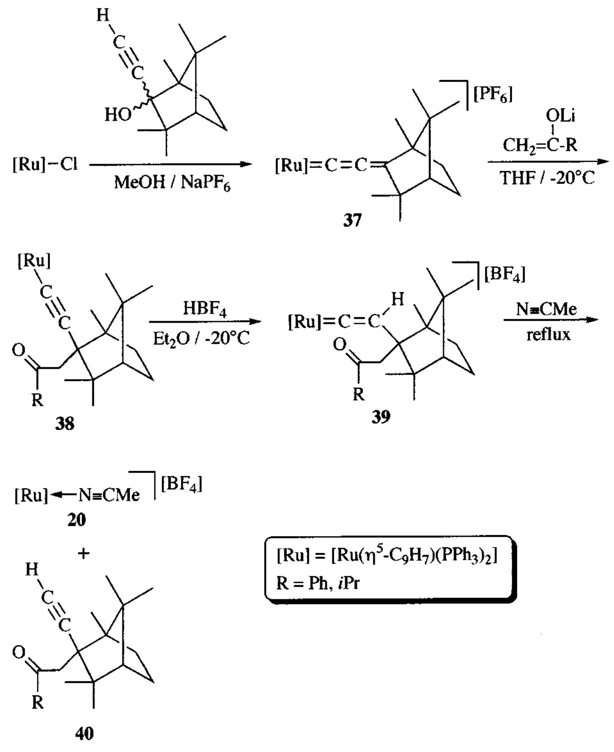
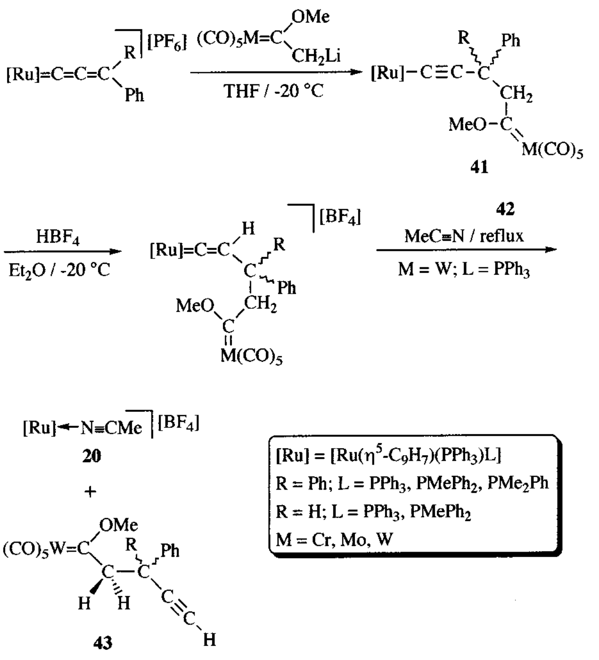


Figure 5. Structure of optically active alkynylruthenium(II) complexes

Cationic indenylruthenium(II)−allenylidene derivatives are also suitable starting materials for the preparation of dimetallic species containing hydrocarbon bridges through carbon−carbon coupling reactions with organometallic anionic nucleophiles. We have reported that $[Ru\{=C=C=C(R)Ph\}(\eta^5\text{-}C_9H_7)(PPh_3)L][PF_6]$ (R = Ph, L = PPh_3, $PMePh_2$, PMe_2Ph; R = H, L = PPh_3, $PMePh_2$) reacts regioselectively with anionic Fischer-type methoxycarbene derivatives $[(CO)_5M\{=C(OMe)CH_2\}]^-$ (M= Cr, Mo, W) to yield unprecedented neutral alkynylcarbene complexes **41** (Scheme 13).[60] Protonation of these compounds leads to the formation of **42**, which represent the first examples of dimetallic complexes containing a vinylidenecarbene type hydrocarbon bridge. In addition, the novel tungsten−methoxycarbenes **43**, bearing a terminal alkyne functionality, could be prepared by selective demetalation of the ruthenium fragment in refluxing acetonitrile.

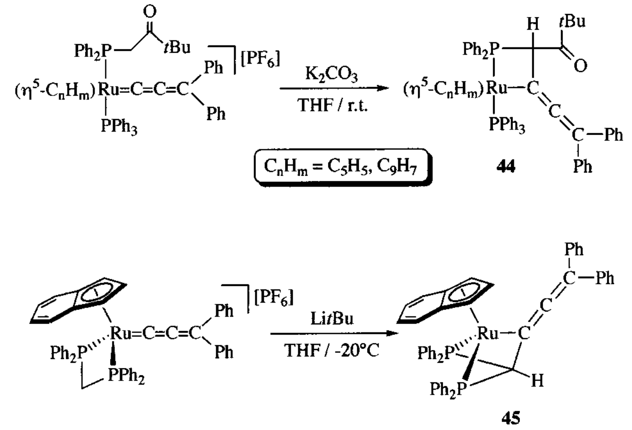


Scheme 12. Synthesis of optically active alkynyl and vinylidene complexes, and terminal alkynes derived from (−)-fenchone



Scheme 13. Preparation of dimetallic complexes containing alkynylcarbene and vinylidenecarbene bridges

Nucleophilic additions of carbanions at C_α of cationic allenylidenes to afford neutral allenyl species are also known.[4a−4b] As an example, we have described the synthesis of allenylmetallacyclic derivatives **44** and **45** (Scheme 14) by deprotonation of an auxiliary phosphane ligand and subsequent carbon−carbon coupling between the electrophilic C_α and the initially generated carbanion.[51,57] We note that formation of **44** is diastereoselective since only one pair of enantiomers $S_{Ru},R_C/R_{Ru},S_C$ is obtained as confirmed by X-ray crystal structure determinations.[57]



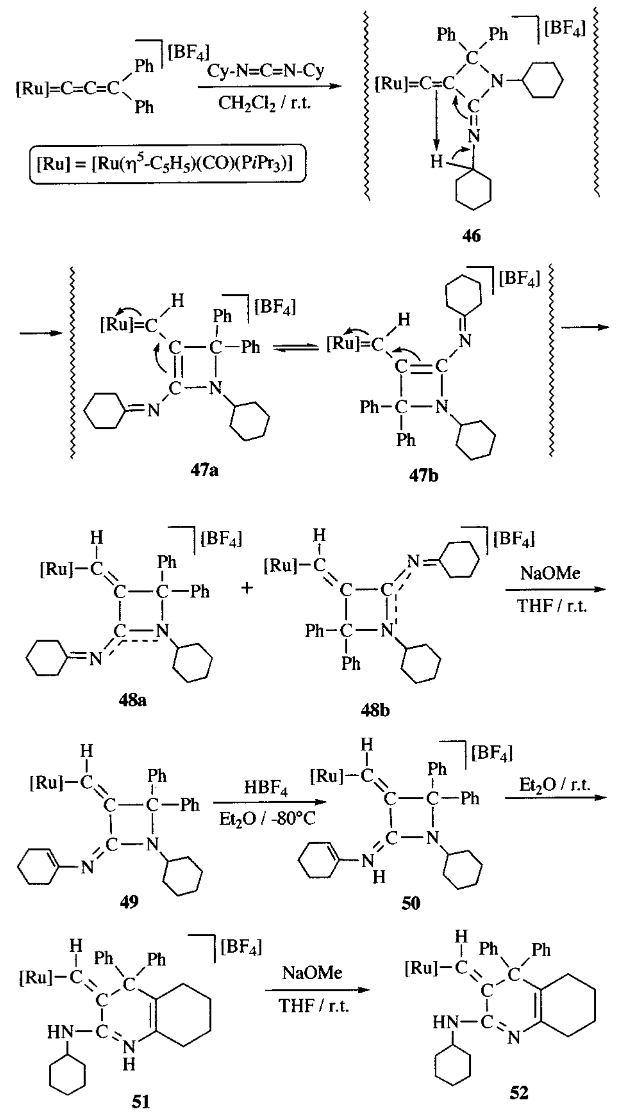
Scheme 14. Intramolecular C−C coupling reactions between allenylidene and phosphane ligands

IV.3 Cyclization Reactions

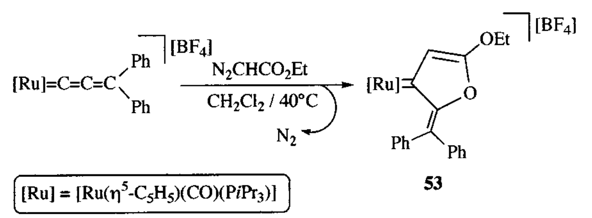
Cationic transition metal allenylidene complexes are useful starting materials to generate unsaturated cyclic structures by the reaction of their highly polarized unsaturated chain with organic substrates.[4a−4b] In this context, Esteruelas and co-workers have recently reported[63] that $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_5H_5)(CO)(PiPr_3)][BF_4]$ reacted with dicyclohexylcarbodiimide to afford the unprecedented iminium azetidinylidenemethyl complex **48** which was isolated as a mixture of the corresponding (*Z*) (**48a**) and (*E*) (**48b**) stereoisomers (Scheme 15). Formation of **48** can be rationalized as the result of a [2+2] cycloaddition between the $C_\beta-C_\gamma$ double bond of the allenylidene ligand and one of the two carbon−nitrogen double bonds of the carbodiimide group. Thus, intermediate **46** was formed and rapidly evolved into carbene **47**, probably as a mixture of isomers, through an Alder-ene type process. A final charge redistribution within **47** gave the observed species **48**. Complex **48** was used as a suitable precursor for the preparation of other heterocyclic species such as **49−52** (Scheme 15).

The doubly α,β-unsaturated oxygen-containing cyclic carbene complex **53** has been prepared by the addition of ethyl diazoacetate to $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_5H_5)(CO)(P\text{-}iPr_3)][BF_4]$ (Scheme 16).[64] In this case, a formal 1,3-addition of the organic reagent at the $C_\alpha-C_\beta$ double bond takes place.

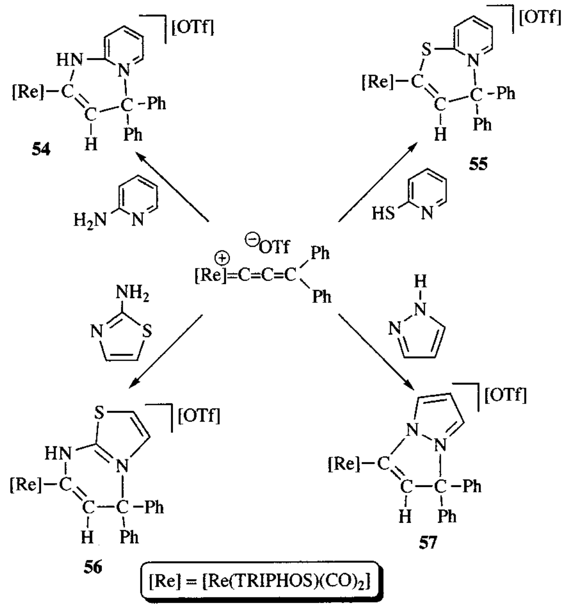
Since allenylidenes have two electrophilic and one nucleophilic centers, the reactions of these compounds with organic molecules containing two nucleophilic heteroatoms and one electrophilic hydrogen atom give rise to 1,2,3-diheterocyclization processes. Following the previously reported reactions with the allenylidene complex $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_5H_5)(CO)(PiPr_3)][BF_4]$,[65a] Bianchini and co-workers have similarly found that the cationic (diphenylallenylidene)rhenium(I) complex $[Re(=C=C=CPh_2)(TRIPHOS)(CO)_2][CF_3SO_3]$ reacts with N,S- and N,N-heterocycles to generate heterobicyclic compounds **54−57** (Scheme 17).[65b] All these species are formed by the initial addition of the heteroatom−H bond to the $C_\alpha-C_\beta$ double bond of the allenylidene ligand, to produce intermediate α,β-unsaturated carbenes which undergo a further nucleophilic attack of the second heteroatom at C_γ of the unsaturated chain.[65c]



Scheme 15. Reactivity of $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_5H_5)(CO)(P\text{-}iPr_3)][BF_4]$ towards dicyclohexylcarbodiimide

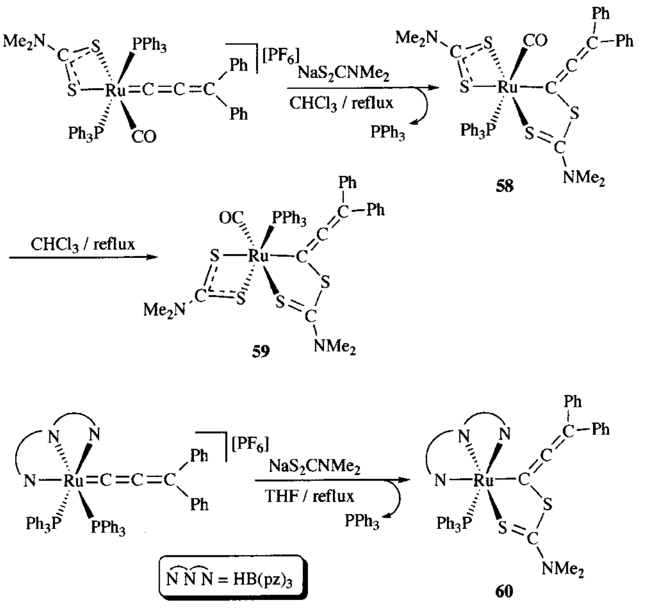


Scheme 16. Cyclization of $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_5H_5)(CO)(P\text{-}iPr_3)][BF_4]$ with ethyl diazoacetate



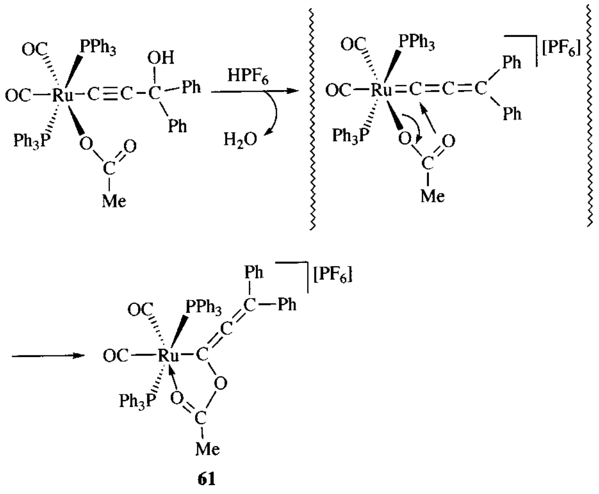
Scheme 17. 1,2,3-diheterocyclizations on [Ru(=C=C=CPh$_2$)(TRIPHOS)(CO)$_2$][OTf]

Other cyclization processes involving direct metal−carbon double-bond additions are also known. Hill and co-workers have recently reported the preparation of metallacyclic allenyl complexes **58** and **60** by the addition of sodium dimethyldithiocarbamate to diphenylallenylidenes [Ru(=C=C=CPh$_2$)(S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$][PF$_6$] and [Ru(=C=C=CPh$_2$){HB(pz)$_3$}(PPh$_3$)$_2$][PF$_6$], respectively (Scheme 18).[66] Complex **58** is not stable and slowly generates the thermodynamically stable isomer **59**. A plausible mechanism to explain the formation of **58** and **60** may involve the initial attack of dimethyldithiocarbamate at C$_\alpha$, followed by the substitution of a triphenylphosphane ligand with the C=S group.



Scheme 18. Coupling of allenylidene ligands with dithiocarbamate

A related intramolecular coupling between an acetate ligand and a transient diphenylallenylidene moiety also occurs when hydroxyalkynyl complex [Ru{C≡CC(OH)Ph$_2$}{κ^1-(*O*)-COOMe}(CO)$_2$(PPh$_3$)$_2$] is treated with HPF$_6$, affording metallacycle **61** (Scheme 19).[67]

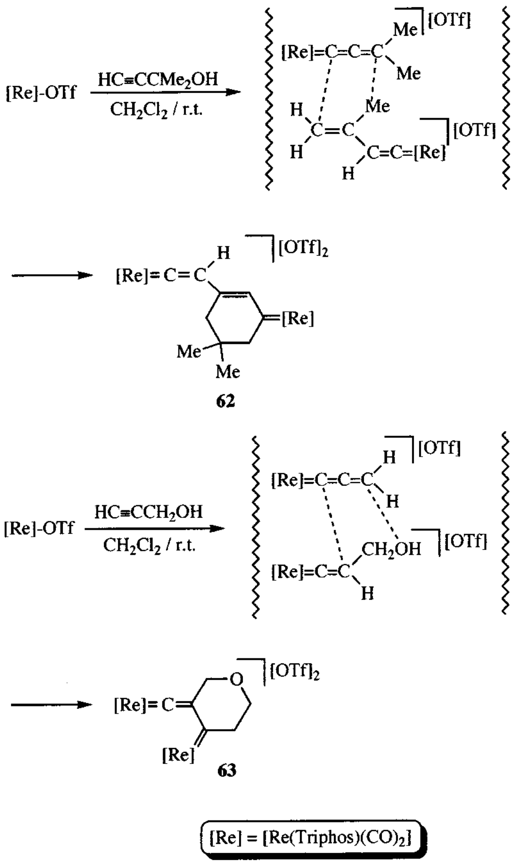


Scheme 19. Intramolecular coupling of an allenylidene ligand with acetate

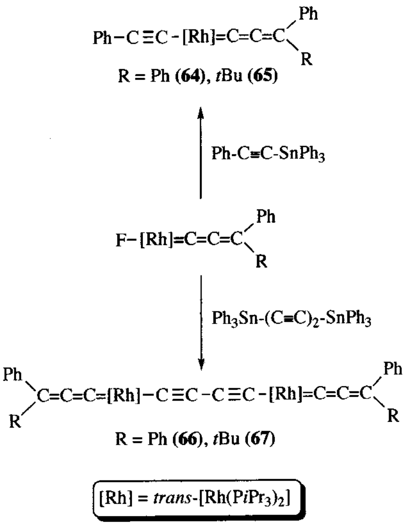
Finally, dinuclear cyclic complexes **62** and **63** (Scheme 20) have been prepared by Bianchini and co-workers through direct activation of 2-methyl-3-butyn-2-ol or propargyl alcohol by [Re(OTf)(TRIPHOS)(CO)$_2$].[46] In the first case, carbene vinylidene complex **62** seems to be formed by the coupling of transient allenylidene [Re(=C=C=CMe$_2$)(TRIPHOS)(CO)$_2$][CF$_3$SO$_3$] and alkenylvinylidene [Re{=C=C(H)−C(Me)=CH$_2$}(TRIPHOS)(CO)$_2$][CF$_3$SO$_3$] species which are simultaneously generated in the initial dehydration process.[68] An unprecedented coupling between the allenylidene [Re(=C=C=CH$_2$)(TRIPHOS)(CO)$_2$][CF$_3$SO$_3$] and its hydroxyvinylidene precursor [Re{=C=C(H)CH$_2$(OH)}(TRIPHOS)(CO)$_2$][CF$_3$SO$_3$] was proposed in the formation of complex **63**.

V. Reactivity of Neutral Allenylidene Complexes

The reactions of several square-planar (allenylidene)rhodium(I) and -iridium(I) chloride complexes with nucleophiles do not proceed through the typical addition, but instead result in substitution products. For instance, the iridium complex *trans*-[IrCl(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] reacts with KOH to give the hydroxo derivative *trans*-[Ir(OH)(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$].[20] The rhodium complexes *trans*-[RhX{=C=C=CPh(R)}(P*i*Pr$_3$)$_2$] (X = OH, NCO, N$_3$) have been prepared in a similar fashion.[24][69] The fluoride complexes obtained by the treatment of the hydroxo complexes with NEt$_3$·3HF have been used as appropriate starting materials for the preparation of mononuclear (**64**, **65**) and dinuclear (**66**, **67**) alkynyl derivatives (Scheme 21).[70] Alternatively, complexes **66** and **67** can be prepared directly by treatment of the hydroxo derivatives with (Ph$_3$Sn)$_2$C$_4$.

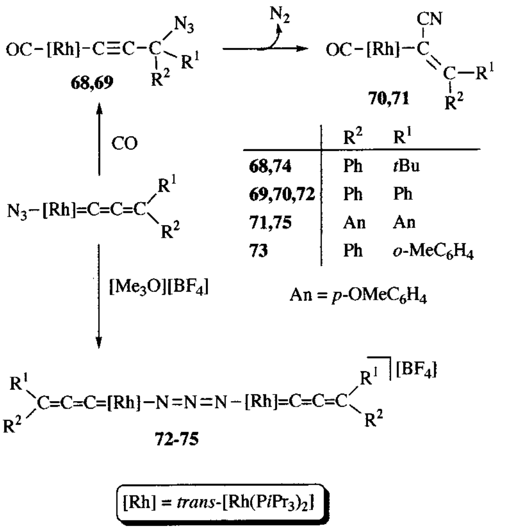


Scheme 20. Couplings between allenylidene and alkenylvinylidene or hydroxyvinylidene ligands



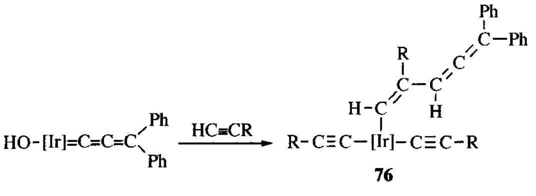
Scheme 21. Substitution reactions on square-planar (allenylidene)rhodium(I) complexes

The reactions of rhodium azide complexes with CO lead either to the formation of the azidoalkynyl complex **68** or of the cyanoalkenyl derivatives **70** and **71** (Scheme 22).[24] A formal addition of the azide anion to C_α or C_γ is postulated as a possible route to the intermediates which give **70** and **71** by elimination of nitrogen. The azidoalkynyl complex **69** was characterized by NMR at low temperature. No electrophilic addition product was observed in the reaction of the rhodium azide derivatives with $[Me_3O][BF_4]$ leading instead to the formation of the dinuclear bis(allenylidene) complexes **72–75** (Scheme 22).[24]



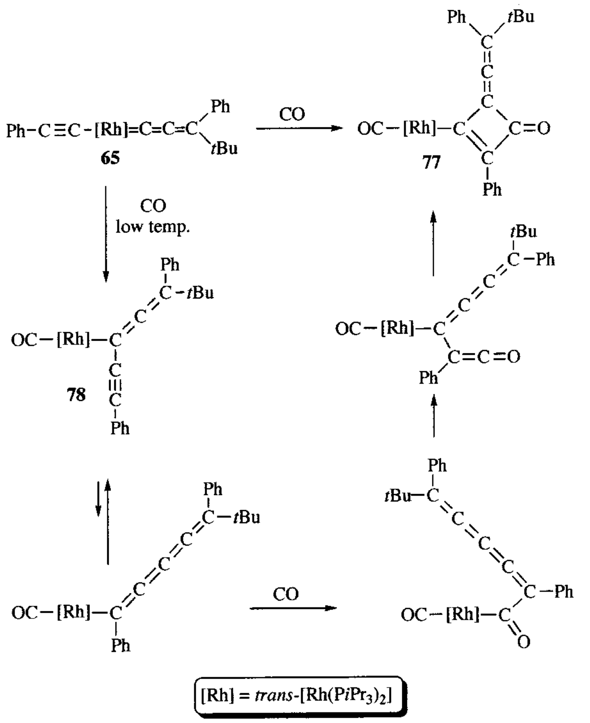
Scheme 22. Reactivity of (allenylidene)rhodium(I) azide complexes

New metal-assisted C–C coupling reactions have been described. *trans*-$[Ir(OH)(=C=C=CPh_2)(PiPr_3)_2]$ reacts with an excess of the terminal alkynes RC≡CH (R = Ph, CO_2Me) to give complexes **76** (Scheme 23). The formation of **76** presumably involves the substitution of OH by C_2R, followed by the oxidative addition of a second molecule of the alkyne to give the iridium hydride intermediate $[IrH(C{\equiv}CR)_2(=C=C=CPh_2)(PiPr_3)_2]$. This intermediate could undergo a rearrangement to form a metal–allenyl species followed by a C–C coupling process with a third molecule of alkyne.[20]

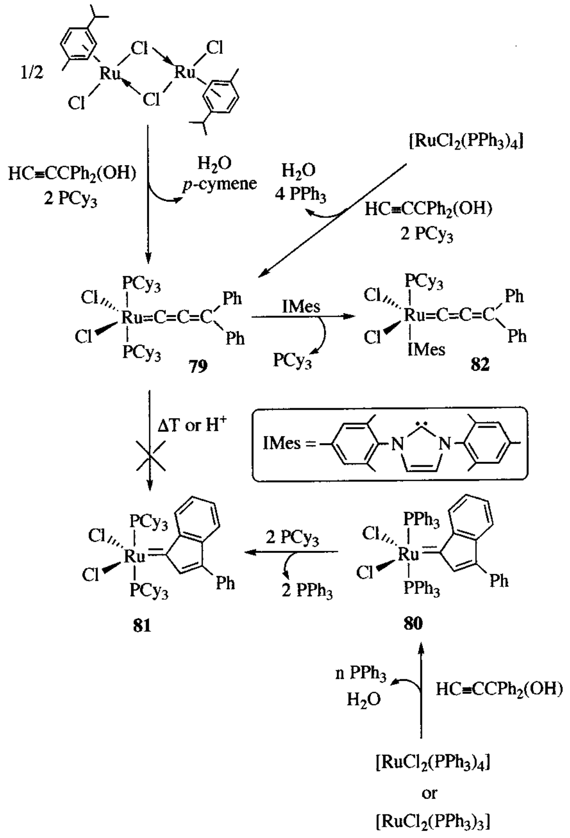


Scheme 23. C–C coupling reactions promoted by *trans*-$[Ir(OH)(=C=C=CPh_2)(PiPr_3)_2]$

An unprecedented triple coupling $[C_2+C_1+C_1]$ of alkynyl, allenylidene, and carbonyl groups has been described by Werner and co-workers.[70] This coupling involves the reaction of complex **65** with CO leading to the formation of **77**, a complex containing a highly unsaturated cyclobutenone ligand in the coordinating sphere of the rhodium atom. A possible mechanism for this conversion is shown in the Scheme 24. The proposed intermediate complex **78** was isolated as a thermally unstable solid.



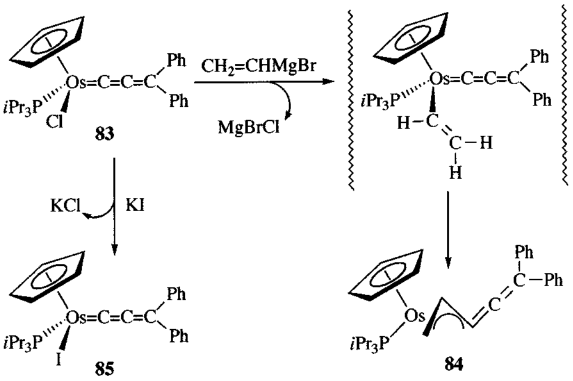
Scheme 24. Unprecedented $[C_2+C_1+C_1]$ coupling of an allenylidene, an alkynyl and a CO ligand



Scheme 25. Synthesis and reactivity of 16-electron ruthenium(II)−allenylidene complexes

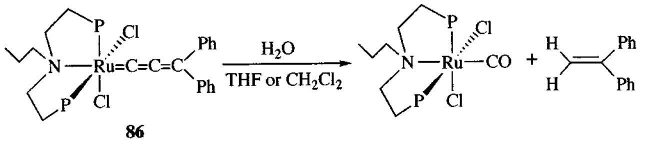
A series of 16-electron ruthenium(II)−allenylidene species have been described as the first unsaturated allenylidene complexes (Scheme 25). The parent complex $[RuCl_2(=C=C=CPh_2)(PCy_3)_2]$ (**79**) is obtained in good yield from the reaction of $[RuCl_2(PPh_3)_4]$ or 0.5 equiv. of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ with 1,1-diphenyl-2-propyn-1-ol and 2 equiv. of PCy_3. However, the reaction of either $[RuCl_2(PPh_3)_3]$ or $[RuCl_2(PPh_3)_4]$ with $HC{\equiv}CC(OH)Ph_2$ leads only to the 3-phenyl-1-indenylidene complex **80** which then undergoes phosphane exchange with PCy_3 to provide complex **81**. The allenylidene complex **79** is stable at elevated temperatures and towards protic acids, and no conversion into 3-phenyl-1-indenylidene complex **81** was observed.[8,71] The exchange of one PCy_3 ligand for IMes affords the allenylidene complex **82** in high yield (Scheme 25). The similar 16-electron complex $[OsCl_2(=C=C=CPh_2)(PPh_3)_2]$ has been isolated and is stable in methanol at room temperature.[72]

An intramolecular nucleophilic addition at the allenylidene chain has been described[15][66] in the reaction of the trispyrazolylborate neutral complex $[RuCl(=C=C=CPh_2)\{HB(pz)_3\}(PPh_3)]$ with $Na[S_2CNMe_2]$ resulting in the metallacyclic allenyl complex **60** (see Scheme 18). Another type of intramolecular addition was observed in the reaction of $[OsCl(=C=C=CPh_2)(\eta^5\text{-}C_5H_5)(PiPr_3)]$ (**83**) with $CH_2=CHMgBr$ which gives the pentatrienyl complex $[Os(\eta^3\text{-}CH_2CHC=C=CPh_2)(\eta^5\text{-}C_5H_5)(PiPr_3)]$ (**84**) (Scheme 26).[73] This complex is formed by migratory insertion of the allenylidene ligand into the $Os-CH=CH_2$ bond of the vinylosmium intermediate which cannot be isolated. Complex **83** also reacts with KI to give the iodo derivative **85**.



Scheme 26. Reactivity of the neutral allenylidene $[OsCl(=C=C=CPh_2)(\eta^5\text{-}C_5H_5)(PiPr_3)]$

Nucleophilic addition of water to the allenylidene chain in the complex *fac,cis*-$[RuCl_2(=C=C=CPh_2)(PNP)]$ (**86**) has been reported to occur both in THF or CH_2Cl_2 at room temperature, to give the carbonyl derivative *fac,cis*-$[RuCl_2(CO)(PNP)]$ and the corresponding free alkene $H_2C=CPh_2$ (Scheme 27).[18] The reaction proceeds by regioselective cleavage of the $C_\alpha-C_\beta$ bond. The use of D_2O gives the corresponding deuterated alkene $D_2C=CPh_2$.



Scheme 27. Selective $C_\alpha-C_\beta$ bond cleavage by water in a ruthenium(II)−allenylidene complex

Dötz and co-workers[74] have reported the synthesis of a series of sugar-derived or (disaccharide)metal−(alkenyl)-(methoxy)carbene complexes obtained from the reactions of sugar-based propargylic alcohols and [W(CO)$_5$(THF)]. The formation of these carbene species is rationalized through the typical addition of alcohols to the transient allenylidene species generated from the propargylic alcohols.

A series of neutral carbonylruthenium trinuclear clusters containing bridging allenylidene groups of type **D** shown in Figure 3 have been reported.[27] These derivatives undergo substitution reactions of the carbonyl groups by phosphane ligands. The formation of a tetranuclear Ru$_3$Au cluster is also described. Furthermore, a C−C coupling between an allenylidene bridging moiety and a phenyl group of a coordinated dppm ligand in a related Ru$_3$ cluster to give a 1,3-diphenylindenyl ligand has been also reported.[75]

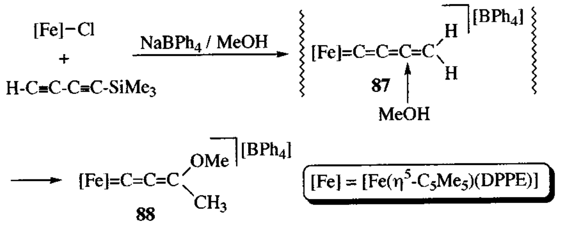
VI. Reactivity of Complexes Containing Higher Cumulenylidene Ligands

Although the chemistry of higher cumulenylidene complexes $[M]=C(=C)_n=CR^1R^2$ ($n > 1$) has not received as much attention as that of allenylidenes ($n = 1$), theoretical[40] and experimental[4b,4e] evidence point also to the alternating electron deficiency and richness of the carbon atoms of the unsaturated chain as one moves along the chain from the metal atom. Therefore nucleophilic additions at the odd-numbered carbon atoms and electrophilic additions at the even-numbered carbon atoms can be expected.

VI.1 Butatrienylidene Complexes

Mononuclear transition metal complexes containing butatrienylidene ligands $[M]=C(=C)_2=CR^1R^2$ have usually been reported as highly reactive intermediates in different reactions.[4b][4e] Indeed, complexes $[(\eta^5\text{-}C_5Me_5)L^1L^2Fe\{=C=C=C=C(R)Fe(CO)_2(\eta^5\text{-}C_5Me_5)\}]^+$ (L^1L^2 = DPPE, DIPPE; R = H, Me), obtained by protonation or methylation at C_δ of neutral dimetallic butadiynes $[(\eta^5\text{-}C_5Me_5)L^1L^2Fe\{C{\equiv}CC{\equiv}CFe(CO)_2(\eta^5\text{-}C_5Me_5)\}]$, are the only butatrienylidene complexes stable enough to be isolated and spectroscopically characterized to date.[32] These stable species have been studied by cyclic voltammetry (CV). Thus, while tertiary butatrienylidenes $[(\eta^5\text{-}C_5Me_5)L^1L^2Fe\{=C=C=C=C(Me)Fe(CO)_2(\eta^5\text{-}C_5Me_5)\}][CF_3SO_3]$ display a reversible one-electron oxidation process and an irreversible reduction process, complexes $[(\eta^5\text{-}C_5Me_5)L^1L^2Fe\{=C=C=C=C(H)Fe(CO)_2(\eta^5\text{-}C_5Me_5)\}][BF_4]$ show a more complicated pattern, owing to the acidic character of the hydrogen atom on C_δ, and signals assigned to $[(\eta^5\text{-}C_5Me_5)L^1L^2Fe\{C{\equiv}CC{\equiv}CFe(CO)_2(\eta^5\text{-}C_5Me_5)\}]$ are also observed in the voltammograms. In fact, these monosubstituted complexes can be readily deprotonated with DBU or traces of water to afford the starting butadiynes $[(\eta^5\text{-}C_5Me_5)L^1L^2Fe\{C{\equiv}CC{\equiv}CFe(CO)_2(\eta^5\text{-}C_5Me_5)\}]$.

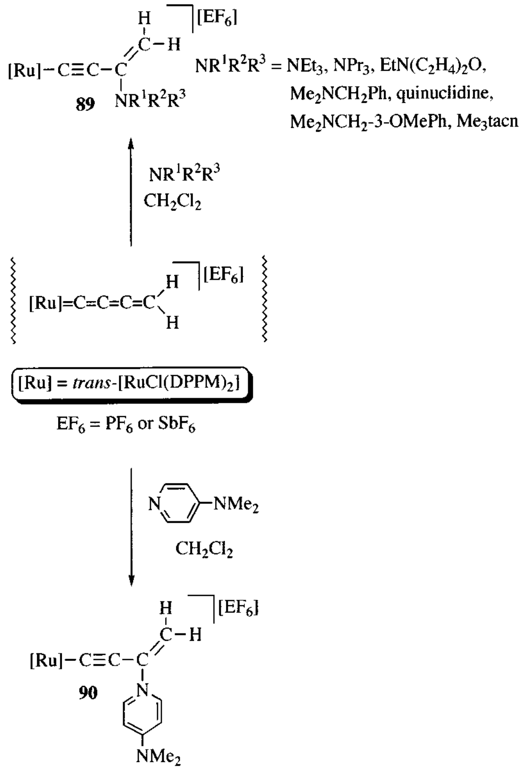
Activation of trimethylsilyl-1,3-butadiyne $HC{\equiv}CC{\equiv}CSiMe_3$ by $[FeCl(\eta^5\text{-}C_5Me_5)(DPPE)]$ in methanol has been reported to yield the methoxyallenylidene $[Fe\{=C=C=C(OMe)CH_3\}(\eta^5\text{-}C_5Me_5)(DPPE)][BPh_4]$ (**88**) (Scheme 28).[31] Formation of **88** involves the generation of the unstable butatrienylidene derivative $[Fe(=C=C=C=CH_2)(\eta^5\text{-}C_5Me_5)\ (DPPE)][BPh_4]$ (**87**), by an initial 1,4-H shift and subsequent desilylation of the intermediate $[Fe\{=C=C=C=C(H)SiMe_3\}(\eta^5\text{-}C_5Me_5)(DPPE)][BPh_4]$, which readily undergoes addition of methanol to the $C_\gamma-C_\delta$ double bond.



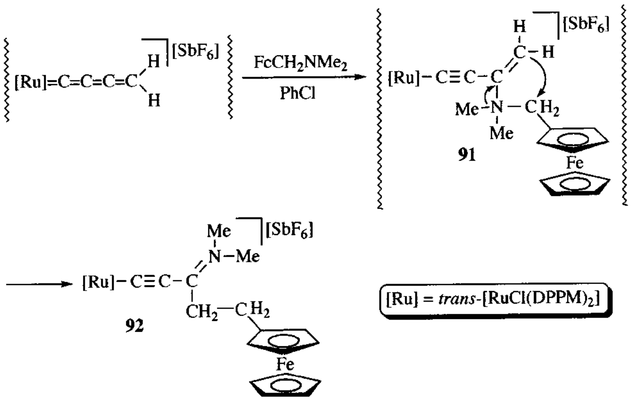
Scheme 28. Synthesis of the iron(II)−allenylidene $[Fe\{=C=C=C(OMe)CH_3\}(\eta^5\text{-}C_5Me_5)(DPPE)][BPh_4]$

Protonation of the neutral diynylruthenium(II) complex *trans*-$[RuCl(C{\equiv}CC{\equiv}CPh)(DPPE)_2]$ or direct activation of 1,3-butadiyne $HC{\equiv}CC{\equiv}CPh$ by *cis*-$[RuCl_2(DPPE)_2]$ allows the formation of the cationic buta-1,2,3-trienylidene derivative *trans*-$[RuCl\{=C=C=C=C(H)Ph\}(DPPE)_2]^+$.[50] This complex is a very reactive species which cannot be isolated since it adds water or methanol from the reaction media to the electrophilic C_γ atom to yield the acylvinylidene *trans*-$[RuCl\{=C=C(H)C(=O)CH_2Ph\}(DPPE)_2]^+$ or the methoxyallenylidene *trans*-$[RuCl\{=C=C=C(OMe)CH_2Ph\}(DPPE)_2]^+$, respectively.[50]

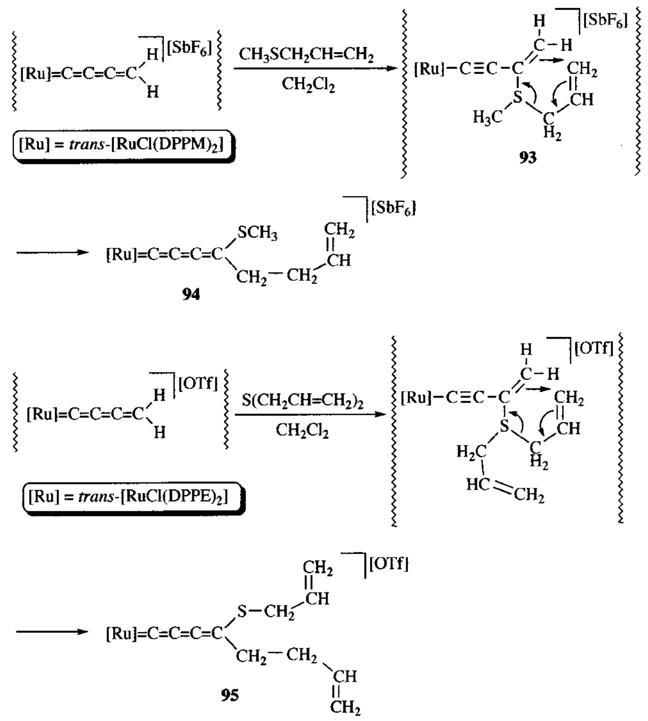
Treatment of *cis*-$[RuCl_2(DPPM)_2]$ with an excess of butadiyne ($HC{\equiv}CC{\equiv}CH$) in the presence of a halide-abstracting reagent ($NaPF_6$ or $NaSbF_6$), allows the generation of *trans*-$[RuCl(=C=C=C=CH_2)(DPPM)_2]^+$, which can be trapped in situ by the addition of tertiary amines to C_γ, to yield stable 2-ammoniobutenynyl complexes **89** (Scheme 29).[76] When 4-(dimethylamino)pyridine is used, this ambident nucleophile binds regioselectively to the unsaturated carbon chain through the pyridine nitrogen atom to give **90**.[76] The reaction of *trans*-$[RuCl(=C=C=C=CH_2)(DPPM)_2]^+$ with (ferrocenylmethyl)dimethylamine has been also reported.[77] In this case the initially generated 2-ammoniobutenynyl derivative **91** evolves into the iminium alkynyl complex **92** by migration of the resonance-stabilized ferrocenylcarbenium ion from the quaternary nitrogen atom to the neighboring nucleophilic C_δ atom (Scheme 30).



Scheme 29. Reactivity of *trans*-[RuCl(=C=C=C=CH$_2$)(DPPM)$_2$][EF$_6$] towards tertiary amines



Scheme 30. Reactivity of *trans*-[RuCl(=C=C=C=CH$_2$)(DPPM)$_2$][SbF$_6$] towards (ferrocenylmethyl)dimethylamine



Scheme 31. Synthesis of thioallenylidene complexes from ruthenium(II)−buta-1,2,3-trienylidene intermediates

Addition of sulfur nucleophiles at *trans*-[RuCl(=C=C=C=CH$_2$)(DPPM)$_2$][SbF$_6$] has been reported to yield thioallenylidene derivatives.[78] Thus, while the reaction with ethanethiol produces *trans*-[RuCl{=C=C=C(SEt)CH$_3$}(DPPM)$_2$][SbF$_6$], by addition of the S−H bond to the $C_\gamma-C_\delta$ double bond of the cumulene chain, thioallenylidene **94** is obtained when allyl methyl sulfide is used (Scheme 31). Formation of **94** involves the initial nucleophilic attack of the sulfide at the electrophilic C_γ atom to generate the unstable enynyl derivative **93** which undergoes a [3,3] thia-Claisen-type rearrangement. In a similar way, thioallenylidene **95** has been prepared from the butatrienylidene *trans*-[RuCl(=C=C=C=CH$_2$)(DPPE)$_2$][CF$_3$SO$_3$] generated in situ and diallyl sulfide (Scheme 31).

Full details on the reactivity of the highly reactive butatrienylidene[Ru(=C=C=C=CH$_2$)(η^5-C$_5$H$_5$)(PPh$_3$)$_2$][PF$_6$], formed from butadiyne and [Ru(η^5-C$_5$H$_5$)(THF)(PPh$_3$)$_2$][PF$_6$], have recently been reported.[12][79] Complexes [Ru{C≡CC(PPh$_3$)=CH$_2$}(η^5-C$_5$H$_5$)(PPh$_3$)$_2$][PF$_6$], [Ru{=C=C=C(NPh$_2$)Me}(η^5-C$_5$H$_5$)(PPh$_3$)$_2$][PF$_6$], [Ru{C≡CC(=O)Me}(η^5-C$_5$H$_5$)(PPh$_3$)$_2$], and [Ru{=C=C=C(C$_4$H$_3$NMe-2)Me}(η^5-C$_5$H$_5$)(PPh$_3$)$_2$][PF$_6$] were prepared by trapping this cumulenylidene derivative with triphenylphosphane, diphenylamine, water, and *N*-methylpyrrole, respectively.[12] In addition, a wide series of functionalized alkynyl derivatives containing either quinoline **96** or 1-azabuta-1,3-diene fragments **97** (Figure 6) can be obtained when complexes [Ru(=C=C=C=CH$_2$)(η^5-C$_5$H$_5$)L^{1}L^2][PF$_6$] [L^1 = L^2 = PPh$_3$, P(OMe)$_3$] are treated with an excess of aromatic imines.[79]

The synthesis and reactivity of Ru$_4$−butatrienylidene clusters of type **B−C** (Figure 3) have also been reported.[26]

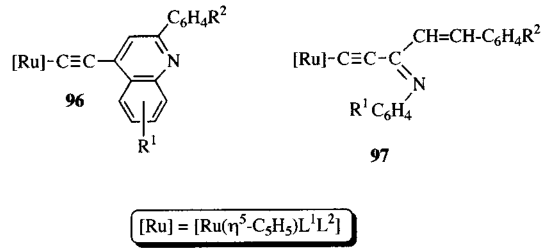


Figure 6. Structures of alkynyl complexes containing quinoline and 1-azabuta-1,3-diene fragments

VI.2 Pentatetraenylidene Complexes

The dimetallic complex [(η^5-C_5Me_5)(PPh_3)(NO)Re=C=C=C=C=C=Mn$(CO)_2$(η^5-C_5Cl_5)][BF_4], obtained by treatment of [(η^5-C_5Me_5)(PPh_3)(NO)Re−C≡C−C≡C−C(OMe)=Mn$(CO)_2$(η^5-C_5Cl_5)] with an excess of BF_3 gas, is the only pentatetraenylidene derivative reported during the period covered by this review.[30] This cumulenylidene complex is stable towards dimethyl sulfide, ethylene or tetracyanoethylene, but readily reacts with trimethylphosphane, even at −80 °C, to afford complicated mixtures of products which have not been identified.

VII. Catalytic Studies

The role of allenylidene species in catalytic processes has been previously described for ruthenium(II) complexes, albeit in a small number of organic transformations.[80] Remarkably, Fürstner, Dixneuf and co-workers have reported for the first time the catalytic activity of an allenylidene complex, namely [RuCl(=C=C=CPh_2)(η^6-*p*-cymene)(PR_3)][PF_6] (PR_3 = PCy_3, P*i*Pr_3), in ring-closing metathesis of olefins which proves to be comparable in efficiency to the alkylidene derivatives developed by Grubbs.[44] Similarly, the allenylidene complex [RuCl(=C=C=CPh_2)(η^6-*p*-cymene)(PCy_3)][PF_6] is also a good catalyst for the yne-ene ring-closing metathesis of the mixed propargylic allyl ethers HC≡C−$CR^1R^2OCH_2$−CH=CH_2 into 3-vinyl-2,5-dihydrofurans.[81] It was shown that an initial photochemical irradiation of the catalyst efficiently promotes the catalytic activity. Following these pioneering works, Dixneuf and co-workers studied the scope of these catalytic transformations.[82] It was demonstrated that the efficiency of these cationic 18-electron allenylidene precatalysts depends on the nature of the counter-anion. The use of $[CF_3SO_3]^-$ improves the activity, which leads to high-yield transformations of *N*,*N*-diallyltosylamine into *N*-tosyldihydropyrrole at room temperature, while the metathesis of the ene-yne ether HC≡C−C(Me)(Ph)OCH_2−CH=CH_2 was completed in a shorter time. New catalytic reactions are produced by using $[BF_4]^-$. Although mechanistic studies have not yet been explored, these preliminary results seem to suggest that the dissociation of the *p*-cymene ligand takes place in the precatalyst complex (either thermally or photochemically), generating a 14-electron allenylidene species [RuCl(=C=C=CPh_2)(PR_3)]$^+$ which effectively acts as the active catalyst.

The catalytic activity of the novel 16-electron allenylidene complexes [$RuCl_2$(=C=C=CPh_2)L^1L^2] (L^1 = PCy_3, L^2 = PCy_3, IMes) in RCM reactions involving diethyl allylmalonate and *N*,*N*-diallyltosylamine has been investigated[8] showing that the catalytic activity is much poorer than that shown by the above-mentioned cationic 18-electron (allenylidene)ruthenium(II) complexes.[44] This behavior probably arises from the significantly higher bonding energy of the allenylidene moiety at the metal center (see X-ray discussion above). Catalytic studies by Fürstner, Hill, and co-workers in the RCM of α,ω-dienes and -dienynes using mononuclear and dinuclear (allenylidene)ruthenium(II) complexes as catalysts have been also reported.[83] However, the actual nature of the catalysts was recently revisited and reformulated as indenylidene species after full characterization (see complexes **80−81** in Scheme 25).[71,84] The first example of a water-soluble allenylidene complex, the dinuclear salt [$(TPPMS)_4Ru_2Cl_4$(=C=C=CPh_2)$_2$] (TPPMS = [Na][Ph_2P-{2-$OSO_2C_6H_4$}]) which shows catalytic activity in ROM and ROMP of olefins, was recently prepared.[85]

Concluding Remarks

Studies on the reactivity of allenylidene and higher cumulenylidene complexes have been widely developed since the discovery of the first derivatives by Fischer and Berke. Both experimental and theoretical studies on allenylidene complexes [M]=C=C=CR^1R^2 are now well established, indicating that the electrophilic centers are located at C_α and C_γ, while the C_β atom is a nucleophile site. Nucleophilic attacks dominate the reactivity of allenylidene complexes relative to the electrophilic additions which usually occur in neutral complexes. Recently, an unusual protonation of the cationic complex [Os(=C=C=CPh_2)(η^5-C_5H_5)(P*i*Pr_3)$_2$][PF_6] with HPF_6 to give the alkenylcarbyne [Os{≡C−C(H)=CPh_2}(η^5-C_5H_5)(P*i*Pr_3)$_2$][PF_6]$_2$ was reported. Recent theoretical calculations on higher cumulenylidene chains =C(=C)$_n$=CH_2 (n = 0−7) also confirm that the electrophilic and nucleophilic attacks are frontier orbital controlled, showing that the carbon atoms are alternatively electron-poor and electron-rich, starting from the metal. Reactivity studies on butatrienylidene and pentatetraenylidene complexes, which are now emerging, seem to agree with these expectations.

Most of the results on the reactivity of allenylidene complexes continue to reveal the potential utility in selective C−C and C−heteroatom bond formation. Relevant developments which have been disclosed are: (*i*) regio- and stereoselective additions at the C_γ atom which provide a valuable methodology for the synthesis of functionalized alkynyl complexes, some of them being of interest for the synthesis of polyen(yn)yl chains; (*ii*) inter- and intramolecular cyclization reactions involving C_α−C_β and C_β−C_γ double bonds; (*iii*) intramolecular C−C coupling reactions with alkynes, alkenyl and alkynyl groups, leading to the selective formation of highly unsaturated hydrocarbon moieties.

Although the utility of allenylidene complexes in catalytic processes are still scarce, studies of the catalytic activity in ring-closing metathesis (RCM) of olefins have been reported for the first time. Provided that the efficiency is comparable to that of Grubbs' alkylidene complexes, it is apparent that this achievement would enhance the rapid progress of this field in the near future.

Acknowledgments

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Note Added in Proof: (i) Novel examples of catalytic ring-closing olefin metathesis using the 18-electron allenylidene complexes $[RuCl(=C=C=CR_2)(\eta^6\text{-}p\text{-cymene})(PR_3)]_+$ (PR_3 = PPh_3, PCy_3, $PiPr_3$) have been described.[86] – (ii) The allenylidene derivative $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_5H_5)(CO)(PiPr_3)][BF_4]$ reacts with 2-aminopyridine and thioisonicotinamide to afford unprecedented pyrido-[1,2-*a*]pyrimidinyl and 1,3-thiazinyl complexes, respectively, which are formed through 1,2,3-diheterocyclization processes.[87]. In addition, novel functionalised [alkenyl(methoxy)carbene]Ru^{II}, -Cr^0 and -W^0 derivatives have been synthesized by addition of methanol on unstable allenylidene complexes.[88]. – (iii) The isolation and structural characterization of the butatrienylidene complex *trans*-$[IrCl(=C=C=C=CPh_2)(PiPr_3)_2]$,[89] as well as the preparation of pentatetraenylidene derivatives of general formula $[Re(=C=C=C=C=CAr_2)(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)][BF_4]$ (CAr_2 = 9-fluorenylidene moieties),[90]) have been described. – (iv) The zwitterionic μ-but-2-yn-1-ylidene-4-ylidyne complex $[Ru_3(CO)_{10}(\mu_3\text{-}C{-}C{\equiv}C\text{-}\mu\text{-}C)\text{-}Fe_2(\eta^5\text{-}C_5Me_5)_2(CO)_3]$ and its dimerized product containing a cumulenic μ-C_8 ligand $[\{(\eta^5\text{-}C_5Me_5)Fe\}_4\{\mu\text{-}C_8\text{-}C(=O)\}\text{-}\{Ru_2(CO)_{13}\}]$ have been prepared.[91]

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