Allenylidene and Higher Cumulenylidene Complexes

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Contents

1. Introduction

Although the free allenylidene species :C═C═CH_2 was originally identified in 1961 (trapped in cold matrixes),[1] it is 1976 when the isolation of the first allenylidene complexes [M{═C═C═CPh(NMe_2)}($CO)_5$] (M = Cr, W)[2] and [MnCp(═C═C═C^{t}Bu$_2$)($CO)_2$] (Cp = η^5-cyclopentadienyl)[3] was achieved. Unlike the very unstable free species (theoretically characterized as a singlet carbene in the ground state), the coordination to a transition metal gives rise to the stabilization of the cumulene chain. Some years later (1982), Selegue reported the systematic synthesis of cationic ruthenium allenylidenes [RuCp(═C═C═CR^1R^2)($PR_3)_2$]$^+$ in high yields starting from readily available propargylic alcohols HC≡CCR^1R^2(OH).[4] Since then, the application of Selegue's methodology to other electron-rich metal fragments, as well as the subsequent availability of a number of alternative efficient synthetic routes, has allowed easy access to these derivatives. This has triggered the reactivity studies disclosing a very rich and versatile chemistry, which launched the modern interest in the chemistry of metal allenylidenes.

Higher metallacumulenylidene complexes [M]═C═$(C)_n$═CR_2 (n = 2, 3, 4, 5) containing longer chains are much scarcer. Although experimental detection of :C═$(C)_n$═CH_2 (also proposed to be constituents of interstellar gas)[5] and ab initio calculations[6,7] confirmed their singlet character in the ground state, likewise allenylidene species, the stabilization of these highly unsaturated chains can only be achieved by coordination, via the use of their lone pair together with an electron back-donation from the appropriate metal fragment. The hexapentaenylidene complex *trans*-[RuCl{═C═C═C═C═C═CH($SiMe_3$)}($dppe)_2$][OTf] (dppe = 1,2-bis(diphenylphosphino)ethane), proposed as an undetected intermediate,[8] and the isolated heptahexaenylidene derivatives [M{═C═C═C═C═C═C═C($NMe_2)_2$}($CO)_5$] (M = Cr, W)[9] exhibit the longest cumulenylidene chains to date.

Although the allenylidene moiety mostly acts as a terminal ligand, a short number of dinuclear and cluster complexes containing bridging allenylidene groups [(M_nL_m)(μ-η^x═C═C═CR^1R^2)$_y$] have been isolated. So far, no transition metal allenylidene or higher cumulenylidenes of Groups 5 and 11 have been described.[10] Only one mononuclear example of Group 4 is known, namely, [$TiCp_2$(═C═C═CPh_2)(PMe_3)].[11] Very recently, the first palladium allenylidene complexes, of general composition *trans*-[PdBr{═C═C═C(OR)NR_2}($PR_3)_2$][X], have been prepared, but no further Group 10 metal complexes are known.[12]

Since the last previous general reviews on allenylidene and cumulenylidene complexes in 1991[13] and 1998,[14] their chemistry has grown rapidly. Specially, much progress has been made in the synthesis and reactivity of the former

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Victorio Cadierno studied chemistry at the University of Oviedo and obtained his Ph.D. degree in 1996 working under the supervision of Prof. J. Gimeno. He then joined the group of Prof. J. P. Majoral at the LCC-CNRS (Toulouse, France) for a two-year postdoctoral stay. Thereafter, he returned to the University of Oviedo, where he is currently Associated Professor of Inorganic Chemistry. In 2002 he was awarded with the Spanish Royal Society of Chemistry (RSEQ) Young Investigator Award. His research interests cover the chemistry of ruthenium complexes and their catalytic applications, and he is coauthor of more than 90 publications in the field of organometallic chemistry.

complexes mainly due to their applications in organic synthesis involving C−C and C−heteroatom bond formation, both through stoichiometric and catalytic processes. Several surveys[15,16] and a book[17] have been given on this subject to date. Specific accounts on chromium and tungsten,[18] Group 8 metals,[19] iridium,[20] ruthenium,[21−26] and osmium[27,28] complexes are also available. The chemistry of ruthenium and osmium allenylidene complexes bearing macrocyclic ligands has also been reviewed.[29] In addition, brief accounts dealing with particular aspects of mono- and polynuclear metal−allenylidenes[30−32] and a series of polynuclear or cluster species containing bridging allenylidene groups[24,32−38] have also appeared. We refer the reader to the general reviews mentioned above for information on the main molecular structural features in the solid state, spectroscopic data, and properties of representative examples of these derivatives.[13−15,21,38]

In the following review, we present an updated "state of the art" covering this topic from the middle of 1998 up to January 2009. Recent advances in theoretical studies that shed light on the chemical behavior are first discussed. This is followed by a general updated presentation of the most efficient synthetic routes. Special attention is devoted to survey the reactivity patterns of metal−allenylidene and cumulene complexes by Periodic Group, involving both mononuclear and polynuclear derivatives. The review concludes with the synthetic applications of metal allenylidenes. Catalytic reactions in which allenylidene complexes are catalyst precursors or proposed as active intermediate species will also be discussed.

2. Theoretical Calculations and Related Structural Studies

Pioneering theoretical studies on allenylidene complexes were reported in 1979 by Hoffmann and co-workers.[39] Using the Extended Hückel molecular orbital (EHMO) methodology, they established that the allenylidene fragment is a σ-donor π-acceptor ligand with a dominant contribution to the bonding of the latter component. These studies were extensively developed years later through the applications of the DFT (density functional theory) method and more powerful computational tools. Nevertheless, the initial results on the electronic structure and the reactivity of allenylidenes, obtained from the calculations at the empirical level, were mainly confirmed.[40] The former studies involving half-sandwich (mainly η^5-C_xH_y cyclopentadienyl- and indenyl-type derivatives) and five-coordinate d^6 metal allenylidenes have been further extended to higher cumulenylidenes and other structural metal fragments.

2.1. Electronic Structure of Allenylidene Complexes

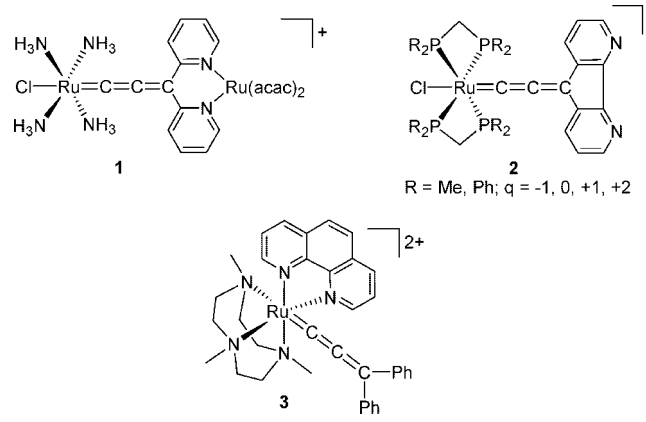
The rationalization of the reactivity studies has been a prevalent goal of theoretical studies. Regioselectivity of both electrophilic and nucleophilic additions is frontier-orbital controlled with LUMO (lowest unoccupied molecular orbital) mainly localized at the C_α and C_γ atoms and HOMO (highest occupied molecular orbital) at the C_β atom. LUMO and HOMO distribution as well as net charges at the carbon atoms of the allenylidene chain have been estimated in a series of cationic ruthenium(II) and osmium(II) derivatives $[M(\eta^5\text{-}C_xH_y)(=C=C=CH_2)(CO)(PH_3)]^+$ and $[M(\eta^5\text{-}C_xH_y)(=C=C=CH_2)(PH_3)_2]^+$ ($C_xH_y = C_5H_5$, C_9H_7; M = Ru, Os), as well as the neutral $[OsCl(\eta^5\text{-}C_5H_5)(=C=C=CH_2)(PH_3)]$ complex, as models.[15,41] Remarkably, the data obtained showed that 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. The electron-rich fragments $[M(\eta^5\text{-}C_xH_y)(PH_3)_2]^+$ showed total charge transfer values notably higher (ca. 57−86%) than those of $[M(\eta^5\text{-}C_xH_y)(CO)(PH_3)]^+$ (M = Ru, $C_xH_y = C_9H_7$; M = Os, $C_xH_y = C_5H_5$) and $[Ru(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4)(CO)(PH_3)]^+$. These results allowed the rationalization of the reactivity of these species, which can be classified depending on the type of the addition as electrophilic and nucleophilic allenylidenes (see below). As a general trend, it was observed that the cationic complexes undergo orbitally controlled

nucleophilic additions at either C_α and C_γ atoms, with the regioselectivity depending on the steric and/or electronic properties of the ancillary ligands (see below). It is worth mentioning the versatile chemical behavior of [Os(η^5-C_5H_5)(=C=C=CPh_2)(P^iPr_3)$_2$][PF_6], arising probably from the particular total charge transfer value and its cationic character, which was able to undergo both electrophilic and nucleophilic additions (see below).[41]

DFT calculations on a series of six-coordinate models of the type [Cr{=C(=C)$_n$=CH_2}$(CO)_5$] confirmed the typical electronic features of allenylidenes. The electronic structure was analyzed in terms of the synergistic σ-donation π-back-donation model, and the contribution from π-back-donation was found to be slightly higher than that from σ-donation.[42] Calculations have also been performed on the series [RuCl{=C(=C)$_n$=CH_2}$(PH_3)_4]^{q+}$ (n = 1−8; q = 0, 1) including allenylidenes (n = 1).[43] Detailed analyses of HOMOs and LUMO localization and atomic net charges followed qualitative trends similar to those obtained for the chromium derivative.[43] Calculations in the amino-substituted allenylidene model *trans*-[RuCl{=C=C=C(Me)NMe_2}$(PH_3)_4]^+$ also provided information on its electronic structure. The breakdown contributions from the metal fragment and carbon atoms of the chain to the LUMO were estimated, being largely dominated by the latter (81%) with major values from C_α (27%), C_γ (34%), and NMe_2 (18%) (Mulliken charges: C_α = −0.255, C_β = −0.265, and C_γ = −0.118).[44] Similarly, in complexes [Cr{=C=C=C(R^1)R^2}$(CO)_5$] (R^1/R^2 = Ph/Ph, Ph/OMe, NMe_2/OMe, NMe_2/NMe_2) were found LUMO-contribution values of 20−28% (C_α), 1−5% (C_β), and 25−33% (C_γ) and the following partial atomic charges: C_α = 0.11 up to 0.14, C_β = −0.38 up to −0.18, and C_γ = 0.06 up to 0.57.[45] From these data, there is no apparent preference for the nucleophilic attack at either C_α or C_γ. By introducing amino substituents at C_γ, it was observed that HOMO and LUMO are more localized on the metal and allenylidene chain, respectively, as compared to related complexes bearing the parent C=C=CH_2 ligand. This is consistent with the proposed electronic structure of the allenylidene group based on the σ-donor/π-acceptor model, which is dependent on the nature of the substituents. Similar trends were calculated in complexes [Cr(C=C=CR_2)$(CO)_5$] (R = F, SiH_3, CH=CH_2, NH_2, NO_2).[46] It is important to note that the electronic properties of the substituents strongly affect the HOMO and LUMO energies in a markedly different way, i.e., an increased energy for π-donor amino groups versus a decreased energy for π-acceptor nitro substituents. Therefore, provided that the contribution of C_α and C_γ atoms to LUMO is dominant, the nitro substituents lead to a favored reactivity in contrast to π-donor groups, which leads to a significant stability toward nucleophilic attacks. This is in agreement with the experimental behavior (see below).

Theoretical studies on *trans*-[RuCl(=C=C=CPh_2)$(NH_3)_4]^+$, taken as a model of allenylidene complexes *trans*-[RuCl(=C=C=CR^1R^2)(16-TMC)][PF_6], which contain the macrocyclic 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane (TMC) ligand, have revealed unusual electronic structures.[47] Thus, ab initio calculations of its ground state at the MP2 level showed that the HOMO is delocalized along the Ru=C=C=CPh_2 unit, in marked contrast to the half-sandwich [M(η^5-C_xH_y)(=C=C=CH_2)$(PH_3)_2]^+$ and six-coordinate *trans*-[RuCl(C=C=CH_2)$(PH_3)_4]^+$ ruthenium(II) complexes, whose HOMO is mainly localized on the metal fragment.[15,43] On the other hand, it was found that Mulliken charges alternate along the allenylidene chain (Ru = 0.55, C_α = 0.17, C_β = −0.72, and C_γ = 0.04), a fact which had not been observed earlier, probably because of the use in the calculations of the nonsubstituted allenylidene =C=C=CH_2 rather than the diphenyl-substituted one. Distribution of the LUMO mainly lies along the allenylidene =C=C=CPh_2 chain with an important localization on the Ph rings (Ru = 13%, C_α = 18%, C_β = 2.6%, C_γ = 27.2%, and Ph = 36%). Similarly, DFT calculations performed in the heteroscorpionato complex [RuCl{κ^3(*N*,*N*,*O*)-bdmpza}{=C=C=CPh_2}(PPh_3)] (bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetato) showed that HOMO is mainly located at the metal center and the chloro ligand while the LUMO is delocalized over the three double bonds and the aromatic rings.[48]

Chart 1

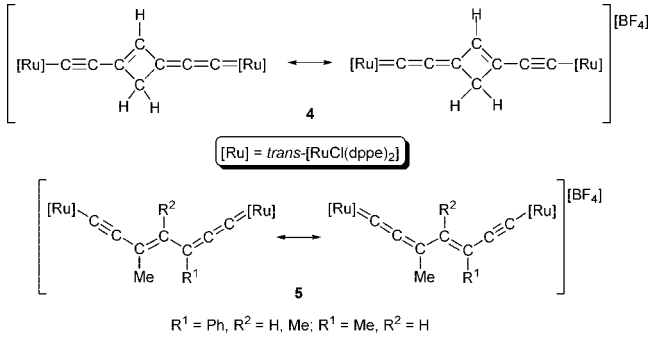


As a continuation of their initial studies,[47] Che and co-workers also performed DFT calculations in the dinuclear model **1** (Chart 1). On the basis of the distribution of highest occupied molecular orbital HOMO, they concluded that there is no communication between the two ruthenium atoms in the ground state. However, the orbital LUMO, which is composed of both π* (Ru{C=C=C(2-py)$_2$}) and dπ (Ru_{acac}), is delocalized over both ruthenium atoms and the allenylidene bridge. This allows, in the excited state, an electronic communication between the {Ru$(acac)_2$} moiety and that bonded to the allenylidene ligand. Redox measurements are in accordance with this MO description. Time-dependent DFT calculations revealed a similar delocalization along the {Ru{C=C=C(py-2)$_2$}Ru} moiety in the MLCT (metal-to-ligand charge transfer) excited states with near-infrared (NIR) absorption energies.[49]

DFT studies performed in octahedral complexes **2** (Chart 1), bearing a related bipyridyl allenylidene group derived from the propargylic alcohol 9-hydroxy-9-ethynyl-4,5-diazafluorene, and subsequent solvent-corrected calculations have been reported.[50] Dielectric constant ε values of 4 and 10 were used. However, the applications of solvent corrections on all charge states did not overturn the identity of the electronic configurations, the electronic transitions in various oxidation states, and the Ru=C_α and allenylidene C=C bond lengths with respect to those obtained for vacuum-phase species.

DFT calculations, charge decomposition analysis (CDA), and natural bond orbital (NBO) analysis on allenylidene [Ru(=C=C=CPh_2)(Me_3Tacm)(phen)]$^{2+}$, bearing the 1,4,7-trimethyl-1,4,7-triazacyclononane ligand Me_3Tacm (**3** in Chart 1), have recently been reported and compared to analogous Fischer-type carbenes [Ru{=C(OMe)R}(Me_3-

Chart 2



Tacm)(phen)]$^{2+}$. Although the σ-donor π-acceptor properties of the allenylidene chain were similarly shown, the calculations suggested that it is a better electron donor and poorer acceptor than the methoxycarbene group. The Ru−C interactions in Ru−allenylidene and methoxycarbene complexes can be depicted by the polarized formulation Ru$^{\delta+}$=C$^{\delta-}$ and nonpolarized formulation Ru=C, respectively. Rotational barriers of 8.3 (C(OMe)Bn), 6.3 (C(OMe)CH=CPh), and 1.5 (=C=C=CPh$_2$) kcal mol^{-1} were calculated.[51]

Theoretical investigations have also been undertaken in bimetallic complexes **4** and **5** featuring C_7 carbon-rich bridges containing allenylidene groups as a part of the skeletal carbon framework (Chart 2).[8] DFT calculations on simplified models in which the phenyl groups of the dppe ligands were substituted by hydrogen atoms for monoreduced and monooxidized states were computed. MO diagrams of **4**$^+$ and **5**$^+$ were calculated showing that the electronic structures are very similar. Among different skeletal conformations of the nonannelated C_7 bridge, the "W"-shaped configuration is preferred. On the basis of a combination of chemical, electrochemical, and spectroscopic (UV−vis, IR, NIR, electron paramagnetic resonance (EPR)) data in solution and in solid state, it was assumed that this is the actual conformation, accounting also for reduced and oxidized species. It was found that the unpaired electron in the reduced state is delocalized mainly over the carbon chain with very little metal contribution, whereas in the oxidized form the odd electron is fully delocalized over the chain and the metal centers. All species exhibited similar spin distribution in each oxidation state with no preferred tendency to be localized on one of the metal fragments. These results resemble those obtained from single-point DFT calculations in the simplified bis-allenylidene model *trans*-[Ru(=C=C=CH$_2$)$_2$(PH$_3$)$_4$]$^{n+}$ (n = 1, 2), in which an identical delocalization of the unpaired electron of the radical (n = 1) over both chains and specially on the C_α and C_γ atoms was evidenced.[52]

2.2. Electronic Structure of Higher Cumulenylidene Complexes

Extensive calculations have established the basic knowledge on the electronic structures and bonding patterns. The most important features are as follows: (i) The electronic structure is described on the basis of a synergic σ-donation π-back-donation model with a slightly higher contribution of the latter component. (ii) Regardless of the length of the chain, the substituents, and the metal fragment, the LUMO is mostly localized on the odd carbon atoms whereas the HOMO has contributions mainly from the metal fragment and the even carbon atoms of the chain. Hence, electrophilic and nucleophilic sites are alternatively localized where the regioselective additions of nucleophiles and electrophiles are expected to occur.

Re and co-workers have carried out detailed density functional calculations on cumulenylidene complexes [Cr{(=C)$_n$R$_2$}(CO)$_5$] (R = H, n = 4−9; R = F, SiH$_3$, CH=CH$_2$, NH$_2$, NO$_2$, n = 4−8)[42,46] and [M](=C)$_n$H$_2$ (n = 4−5), with the latter including the following types of metal fragments: (a) [Mo(CO)$_5$], [W(CO)$_5$], [FeCp(dppe)]$^+$, *trans*-[RuCl(dppe)$_2$]$^+$, [RuCp(PMe$_3$)$_2$]$^+$ and [RuClBz(PH$_3$)]$^+$ (all d^6); (b) *trans*-[RhCl(PH$_3$)$_2$]$^+$ and *trans*-[IrCl(PH$_3$)$_2$]$^+$ (both d^8); (c) [TiCp$_2$(PH$_3$)] (d^2); and (d) [MoCp(PH$_3$)$_2$]$^+$ (d^4).[53] Bond dissociation energies have been found to be essentially independent of the chain length, but they are affected by the π-donor and π-acceptor electronic properties of the substituents. In particular, the amino groups lead to a decrease of the Cr−C bond energy, which mainly affects odd chains, whereas an increase of the dissociation energies is more evident for even chains. It was also found that an increase in the electron richness within d^6 metal fragments gave rise to a slight decrease in the metal−cumulene bond energy. Conversely, bond energies for d^8 and, to a lesser extent, d^4−d^2 complexes are larger than those of d^6 analogues. Breakdown of the contributions from the metal fragments and the carbon atoms along the chain have been thoroughly analyzed. The localization of the HOMO and LUMO on even/odd carbon atoms is essentially unaltered by variations in the metal electron count from d^6 to d^8 or in the electron richness, and therefore, no change in the regioselectivity of additions are foreseen. However, for d^4 complexes, the HOMO is mainly localized on the odd carbons while the LUMO is localized on the even carbon atoms, which is inverted to that found in d^6 and d^8 complexes. Since no d^4 metallacumulene complex has been isolated to date, a comparison with experimental reactivity pattern is not possible yet. Different contributions were found from d^2 complexes since the LUMO and HOMO are mainly localized on the odd carbons, where both nucleophilic and electrophilic attacks are expected to take place. Hence, the regioselectivity of the former attack is the same as d^6 and d^8 complexes being inverted for the latter.

On increasing the chain length, there is an energy rise of the HOMO and a lowering of the LUMO (specially with electron-withdrawing metal fragments [M(CO)$_5$]; M = Cr, Mo, W), which determine an increase of the reactivity toward electrophilic and nucleophilic attacks. This is probably responsible for the synthetic difficulties in preparing higher metallacumulenes. Substitution of H in [Cr{(=C)$_n$H$_2$}(CO)$_5$] by π-donor groups causes an increase of both HOMO and LUMO energies, which is much pronounced for odd chains. Likewise for allenylidene complexes (see above), it leads to a decreased reactivity of these odd chain complexes toward nucleophilic attacks. This is in agreement with the experimental results, which show a high stability of amino-substituted allenylidenes and pentatetraenylidenes (see below). On the other hand, even higher chain metallacumulenes are expected to be stabilized by π-acceptor substituents such as NO$_2$, CN, COOR, etc. Charge distribution along the carbon atoms of the cumulenic chain, which bear very small positive or negative charges, are very similar except for the first and last atom, which support higher negative charges. Only in difluoro-substituted complexes [Cr{(=C)$_n$F$_2$}(CO)$_5$], the last carbon atom of the chain is positively charged.[46] The results clearly show that charge distribution is not important

in determining the regioselectivity of both electrophilic and nucleophilic additions.[42,53]

Further studies on related metallacumulene complexes involving ruthenium, manganese, and rhenium metal fragments have also been reported. In general, the studies confirmed the electronic structures and bonding descriptions of metallacumulenes obtained from the studies by Re and co-workers. Thus, Winter and co-workers studied the model complex *trans*-$[RuCl(=C=C=C=CH_2)(PH_3)_4]^+$,[44] showing complementary results to those obtained for the related butatrienylidene $[Cr(=C=C=C=CH_2)(CO)_5]$ derivatives.[42] From extensive calculations on the models *trans*-$[RuCl\{(=C)_nH_2\}(PH_3)_4]^{q+}$ ($q = 0, 1$) and *trans*-$[RuCl\{(=C)_nH_2\}(PH_3)_4]^-$ ($n = 4-8$),[43] it was concluded that the linear C_nH_2 ligand is somewhat more strongly bonded to the metal fragment when n is an odd number, in agreement with the fact that no ruthenium complexes with an even n number have been isolated to date. Calculations in complexes arising from one and two electron reductions of complexes $[RuCl\{(=C)_nH_2\}(PH_3)_4]^+$ provided interesting properties of the reduced species. It was found that it is easier to undergo the reductions when n = odd rather than when n = even. The neutral complexes $[RuCl\{(=C)_nH_2\}(PH_3)_4]$ are better described as Ru(II) 18-electron species with a reduced $(C_nH_2)^-$ ligand. On the other hand, the anions $[RuCl\{(=C)_nH_2\}(PH_3)_4]^-$ were found to be stable, corresponding to singlet species in the ground state. It is worth mentioning that they show a bending structure at C_α, which allows an extra charge localization on C_α, tending to preserve the metal 18-electron configuration.

Group 7 metallacumulenes $[MnCp(dHpe)(=C=C=C=CR_2)]$ (dHpe = $PH_2CH_2CH_2PH_2$; R = H, $SnMe_3$),[54] $[MnCp\{(=C)_nH_2\}(CO)_2]$, and $[ReCp\{(=C)_nH_2\}(PH_3)(NO)]^+$ ($n = 5, 7, 9$)[55] have been also analyzed by DFT calculations. On the basis of this analysis, the unexpected high stability of the tin-substituted manganese butatrienylidene complex could be explained, with the high-lying and, thus, strongly donating σ-orbitals of $SnMe_3$ groups being the most important factor. As far as the $[M]\{(=C)_nH_2\}$ complexes are concerned (M = Mn, Re), the Mn−C bond contracts slightly as the chains are extended, while for rhenium a lengthening of the metal−carbon bond was found. Besides these facts, no differences with respect to the other metal fragments were found.

Recently, the first heptahexaenylidene complexes have been isolated.[9] Analysis of the electronic structure in the model complex $[W(CO)_5\{=C(=C)_5=C(NMe_2)_2\}]$ was in agreement with the expected data. Thus, the LUMO is mostly localized on the odd carbon atoms of the chain, whereas the HOMO is on the even carbon atoms.

2.3. Other Theoretical Calculations

Although most theoretical studies have been focused on the electronic structures, analysis of conformational orientation of the allenylidene group $=C=C=CR^1R^2$ has also attracted some interest. Early studies on half-sandwich $[M(\eta^5\text{-}C_xH_y)L_2]^+$ (M = Fe, Ru, Os) metal fragments showed a marked preference of the allenylidene group to adopt a "vertical" orientation in which the *ipso* carbon atoms of the R^1/R^2 substituents are contained in the molecular plane (pseudo-mirror plane bisecting the half-sandwich metal fragment).[13−15] Preference for this conformation arises from the dominant $metal_{dxy}-C_{p\pi}$ back-donation of the metal−HOMO into the allenylidene−LUMO π^*-orbital (see Chart 3).

Chart 3

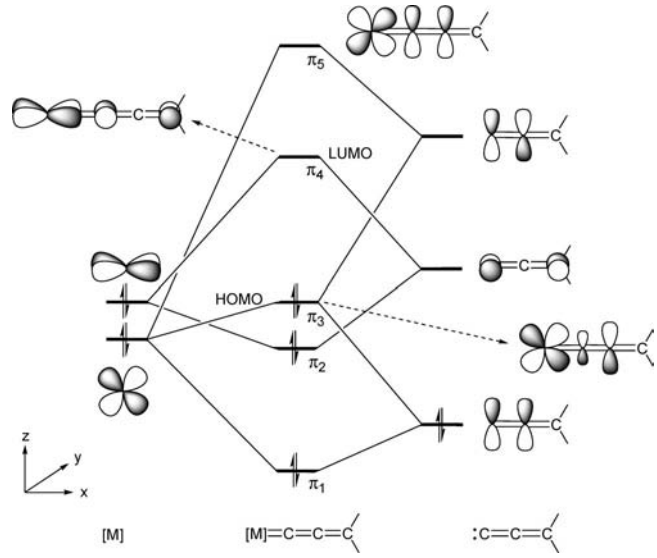
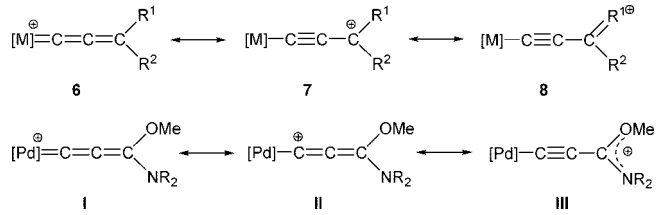


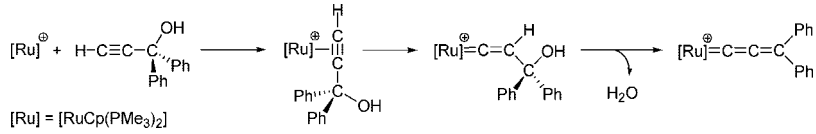
Chart 4



Vertical orientation has also been found in the analogous heteroscorpionato complex $[RuCl\{\kappa^3(N,N,O)\text{-bdmpza}\}\{=C=C=CPh_2\}(PPh_3)]$ (bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetato).[48] In contrast, an unusual "horizontal" orientation of the allenylidene group is favored by the metal fragment $[Mo(dppe)(\eta^7\text{-}C_7H_7)]^+$. The theoretical analysis of the allenylidene conformation revealed that the HOMO is generated by a significant contribution from the metal d_{z2} orbital and the vacant LUMO of the allenylidene ligand, giving rise to the preferred horizontal conformation.[56] Determination of the energy barrier to allenylidene group rotation by variable temperature $^{31}P\{^1H\}$ NMR experiments was reported to be 57.8 kJ mol^{-1} at a coalescence temperature (T_c) of 290 K.[56] This value compares well with that of $[RuTp\{C=C=C(Ph)Fc\}(dppf)]^+$ (Fc = ferrocenyl, dppf = 1,1′-bis(diphenylphosphino)ferrocene, Tp = $HB(pz)_3$) estimated as 47 kJ mol^{-1} (T_c = 238 K).[57]

Description of the allenylidene bonding as a resonance of metal−carbene **6** and metal alkynyl mesomers **7**−**8** (Chart 4), with the latter being the dominant contribution (zwitterionic species $[M]^-C{\equiv}CC^+R^1R^2$ for neutral allenylidene complexes), is commonly proposed. The degree of bond length alternation along the cumulene chain from crystallographic data is usually taken as a reference of the contribution from the different possible mesomeric forms (extensive data have been collected in the previous Bruce's reviews).[13,14] Calculations of the optimized geometries (generally using the LANL2DZ basis set) are commonly associated to all DFT studies and confirm the experimentally observed bond-length alternation. As a representative example, calculated values of Cr−C and C−C bond lengths in $[Cr(=C=C=CH_2)(CO)_5]$ show deviations that are within only 0.04 Å with respect to the experimental parameters (these slight deviations can be attributed to the use of hydrogen susbstituents instead of the actual phenyl groups).[42]

Scheme 1



Complexes bearing heteroatom substituents at the C_γ atom of the allenylidene chain show a greater difference among the M=C and C=C bond lengths arising from the ability of the heteroatom to stabilize a positive charge through the enynyl mesomer form (**8**). Typical examples are the amino−allenylidene ruthenium(II) complexes *trans*-[RuCl{=C=C=C(NRR′)Me}(dppm)$_2$]$^+$, which show a dominant contribution of the iminium−alkynyl resonance form *trans*-[RuCl{C≡C−C(=NRR′)Me}(dppm)$_2$]$^+$.[58] The rotational barrier around the C−N bond in these complexes was calculated. It was found that the rotamer in which the $N(CH_3)_2$ moiety is perpendicular to the Ru=C=C=C(CH_3)N plane is 26 kcal mol^{-1} higher in energy. This result indicates that the rotation around the iminium type C−N bond decouples the nitrogen lone pair and the π-system of the allenylidene ligand, giving a high-energy structure with a tetrahedral nitrogen atom and resulting in a significantly longer CN bond. The comparison of the spectroscopic data of the recently reported palladium−allenylidenes with those of the related neutral complexes [M{=C=C=C(OMe)-NMe_2}$(CO)_5$] (M = Cr, W) revealed that, in the cationic palladium derivatives, the alkynyl character (**III** in Chart 4) is significantly more pronounced than in the corresponding Group 6 complexes, evidenced by the υ(CC) vibration at higher energy by ∼70−90 cm^{-1}.[12] In contrast, complexes *trans*-[RuCl(=C=C=CR^{1}R^2)(16-TMC)][PF_6], containing the strongly σ-donating macrocycle ligand 16-TMC, favor the stabilization of the mesomer form [M]$^+$=C=C=CR^{1}R^2 (**6**) with respect to the alkynyl mesomer **7**, in agreement with the inertness of these complexes to undergo nucleophilic attack by methoxide or refluxing methanol at C_γ.[47]

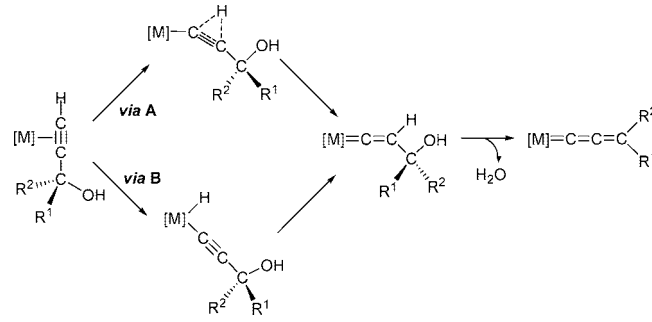
Optimized geometries calculated for higher metallacumulene complexes also showed good agreement with available data from X-ray crystallography. The metal−carbon chains in these complexes either are linear or deviate only slightly from linearity. The geometries of even-chain cumulenes are consistent with a purely cumulenic structure, while odd-chain cumulenes show a small but significant polyyne-like carbon−carbon bond-length alternation superimposed to an average cumulenic structure.[42] Theoretical studies on reaction mechanisms involving allenylidene complexes have been also undertaken, but they will be discussed in the appropriate section.[59]

3. Preparation of Allenylidene Complexes

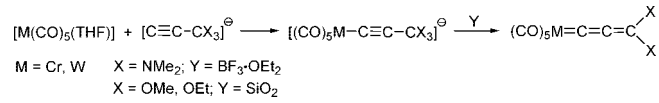
The most general synthetic approach of allenylidene complexes employs propargylic alcohols HC≡CCR^{1}R^2(OH) as sources of the allenylidene C_3 skeleton. In 1982, Selegue introduced for the first time this synthetic strategy for the high-yield preparation of the ruthenium(II) complex [Ru(η^5-C_5H_5)(=C=C=CPh_2)(PMe_3)$_2$][PF_6] starting from 1,1-diphenyl-2-propyn-1-ol, which is converted smoothly into the allenylidene unit via elimination of water (Scheme 1).[4]

The reaction mechanism is now well-established and involves the spontaneous dehydration of the intermediate 3-hydroxyvinylidene species formed, either via **A** or via **B** (Scheme 2), after the coordination of 2-propyn-1-ols at the

Scheme 2



Scheme 3



metal center. A major drawback of this synthetic methodology is the competitive formation of vinylvinylidene versus allenylidene tautomers when alkynols bearing a C−H bond in β-position with respect to the alcohol group are used as substrates. In this context, ab initio molecular orbital calculations on the models [Ru(η^5-C_5H_5){=C=C=C(H)CH_3}$(PH_3)_2$]$^+$ and [Ru(η^5-C_5H_5){=C=C(H)CH=CH_2}$(PH_3)_2$]$^+$ showed that the vinylvinylidene tautomer is 2.1 kcal mol^{-1} more stable than the allenylidene one, explaining its competitive formation.[60]

The Selegue's synthetic strategy proved to not be suitable for [$M(CO)_5$] (M = Cr, W) metal fragments due to the thermal instability of the corresponding nondonor substituted allenylidenes (R^1/R^2 = usually alkyl or aryl groups). Overcoming the synthetic drawbacks of pioneering synthetic routes of Group 6 allenylidenes starting from Fischer-type carbenes,[13,14] an alternative general synthetic procedure using deprotonated tris-amino or alkoxyprop-1-ynes has been successfully applied (Scheme 3).

These two synthetic routes have found many applications over the past decade and many new allenylidenes could be prepared, proving the wide utility of these methodologies.[13,14] Other synthetic alternatives of allenylidenes are also known, but only a few applications have been found. In the following subsections, updated syntheses of allenylidene complexes are presented by periodic group number.

3.1. Group 6 Metals

Following earlier works, Fischer and co-workers have exploited thoroughly the synthetic route based on functionalized acetylides. Thus, by using deprotonated propynoic acid amides (alkynyl metallate), the reaction with [$M(CO)_5$(THF)] followed by treatment with [R_3O][BF_4] afforded N/O-substituted allenylidene complexes **9** (Scheme 4).[61]

Analogous N/C-substituted allenylidenes **10**−**13** (Chart 5) were obtained by using C-ethynylimines, such as HC≡CC(=NMe)Ph, 2-ethynylpyridines, 2-ethynylquinoline, or 2-ethynylpyrimidine, instead of propynoic acid amides.[61−63]

Scheme 4

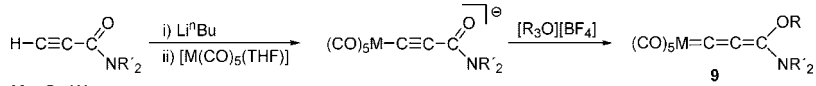
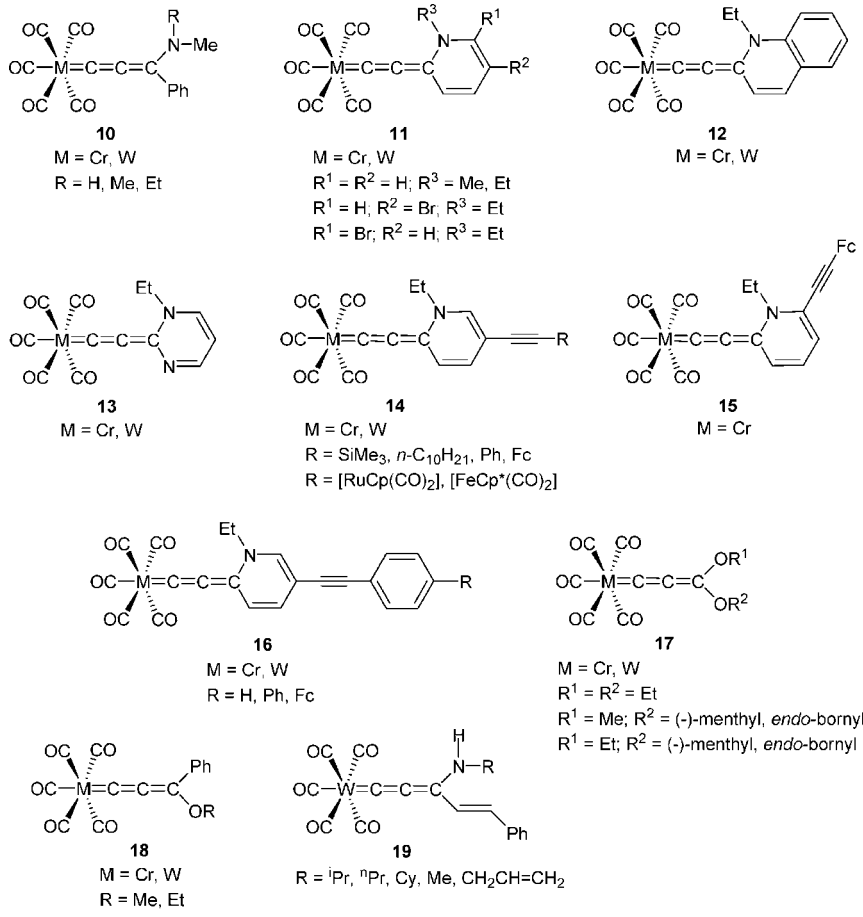


Chart 5



Allenylidenes **11** containing six-membered *N*-heterocycle substituents brominated at 3- and 4-position were used to introduce various alkynyl groups through classical Pd-catalyzed coupling processes with terminal alkynes, yielding complexes **14**−**16** (Chart 5) in moderate-to-high yields.[62] Desilylation of the tetramethylsilane (TMS)-containing chromium−allenylidene **14** led to the corresponding ethynyl-terminated derivative, which was used to prepare heterobinuclear Cr−Ru and Cr−Fe complexes through CuI-catalyzed coupling reactions of the generated terminal C≡CH unit with [RuBrCp(CO)$_2$] and [FeBrCp*(CO)$_2$], respectively. Oxidative coupling of this ethynyl-terminated allenylidene with Cu(OAc)$_2$ was described, affording an unusual homobinuclear bis-allenylidene.[62] Bimetallic Cr−Cr and W−W species were also prepared starting from allenylidenes **13** after coordination of [M(CO)$_5$] units to the nonalkylated nitrogen atom of the pyrimidyl unit.[63]

Related metal O/C-, O/O-, and N/S-substituted allenylidenes, such as complexes **17** and **18** (Chart 5), are also accessible from ethynyl ketones HC≡CC(=O)R, propynoic acid esters HC≡CC(=O)OR, and propynethioic acid amides HC≡CC(=S)NR$_2$, respectively, after the sequential deprotonation and corresponding alkylation.[18,64] Some of these complexes have also been used as suitable precursors of related metal allenylidenes obtained through substitution, insertion, and carbene-transfer reactions (see reactivity studies below). A further series of tungsten−allenylidene derivatives are complexes **19** (Chart 5), formed in low yield (along with other byproducts) through condensation of the (methyl)thiocarbene complex [(CO)$_5$W=C(SEt)Me] with α,β-unsaturated secondary acid amides.[65]

The first mononuclear molybdenum derivatives containing an allenylidene group, namely, [Mo(η^7-C$_7$H$_7$){C=C=C(R)Ph}(dppe)][PF$_6$] (R = Ph, Me) and [(CO)$_5$Mo(=C=C=CFc$_2$)], have been described. The former, generated as mixtures with the corresponding hydroxyvinylidene intermediates [Mo(η^7-C$_7$H$_7$){=C=C(H)C(OH)(R)Ph}(dppe)][PF$_6$], were obtained through the Selegue's methodology by reacting [MoBr(η^7-C$_7$H$_7$)(dppe)] with the corresponding disubstituted propargylic alcohol in methanol and in the presence of KPF$_6$.[56] The latter was synthesized by reacting the dilithiated alkynol [LiC≡CCFc$_2$(OLi)] with [Mo(CO)$_5$(THF)], followed by deoxygenation of the resulting metal−acetylide with phosgene.[66]

Dinuclear molybdenum derivatives in which the allenylidene group acts as a bridging ligand are also known. They were obtained via classical activation of propargylic alcohols HC≡CC(OH)R$_2$ by the bis-nitrile complex [Mo$_2$Cp$_2$(μ-SMe)$_3$(NCMe)$_2$][BF$_4$]. When 1,1-diphenyl-2-propyn-1-ol was used, the reaction gave the allenylidene complex **20** in good

Scheme 5

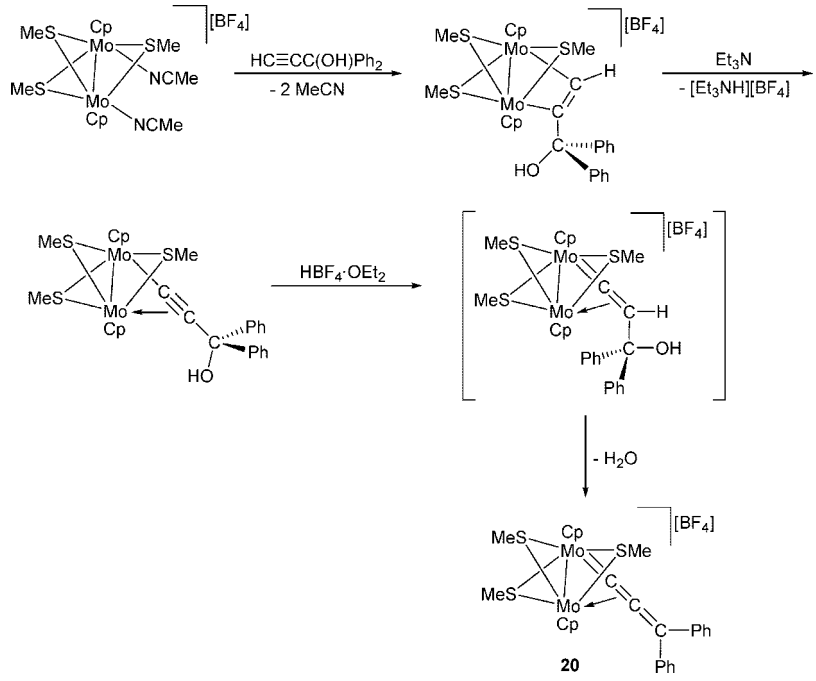
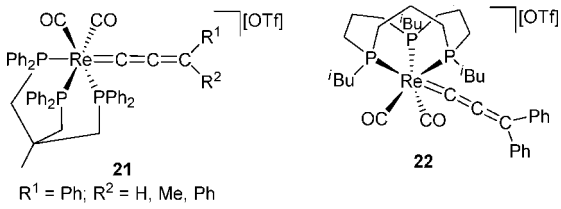


Chart 6

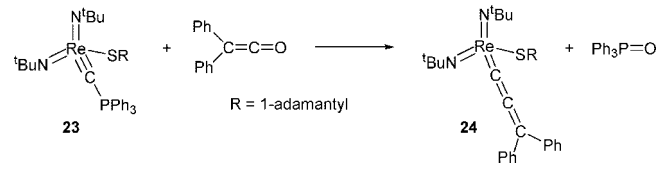


yield, via a μ-alkynyl derivative, implying a four-step process (Scheme 5).[67] However, the reaction of $[Mo_2Cp_2(\mu\text{-}SMe)_3(NCMe)_2][BF_4]$ with $HC{\equiv}CC(OH)Me_2$ in the presence of $HBF_4 \cdot OEt_2$ (1 equiv) led to a complex mixture of several dinuclear complexes containing the corresponding allenylidene complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^2{=}C{=}C{=}CMe_2)][BF_4]$ as a minor component.[68]

3.2. Group 7 Metals

After the preparation of the pioneering manganese derivatives $[MnCp(=C=C=CR_2)(CO)_2]$,[3,69] no further examples have been reported to date despite the fact that chemistry of related vinylidenes and butatrienylidenes is presently an active area of research.[70] The most significant advances stem from the isolation of the first allenylidene−rhenium derivatives. Bianchini, Peruzzini, and co-workers have extensively studied the chemistry of octahedral complexes $[Re(=C=C=CR^1R^2)(CO)_2(triphos)][OTf]$ (triphos = $MeC(CH_2PPh_2)_3$; $TfO^- = CF_3SO_3^-$; **21** in Chart 6). Following Selegue's protocol, rhenium(I) allenylidenes **21** could be prepared in CH_2Cl_2 from mono- and disubstituted propargylic alcohols $HC{\equiv}CCR^1R^2(OH)$ (R^1 = Ph; R^2 = H, Me, Ph) and isolated as air-stable solids.[71,72] A rhenium(I) fragment containing the triphosphorus macrocyclic ligand 1,5,9-triisobutyl-1,5,9-triphosphacyclododecane has also been used to prepare the analogous allenylidene complex **22** (Chart 6).[73] Other six-coordinate Re(I) allenylidenes, namely, $[Re(=C=C=CPh_2)(CO)_2(PR_3)_3][BF_4]$ (PR_3 = $PPh(OEt)_2$, $PPh_2(OEt)$), are also known.[74]

Scheme 6



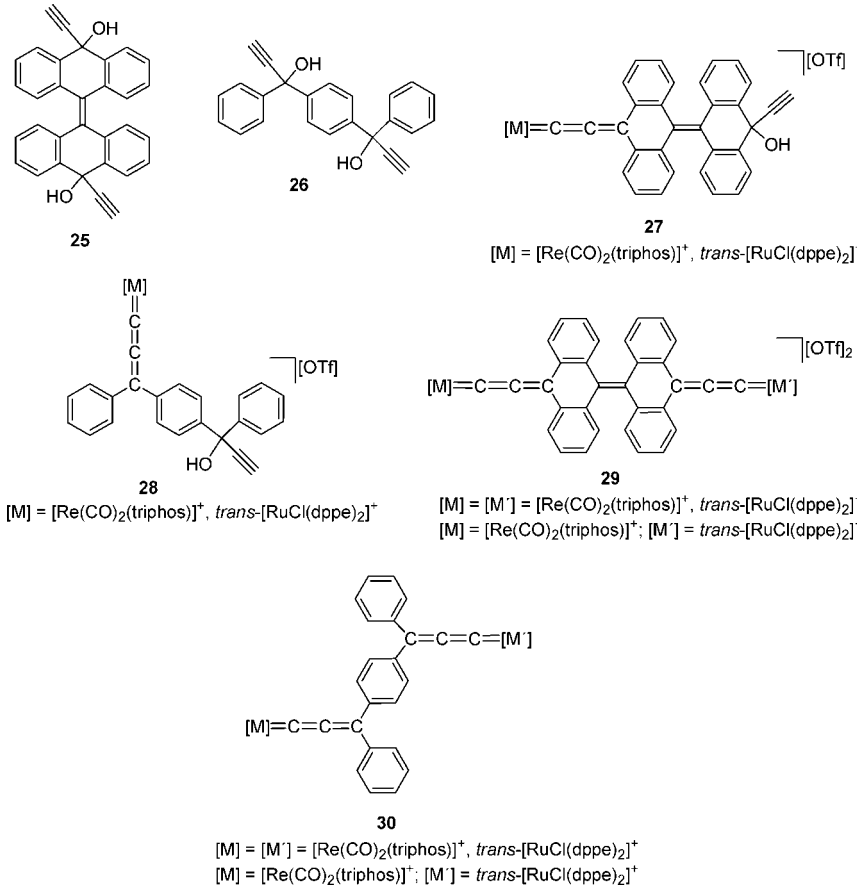
The unusual tetrahedral rhenium(VII) derivative $[Re(N^tBu)_2(SR)(=C=C=CPh_2)]$ (**24**), which represents the first d^0-allenylidene complex characterized crystallographically, has been isolated as an air-stable solid.[75] Complex **24** was obtained through a new synthetic strategy involving the reaction of the phosphonioalkylidyne rhenium complex **23** with diphenylketene (Scheme 6).

Starting from bis-α-alkynols **25** and **26**, functionalized allenylidene Re(I) and Ru(II) complexes **27** and **28** were prepared (Chart 7).[76] These species bear a free propargylic group amenable to react with a second metal fragment to form homo- and heterobimetallic derivatives. This has been achieved by the reaction of **27**−**28** with $[RuCl(dppe)_2][OTf]$ or $[Re(CO)_2(triphos)][OTf]$, affording the dinuclear complex **29**−**30** in which the two allenylidene groups are held together by an organic spacer.

3.3. Group 8 Metals

The chemistry of allenylidene complexes is dominated by these metals mainly due to the efficiency and versatility of Selegue's synthetic approach (Schemes 1 and 2). Although a series of five-coordinated iron(0) derivatives $[Fe(=C=C=CR_2)(CO)_2L_2]$ (L = CO, R = ^{t}Bu; L = PEt_3, R = Ph, ^{t}Bu) were known,[77] the synthetic routes employed did not find further utility. Only the application of the classical methodology has given rise to the systematic synthesis of stable allenylidene complexes. The reactions usually proceed in a one-pot manner by reacting the precursor halide complex with the appropriate propargylic alcohol in the presence of a halide abstractor ($NaBF_4$, KPF_6, $AgSbF_6$, etc.). Addition of nucleophiles to the allenylidene ligand dominates the

Chart 7



reactivity of these electrophilic groups (see below). Therefore, the use of methanol or ethanol as solvents (or sometimes the molecule of water resulting from the spontaneous dehydration) often leads to the isolation of Fischer-type alkoxy- or hydroxycarbenes $[M]{=}C(OR)CH{=}CR^1R^2$ instead of the desired allenylidene complexes. The use of silver(I) salts AgX ($X^- = PF_6^-$, TfO^-, BF_4^-) mostly soluble in chlorinated organic solvents avoids this drawback since the use of nucleophilic polar solvents can be avoided. The synthetic methodology turns out to be quite general regardless of the precursor metal complex used, including six-coordinate, five-coordinate, and half-sandwich metal fragments.

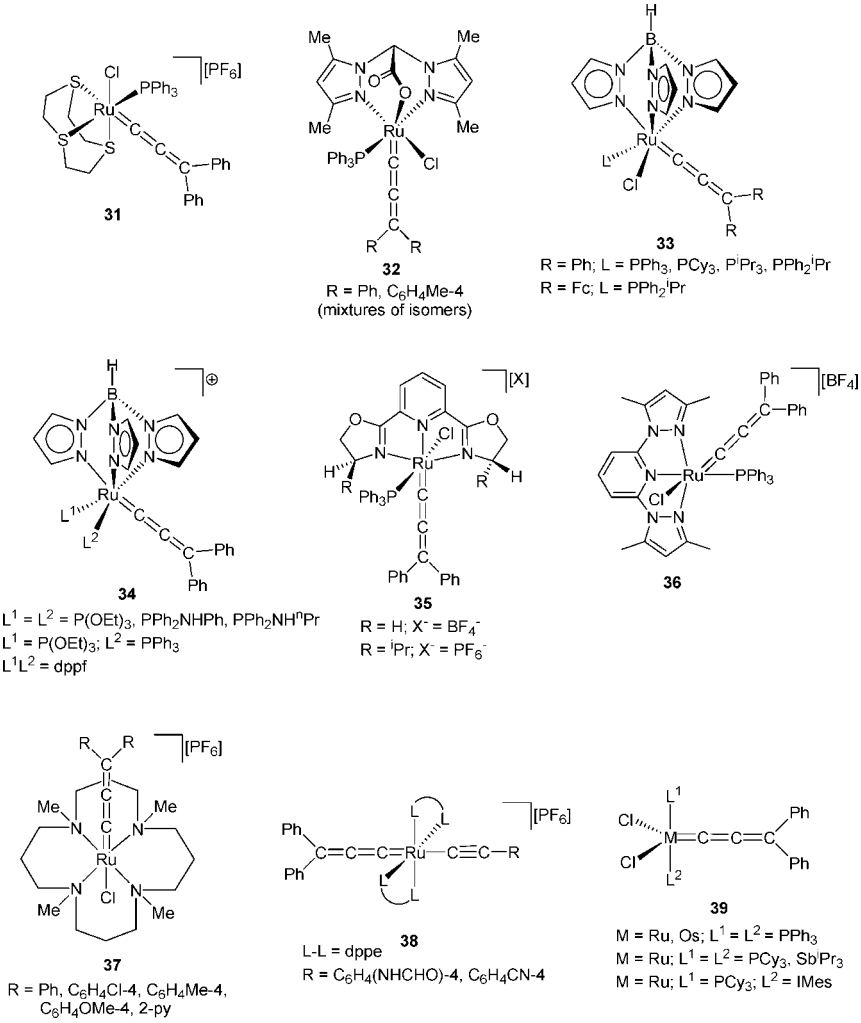
3.3.1. Octahedral and Five-Coordinate Complexes

Chart 8 shows illustrative examples of new allenylidene complexes in which the cumulenic chain was generated from propargylic alcohols $HC{\equiv}CC(OH)R^1R^2$. The reactions imply the formation of a coordinatively unsaturated 16-electron complex, either of the type $[ML_4X]^+$ (generated from the appropriate six-coordinate precursor $[ML_4X_2]$ by abstraction of halide, usually chloride) or $[ML_3X_2]$ (formed by dissociation of a labile ligand such as dmf, hemilabile P−O ligands, and P^iPr_3 or analogous bulky phosphines). In addition to commercially available alkynols, new functionalized substrates such as 9-hydroxy-9-ethynyl-4,5-diazafluorene,[50,78] $HC{\equiv}CC(OH)(4\text{-}XC_6H_4)_2$ (X = Cl, Me, OMe),[47] and $HC{\equiv}CC(OH)(2\text{-py})_2$[49] have eventually been used. Ancillary ligands include carbonyl (Os, Ru),[79,80] acetonitrile (Os),[81] *N*-heterocyclic carbene ligands (Ru, Os),[81] monodentate phosphines and/or phosphites (Fe, Ru, Os),[82−87] bidentate phosphines (Ru-dppe and Ru-dppm;[24,25,47,50,88−91] Os-dppe and Os-dppm;[47,50] Ru-κ^2(*P*,*P*)-aminodiphosphine;[92] Ru-dippe (1,2-bis(diisopropylphosphino)ethane);[93] Fe-dppe[94−96]), hemilabile phosphino-ether *P*,*O*-donor ligands (Ru),[97] κ^2(*N*,*N*)-coordinated pyrazolylphosphines and related ligands (Ru),[98] κ^3(*P*,*P*,*N*)-coordinated aminodiphosphines (Ru),[99] the κ^3(*S*,*S*,*S*)-coordinated 1,4,7-trithiacyclononane ligand (Ru; **31**),[80] the κ^3(*O*,*O*,*O*)-coordinated organometallic tripod ligand $[CpCo\{P(OEt)_2{=}O\}_3]$ (Ru),[100] the κ^3(*N*,*N*,*O*)-coordinated bis(3,5-dimethylpyrazol-1-yl)acetato ligand (Ru; **32**),[48] κ^3(*N*,*N*,*N*)-coordinated tris(pyrazolyl)borates (Ru; **33**−**34**),[57,80,101−104] and related polydentate *N*-donor ligands such as κ^3(*N*,*N*,*N*)-2,6-bis(oxazolyn-2′-yl)pyridines (Ru; **35**),[105] κ^3(*N*,*N*,*N*)-bis(pyrazol-1-yl)pyridines (Ru, **36**),[106] κ^3(*N*,*N*,*N*)-1,4,7-trimethyl-1,4,7-triazacyclononane (Ru; **3** in Chart 1),[51] and κ^4(*N*,*N*,*N*,*N*)-macrocycles (Ru; **37**).[47,49,80]

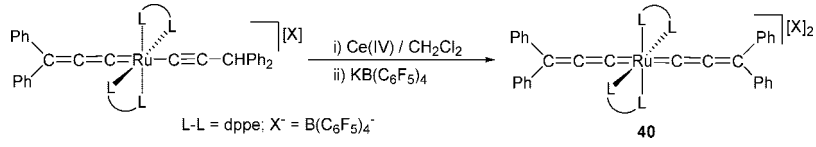
σ-Acetylide−allenylidene complexes **38** (Chart 8) have recently been isolated from *trans*-$[RuCl\{{=}C{=}C(H)C_6H_4R\text{-}4\}(dppe)_2][PF_6]$ after the abstraction of chloride in the presence of $NaPF_6/NEt_3$ and $HC{\equiv}CC(OH)Ph_2$.[107] It is worth mentioning that the use of bulky ligands in five-coordinate allenylidene complexes $[RuCl_2(=C=C=CPh_2)(Sb^iPr_3)_2]$,[108] $[MCl_2(=C=C=CPh_2)(PPh_3)_2]$ (M = Ru,[85] Os[80]) and $[RuCl_2(=C=C=CPh_2)(PCy_3)L]$ (L = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), PCy_3) allows the stabilization of 16e$^-$ complexes (**39** in Chart 8).[109]

Besides the use of coordinatively unsaturated 16-electron precursors $[ML_4X]^+$ and $[ML_3X_2]$, alternative synthetic methodologies of allenylidenes based on different starting materials have also been used for the preparation of (i) $[RuCl_2(=C=C=CPh_2)(CO)(Sb^iPr_3)_2]$ obtained from $[RuHCl(CO)(Sb^iPr_3)_3]$ and 1,1-diphenyl 2-propyn-1-ol;[108] (ii) $[Ru(\kappa^1\text{-}O_2CMe)(=C=C=CPh_2)(CN^tBu)_2(PPh_3)_2]$, which results from the protonation of the alkynyl−isocyanide com-

Chart 8

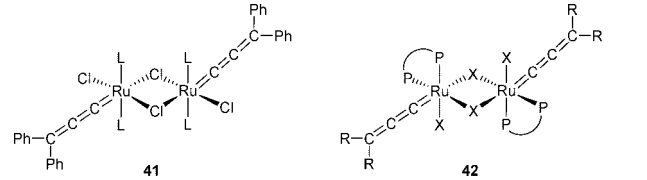


Scheme 7



plex [Ru(κ^1-O_2CMe){C≡CC(OH)Ph_2}(CN^tBu)$_2$(PPh_3)$_2$];[87] (iii) [Ru(acac)$_2$(=C=C=CPh_2)(P^iPr_3)] generated from [Ru(acac)$_2$(P^iPr_3)$_2$];[86] (iv) [$RuCl_2$(=C=C=CPh_2)(PPh_3)$_2$(L)] (L = H_2O, MeOH, EtOH, 4-(*N*,*N*-dimethylamino)pyridine) obtained by reaction of the five-coordinate complex [$RuCl_2$(=C=C=CPh_2)(PPh_3)$_2$] (prepared by treatment of carbyne [$RuCl_2${≡CC(H)=CPh_2}(PPh_3)$_2$]$^+$ with base) with the ligands L;[85] (v) cationic complexes [RuCl{=C=C=C(NMe_2)(CH_2Fc)}(dppm)$_2$]$^+$[110] and [RuCl{=C=C=C-(ER_n)Me}(dppm)$_2$]$^+$, with a broad range of heteroatom substituents,[58,111−115] which are prepared from the transient butatrienylidene complex [RuCl(=C=C=C=CH_2)(dppm)$_2$]$^+$ (see reactivity studies); (vi) the cationic osmium derivative [Os{κ^2(*C*,*O*)-C(CO_2Me)=CH_2}(=C=C=CPh_2)(CO)(P^iPr_3)$_2$]-[BF_4] obtained by the displacement of the acetone ligand in [Os{κ^2(*C*,*O*)-C(CO_2Me)=CH_2}($OCMe_2$)(CO)(P^iPr_3)$_2$][BF_4] by 1,1-diphenyl-2-propyn-1-ol;[116] (vii) complex *trans*−*cis*-[OsH(=C=C=CPh_2)(N$CMe)_2$(P^iPr_3)$_2$][BF_4], which results from the deprotonation of the carbyne complex [OsH{≡CC(H)=CPh_2}(N$CMe)_2$(P^iPr_3)$_2$][BF_4];[117] and (viii) [Os(=C=C=CPh_2){P($OEt)_3$}$_5$][BPh_4]$_2$, which results from the reaction of [Os{κ^2(*O*,*O*)-OTf}$_2${P($OEt)_3$}$_4$] with HC≡CC(OH)Ph_2 and P($OEt)_3$ in the presence of $NaBPh_4$.[118] The preparation of a unique example of a bisallenylidene complex **40** and its reduced one-electron radical has also been reported (Scheme 7).[52]

Chart 9



Along with the previously reported dinuclear allenylidene complex [Ru_2(μ-Cl)$_3$(=C=C=CPh_2)$_2$(PPh_3)$_4$][PF_6],[85,119] new derivatives containing (μ-X)$_2$ halide systems have also been reported (Chart 9). Thus, while complex **41** was formed through the classical route starting from [{$RuCl_2$(TPPMS)$_2$}$_2$] (TPPMS = (3-sulfonatophenyl)diphenylphosphine sodium

Scheme 8

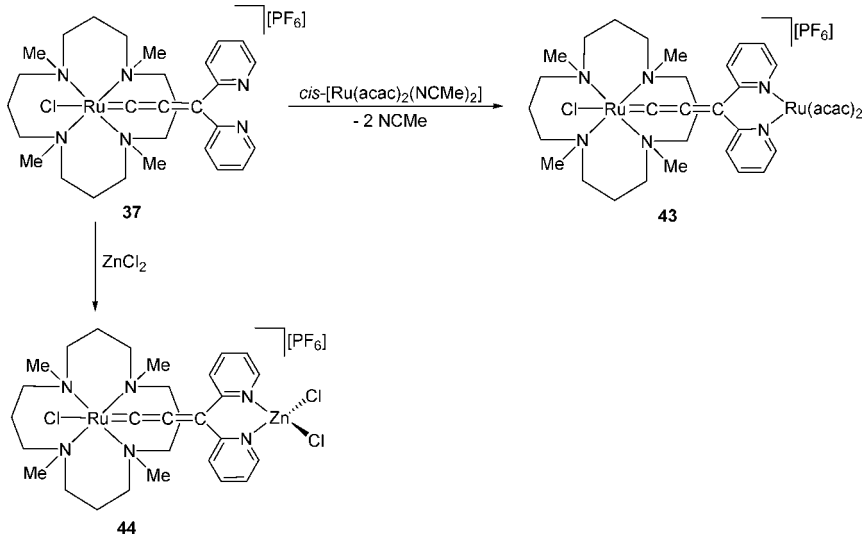
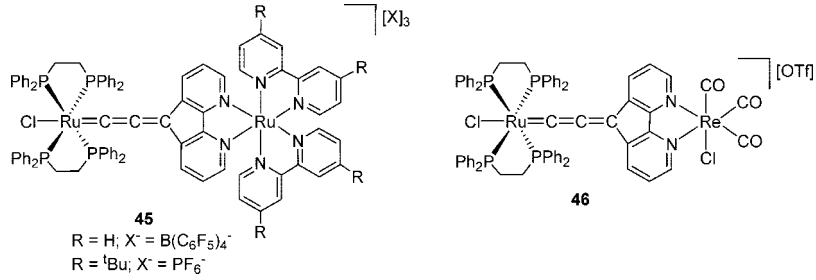


Chart 10



salt),[120] complexes **42** were obtained by the treatment of the corresponding carbyne complex [RuX_3{≡CC(H)═CR}(dppf)] with 1 equiv of $AgSbF_6$.[121]

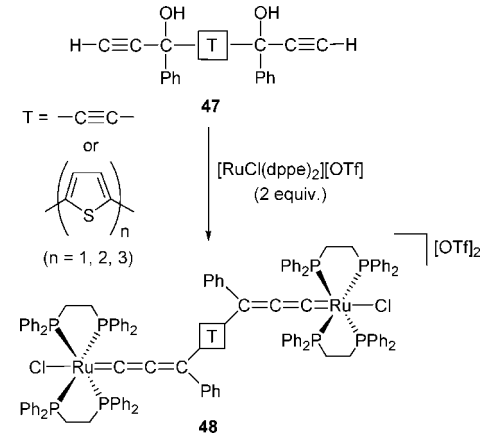
Dimetallic fragments linked by allenylidene groups are more common. Besides the heterobimetallic Ru−Re and homobimetallic Ru−Ru complexes **29**−**30** (Chart 7),[76] reported examples include the following:

(i) Diruthenium(II) **43** and mixed Ru(II)−Zn(II) **44** derivatives, prepared from **37**, which acts as a metalla-ligand for coordination to the [$Ru(acac)_2$] and $ZnCl_2$ fragments (Scheme 8).[49]

(ii) The related species **45** and **46** (Chart 10) obtained by coordination of the diazafluorene-based Ru(II)−allenylidene *trans*-[$RuCl(═C═C═CC_{10}H_6N_2)(dppe)_2$][OTf] to $[Ru(bipy)_2]^{2+}$ and $[ReCl(CO)_3]^{+}$ moieties, respectively.[78]

(iii) Diruthenium(II) complexes **5** (Chart 2) containing a planar "W"-shaped π-conjugated C_7 bridge, which were formed by coupling cationic allenylidene complexes *trans*- [$RuCl\{═C═C═C(R^1)CH_2R^2\}(dppe)_2$][$BF_4$], featuring an acidic methylenic unit, with the neutral diynyl complex *trans*-[$RuCl\{(C≡C)_2H\}(dppe)_2$]. The process involves the initial protonation of the latter by the methylenic unit of the former and subsequent C−C coupling between the resulting organometallic species.[8] Similar C_9-bridged species were synthesized using the triynyl derivative *trans*-[$RuCl\{(C≡C)_3SiMe_3\}(dppe)_2$].[8] Oxidation with ferrocenium hexafluorophosphate, or protonation with HOTf, of the diynyl complex *trans*-[$RuCl\{(C≡C)_2H\}(dppe)_2$] was reported to yield the related C_7-annelated dinuclear complex **4** (Chart 2), with the process involving a highly reactive butatrienylidene intermediate $[Ru]^{+}═C═C═C═CH_2$.[8]

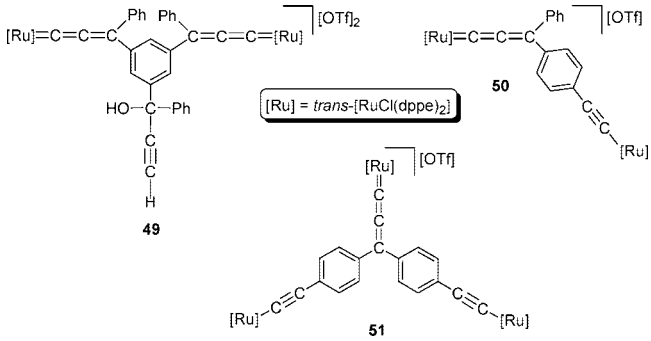
Scheme 9



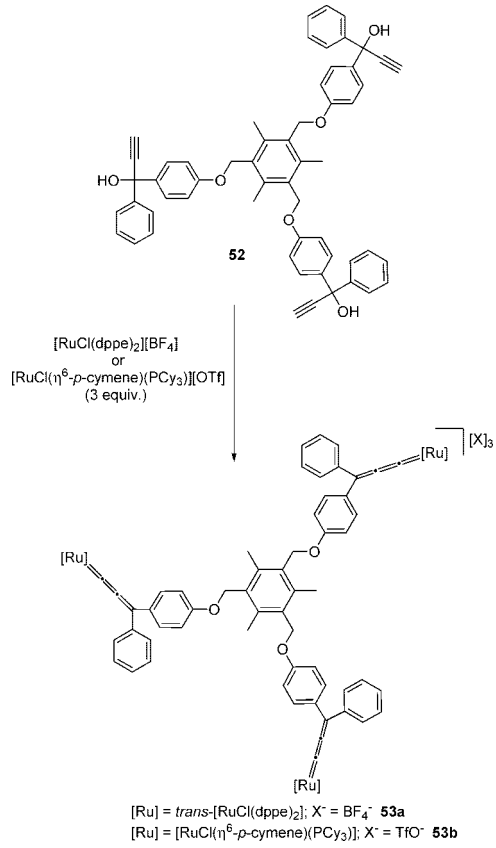
(iv) Bis(allenylidene)−ruthenium(II) complexes **48** obtained by treatment of [$RuCl(dppe)_2$][OTf] with 2 equiv of bis(propargylic) alcohols **47** (Scheme 9).[90] The same reactions performed with 1 equiv of **47** afforded the expected monoallenylidene derivatives.[90] In the same work, the preparation of bis(allenylidene) complex **49** and the new dimetallic and trimetallic complexes **50** and **51**, containing mixed alkynyl−allenylidene bridges, was also described (Chart 11).

(v) The tricationic trinuclear tris(allenylidene)−ruthenium(II) complex **53a**, which was synthesized by reacting the new triyne C_6Me_3-1,3,5-[$CH_2O(p\text{-}C_6H_4)PhC(OH)C≡CH]_3$ (**52**) with 3 equiv of the tetrafluoroborate salt [$RuCl(dppe)_2$][BF_4] (Scheme 10).[122]

Chart 11



Scheme 10



3.3.2. Half-Sandwich Complexes

Following former synthetic approaches[13,14] based on the Selegue's methodology,[4] halide complexes have continued to be used as suitable precursors for the activation of propargylic alcohols. Limitations of this synthetic route mainly stem from (i) the reluctance of the 3-hydroxyvinylidene intermediate **54** (Scheme 11) to undergo dehydration especially when strong electron-releasing metal fragments are used and (ii) the competitive formation of an alkenylvinylidene isomer **55** versus the expected allenylidene **56** arising from the activation of propargylic alcohols containing a C−H bond in β-position with respect to the OH group (Scheme 11).[60,123−125] Although spontaneous dehydration usually occurs, eventually 3-hydroxyvinylidene intermediates $[M]{=}C{=}C(H)C(OH)(R^1)(R^2)$ (**54**) are stable and the transformations into the allenylidenes **56** require treatment with acidic Al_2O_3.[126,127] In this context, it is worth noting that recent theoretical calculations on the propargylic alcohol−allenylidene transformation using the half-sandwich ruthenium fragments $[RuCp(PH_3)_2]^+$ and $[CpRuCl(\mu_2\text{-SMe})\text{-}RuCp]^+$ as models have pointed out the important role played by protic solvents (e.g., MeOH) in the dehydration process (Scheme 12).[128]

Typical half-sandwich metal fragments employed in allenylidene synthesis include not only the classical η^5-cyclopentadienyl, η^5-indenyl, and η^6-arene chloride derivatives but also tethered-type ligands in which the rings are linked to the metal through an ancillary κ^1-coordinated donor atom as well, giving rise to $\eta^5{:}\kappa^1(L)$- or $\eta^6{:}\kappa^1(L)$-coordination modes (Chart 12).

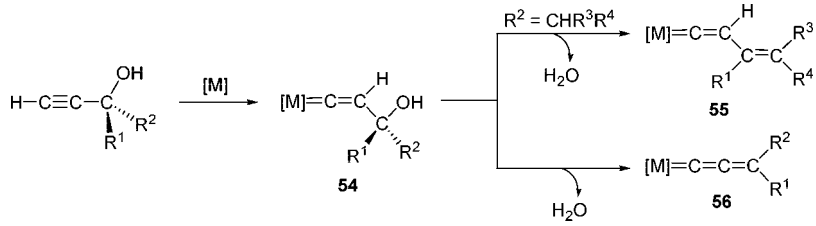
3.3.2.1. η^5-Cyclopentadienyl and η^5-Indenyl Complexes. Continuing the fate of previously reported examples,[13,14] the most common derivatives are cationic complexes $[M(\eta^5\text{-Ring})(=C=C=CR^1R^2)(L^1)(L^2)][X]$ (X^- = BF_4^-, BPh_4^-, PF_6^-, TfO^-, $B(Ar_F)_4^-$, etc.; Ar_F = 3,5-$C_6H_3(CF_3)_2$). Ruthenium(II) fragments involve both η^5-C_5R_5 (R = H, Me) and η^5-C_9H_7 or η^5-1,2,3-$C_9H_4Me_3$ rings mostly containing mono- and bidentate phosphines. Examples of η^5-C_5R_5 derivatives described include $[RuCp(=C=C=CPh_2)(PPh_3)_2][PF_6]$,[129] $[RuCp(=C=C=CPh_2)(PPh_2NHR)_2][OTf]$ (R = Ph, ^{n}Pr),[103] complexes **57** (Chart 13),[130] and a large series of Cp*Ru(II) allenylidenes of the type $[RuCp^*\{=C=C=C(R^1)(R^2)\}(L^1)(L^2)][X]$ (L^1L^2 = dippe, R^1 = R^2 = Me, Ph, X^- = BPh_4^-;[126] L^1L^2 = dippe, R^1 = Ph, R^2 = H, Me, X^- = BPh_4^-;[126] L^1 = L^2 = PEt_3, R^1 = Ph, R^2 = H, Me, Ph, X^- = BPh_4^-;[131,132] L^1 = L^2 = PEt_3, R^1 = H, R^2 = C_6H_4OMe-4, C_6H_4F-4, X^- = BF_4^-;[133] L^1 = L^2 = PMe^iPr_2, R^1 = Ph, R^2 = H, Me, Ph, X^- = $B(Ar_F)_4^-$;[127] L^1 = CO, L^2 = PMe^iPr_2, R^1 = R^2 = Ph, X^- = $B(Ar_F)_4^-$[134]). Recently, several examples of chiral ruthenium(II) complexes bearing a fullerene−cyclopentadienyl ligand (**58** in Chart 13) have been isolated.[135]

Another large family of allenylidene complexes is formed by the η^5-indenyl derivatives. They were generated by activation of 1,1-diphenyl-2-propyn-1-ol, 1-phenyl-2-propyn-1-ol, and 9-ethynyl-9-fluorenol by indenyl−ruthenium(II) chloride complexes $[RuCl(\eta^5\text{-}C_9H_7)(L^1)(L^2)]$, in methanol and in the presence of $NaPF_6$, affording the corresponding cationic derivatives $[Ru(\eta^5\text{-}C_9H_7)(=C=C=CR^1R^2)(L^1)(L^2)][PF_6]$ (R^1 = R^2 = Ph, L^1 = PPh_3, L^2 = PPh_3, $PMePh_2$, PMe_2Ph, $Ph_2PCH_2CH{=}CH_2$; R^1 = R^2 = Ph, L^1L^2 = dppm, dppe; R^1 = H, R^2 = Ph, L^1 = PPh_3, L^2 = PPh_3, $PMePh_2$; R^1R^2 = $C_{12}H_8$ (2,2′-biphenyldiyl), L^1 = PPh_3, L^2 = PPh_3; R^1R^2 = $C_{12}H_8$ (2,2′-biphenyldiyl), L^1L^2 = dppm, dppe).[19,136,137] Some examples containing chiral phosphines, such as (*R*)-BINAP, have also been described.[138,139]

In a similar way, the chiral allenylidene−ruthenium(II) complexes (*R*,*S*)-**59**, (*R*,*R*)-**60**, and (*S*,*S*)-**61** have been prepared by reacting $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ with $NaPF_6$ and propargylic alcohols derived from the optically active ketones (−)-fenchone, (+)-camphor, and (−)-verbenone (Chart 14).[140,141] The reaction of $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ with an excess of 1-ethynyl-1-cyclohexanol and $NaPF_6$ in refluxing methanol gave the unusual allenylidene complex **62**, containing a spirobicyclic organic skeleton, via an unprecedented coupling of two dehydrated molecules of the propargylic alcohol.[142] The initial product in this reaction is the alkenyl−vinylidene complex $[Ru\{=C=C(H)C_6H_9\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (C_6H_9 = 1-cyclohexenyl), which undergoes the addition of a second molecule of 1-ethynyl-1-cyclohexanol.

A different synthetic route has been used to prepare heteroatom-substituted allenylidenes $[RuCp(PPh_3)_2\{=C=C=C(NPh_2)Me\}][PF_6]$ and $[RuCp\{=C=C=C(-2\text{-}MeC_4H_3N)Me\}(PPh_3)_2][PF_6]$,[113] the binuclear butenynylallenylidene

Scheme 11



Scheme 12

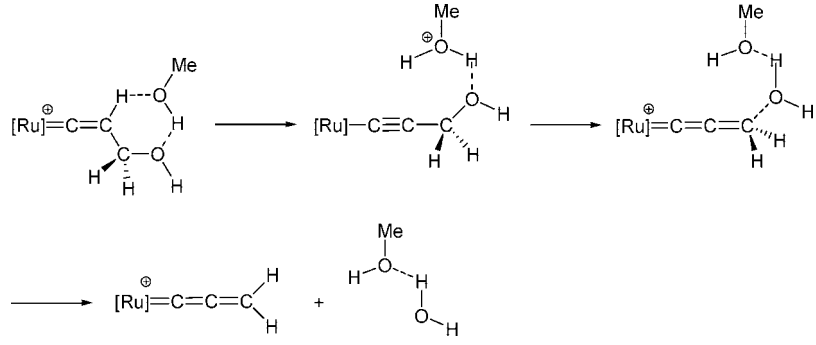


Chart 12

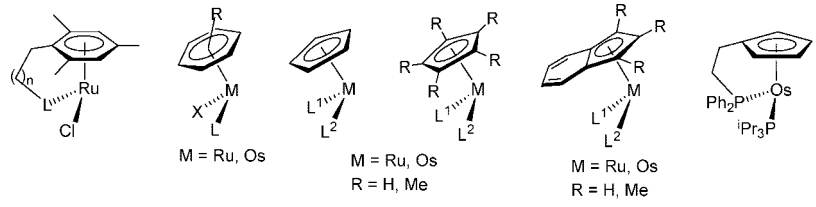
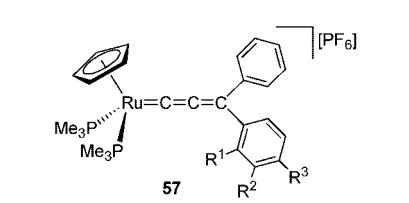
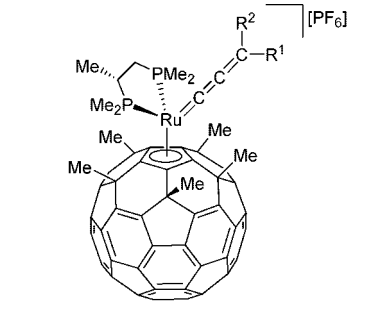


Chart 13



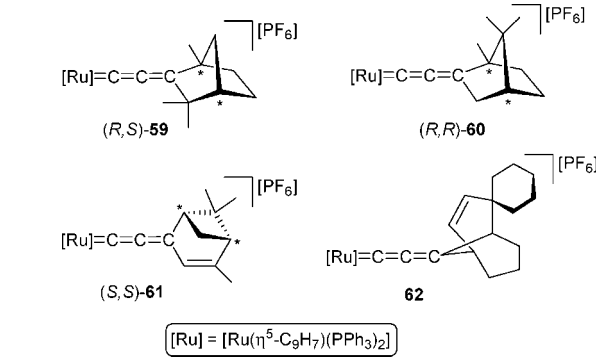
$R^1 = R^2 = H$; $R^3 = NO_2$, C≡CPh, C≡C-$C_6H_4NO_2$-4, C≡C-$C_6H_4NMe_2$-4, (*E*)-C(H)=C(H)^{n}Bu
$R^2 = R^3 = H$; R^1 = (*E*)-C≡C$(CH_2)_2$C(H)=C(H)CO_2Et, $CH_2C{\equiv}C^nBu$, I, ^{n}Hex, C≡CMe, C≡C^{n}Bu
$R^1 = R^3 = H$; R^2 = C≡C^{n}Bu



$R^1 = R^2$ = Ph
$R^1 = H$; R^2 = Ph, Fc, $C_6H_4NMe_2$-4, C_6H_4OMe-4

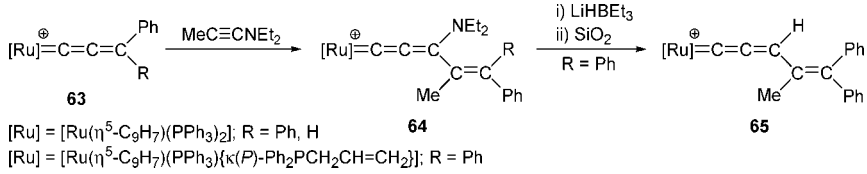
[{RuCp*(dppe)}$_2${μ-C≡CC(OMe)=C(H)C(Me)=C=C=C}][PF_6],[143] and [FeCp*(dppe){=C=C=C(OMe)Me}][BPh_4].[144] They were prepared by trapping the corresponding transient butatrienylidene complexes with the appropriate nucleophile (see reactivity section). A systematic route to prepare sequentially polyalkenyl−allenylidene complexes has been reported (more details can be found in the reactivity section).[145,146] The first step consists of the insertion of the ynamine MeC≡CNEt_2 into the C_β=C_γ bond of indenyl−allenylidene complexes **63**, which leads to the stereoselective formation of cationic amino−allenylidenes **64** (Scheme 13). When R = Ph, complexes **64** can be transformed into the secondary derivatives **65** via treatment with $LiBHEt_3$ and subsequent purification on silica-gel column. Further insertions of MeC≡CNEt_2 into **65** allow the preparation of polyunsaturated cumulene chains (see below).

Chart 14



In contrast to their cationic counterparts, neutral η^5-C_5R_5-based ruthenium(II)−allenylidenes are much scarcer. Thus, within the period covered by this review, only complex

Scheme 13

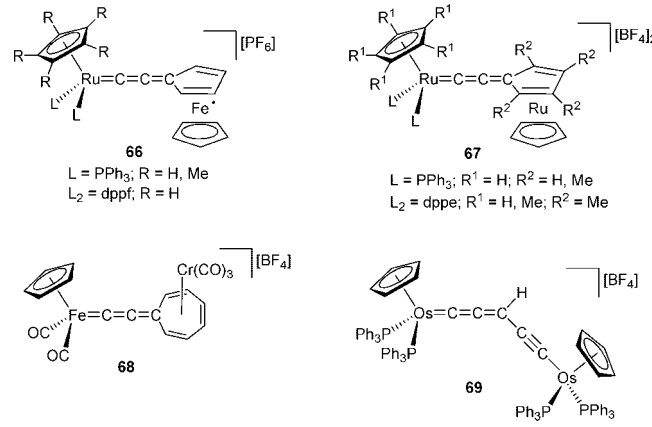


[RuClCp(=C=C=CPh$_2$)(PPh$_3$)] resulting from the treatment ofallylcomplex[Ru(η^3-2-C$_3$H$_4$Me)Cp(PPh$_3$)]withHC≡CCPh$_2$-(OH)/HCl has been reported.[147] The use of acidic Al$_2$O$_3$ as dehydrating agent was required.

Allenylidene−osmium complexes have also been described. Thus, complex [OsClCp(P^{i}Pr$_3$)$_2$] was found to react with 1,1-diphenyl-2-propyn-1-ol in the presence of TlPF$_6$ to give the stable hydrido−hydroxyalkynyl−osmium(IV) derivative [OsH{C≡CCPh$_2$(OH)}Cp(P^{i}Pr$_3$)$_2$][PF$_6$], as the result of the extraction of the chloride ligand and the oxidative addition of the alkynol C(sp)−H bond to the metal. Dehydration of this complex to generate the cationic osmium allenylidene derivative [OsCp(=C=C=CPh$_2$)(P^{i}Pr$_3$)$_2$][PF$_6$], catalyzed by HCl, could be achieved in refluxing chloroform.[41] The analogous complexes [OsCp(=C=C=CPh$_2$)-(P^{i}Pr$_3$)(L)][PF$_6$] (L = CO, PHPh$_2$) are also known. They were prepared from the unsaturated π-alkyne complex [OsCp{η^2-HC≡CCPh$_2$(OH)}(P^{i}Pr$_3$)][PF$_6$] by treatment with CO and PHPh$_2$ in refluxing dichloromethane, with the process also involving the intermediate formation of a hydride−hydroxyalkynyl−osmium(IV) species [OsHCp{C≡CCPh$_2$-(OH)}(P^{i}Pr$_3$)(L)][PF$_6$], which, in the case of L = PHPh$_2$, could be isolated and characterized.[148] The reaction of [OsBrCp(PPh$_3$)$_2$] with HC≡CC(OH)Ph$_2$ and NH$_4$PF$_6$ proceeded in a different way since it led directly to the allenylidene complex [OsCp(=C=C=CPh$_2$)(PPh$_3$)$_2$][PF$_6$].[149] Apparently, the replacement of P^{i}Pr$_3$ by PPh$_3$ in the coordination sphere of the metal destabilizes the hydride−alkynyl intermediates and facilitates the formation of the allenylidene derivatives. In addition to these cationic derivatives, the neutral species [OsXCp(=C=C=CPh$_2$)(P^{i}Pr$_3$)] (X = Cl, I) are also known.[150]

Atypical dinuclear allenylidene complexes [Cp*RuCl(μ-SMe)$_2$Ru{=C=C=C(H)Ph}Cp*][BF$_4$] and [Cp*RuCl(μ-EMe)$_2$RuCp*{=C=C=C(4-MeC$_6$H$_4$)$_2$}][OTf] (*E* = S, Se, Te) have been synthesized by reaction of chalcogenolate-bridged diruthenium(III) precursors [{Cp*RuCl(μ-SMe)}$_2$] or [Cp*RuCl(μ-EMe)$_2$RuCp*(OH$_2$)][OTf] with the corresponding alkynol.[151,152] The related hybrid phosphido/thiolate-bridged derivative [Cp*RuCl(μ-S^{i}Pr)(μ-PMe$_2$)RuCp*{=C=C=C(4-MeC$_6$H$_4$)$_2$}][BF$_4$] is also known.[153] These species, which are the only known ruthenium(III) allenylidenes, have been widely used in catalytic transformations of propargylic alcohols (see below). Other dinuclear derivatives (prepared by chemical oxidation of acetylide complexes) in which the allenylidene group is acting as a bridging ligand have also been described. Thus, the one-electron oxidation of ferrocenyl−acetylide complexes [Ru(C≡CFc)(η^5-C$_5$R$_5$)L$_2$] (L = PPh$_3$, R = H, Me; L$_2$ = dppf, R = H) with ferrocenium hexafluorophosphate yielded the cationic allenylidene radicals **66** (Chart 15),[154] while the dicationic species **67** were prepared by two-electron oxidation of [Ru(C≡CRc)(η^5-C$_5$H$_5$)(PPh$_3$)$_2$] (Rc = ruthenocenyl) and [Ru(C≡CRc′)(η^5-C$_5$R$_5$)L$_2$] (L = PPh$_3$, R = H; L$_2$ = dppe, R = H, Me) (Rc′ = 2,3,4,5-tetramethylruthenocenyl) using 2 equiv of a *p*-benzoquinone/BF$_3$·OEt$_2$ mixture.[155] Another analogous

Chart 15

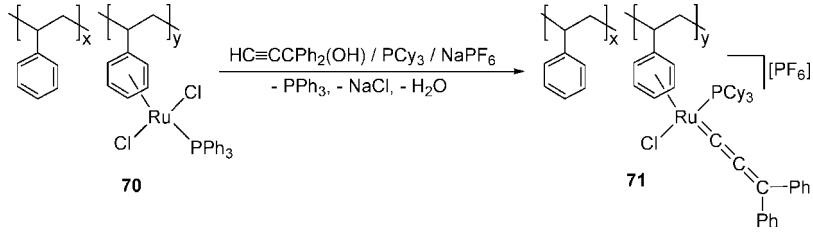


dinuclear example is the iron(II)−chromium(0) complex [(CO)$_2$CpFe(μ-η^1:η^7-C$_2$C$_7$H$_6$)Cr(CO)$_3$][BF$_4$] (**68**), although structural parameters of the Fe−C$_\alpha$−C$_\beta$−C$_\gamma$ chain indicate that the bridging moiety can better be described as a substituted tropylium alkynyl group.[156] The dinuclear cationic osmium(II) complex **69** and an analogous iron derivative [Cp(dppe)Fe=C=C=CHC≡CFe(dppe)Cp][BF$_4$] have also been described.[157]

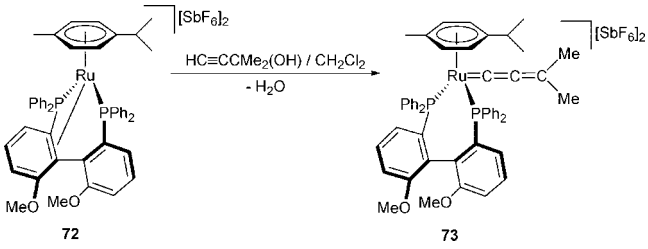
3.3.2.2. η^6-Arene Complexes. Most of the reported examples belong to the series of cationic complexes with general formula [RuCl(=C=C=CR^{1}R^2)(η^6-*p*-cymene)(L)][X]. These complexes have attracted special attention in the past few years since they can act as efficient precatalysts for olefin metathesis. The most general synthetic route for the preparation of complexes [RuCl(=C=C=CR$_2$)(η^6-arene)(PR$_3$)][X] is the direct treatment of the appropriate dichloride precursor [RuCl$_2$(η^6-arene)(PR$_3$)] in MeOH with a propargylic alcohol HC≡CCR$_2$(OH) in the presence of NaPF$_6$ or NaBPh$_4$. Nevertheless, in some cases, the replacement of the sodium salt by AgX (X$^-$ = PF$_6^-$, TfO$^-$, BF$_4^-$) results in a more practical and flexible synthetic method, allowing work under aprotic conditions. Thus, treatment of [RuCl$_2$(η^6-arene)(PR$_3$)] with AgX in CH$_2$Cl$_2$ initially generates the isolable 16-electron species [RuCl(η^6-arene)(PR$_3$)][X], which readily reacts with suitable propargylic alcohol derivatives in CH$_2$Cl$_2$ to afford the desired allenylidene complexes. This latter route prevents side-reactions such as the well-known nucleophilic attack of MeOH at the α-carbon of the allenylidene chain to yield catalytically inert Fischer-type carbene complexes of the type [RuCl{=C(OMe)C(H)=CR$_2$}(η^6-arene)(PR$_3$)][X] (see reactivity studies below).

The following allenylidene derivatives have been obtained following these approaches: [RuCl(=C=C=CR^{1}R^2)(η^6-*p*-cymene)(PR$_3$)][X] (R^1 = R^2 = Ph, PR$_3$ = PCy$_3$, X$^-$ = PF$_6^-$, BF$_4^-$, BPh$_4^-$, TfO$^-$, SbF$_6^-$; R^1 = R^2 = Ph, PR$_3$ = PPh$_3$, X$^-$ = PF$_6^-$, TfO$^-$; R^1 = R^2 = Ph, PR$_3$ = P^{i}Pr$_3$, X$^-$ = PF$_6^-$, TfO$^-$; R^1 = R^2 = Ph, PR$_3$ = Cy$_2$PCH$_2$CH$_2${(η^5-C$_5$H$_4$)TiCpCl$_2$}, X$^-$ = TfO$^-$; R^1 = R^2 = C$_6$H$_4$Cl-4, PR$_3$ = PCy$_3$, X$^-$ = BF$_4^-$, TfO$^-$; R^1 = R^2 = C$_6$H$_4$OMe-4, PR$_3$ =

Scheme 14



Scheme 15



PCy_3, $X^- = TfO^-$; $R^1 = R^2 = C_6H_4F$-4, $PR_3 = PCy_3$, $X^- = TfO^-$; $R^1 = H$, $R^2 = (E)$-CH=CH-$C_6H_4NMe_2$-4, $PR_3 = PCy_3$, $X^- = BF_4^-$; $R^1R^2 = 2,2'$-biphenyldiyl, $PR_3 = PCy_3$, $X^- = BF_4^-$; $R^1 = Ph$, $R^2 = Me$, $PR_3 = PCy_3$, $X^- = TfO^-$),[158−164] [RuCl(=C=C=CPh_2)(η^6-1,2,4,5-$C_6H_2Me_4$)(PCy_3)][OTf],[161] and the trinuclear species **53b** (Scheme 10).[122] The synthesis of the polystyrene-supported allenylidene **71**, which can be recovered quantitatively and reused in catalytic RCM reactions, could also be successfully achieved starting from the immobilized dichloride precursor **70** (Scheme 14).[165]

Taking advantage of the hemilabile properties of the $\kappa^2(P,N)$-coordinated iminophosphorane−phosphine ligand $Ph_2PCH_2P(=NR)Ph_2$ (R = 4-C_5F_4N), the stable diphenylallenylidene complexes [RuCl(=C=C=CPh_2){$\kappa^1(P)$-$Ph_2PCH_2P(=NR)Ph_2$}(η^6-arene)][SbF_6] (arene = 1,3,5-$C_6H_3Me_3$, C_6Me_6) were prepared by reacting a dichloromethane solution of [RuCl{$\kappa^2(P,N)$-$Ph_2PCH_2P(=NR)Ph_2$}(η^6-arene)][SbF_6] with 1,1-diphenyl-2-propyn-1-ol.[166] In a similar way, treatment of complex **72** with HC≡CMe_2(OH) resulted in the formation of the dicationic derivative **73**, via displacement of the labile olefinic unit of the diphosphine ligand (Scheme 15).[167] The related dicationic complex [Ru(=C=C=CPh_2){$\kappa^2(P,N)$-PPh_2Py}(η^6-C_6Me_6)][BF_4]$_2$ (PPh_2Py = diphenyl-2-pyridylphosphine) was also described.[168]

Allenylidene−ruthenium(II) complexes containing *N*-heterocyclic carbenes, instead of the classical phosphines, as ancillary ligands are known. Thus, complex [RuCl(=C=C=CPh_2)(η^6-*p*-cymene)(IMes)][X] (**74**; $X^- = PF_6^-$, TfO^-; IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) was obtained by reacting [$RuCl_2$(η^6-*p*-cymene)(IMes)] with HC≡CPh_2(OH) in the presence of $NaPF_6$[169] or AgOTf.[164] In contrast, the related complex [RuCl(=C=C=CPh_2)(η^6-*p*-cymene)($IMesH_2$)][PF_6] (**75**; $IMesH_2$ = 1,3-bis(2,4,6-trimethylphenyl)dihydroimidazol-2-ylidene), which is an active catalyst for the atom transfer radical polymerization of vinyl monomers, was synthesized starting from [RuCl(=C=C=CPh_2)(η^6-*p*-cymene)(PCy_3)][PF_6] via substitution of the PCy_3 ligand by the *N*-heterocyclic carbene (NHC).[170]

It has also been reported that the treatment of a series of imidazoline−ruthenium(II) and benzimidazole−ruthenium(II) complexes of general formula [$RuCl_2$(η^6-arene)(*N*-donor)] (arene = *p*-cymene, C_6Me_6) with AgOTf and HC≡CPh_2-(OH) generates in situ the corresponding allenylidenes [RuCl(=C=C=CPh_2)(η^6-arene)(*N*-donor)][OTf], which are able to catalyze the cycloisomerization of diallylamines into pyrrolidines (see below). Nevertheless, these species were not stable enough to be isolated and properly characterized.[171]

Arene−osmium(II) allenylidenes are much scarcer. Only the series of the type [OsX(=C=C=CR_2)(η^6-arene)(L)][PF_6] (arene = 1,3,5-$C_6H_3Me_3$, = XCl, R = Ph, L = PMe_3, PPh_3, PCy_3, As^iPr_3, Sb^iPr_3; arene = 1,3,5-$C_6H_3Me_3$, = XCl, R = C_6H_4Me-4, L = PCy_3; arene = C_6H_6, = XI, R = Ph, L = PCy_3; arene = *p*-cymene, = XCl, R = Ph, L = PCy_3),[172] and [OsCl(=C=C=CPh_2)(η^6-arene)(IPr)][OTf] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)[81] are known. They were obtained by reaction of the corresponding dihalide precursor [OsX_2(η^6-arene)(L)] with the appropriate propargylic alcohol in the presence of $AgPF_6$. Treatment of [OsCl(=C=C=CPh_2)(η^6-1,3,5-$C_6H_3Me_3$)(PCy_3)][PF_6] with KBr, NaI, and AgO_2CCF_3 led to the formation of the corresponding bromo-, iodo-, and trifluoroacetato complexes [OsX(=C=C=CPh_2)(η^6-1,3,5-$C_6H_3Me_3$)(PCy_3)][PF_6] (X = Br, I, CF_3CO_2).[172] Further examples bearing η^6-arene tethered ligands are also known (see next section).

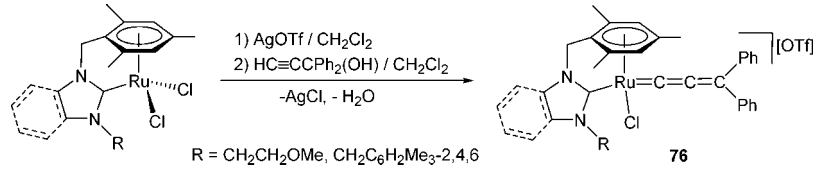
3.3.2.3. η^5-Cyclopentadienyl and η^6-Arene Tethered Complexes. Selegue's route using halide precursors has led to the synthesis of the following cationic complexes: [Os{η^5:$\kappa^1(P)$-$C_5H_4(CH_2)_2PPh_2$}(=C=C=CPh_2)(P^iPr_3)][PF_6],[173] [Ru{η^5:$\kappa^2(P,P)$-$C_5H_4CH_2CMe(CH_2PPh_2)_2$}(=C=C=C$Ph_2$)][$PF_6$],[174] [RuCl(=C=C=C$Ph_2$){$\eta^6$:$\kappa^1(P)$-$C_6H_5O(CH_2)_2P^tBu_2$}][$PF_6$],[175] and [RuCl(=C=C=C$Ph_2$){$\eta^6$:$\kappa^1(P)$-$C_6H_5(CH_2)_nPR_2$}][X] (R = Cy, *n* = 3, $X^- = TfO^-$, PF_6^-; R = ^{t}Bu, *n* = 2, $X^- = PF_6^-$).[160,175] Related tethered η^6-arene allenylidene complexes **76** containing NHC−carbenes as side arms have also been described (Scheme 16).[176]

3.4. Group 9 Metals

New achievements continue being focused to rhodium and iridium since no cobalt allenylidene has been reported to date. Pursuing earlier studies,[20,33] Werner and co-workers have synthesized from substituted 2-propyn-1-ols novel typical square-planar rhodium(I) and iridium(I) allenylidenes *trans*-[MCl(=C=C=CR^1R^2)$(L)_2$] (M = Ir, L = P^iPr_3, R^1 = Ph, R^2 = ^{t}Bu;[177] M = Rh, L = P^iPr_3, R^1 = Ph, R^2 = CF_3;[178] M = Rh, L = ^{i}$Pr_2PCH_2CH_2Ph$, $R^1 = R^2$ = Ph[179]). Synthetic routes proceeded via 3-hydroxyvinylidene intermediates *trans*-[MCl{=C=C(H)C(OH)R^1R^2}$(L)_2$], which yield the desired allenylidene complexes by abstraction of water. The generation of iridium allenylidenes required treatment with trace amounts of CF_3CO_2H and was also facilitated by using UV irradiation.[177] Similarly, the novel phenylene-bridged bis(allenylidene)rhodium compound **78** was obtained by dehydration of the binuclear 3-hydroxyvinylidene **77** upon treatment with acidic Al_2O_3 (Scheme 17).[180]

In agreement with the expected *trans* influence of the π-acceptor allenylidene unit, substitution of the chloride ligand by different anionic nucleophiles in complexes *trans*-

Scheme 16



Scheme 17

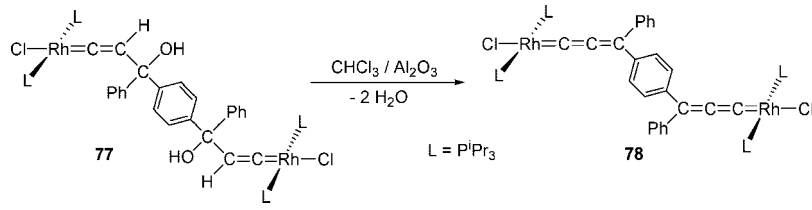
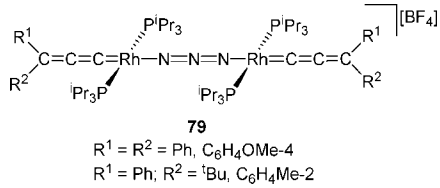
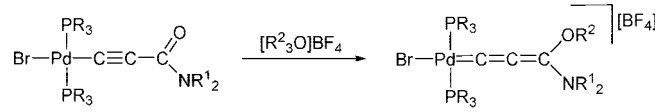


Chart 16



Scheme 18



[MCl(=C=C=CR^{1}R^2)(P^{i}Pr$_3$)$_2$] is favored, affording new rhodium(I) and iridium(I) allenylidenes *trans*-[MX(=C=C=CR^{1}R^2)(P^{i}Pr$_3$)$_2$] (M = Rh, X = I, F, OH, C≡CPh, N$_3$, OCN, R^1 = Ph, R^2 = Ph, ^{t}Bu, C$_6$H$_4$Me-2;[181−183] M = Ir, X = N$_3$, Br, OH, I, OCN, SCN, R^1 = Ph, R^2 = Ph, ^{t}Bu[177]). It is worth noting the interesting formation of the hydroxo derivatives that constitute the gate for the synthesis of a variety of square-planar complexes, via OH$^-$/X$^-$ (X$^-$ = F$^-$, PhO$^-$, MeCO$_2^-$, PhCO$_2^-$, TsO$^-$) exchange reactions, not accessible through any other route.[177,182−184] The cationic derivative *trans*-[Rh(OH$_2$)(=C=C=CR^{1}R^2)(L)$_2$][PF$_6$] (L = ^{i}Pr$_2$PCH$_2$CH$_2$Ph) could also be synthesized by protonation of the corresponding hydroxo−allenylidene complex and, in acetone solution, was found to undergo water/acetone ligand exchange.[179]

Other examples of Group 9 metal allenylidenes described include (i) the cationic species *trans*-[Rh(=C=C=CPh$_2$)(acetone)(P^{i}Pr$_3$)$_2$][PF$_6$] generated from the reaction of the bis(acetone)rhodium(I) complex [Rh(acetone)$_2$(P^{i}Pr$_3$)$_2$][PF$_6$] with 1,1-diphenyl-2-propyn-1-ol (substitution of the labile acetone ligand by both neutral and anionic ligands was also described);[185] (ii) the half-sandwich Rh(I) complexes [RhCp(=C=C=CR^{1}R^2)(L)] (R^1 = Ph, R^2 = Ph, C$_6$H$_4$Me-2, L = P^{i}Pr$_3$, ^{i}Pr$_2$AsCH$_2$CH$_2$OMe), which were obtained by reacting the corresponding square-planar precursor *trans*-[RhCl(=C=C=CR^{1}R^2)(L)$_2$] with NaCp;[178] (iii) the six-coordinate hydrido−iridium(III) complexes [IrHCl$_2$\{=C=C=C(Ph)R\}(P^{i}Pr$_3$)$_2$] (R = Ph, ^{t}Bu) obtained by oxidative addition of HCl to the corresponding iridium(I) compound;[186] and (iv) the dinuclear complexes **79** (Chart 16) containing an almost linear eleven-membered C$_3$RhN$_3$RhC$_3$ chain, which were generated by treatment of the corresponding mononuclear derivatives *trans*-[Rh(N$_3$)(=C=C=CR^{1}R^2)(P^{i}Pr$_3$)$_2$] with the Meerwein's salt [Me$_3$O]BF$_4$.[181]

3.5. Group 10 Metals

The preparation of the first palladium−allenylidene complexes **81**, generated by selective alkylation of the carbonyl group in σ-alkynyl derivatives **80** (Scheme 18), has recently been reported, but no further Group 10 metal complexes are known.[12]

4. Preparation of Higher Cumulenylidene Complexes

After pioneering reports on pentatetraenylidene ruthenium,[187] rhodium,[188] iridium,[189] and Group 6[190] complexes [M]=C(=C)$_n$=CR$_2$ (n = 3), several new pentatetraenylidenes as well as butatrienylidenes (n = 2) have been isolated.

Early identifications of butatrienylidene complexes stem from highly reactive intermediate species.[37] To this regard, trapping the transient butatrienylidene cations *trans*-[RuCl(=C=C=C=CH$_2$)(dppm)$_2$]$^+$, [RuCp(=C=C=C=CH$_2$)(PPh$_3$)$_2$]$^+$, [RuCp*(=C=C=C=CH$_2$)(dppe)]$^+$, and [FeCp*(=C=C=C=CH$_2$)(dppe)]$^+$ through reactions with nucleophiles has been used to obtain functionalized allenylidene complexes. They were generally prepared in situ by reacting a THF solution of the corresponding chloride derivative with buta-1,3-diyne or HC≡CC≡CSiMe$_3$ (see reactivity studies below).[143,144] Stabilization of this cumulenylidene chain has been achieved by generating the following substituted derivatives (Chart 17): (i) Iron complexes **82** obtained by treatment of the binuclear μ-butadiyndiyl derivatives [Cp*(CO)$_2$FeC≡CC≡CFeCp*(L−L)] with HBF$_4$ or MeOTf. They were characterized by spectroscopic methods (NMR, IR, UV−vis, and Mössbauer), mass spectrometry, and cyclic voltammetry.[191] (ii) Manganese complexes **83** generated by irradiation of the corresponding vinylidenes [Mn(η^5-C$_5$H$_4$R^2)\{=C=C(SnPh$_3$)C≡CSnPh$_3$\}(P−P)]. Deprotection with [N^{n}Bu$_4$]F afforded the parent butatrienylidenes [Mn(η^5-C$_5$H$_4$R^2)(=C=C=C=CH$_2$)(P−P)] identified only by NMR spectroscopy at −40 °C since they decompose above −5 °C.[70,192] (iii) The iridium complexes **84** prepared through metathetical processes from the parent chloride derivative

Chart 17

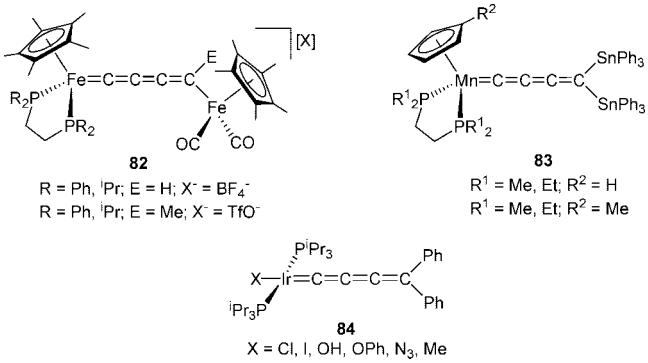
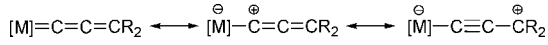


Chart 18



trans-[IrCl(=C=C=C=CPh$_2$)(P^{i}Pr$_3$)$_2$], which is synthesized by reaction of the dihydride−Ir(III) precursor [IrH$_2$Cl(P^{i}Pr$_3$)$_2$] with the functionalized 1-alkyne HC≡CC(OTf)=CPh$_2$ and NEt$_3$ at −100 °C.[193]

Novel synthetic procedures of pentatetraenylidene complexes include the synthesis of the rhenium species [ReCp*(=C=C=C=CAr$_2$)(NO)(PPh$_3$)][BF$_4$] (CAr$_2$= 9-fluorenylidene and halide-substituted derivatives), which were obtained from the reactions of diynyl complexes [ReCp*{C≡CC≡C(OMe)Ar$_2$}(NO)(PPh$_3$)] with BF$_3$·OEt$_2$ at −45 °C.[194]

So far, the hexapentaenylidene complex *trans*-[RuCl{=C=C=C=C=C=CH(SiMe$_3$)}(dppe)$_2$][OTf][8] and the heptahexaenylidene derivatives [M{=C=C=C=C=C=C=C(NMe$_2$)$_2$}(CO)$_5$] (M = Cr, W)[9] are the longest cumulenylidene complexes reported to date. The former is proposed in the formation of a C$_9$-bridged dinuclear ruthenium(II) complex as an undetected intermediate, resulting from the coupling between *trans*-[RuCl(=C=C=CMe$_2$)(dppe)$_2$] and the polyynyl derivative *trans*-[RuCl(C≡CC≡CC≡CSiMe$_3$)(dppe)$_2$]. The latter, which could be isolated as microcrystalline solids, were generated by a sequential five-step reaction of Me$_3$Si(C≡C)$_3$SiMe$_3$ with LiMe·LiBr, [(Me$_2$N)$_3$C]$^+$Cl$^-$, Li^{n}Bu, and [M(CO)$_5$(THF)] (overall yield 3%).

5. Reactivity of Allenylidene Complexes

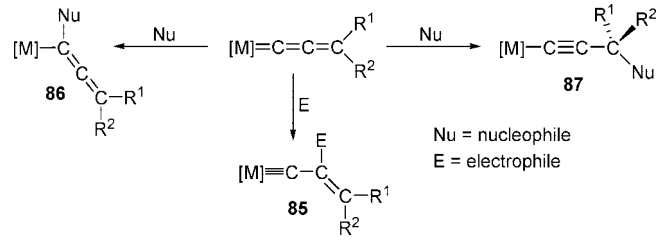
5.1. General Considerations

On the basis of a large number of stoichiometric studies, the main trends of allenylidene reactivity are presently well-established, being governed by the electron-deficient character of the C$_\alpha$ and C$_\gamma$ carbon atoms in the cumulenic chain, with the C$_\beta$ exhibiting a nucleophilic character. This can also be rationalized by considering the mesomeric forms depicted in Chart 18. Theoretical calculations (see above) are in accordance with these general reactivity patterns.

The alternating array of electrophilic/nucleophilic carbon sites makes allenylidene complexes unique organometallic reagents for C−C and C−heteroatom couplings via simple addition reactions. Thus, while electrophiles add selectively to C$_\beta$, yielding alkenylcarbyne derivatives **85**, the nucleophilic attacks can take place both at the C$_\alpha$ or C$_\gamma$ atoms affording metal−allenyl **86** or metal−alkynyl **87** complexes, respectively (Scheme 19).

The regioselectivity of the nucleophilic additions on allenylidene complexes (C$_\alpha$ vs C$_\gamma$) is subtly controlled by

Scheme 19



the electronic and steric properties of both the substituents on the unsaturated hydrocarbon chain and the ancillary ligands on the metal atom, as well as by the nucleophile employed. The nucleophilic character of the allenylidene C$_\beta$ was experimentally demonstrated for the first time by Kolobova and co-workers in 1984, who obtained alkenyl−carbyne complexes [MnCp{≡CC(H)=CR$_2$}(CO)$_2$][X] (R = ^{t}Bu, Ph; X$^-$ = Cl$^-$, BF$_4^-$, CF$_3$CO$_2^-$) by treatment of neutral manganese(I) allenylidenes [MnCp(=C=C=CR$_2$)(CO)$_2$] with Brønsted acids (HX).[40c] Since then, a large variety of neutral and cationic transition-metal allenylidenes, mainly of Groups 8 and 9, have been selectively protonated or methylated at the C$_\beta$ atom to afford stable alkenyl−carbyne species [M]≡CC(E)=CR^{1}R^2 (E = H, Me). Nevertheless, nucleophilic additions dominate the reactivity of allenylidene complexes.[13−15]

Moreover, the presence in the allenylidene chain of two electrophilic centers and one nucleophilic center enables cyclization processes with a large variety of organic substrates, allowing the construction of original carbo- and heterocyclic compounds. Although there has been little success on earlier attempts to transfer the allenylidene ligand among metal complexes, this has been achieved recently from chromium into tungsten metal fragments.[63]

In the following subsections, recent reactivity studies of allenylidene complexes are presented by periodic group.

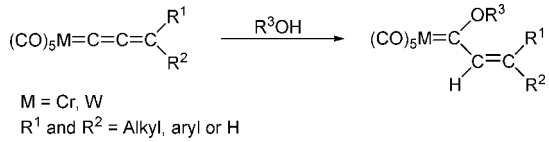
5.2. Reactions of Allenylidene Complexes

5.2.1. Group 6 Metals

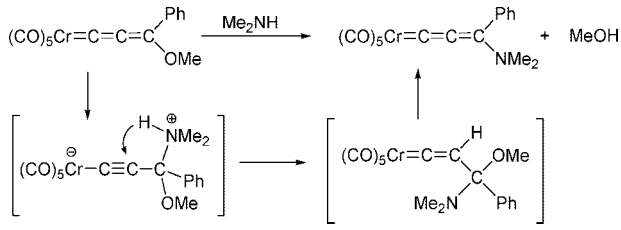
The reactivity of Group 6 allenylidenes [M(=C=C=CR^{1}R^2)(CO)$_5$] (M = Cr, W; R^1 and R^2 = alkyl or aryl group) toward nucleophiles has been extensively documented and is clearly dominated by the regioselective additions at the electrophilic α-carbon (alcohols, phosphines, and amines) and [2 + 2]-cycloadditions of dipolar unsaturated substrates such as ynamines.[13−15] Nevertheless, it was also found that a variety of phosphines, P(OMe)$_3$, AsPh$_3$, and SbPh$_3$, react with [Cr(=C=C=CR^{1}R^2)(CO)$_5$] (R^1 = NMe$_2$, NPh$_2$; R^2 = NMe$_2$, OMe, Ph) in tetrahydrofuran (THF), affording allenylidene tetracarbonyl complexes *cis*-[Cr(=C=C=CR^{1}R^2)(CO)$_4$(L)]. Similarly, tricarbonyl derivatives *mer*-[Cr(=C=C=CR^{1}R^2)(CO)$_3$(L)$_2$] (R^1 = NMe$_2$; R^2 = Ph; L = P(OMe)$_3$, P(C$_6$H$_4$F-4)$_3$, P(4-C$_6$H$_4$Cl-4)$_3$) were formed by photolysis using an excess of the P-donor ligand.[195] Searching for the coupling of CO with an allenylidene moiety by irradiation of [Cr(=C=C=CPh$_2$)(CO)$_5$], as it occurs in the analogous vinylidene complex, it was found that the reaction leads instead to the dimerization of the allenylidene ligand, affording tetraphenylhexapentaene Ph$_2$C(=C)$_4$=CPh$_2$.[196]

Undoubtedly, the most common reaction of these Group 6 allenylidenes (either isolated or generated in situ) is the addition of alcohols R^{3}OH across the C$_\alpha$=C$_\beta$ bond to afford Fischer-type α,β-unsaturated alkoxycarbene derivatives

Scheme 20



Scheme 21

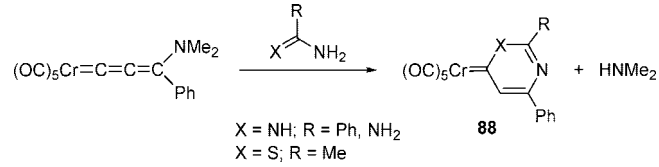


[M{=C(OR^3)CH=CR^{1}R^2}(CO)$_5$], via nucleophilic attack of the alcohol at the electrophilic C$_\alpha$ and subsequent migration of the hydrogen atom to C$_\beta$ (Scheme 20).[197,198]

Pursuing previous studies, Fischer and co-workers have continued with their interest to develop the reactivity of Group 6 allenylidenes.[18] Thus, they have found that bis(aryl)- or bis(alkyl)-substituted amino−allenylidenes [M{=C=C=C(NR′$_2$)R}(CO)$_5$] (M = Cr, W; R = Ph, C(Me)$_2$OEt; R′ = Me, Et, ^{i}Pr, Bn; not all combinations) also add dimethylamine Me$_2$NH across the C$_\alpha$=C$_\beta$ to give alkenyl−aminocarbenes [M{=C(NMe$_2$)CH=C(NR′$_2$)R}(CO)$_5$].[61,64,199] In contrast, when a solution of the alkoxy-substituted complex [Cr{=C=C=C(OMe)Ph}(CO)$_5$] was treated with 1 equiv of Me$_2$NH, the expected aminocarbene was not formed, with the reaction leading instead to the allenylidene derivative [Cr{=C=C=C(NMe$_2$)Ph}(CO)$_5$] by substitution of the methoxy group.[64] This unexpected substitution process, which is initiated by the nucleophilic attack of dimethylamine to the C$_\gamma$ atom of the allenylidene chain followed by elimination of methanol (Scheme 21), can be considered as the "allenylidene version" of the classical aminolysis of Fischer-type alkoxycarbene complexes. Exchange reactions of the alkoxy groups by primary and secondary amines in complexes [Cr{=C=C=C(NMe$_2$)OMe}(CO)$_5$],[45,61,200] and [M{=C=C=C(OR)OEt}(CO)$_5$] (M = Cr, W; R = Et, (−)-menthyl, *endo*-bornyl)[64] have also been described, allowing the preparation of a large variety of novel mono- and diamino-substituted Group 6 allenylidenes. Treatment of [Cr{=C=C=C(NMe$_2$)Ph}(CO)$_5$] with a large excess of ammonia or primary amines RNH$_2$ led also to the substitution of the dimethylamino group, affording [Cr{=C=C=C(NHR)Ph}(CO)$_5$] (R = H, Ph or alkyl groups).[199] All these results seem to indicate a marked preference of the heteroatom-substituted Group 6 allenylidenes for the C$_\gamma$ versus C$_\alpha$ additions opposite to their alkyl or aryl-substituted counterparts. Theoretical calculations have rationalized this reactivity (see above).[42,45,46]

These amino−allenylidene complexes displayed a fruitful reactivity against *N*,*N*- or *N*,*S*-dinucleophiles, yielding a series of heterocyclic carbenes. Thus, treatment of [Cr{=C=C=C(NMe$_2$)Ph}(CO)$_5$] with benzamidine, guanidine, or thioacetamide yields selectively α,β-unsaturated carbenes **88** (Scheme 22),[200] arising from nitrogen attack at C$_\gamma$, subsequent HNMe$_2$ elimination, and further reorganization of the molecule through a ring-closing process. Starting from [Cr{=C=C=C(NMe$_2$)Ph}(CO)$_5$], the proper choice of other bifunctional nucleophiles also allowed the preparation, in moderate-to-high yields, of the five-, seven-, and eight-membered heterocyclic carbene species **89**−**92** (Chart 19), which, in some cases, were formed along with minor amounts of other derivatives.[201] Similar 1,2,3-diheterocyclizations involving (ethoxy)allenylidene complexes have been described, with ethanol instead of HNMe$_2$ being released in this case.[200]

Scheme 22



Treatment of the chromium complex **13** with an excess of [W(CO)$_5$(THF)] afforded the tungsten allenylidene **93** by transmetallation of the allenylidene ligand and addition of W(CO)$_5$ to the N-atom of the heterocyclic substituent (Scheme 23).[63]

Chromium complexes [Cr{=C=C=C(R^1)R^2}CO)$_5$] (R^1 = NMe$_2$, R^2 = NMe$_2$, OMe, Ph; R^1 = N(Et)Me, R^2 = Ph; R^1 = N(^{n}Bu)Me, R^2 = Ph; R^1 = NPh$_2$, R^2 = OMe; R^1 = R^2 = C$_6$H$_4$NMe$_2$-4) were also able to transfer the allenylidene ligand to tungsten. In contrast, the reverse transmetallation from tungsten to chromium could not be achieved. The process was analyzed by DFT calculations, which indicated that the reaction proceeds by an associative rather than a dissociative pathway, with coordination of a [W(CO)$_5$] fragment to the C$_\alpha$−C$_\beta$ bond of the chromium allenylidene ligand being the initial step.[63]

Addition of anionic nucleophiles Nu$^-$ (H$^-$, MeO$^-$, HO$^-$, MeS$^-$) to the dinuclear molybdenum−allenylidene complex [Mo$_2$Cp$_2$(μ-SMe)$_3$(μ-η^1:η^2=C=C=CMe$_2$)][BF$_4$] (**20** in Scheme 5), affording the corresponding neutral acetylide derivatives [Mo$_2$Cp$_2$(μ-SMe)$_3${μ-η^1:η^2-C≡CC(Nu)Ph$_2$}], has also been described.[68]

No electrophilic additions to Group 6 allenylidenes have been reported to date.

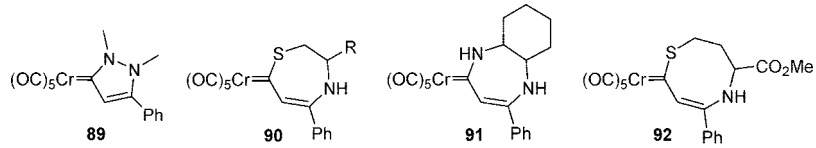
5.2.2. Group 7 Metals

As commented previously, the nucleophilic character of the allenylidene C$_\beta$ was experimentally demonstrated for the first time by Kolobova and co-workers, who obtained alkenyl−carbyne complexes [MnCp{≡CC(H)=CR$_2$}(CO)$_2$][X] (R = ^{t}Bu, Ph; X$^-$ = Cl$^-$, BF$_4^-$, CF$_3$CO$_2^-$) by treatment of neutral manganese(I) allenylidenes [MnCp(=C=C=CR$_2$)(CO)$_2$] with Brønsted acids (HX).[40c] In this context, it has been recently reported that the related allenylidene [MnCp(=C=C=CPh$_2$)(CO)(PPh$_3$)] catalyzes the reduction of protons from HBF$_4$ into hydrogen via carbyne [MnCp{≡C−CH=CPh$_2$}(CO)(PPh$_3$)][BF$_4$] formed by protonation of the catalyst.[202]

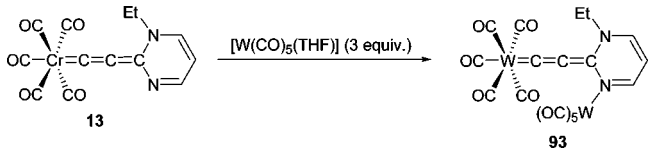
Similarly, protonation and methylation of rhenium allenylidene [Re(=C=C=CPh$_2$)(CO)$_2$(triphos)][OTf] (**21**), affording the corresponding carbyne complexes **94** (Scheme 24), have been described.[203]

Following the previously reported examples of nucleophilic additions to manganese allenylidenes [Mn(η^5-C$_5$R$_5$)(=C=C=CPh$_2$)(CO)$_2$],[13,14] further studies from Bianchini, Peruzzini, and co-workers, have been focused on rhenium complexes [Re(=C=C=CR^{1}R^2)(CO)$_2$(triphos)][OTf] (**21** in Chart 6 and Scheme 24). Although these complexes were found to be unreactive toward alcohols, they underwent regioselective attacks of anionic nucleophiles (Nu$^-$ = MeO$^-$,

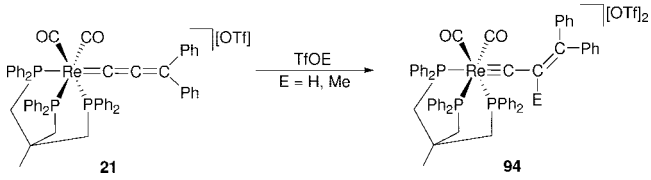
Chart 19



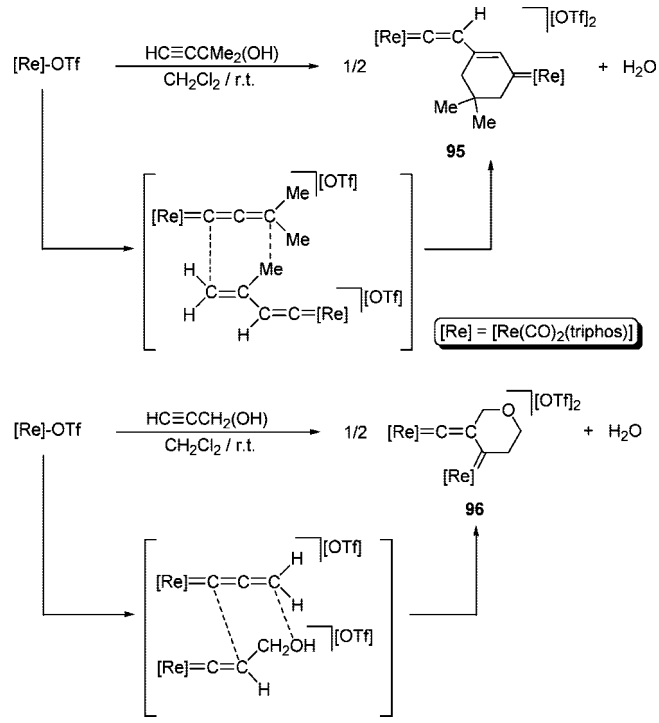
Scheme 23



Scheme 24



Scheme 25



HO$^-$, Me$^-$, H$^-$, enolates, etc.) at the C_γ atom to afford stable neutral σ-alkynyl compounds [Re{C≡CC(Nu)R^{1}R^2}(CO)$_2$(triphos)].[203] Phosphines also attack the allenylidene-C_γ atom to give kinetic phosphonioalkynyl products that transformed thermally into thermodynamically more stable phosphonioallenyl derivatives.[204] Interestingly, when Ph_2PH was employed, the resulting phosphonio−allenyl species [Re{C(PHPh$_2$)=C=CPh$_2$}(CO)$_2$(triphos)][OTf] further evolved into the phosphonio−butadienyl derivative [Re{C(=PPh$_2$)-C(H)=CPh$_2$}(CO)$_2$(triphos)][OTf] via selective 1,3-P,C-H shift.[204] Diphenylallenylidene [Re(=C=C=CPh$_2$)(CO)$_2$-(triphos)][OTf] also reacted with thiols to give thiocarbenes [Re{=C(SR)CH=CPh$_2$}(CO)$_2$(triphos)][OTf] (R = Ph, 1-Napht, allyl).[205] Related N−H additions of primary amines and ammonia have also been described, with the resulting complexes being formulated from X-ray data as azoniabutadienyl compounds [Re{C(=NHR)CH=CPh$_2$}(CO)$_2$-(triphos)][OTf] (R = H, Ph, CH$_2$C≡CH) rather than Fischer-type aminocarbenes [Re{=C(NHR)CH=CPh$_2$}(CO)$_2$(triphos)][OTf].[205]

Remarkably, in contrast to their disubstituted counterparts, the monosubstituted derivatives [Re(=C=C=CHR)(CO)$_2$(triphos)][OTf] (R = Me, Ph) undergo O−H additions of methanol or water across the C_α=C_β bond to afford the corresponding carbenes [Re{=C(OR′)CH=CHR}(CO)$_2$-(triphos)][OTf] (R′ = Me, H).[71,72] On the basis of all these results, it was concluded that the fragment [Re(CO)$_2$-(triphos)]$^+$ orients the addition of hard nucleophiles to the C_γ atom, with soft nucleophiles giving thermodynamically stable C_α-adducts.

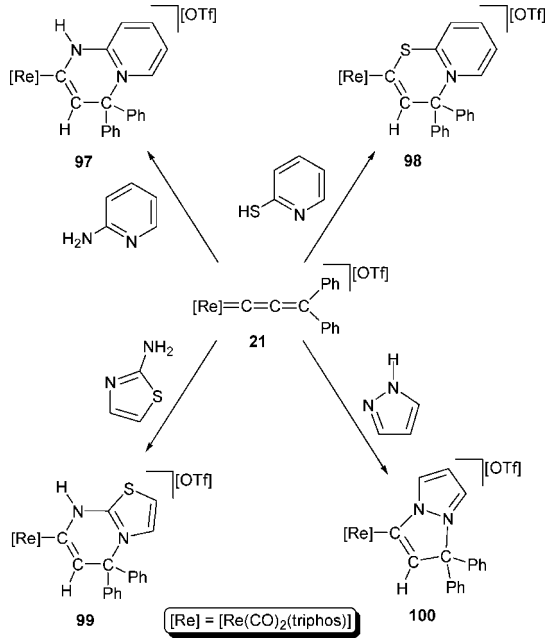
Direct activation of 2-methyl-3-butyn-2-ol or propargyl alcohol by [Re(OTf)(CO)$_2$(triphos)] was found to produce the dinuclear cyclic complexes **95** and **96**, respectively (Scheme 25).[71] In the first case, carbene−vinylidene **95** is generated by the coupling of the transient allenylidene [Re(=C=C=CMe$_2$)(CO)$_2$(triphos)][OTf] with its alkenyl−vinylidene tautomer [Re{=C=C(H)C(Me)=CH$_2$}(CO)$_2$-(triphos)][OTf], which are simultaneously generated in the initial dehydration process. An unprecedented coupling between the allenylidene [Re(=C=C=CH$_2$)(CO)$_2$(triphos)][OTf] and its hydroxy−vinylidene precursor [Re{=C=C(H)CH$_2$OH}(CO)$_2$(triphos)][OTf] was proposed in the formation of complex **96**.

Similarly to the reported reactions for the ruthenium−allenylidene complex [RuCp(=C=C=CPh$_2$)(CO)(P^{i}Pr$_3$)]-[BF$_4$],[206] Bianchini and co-workers have also found that the related cationic diphenylallenylidene−rhenium(I) complex [Re(=C=C=CPh$_2$)(CO)$_2$(triphos)][OTf] (**21**) readily reacts with *N,S*- and *N,N*-heterocycles such as pyrazole,[207] 1*H*-benzotriazole, 2-aminopyridine, and 2-aminothiazole to generate heterobicyclic compounds **97**−**100** (Scheme 26).[208] All these species are formed through the initial addition of the heteroatom-H bond across the C_α−C_β double bond of the allenylidene ligand to produce intermediate α,β-unsaturated carbenes, which evolve by nucleophilic attack of the second heteroatom at the C_γ of the unsaturated chain.

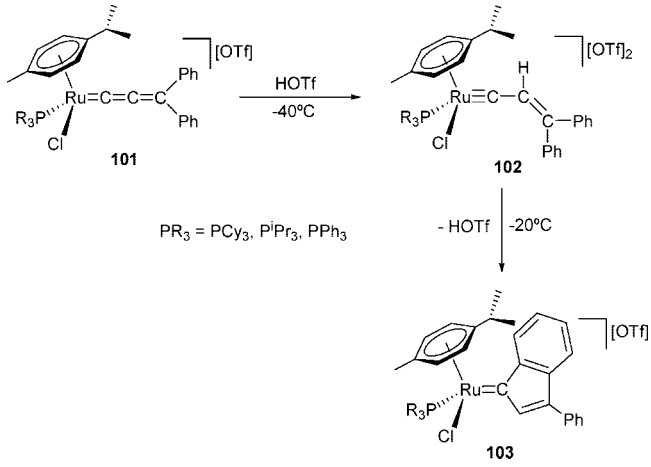
5.2.3. Group 8 Metals

5.2.3.1. Electrophilic Additions. Although the protonation of the first neutral ruthenium−allenylidene [RuCl$_2$(=C=C=CPh$_2$){κ^2(*P*,*O*)-^{i}Pr$_2$PCH$_2$CO$_2$Me}{κ^1(*P*)-^{i}Pr$_2$PCH$_2$CO$_2$Me}] with HCl led to the α,β-unsaturated carbene [RuCl$_2$-{=C(Cl)C(H)=CPh$_2$}{κ^2(*P*,*O*)-^{i}Pr$_2$PCH$_2$CO$_2$Me}{κ^1(*P*)-^{i}Pr$_2$-PCH$_2$CO$_2$Me}] via HCl addition across the C_α=C_β double bond,[209] protonation of other neutral and cationic allenylidenes,i.e.,[OsCpCl(=C=C=CPh$_2$)(P^{i}Pr$_3$)],[150][OsCp(=C=C=CPh$_2$)(P^{i}Pr$_3$)$_2$][PF$_6$],[41] [OsH(=C=C=CPh$_2$)(NCMe)$_2$-(P^{i}Pr$_3$)$_2$][BF$_4$],[210] [Os{η^5:κ^1(*P*)-C$_5$H$_4$CH$_2$CH$_2$PPh$_2$}(=C=C=CPh$_2$)(P^{i}Pr$_3$)][PF$_6$],[173] [Os{(*E*)−CH=CHPh}(=C=C=CPh$_2$)(CH$_3$CN)$_2$(P^{i}Pr$_3$)][BF$_4$],[211] [RuTpCl(=C=C=

Scheme 26



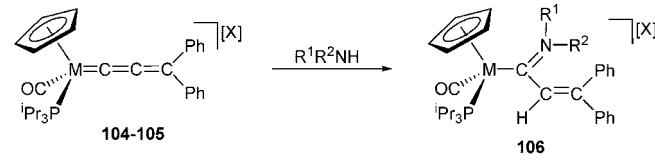
Scheme 27



$CR_2)(PR_3)]$ (PR_3 = PPh_3, $PPh_2{}^iPr$; R = Ph, Fc),[102] [{RuX(μ-X)(=C=C=CR_2)(dppf)}$_2$] (R = Ph, ^{i}Pr; X = Cl, Br),[121] *trans*-[RuCl{=C=C=C(Me)R}(dppe)$_2$][BF_4] (R = Me, Ph),[212] [RuCp*{=C=C=C(R)Ph}(dippe)][$B(Ar_F)_4$] (R = H, Ph),[213] and [RuCp*(=C=C=CR^1R^2)(PEt_3)$_2$][BF_4] (R^1 = R^2 = Ph; R^1 = H, R^2 = Ph, C_6H_4F-4, C_6H_4OMe-4)[133] has been reported to yield the expected α,β-unsaturated carbynes $[M]^{n+}$≡CC(H)=CR^1R^2 (n = 1, 2).

Probably, the most striking discovery related to the reactivity of Group 8 allenylidenes toward electrophiles is the evidence that allenylidene−ruthenium complexes **101** rearrange, upon treatment with HOTf, into the indenylidene derivatives **103**, which display extremely high catalytic activity in alkene metathesis (Scheme 27).[164] The process involves the initial formation of alkenyl−carbynes **102**, which evolve into **103** through a formal electrophilic substitution of an *ortho*-proton of one of the phenyl groups by the C_α-atom of the carbyne moiety, with concomitant elimination of HOTf. An analogous transformation was also observed in the protonation of the osmium derivative [OsCp(=C=C=CPh_2)(CO)(P^iPr_3)][PF_6] to give the corresponding 3-phenyl-1-indenylidene complex, which was isolated as an air-stable solid.[148] Remarkably, the direct

Scheme 28



M = Os; X$^-$ = PF_6^-; R^1 = H; R^2 = Ph
M = Ru; X$^-$ = BF_4^-; R^1 = H; R^2 = Ph, ^{n}Pr, $CH_2CH{=}CH_2$, $CH_2C{\equiv}CH$, 2-Py
M = Ru; X$^-$ = BF_4^-; R^1 = Me; R^2 = $CH_2C{\equiv}CH$
M = Ru; X$^-$ = BF_4^-; R^1 = R^2 = Et
M = Ru; X$^-$ = BF_4^-; R^1R^2 = -$(CH_2)_5$-

activation of HC≡$CCPh_2$(OH) by [$RuCl_2(PPh_3)_4$] led also to the formation of an indenylidene complex, with an acidic media not being required in this case to promote the intramolecular allenylidene rearrangement.[109]

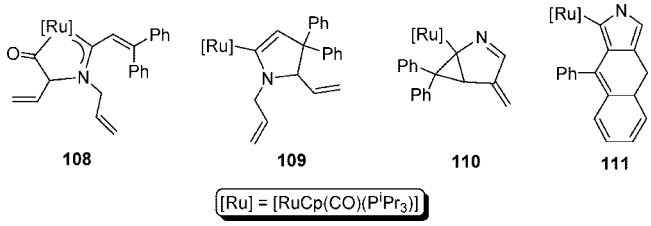
5.2.3.2. Nucleophilic Additions. The reactivity of cationic half-sandwich ruthenium(II) allenylidenes toward nucleophiles is well-documented.[13,14] This feature has continued to be of interest in the past decade, disclosing new examples and confirming that the C_γ versus C_α preference to undergo a selective addition is strongly dependent on the steric and electronic properties of the ancillary ligands in the metal fragment. This is clearly exemplified by the behavior toward alcohols. Thus, while allenylidene ligands attached to the fragments [RuCl(η^6-arene)(L)]$^+$ (L = PR_3 or CNR)[198,214,215] and [RuCp(CO)(PR_3)]$^+$ (PR_3 = PPh_3, P^iPr_3)[198] were able to add alcohols across the C_α=C_β bond to yield Fischer-type α,β-unsaturated alkoxycarbenes, the more sterically demanding [RuCp(PPh_3)$_2$]$^+$[129] or basic [RuCp*(PEt_3)$_2$]$^+$[133] made the allenylidene ligand resistant to alcohols. Similarly, the corresponding hydroxycarbenes were formed by addition of water to [RuCl(=C=C=CHPh)(η^6-*p*-cymene)(PR_3)][OTf] (PR_3 = PPh_3, PCy_3), which, however, were not stable, evolving into the carbonyl derivatives [RuCl(η^6-*p*-cymene)(CO)(PR_3)][OTf] by releasing styrene.[216] This contrasts with the stability found for the related hydroxycarbene complex [RuCp{=C(OH)CH=CPh_2}(CO)(P^iPr_3)][BF_4].[217]

Likewise to alcohols and water, complex [RuCp(=C=C=CPh_2)(CO)(P^iPr_3)][BF_4] (**104**) and its related osmium counterpart [OsCp(=C=C=CPh_2)(CO)(P^iPr_3)][PF_6] (**105**) also add the N−H bond of primary and secondary amines across the C_α=C_β, generating azoniabutadienyl ruthenium and osmium complexes **106** (Scheme 28).[148,218−220] The preparation of the related azoniabutadienyl species [RuCp*{C(=NR^1R^2)C(H)=CPh_2}(CO)(PMe^iPr_2)][$B(Ar_F)_4$] (R^1 = H, R^2 = Me, $CH_2C{\equiv}CH$; R^1 = R^2 = ^{i}Pr) starting from [RuCp*(=C=C=CPh_2}(CO)(PMe^iPr_2)][$B(Ar_F)_4$] (**107**) has also been described.[221]

The closely related α,β-unsaturated-2-azaallenyl complexes [RuCp{C(=N=CPh_2)C(H)=CPh_2}(CO)(P^iPr_3)][BF_4] and [RuCp*{C(=N=CPh_2)C(H)=CPh_2}(CO)(PMe^iPr_2)][$B(Ar_F)_4$] were similarly obtained by reacting the allenylidene precursors **104** and **107**, respectively, with benzophenoneimine.[217,221] Addition of $MeNH_2$ to the neutral heteroscorpionato allenylidene complex [RuCl{κ^3(*N*,*N*,*O*)-bdmpza}{=C=C=C(C_6H_4Me-4)$_2$}(PPh_3)] (**32** in Chart 8) has also been described, with the resulting product being described as a Fischer-type aminocarbene [RuCl{κ^3(*N*,*N*,*O*)-bdmpza}{=C(NHMe)C(H)=C(C_6H_4Me-4)$_2$}(PPh_3)].[222]

The utility of these N−H addition reactions for the construction of complex molecular architectures was nicely illustrated in the behavior of **104** toward *N*,*N*-diallylamine and *N*-propargylamine, with the reactions leading to the

Chart 20



formation of the heterocyclic derivatives **108**−**109** and **110**−**111** (Chart 20), respectively, via base-promoted intramolecular cyclization of the corresponding azoniabutadienyl intermediates.[219,220]

An intramolecular version of these nucleophilic additions occurred in the reaction of the propargylic alcohol HC≡CCPh$_2$(OH) with complex [RuClCp(PPh$_2$NH^{n}Pr)$_2$] in the presence of AgOTf, which afforded the azaphosphacarbene **112** (Chart 21). This complex is formed through an intramolecular N−H addition of one of the phosphinoamine ligands to the C$_\alpha$=C$_\beta$ on the allenylidene chain of the intermediate species [RuCp(=C=C=CPh$_2$)(PPh$_2$NH^{n}Pr)$_2$][OTf].[103] A related base-promoted intramolecular O−H addition was observed in the activation of 1,1-diphenyl-2-propyn-1-ol by complexes [Ru(η^5-Ring){κ^2(*P*,*O*)-Ph$_2$PCH$_2$C(=O)^{t}Bu}(PMe$_3$)][PF$_6$] (Ring = Cp, indenyl). Thus, addition of the enolic form of the keto-phosphine Ph$_2$PCH$_2$C(=O)^{t}Bu at the C$_\alpha$ atom of the initially formed allenylidenes [Ru(η^5-Ring)(=C=C=CPh$_2$){κ^1(*P*)-Ph$_2$PCH$_2$C(=O)^{t}Bu}(PMe$_3$)][PF$_6$] takes place, leading to metallacycles **113**.[223a] These results contrast with previous studies using the less basic precursors [Ru(η^5-Ring){κ^2(*P*,*O*)-Ph$_2$PCH$_2$C(=O)^{t}Bu}(PPh$_3$)][PF$_6$], which afforded **114** via a C−C coupling process.[223b]

Thiols also reacted with allenylidenes **104** and **107** to afford α,β-unsaturated thiocarbenes, i.e., [RuCp{=C(S^{n}Pr)CH=CPh$_2$}(CO)(P^{i}Pr$_3$)][BF$_4$] and [RuCp*{=C(S^{n}Pr)CH=CPh$_2$}(CO)(PMe^{i}Pr$_2$)][B(Ar$_F$)$_4$], via S−H addition across the C$_\alpha$=C$_\beta$ double bond of the cumulenic chain. Single-crystal X-ray diffraction studies on the latter point out the existence of an important contribution of the tautomeric thiabutadienyl form [RuCp*{C(=S^{n}Pr)CH=CPh$_2$}(CO)(PMe^{i}Pr$_2$)][B(Ar$_F$)$_4$].[217,221]

The crucial role of the ancillary ligands on the C$_\gamma$ versus C$_\alpha$ preference was also clearly reflected in the behavior of half-sandwich Ru(II) allenylidenes toward phosphines. Thus, **107** added phosphines at the C$_\alpha$ atom to yield cationic phosphino−allenyl derivatives [RuCp*{C(PR$_3$)=C=CPh$_2$}(CO)(PMe^{i}Pr$_2$)][B(Ar$_F$)$_4$] (PR$_3$ = PMe$_3$, PMe^{i}Pr$_2$).[221] In contrast, allenylidenes [Ru(η^5-C$_9$H$_7$)(=C=C=CR^{1}R^2)(PPh$_3$)$_2$][PF$_6$] containing the bulkier bis(triphenylphosphine)indenyl fragment reacted selectively at the C$_\gamma$, affording phosphonio−alkynyl species [Ru(η^5-C$_9$H$_7$){C≡CCR^{1}R^2-(PR$_3$)}(PPh$_3$)$_2$][PF$_6$] (R^1, R^2 = alkyl, aryl or H; PR$_3$ = PPh$_3$, PMePh$_2$, PMe$_2$Ph, PMe$_3$).[60,124,224,225] In this context, it should be noted that the phosphonioalkynyl derivatives [Ru(η^5-C$_9$H$_7$){C≡CCH(R^1)(PR$_3$)}(PPh$_3$)$_2$][PF$_6$] (R^1 = H, PR$_3$ = PPh$_3$; R^1 = Ph, PR$_3$ = PMe$_3$) proved to be of particular synthetic interest, since they were excellent substrates for Wittig-type reactions. Thus, deprotonation of phosphonio−alkynyl complexes [Ru{C≡CC(PR$_3$)HR^1}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (R^1 = H, PR$_3$ = PPh$_3$; R^1 = Ph, PR$_3$ = PMe$_3$), containing an acidic hydrogen atom at C$_\gamma$, generates the highly unstable ylide−alkynyl derivatives [Ru{C≡CC(R^1)=PR$_3$)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$] (**115**), which were suitable precursors for the preparation of a wide series of neutral enynyl and polyenynyl **116**−**122** complexes by means of Wittig-type processes with carbonyl compounds (Scheme 29).[225−229]

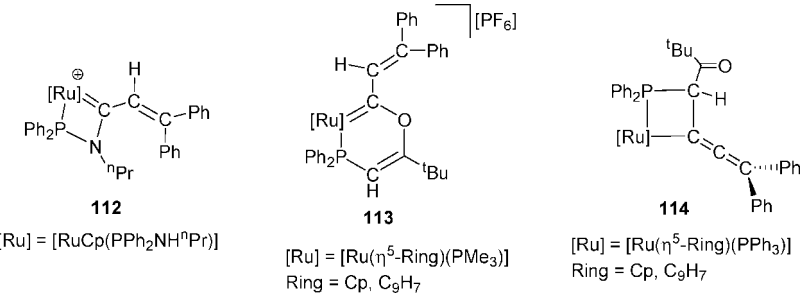
The steric protection of the C$_\alpha$ atom together with the extensive contribution of the metal−alkynyl resonance form [M]−C≡C−C$^+$R^{1}R^2 in these cationic transition-metal−allenylidene complexes [M]$^+$=C=C=CR^{1}R^2, have found synthetic interest. Thus, they have been used as excellent building blocks for the preparation of functionalized alkynyl derivatives through the selective addition of nucleophiles at C$_\gamma$ of the unsaturated chain, leading to a large variety of alkynyl complexes [M]−C≡C−C(Nu)R^{1}R^2. This behavior was nicely illustrated in the chemistry of the indenyl−ruthenium(II) allenylidene complexes [Ru(η^5-C$_9$H$_7$)(=C=C=CR^{1}R^2)(PPh$_3$)$_2$][PF$_6$], which underwent the regioselective C$_\gamma$-addition of a wide range of anionic nucleophiles leading to alkynyl derivatives **123**,[136] **124**,[140,141] **125**,[140,141] **126**,[140,141] **127**,[140,141] **128**,[230] **129**,[231] **130**,[232] **131**,[142,229] **132**,[233] **133**,[140,141] and **134**[140,141] (Chart 22). These nucleophilic additions were, in some cases, not only regioselective but also diastereoselective, as occurred in the formation of compounds **126** and **127**, resulting from the addition of lithium enolates derived from (−)-carvone and (+)-pulegone, respectively, to [Ru(η^5-C$_9$H$_7$)(=C=C=CPh$_2$)(PPh$_3$)$_2$][PF$_6$], or in the formation of **132**−**134** starting from the optically pure allenylidene [Ru(η^5-C$_9$H$_7$){=C=C=C(C$_9$H$_{16}$)}(PPh$_3$)$_2$][PF$_6$] (C(C$_9$H$_{16}$) = (1*R*)-1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene).

Other reported examples of neutral alkynyl−ruthenium complexes generated from nucleophilic additions of anions to cationic allenylidenes are as follows: [RuCp{C≡CCPh$_2$(Nu)}(PPh$_3$)$_2$] (Nu$^-$ = Me$^-$, MeO$^-$, CN$^-$, Cp$^-$),[129] [RuCp*{C≡CC(R)Ph(Nu)}(dippe)] (R = H, Nu$^-$ = MeC(=O)CH$_2^-$, pyrazolyl; R = Ph, Nu = MeC(=O)CH$_2^-$, pyrazolyl),[213] and [Ru(η^5-C$_9$H$_7$){C≡CC(H)(NEt$_2$)C(Me)=CR^{1}R^2}(PPh$_3$)$_2$] (R^1 = R^2 = Ph; R^1 = H, R^2 = C(Me)=CPh$_2$).[145] Regioselective additions at the C$_\gamma$ atom of the fullerene-based allenylidenes [Ru(η^5-C$_{60}$Me$_5$)(=C=C=CR^{1}R^2){(*R*)-prophos}][PF$_6$] (**58** in Chart 13) have also been described.[135]

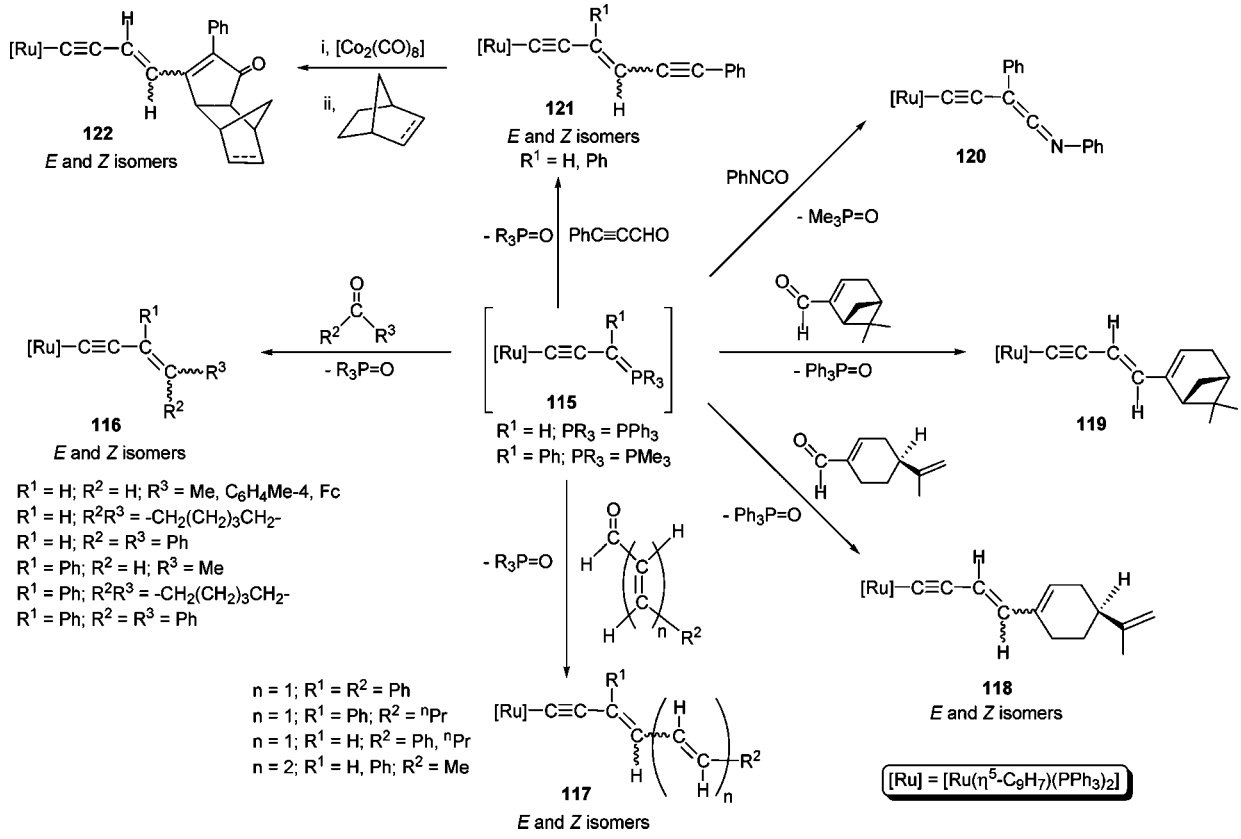
By taking advantage of the regioselectivity shown by the indenyl−ruthenium(II) complexes [Ru(η^5-C$_9$H$_7$)(=C=C=CR^{1}R^2)(PPh$_3$)$_2$][PF$_6$], an efficient synthetic procedure for the propargylic substitution of 2-propyn-1-ols mediated by the metallic fragment [Ru(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]$^+$ was developed (Scheme 30). Thus, in a first step, allenylidene complexes **135** were formed and subsequently transformed into the corresponding σ-alkynyl derivatives **136**, which undergo a selective C$_\beta$-protonation to afford the vinylidene complexes **137**. Finally, demetallation of **137** with acetonitrile led to the functionalized terminal alkynes **138** in excellent yields. Following this route, a large variety of γ-ketoalkynes (including optically active representatives),[140,141,230] 1,4-diynes,[229,233,234] and 1,5- and 1,6-enynes[231,232] could be synthesized. Related processes have also been described starting from the chiral allenylidene [Ru(η^5-C$_9$H$_7$)(=C=C=CHPh){(*R*)-BINAP}][PF$_6$], allowing the preparation of propargylic-substituted compounds with complete enantioselectivity.[138] In all cases, the metal is recovered as the corresponding acetonitrile solvate.

The behavior of osmium−allenylidenes toward nucleophiles follows similar trends to that observed for their analogous ruthenium counterparts. Thus, while the electron-rich bisphosphine complex [OsCp(=C=C=CPh$_2$)(P^{i}Pr$_3$)$_2$][PF$_6$] was inert toward alcohols and amines,[41] the more

Chart 21



Scheme 29

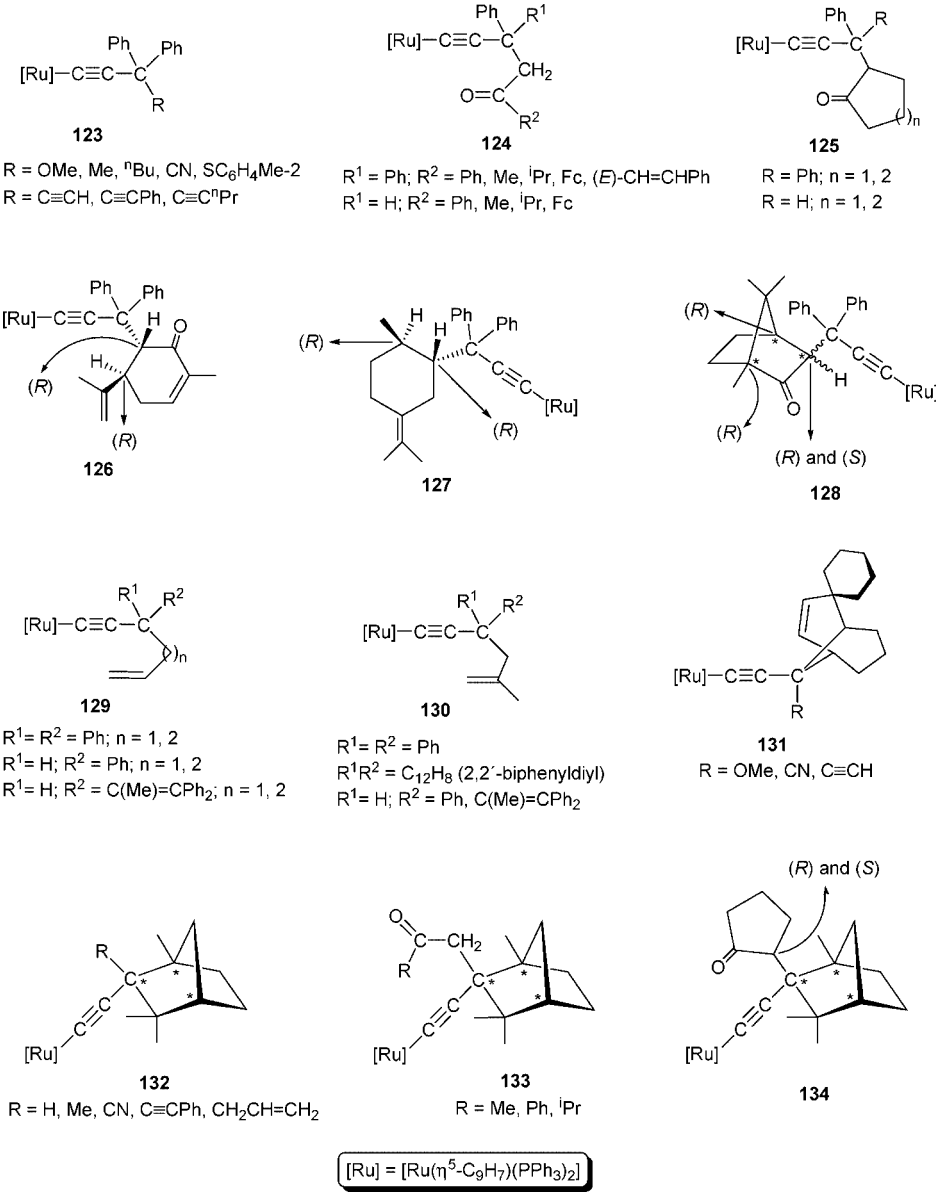


electrophilic carbonyl derivative $[OsCp(=C=C=CPh_2)(CO)(P^iPr_3)][PF_6]$ readily reacted with methanol and aniline to afford $[OsCp\{=C(OMe)CH=CPh_2\}(CO)(P^iPr_3)][PF_6]$ and $[OsCp\{C(=NHPh)CH=CPh_2\}(CO)(P^iPr_3)][PF_6]$, respectively.[148] C_α-additions of alcohols and phosphines to the (η^6-arene)−Os(II) allenylidene $[OsCl(=C=C=CPh_2)(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PMe_3)][PF_6]$ have also been described, allowing the preparation of $[OsCl\{=C(OR)CH=CPh_2\}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PMe_3)][PF_6]$ (R = Me, Et) and $[OsCl\{C(PR_3)=C=CPh_2\}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PMe_3)][PF_6]$ (PR_3 = PMe_3, PPh_3), respectively.[172] As expected, because of the presence of two bulky P^iPr_3 ligands, the addition of anionic nucleophiles (Me^-, MeO^-, $MeC(=O)CH_2^-$) to $[OsCp(=C=C=CPh_2)(P^iPr_3)_2][PF_6]$ took place selectively on the less sterically congested C_γ, generating neutral alkynyl species $[OsCp\{C{\equiv}CCPh_2(Nu)\}(P^iPr_3)_2]$.[41] Related C_γ-additions of anions have also been observed starting from the octahedral derivative $[Os\{\kappa^2(C,O)\text{-}C(CO_2Me)=CH_2\}(=C=C=CPh_2)(CO)(P^iPr_3)_2][BF_4]$.[116]

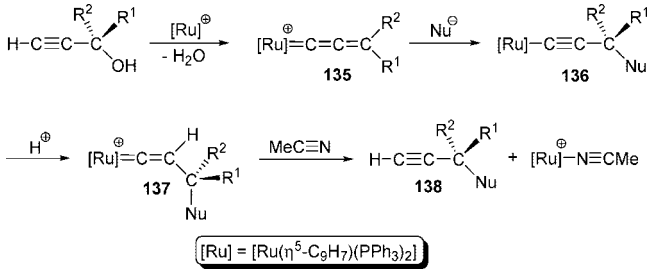
In contrast to ruthenium and osmium, the reactivity of iron allenylidenes remains almost unexplored. Only the behavior of the cationic diphenylallenylidene−Fe(II) derivative *trans*-$[FeBr(=C=C=CPh_2)(depe)_2]^+$ (depe = $Et_2PCH_2CH_2PEt_2$) has been studied in detail. Thus, it has been found that this complex reacts exclusively at C_γ with both neutral (amines, phosphines) and anionic (H^-, MeO^-, CN^-) nucleophiles.[95,96] This behavior contrasts with that of the neutral Fe(0) derivative $[Fe(=C=C=C^tBu_2)(CO)_4]$, which undergoes PPh_3 attack at C_α to afford the zwitterionic phosphonioallenyl species $[Fe\{C(PPh_3)=C=C^tBu_2\}(CO)_4]$.[235]

5.2.3.3. Cycloaddition and Cyclization Reactions. It has been shown that ruthenium and osmium allenylidenes are prone to undergo cycloaddition reactions involving both M=C_α, C_α=C_β, and C_β=C_γ bonds of the cumulenic chain. Concerning the M=C_α bond, Hill and co-workers have studied a series of inter- or intramolecular additions of anionic nucleophiles containing at least two reactive heteroatoms. Thus, sodium dimethyldithiocarbamate was found to react with the cationic allenylidene complex $[RuTp(=C=C=CPh_2)(PPh_3)_2][PF_6]$ (**139**) to generate the allenyl−metallacycle **140** (Scheme 31), as the result of the nucleophilic addition of one of the sulfur atoms at the C_α carbon and subsequent coordination of the second sulfur to the ruthenium center, with concomitant release of a triph-

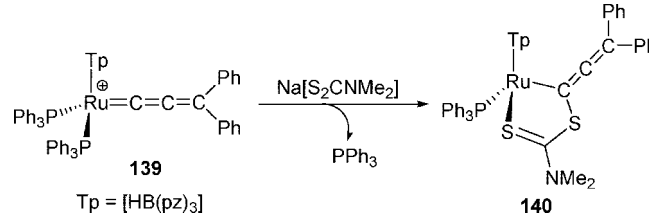
Chart 22



Scheme 30



Scheme 31

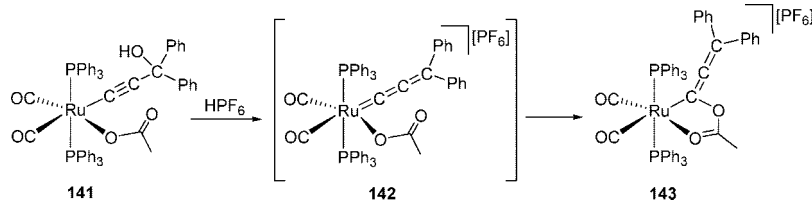


enylphosphine ligand.[236] Complex **140** could also be synthesized by treatment of the neutral derivative [Ru-TpCl(=C=C=CPh$_2$)(PPh$_3$)] with Na[S$_2$CNMe$_2$]. Under similar conditions, the allenylidene complex [Ru{κ^2(*S*,*S*)-S$_2$CNMe$_2$}(=C=C=CPh$_2$)(CO)(PPh$_3$)$_2$][PF$_6$] was transformed into the analogous metallacycle [Ru{κ^2(*S*,*S*)-S=C(NMe$_2$)S−C=C=CPh$_2$}{κ^2(*S*,*S*)-S$_2$CNMe$_2$}(CO)(PPh$_3$)].[236]

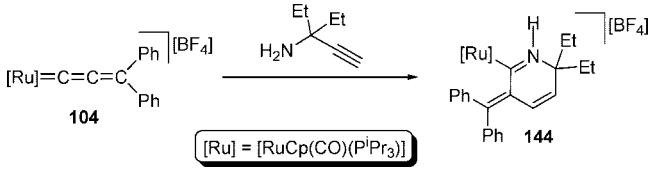
A related intramolecular coupling between a monodentate acetate ligand and a transient diphenylallenylidene moiety was observed when the hydroxyalkynyl derivative **141** was treated with HPF$_6$, affording the ruthenacycle **143** (Scheme 32).[87] This cyclization process was found to be strongly dependent on the electronic properties of the organometallic fragment as evidenced by the stability of the allenylidene species [Ru{κ^1-OAc}(=C=C=CPh$_2$)(CN^{t}Bu)$_2$(PPh$_3$)$_2$][PF$_6$], which is closely related to the intermediate **142**.[87]

The central C$_\alpha$=C$_\beta$ double bond of an allenylidene backbone can also react with a variety of unsaturated organic substrates to yield cyclic adducts. Most of the cyclization processes reported with dipolar substrates occur in a stepwise manner via an initial nucleophilic attack at the C$_\alpha$ atom and further rearrangement of the molecule involving a coupling

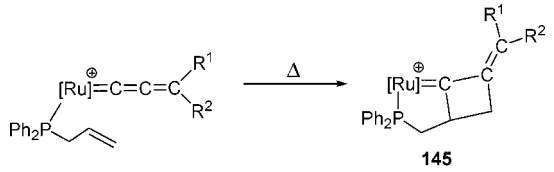
Scheme 32



Scheme 33



Scheme 34



with the C_β carbon. Thus, it was found that the electron-poor ruthenium complex **104** readily adds 1,1-diethylpropargylamine to generate the unprecedented dihydropyridinium species **144** (Scheme 33).[219] Note that the course of the reaction is different when *N*-propargylamine is employed as substrate, with the corresponding azoniabutadienyl complex **106** being selectively formed in this case (see Scheme 28).[219]

Ruthenium allenylidene complexes bearing a $\kappa^1(P)$-allyldiphenylphosphine ligand have been shown to evolve smoothly into the bicyclic derivatives **145**, via an unusual intramolecular [2 + 2]-cycloaddition of two C=C bonds (Scheme 34).[137,146] This process has been carried out starting from isolated as well as in situ generated alkyl- or aryl-substituted allenylidenes but was not observed with the related amino−allenylidene compound $[Ru(\eta^5\text{-}C_9H_7)\{=C=C=C(NEt_2)C(Me)=CPh_2\}\{\kappa^1(P)\text{-}Ph_2PCH_2\text{-}CH=CH_2\}(PPh_3)][PF_6]$.[146] Analogous [2 + 2]-cycloaddition of two C=C bonds involving the $C_\alpha=C_\beta$ double bond of a vinylidene ligand is known.[237]

Cycloaddition reactions of allenylidene ligands with alkynes have also been described. Thus, heating a toluene solution of the neutral osmium complex **146** in the presence of dimethylacetylenedicarboxylate led selectively to the allenyl−vinylidene **148** (Scheme 35).[150] The formal insertion of the alkyne into the $C_\alpha=C_\beta$ double bond can be rationalized through an initial [2 + 2]-cycloaddition followed by the ring-opening of the cyclobutenyl intermediate **147**.

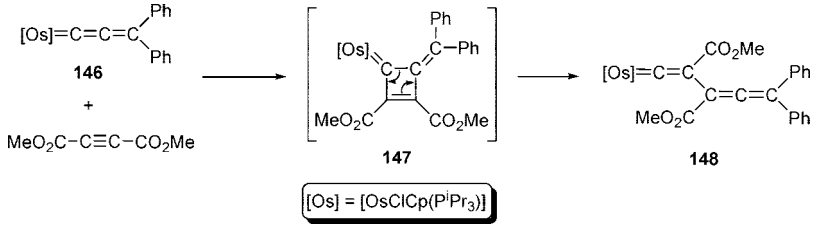
An unusual Diels−Alder cycloaddition involving the $C_\beta=C_\gamma$ bond has been described. The reaction took place by treatment of the electron-deficient allenylidene moiety in complex $[RuCp(=C=C=CPh_2)(CO)(P^iPr_3)][BF_4]$ (**104**) with a 20-fold excess of isoprene at room temperature, affording the cycloadduct **149** (Scheme 36).[238] This Diels−Alder cycloaddition in which the allenylidene moiety acts as a dienophile was completely regioselective, with only the $C_\beta=C_\gamma$ bond of the allenylidene skeleton being implicated. Furthermore, it was also regioselective with regard to the orientation of the diene with the exclusive attack of C(1) and C(4) carbons at the C_β and C_γ positions, respectively. Allenylidene **104** also underwent Diels−Alder reactions with cyclopentadiene and cyclohexadiene in refluxing dichloromethane to afford the bicyclic products **150** and **151**, respectively, as a mixture of diastereomers for the former and as a sole diastereomer for the latter (Scheme 36).[238]

The activation of the allenylidene group by an electron-deficient organometallic fragment was also evidenced when allenylidene complex **104** and its osmium counterpart **105** were treated with carbodiimides in dichloromethane at room temperature. Under these mild conditions, the reactions yielded *Z*- and *E*-iminiumazetidinylidenemethyl species **152** (Scheme 37), while the related bis(phosphine) complex $[OsCp(=C=C=CPh_2)(PHPh_2)(P^iPr_3)][PF_6]$ remained inert.[148,239] The formation of cycloadducts **152** was rationalized in terms of a stepwise [2 + 2]-cycloaddition between the allenylidene $C_\beta=C_\gamma$ and one of the two C=N bonds of the carbodiimide, followed by an Alder-ene rearrangement.

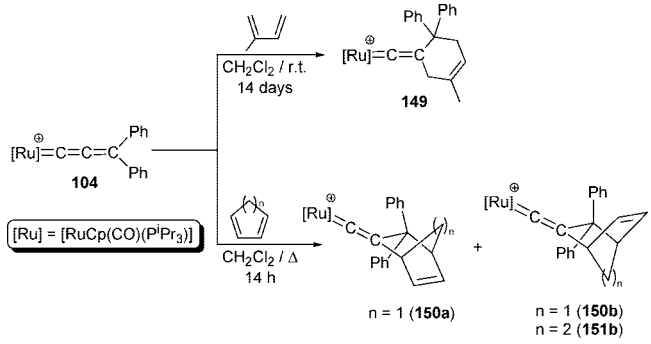
As commented previously, a new synthetic approach of amino−allenylidene ruthenium complexes **64** has been reported (Scheme 13). They result from the regioselective coupling of ynamine $MeC\equiv CNEt_2$ into the $C_\beta=C_\gamma$ double bond of the indenyl−ruthenium(II) allenylidenes **63** to give a cyclobutylidene intermediate that spontaneously undergoes a subsequent ring-opening, yielding exclusively the alkenyl−aminoallenylidene complexes **64**.[145,146] This transformation was also operative with the silylated ynamine $Me_3SiC\equiv CNEt_2$.[145,146] On the basis of this reactivity, an original synthetic route to polyunsaturated allenylidene species could be developed (Scheme 38).[145] Thus, after the first ynamine insertion, a formal substitution of amino group by hydrogen in **64** was performed by consecutive treatments with $LiHBEt_3$ and SiO_2. Like **63**, the resulting monosubstituted alkenyl−allenylidene **65** was able to insert ynamines via a cyclization/cycloreversion pathway to generate the corresponding dienyl−aminoallenylidene species. Further transformations in the presence of $LiHBEt_3$ and SiO_2 furnished the monosubstituted dienyl−allenylidene complex **153**. Finally, a third ynamine insertion provided the highly unsaturated trienyl−aminoallenylidene compound **154**. All the processes involved in this synthetic methodology were totally regio- and stereoselective, giving rise to the formation of **154** as the *trans*,*trans*-isomer exclusively. It is interesting to note that aminoallenylidene compounds, such as **64**, were not prone to insert ynamines even in the presence of a large excess of reagent.

A wide range of dinucleophiles were prone to undergo cyclization processes by addition on both $C_\alpha=C_\beta$ and $C_\beta=C_\gamma$ bonds of a Ru−allenylidene moiety, giving rise to 1,2,3-heterocyclizations. The structure of the products generated was dependent on the number of hydrogen atoms that the organic dinucleophile could deliver. Thus, when only one heteroatom of the dinucleophile contains a hydrogen sub-

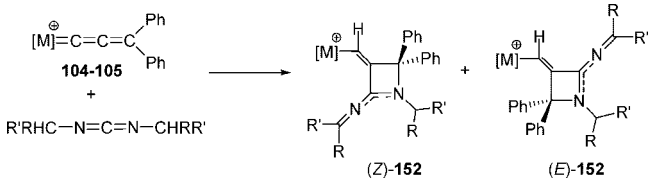
Scheme 35



Scheme 36



Scheme 37



stituent, such as pyrazoles, the reaction with diphenylallenylidene **104** yielded the heterocyclic derivatives **155** (Scheme 39).[206]

Similar 1,2,3-diheterocyclizations have been performed by addition of other *N*,*N*- or *N*,*S*-dinucleophiles, such as pyridine-2-thiol, 2-aminopyridine, 2-aminothiazole, thioisonicotinamide, and 1*H*-benzotriazole, to allenylidene complex **104**, giving rise to the formation of the five- and six-membered cyclic alkenyl derivatives **156**−**158** (Chart 23).[206,240] Related 1,2,3-diheterocyclizations were achieved with rhenium allenylidenes (see Scheme 26).

Another type of coupling involving both C_α═C_β and C_β═C_γ bonds of an allenylidene ligand was observed by heating acetonitrile solutions of the osmium derivatives **159**, with the process yielding the 1-osma-4-hydrocyclopenta[*c*]pyrroles **160** (Scheme 40).[117] They are generated through the assembly of the alkenyl and allenylidene ligands with a molecule of acetonitrile. A plausible reaction pathway consists of the migratory insertion of the allenylidene chain into the Os−alkenyl bond, followed by the addition of the central carbon of the resultant allenyl group to the nitrile function and further electronic reorganization of the molecule. In accordance with this, treatment of **159** (R = Ph) with CO allowed the isolation of the allenyl derivative [Os{C(CH═CHPh)═C═CPh_2}(CO)(P^iPr_3)$_2$(NCMe)$_2$][BF_4].[241]

A cycloaddition process forming a binuclear alkenyl−vinylidene−alkylidene complex of type **95** (see Scheme 25) involving the organometallic fragment [$OsCp(PPh_3)_2$]$^+$ has also been described.[149] As commented in the rhenium case, the suggested mechanism, analogous to that proposed earlier in the reaction of [$RuClCp(PPh_3)_2$] with 2-methyl-3-butyn-2-ol,[242] involves the cycloaddition between a transient allenylidene and its alkenyl vinylidene tautomer, both generated in situ via the dehydration of a 3-hydroxy−vinylidene intermediate.

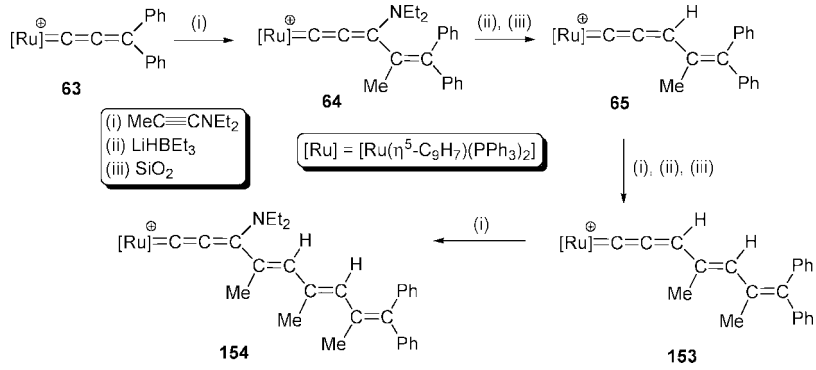
5.2.3.4. Other Reactions. The six-coordinate hydride−allenylidene complex [OsH(═C═C═CPh_2)(CH_3CN)$_2$(P^iPr_3)$_2$]-[BF_4] (**161**) has shown an unusual reactivity toward alcohols.[243] Thus, in contrast to the α-electrophilic character featured by most of its diphenylallenylidene partners, which in the presence of alcohols afford α,β-unsaturated alkoxycarbene derivatives (see above), this hydride complex in methanol, ethanol, *n*-propanol, or 2-propanol was found to evolve into the hydride−alkenylcarbene **162** (Scheme 41). The hydrogenation of the C_α═C_β double bond of the allenylidene ligand of **161** takes place by means of hydrogen transfer from the alcohols to give the carbonyl compounds. However, the reactions with phenol and *tert*-butanol, which have no β-hydrogen, afforded the alkoxy−hydride−carbyne complexes **163** and **164**, respectively, as a consequence of the 1,3-addition of the O−H bond of the alcohols to the metallic center and the C_β atom of the allenylidene chain.

The mechanism of this hydrogenation reaction has been analyzed by DFT calculations (Scheme 42).[243] The highest barrier is the β-hydrogen elimination on the alkoxide ligand, which is favored with regard to the migratory insertion of the carbyne into the Os−H bond and appears to be the rate-determining step for the reduction (81.1 kJ mol^{-1}). It was found that the transformation proceeds via a dihydride carbyne intermediate with the *trans* species being strongly favored with regard to the *cis* one. Subsequent migratory insertion of the carbyne into an Os−H bond of the *trans*-dihydride is only 62.3 versus 160.1 kJ mol^{-1} for the *cis* isomer.

Cationic allenylidene complexes containing a hydrogen atom in δ position, i.e., [M]$^+$═C═C═C(R^1)CHR^2R^3, are known to undergo deprotonation processes upon treatment with bases, affording neutral σ-enynyl derivatives [M]-C≡C$C(R^1)$═CR^2R^3.[13,14] A recent example of deprotonation was observed in the iron allenylidene *trans*-[FeBr(═C═C═CMePh)(depe)$_2$][BPh_4].[95] In this context, it should also be noted that ruthenium(II) allenylidenes *trans*-[RuCl{═C═C═C(R^1)CH_2R^2}(dppe)$_2$][BF_4], containing an acidic methylenic unit, readily react with the neutral diynyl complex *trans*-[RuCl{(C≡C)$_2$H}(dppe)$_2$] to afford the dinuclear C_7-bridged compounds **5** (see Chart 2) via C_δ−H deprotonation.[8]

An unusual reactivity was observed in the one-electron reduction of complexes *trans*-[RuCl(═C═C═CR_2)(dppe)$_2$]-[PF_6] (R = Ph, Me) with cobaltocene, resulting in the formation of highly reactive radicals *trans*-[RuCl(C≡CC$^\bullet$R$_2$)(dppe)$_2$], which, in the presence of Ph_3SnH, could be trapped by H-transfer, yielding alkynyl compounds *trans*-[RuCl(C≡CCHR_2)(dppe)$_2$].[244]

Scheme 38



Scheme 39

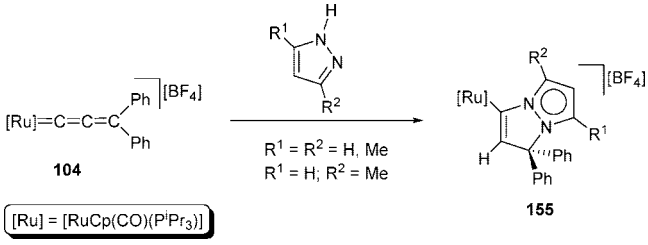
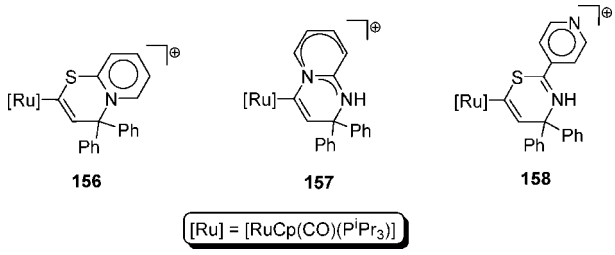
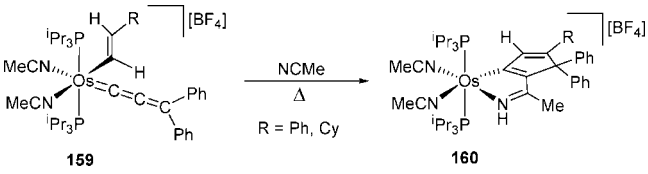


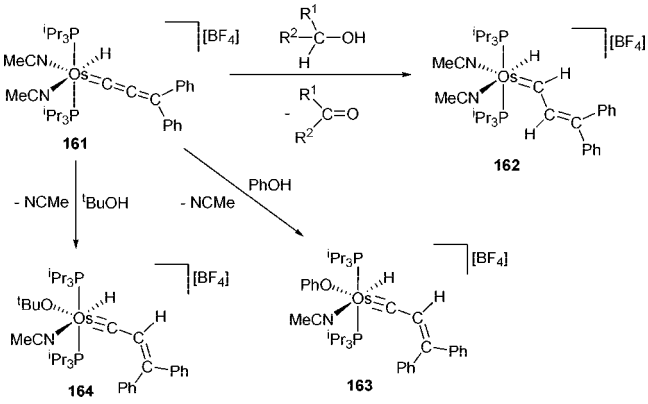
Chart 23



Scheme 40



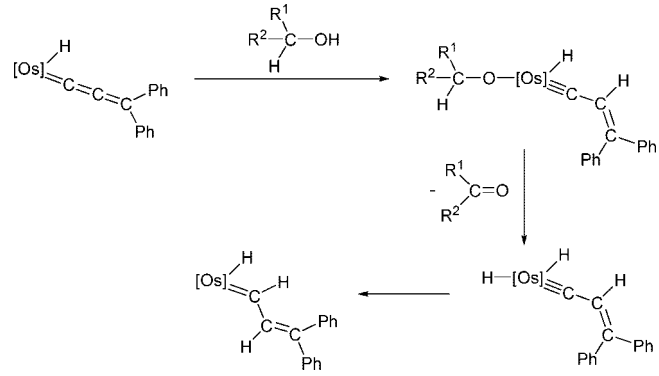
Scheme 41



5.2.4. Group 9 Metals

The reactions of several square-planar allenylidene rhodium(I) and iridium(I) chloride complexes *trans*-[MCl(=C=C=CR^{1}R^2)(P^{i}Pr$_3$)$_2$] with anionic nucleophiles do not proceed through the typical C$_\alpha$ or C$_\gamma$ addition, giving instead

Scheme 42

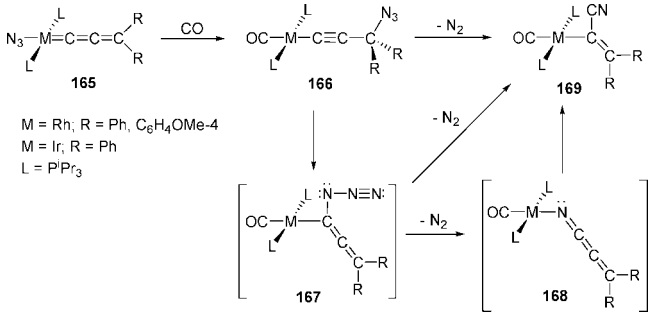


substitution products *trans*-[MX(=C=C=CR^{1}R^2)(P^{i}Pr$_3$)$_2$] (X$^-$ = I$^-$, HO$^-$, RO$^-$, RCO$_2^-$, N$_3^-$, SCN$^-$, etc.), providing therefore an efficient synthetic route of allenylidenes (see above). The strong *trans* influence of the π-acceptor allenylidene unit allows the easy exchange of the chloride ligand by a large variety of anionic nucleophiles. The easy access to these derivatives has triggered the reactivity studies.

In particular, a variety of insertion reactions into the M−X bond have been described. Thus, upon treatment with carbon monoxide, complexes *trans*-[M(OPh)(=C=C=CR^{1}R^2)(P^{i}Pr$_3$)$_2$] (M = Rh, R^1 = Ph, R^2 = Ph, C$_6$H$_4$Me-2; M = Ir, R^1 = Ph, R^2 = ^{t}Bu) and *trans*-[Rh{κ^1(*O*)-O$_2$CMe}(=C=C=CR^{1}R^2)(P^{i}Pr$_3$)$_2$] (R^1 = Ph, R^2 = Ph, C$_6$H$_4$Me-2) were found to undergo migratory insertion of the allenylidene unit into the M−O bond to generate the σ-alkynyl complexes *trans*-[M{C≡CCR^{1}R^2(OPh)}(CO)(P^{i}Pr$_3$)$_2$] and *trans*-[Rh{C≡CCR^{1}R^2(O$_2$CMe)}(CO)(P^{i}Pr$_3$)$_2$], respectively.[177,183] Similarly, the reactions of the hydroxo compounds *trans*-[Rh(OH)(=C=C=CR^{1}R^2)(P^{i}Pr$_3$)$_2$] (R^1 = R^2 = Ph, C$_6$H$_4$OMe-4; R^1 = Ph, R^2 = ^{t}Bu) with CH$_2$(CN)$_2$ and either CO or CNMe yielded the carbonyl or the isocyanide complexes *trans*-[Rh{C≡CCR^{1}R^{2}CH(CN)$_2$}(L)(P^{i}Pr$_3$)$_2$] (L = CO, CNMe), via highly unstable allenylidene intermediates *trans*-[Rh{CH(CN)$_2$}(=C=C=CR^{1}R^2)(P^{i}Pr$_3$)$_2$].[183]

Treatment of the azido complexes **165** with CO also led to the migration of the N$_3^-$ ligand to the allenylidene unit (Scheme 43). Nevertheless, the initially formed azido−alkynyl compounds **166** were, in this case, thermally unstable, evolving slowly into the metallated acrylonitrile derivatives **169** via extrusion of N$_2$. The mechanism of formation of **169** involves the migration of the azido moiety from C$_\gamma$ to the C$_\alpha$ atom of the alkynyl ligand to generate the allenyl intermediates **167**, which by elimination of N$_2$ and shifting of the metal fragment (directly or via intermediate **168**) affords **169**.[177,181]

Scheme 43



An oxidatively induced C_α−P coupling has been observed upon oxidation of complexes *trans*-[RhCl(=C=C=CR_2)(P^iPr_3)$_2$] (R = Ph, C_6H_4OMe-4) with Cl_2 or $PhICl_2$, yielding phosphonio−allenyl products [$RhCl_3${C(P^iPr_3)=C=CR_2}(P^iPr_3)]. They are formed by migration of one P^iPr_3 ligand from the metal to the allenylidene α-carbon in the six-coordinate Rh(III) intermediates [$RhCl_3$(=C=C=CR_2)(P^iPr_3)$_2$].[178]

Werner and co-workers have nicely exploited the ability of square-planar Rh(I) and Ir(I) allenylidenes to undergo C−C couplings. Reported processes include the following:

(i) Insertion of the methylene unit :CH_2 into the Rh=C bond, which took place by treatment of *trans*-[RhCl(=C=C=CR^1R^2)(P^iPr_3)$_2$] (R^1 = R^2 = Ph, C_6H_4OMe-4; R^1 = Ph, R^2 = CF_3, ^{t}Bu) with diazomethane, allowing the isolation of stable butatriene−Rh(I) compounds *trans*-[RhCl(η^2-H_2C=C=C=CR^1R^2)(P^iPr_3)$_2$].[178] Remarkably, their iodide counterparts *trans*-[RhI(η^2-H_2C=C=C=CR_2)(P^iPr_3)$_2$] (R = Ph, C_6H_4OMe-4) were generated by reacting the corresponding allenylidene complexes *trans*-[RhI(=C=C=CR_2)(P^iPr_3)$_2$] with MeI.[178] This unusual C−C coupling reaction, in which MeI behaves as a :CH_2 source, involves oxidative addition of MeI at the rhodium center followed by insertion of the allenylidene unit into the Rh−Me bond. The resulting allenyl−Rh(III) intermediates [RhI_2(η^1-C(Me)=C=CR_2)(P^iPr_3)$_2$] evolve through a β-H shift to give [$RhHI_2$(η^2-H_2C=C=C=CR_2)(P^iPr_3)$_2$], which upon reductive elimination of HI generate the final butatriene−Rh(I) complexes. The same reactivity pattern was also observed in the reaction of *trans*-[IrI(=C=C=CPh_2)(P^iPr_3)$_2$] with MeI.[186]

(ii) A C_3 + C_2 coupling process observed in the reactions of these square-planar Rh(I)−allenylidenes with the Grignard reagent CH_2=CHMgBr to yield η^3-pentatrienyl derivatives. An example is shown in Scheme 44.[178] Thus, starting from **170**, this C−C coupling takes place through an initial substitution of the chloride ligand leading to the vinyl−metal intermediate **171**, which rearranges, by migratory insertion of the allenylidene unit into the Rh−CH=CH_2 bond, to give the final product **172**.

(iii) C−C couplings with alkynes. An unprecedented coupling of this type has been found in the reaction of the Ir(I) derivatives **173** with an excess of the terminal alkynes to afford, under remarkably mild conditions (room temperature, r.t.), the novel five-coordinate compounds **174** (Scheme 45). The proposed mechanism involves an initial $HO^-/R^2C{\equiv}C^-$ ligand exchange followed by the oxidative addition of a second molecule of the alkyne to generate the hydride Ir(III) intermediate [IrH(C≡CR^2)$_2${=C=C=C(R^1)Ph}(P^iPr_3)$_2$]. The rearrangement to an allenyl species followed by the C−C coupling with a third alkyne molecule gives the final product.[177,184]

An intramolecular allenylidene−alkynyl coupling was also observed in the reaction of the rhodium complex **175** with carbon monoxide (Scheme 46). The initially formed thermally unstable allenyl derivative **176** evolved into the metallated cyclobutenone **177** when an excess of CO was present.[182]

A different unexpected coupling involving terminal alkynes was found in the reaction with the rhodium−allenylidene derivative **170**, which resulted in the formation of the zwitterionic π-allyl−allenyl species **179** (Scheme 47).[178] The reaction is assumed to take place through an initial [2 + 2]-cycloaddition between the carbon−carbon triple bond of the alkyne and the Rh=C bond, giving rise to the metallacyclobutene **178**, which spontaneously evolves into **179** by migration of the P^iPr_3 ligand from the metal to the hydrocarbon chain.

Linkage of two allenylidene moieties has also been observed in the thermal decomposition of *trans*-[RhCl(=C=C=CPh_2)(P^iPr_3)$_2$].[178]

6. Reactivity of Higher Cumulenylidene Complexes

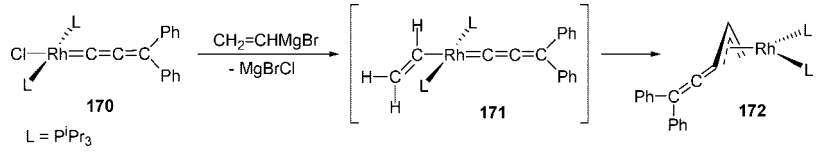
Although the chemistry of higher cumulenylidene complexes [M]=C(=C)$_n$=CR^1R^2 (n > 1) has not received so much attention as that of allenylidenes (n = 1), theoretical (see above) and experimental[14,24] evidence point also to the alternating electron deficiency and richness of the carbon atoms of the unsaturated chain as one moves along the chain from the metal atom. Therefore, nucleophilic additions at the odd-numbered carbons and electrophilic additions at the even-numbered carbons can be envisaged.

6.1. Reactions of Butatrienylidene Complexes

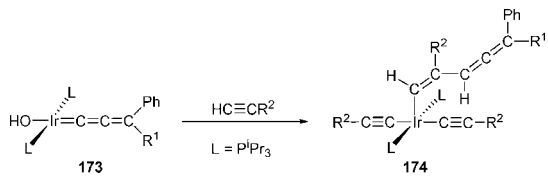
As commented previously, mononuclear transition-metal complexes containing butatrienylidene ligands [M]=C=C=C=CR^1R^2 have usually been reported to be highly reactive intermediates in different reactions.[37] Complexes [Cp*(L−L)Fe{=C=C=C=C(R)FeCp*$(CO)_2$}]$^+$ (**82** in Chart 17) represent rare examples of butatrienylidene complexes stable enough to be isolated and spectroscopically characterized.[191] These stable species have been studied by cyclic voltammetry (CV). Thus, while the disubstituted species [Cp*(L−L)Fe{=C=C=C=C(Me)FeCp*$(CO)_2$}]$^+$ displayed a reversible one-electron oxidation process and an irreversible reduction, monosubstituted complexes [Cp*(L−L)Fe{=C=C=C=C(H)FeCp*$(CO)_2$}]$^+$ showed a more complicated pattern, due to the acidic character of the hydrogen atom on C_δ, and signals attributed to [Cp*(L−L)Fe{C≡CC≡CFeCp*$(CO)_2$}] were also observed in the voltammograms. In fact, these monosubstituted butatrienylidene complexes could be readily deprotonated with DBU or traces of water to afford the starting butadiynes [Cp*(L−L)Fe{C≡CC≡CFeCp*$(CO)_2$}].[191]

Activation of trimethylsilyl−1,3-butadiyne HC≡CC≡$CSiMe_3$ by [FeCp*Cl (dppe)] in methanol has been reported to yield the methoxy−allenylidene [FeCp*{=C=C=C(OMe)Me}(dppe)][BPh_4] (**181**) (Scheme 48).[144] Formation of **181** involves the generation of the unstable butatrienylidene derivative **180**, through an initial 1,4-H shift and

Scheme 44



Scheme 45



subsequent desilylation of the intermediate [FeCp*{=C=C=C=C(H)SiMe$_3$}(dppe)][BPh$_4$], which readily adds methanol at the C_γ=C_δ double bond.

Another transient, very reactive butatrienylidene derivative *trans*-[RuCl{=C=C=C=C(H)Ph}(dppe)$_2$]$^+$, obtained by protonation of the neutral diynyl ruthenium(II) complex *trans*-[RuCl(C≡CC≡CPh)(dppe)$_2$] or by direct activation of 1,3-butadiyne HC≡CC≡CPh with *cis*-[RuCl$_2$(dppe)$_2$] has been described.[245] This complex could not be isolated since it adds water or methanol from the reaction media at the electrophilic C_γ carbon to yield the acylvinylidene *trans*-[RuCl{=C=C(H)C(=O)CH$_2$Ph}(dppe)$_2$]$^+$ or the methoxy−allenylidene *trans*-[RuCl{=C=C=C(OMe)CH$_2$Ph}(dppe)$_2$]$^+$, respectively.

An analogous transient butatrienylidene complex *trans*-[RuCl(=C=C=C=CH$_2$)(dppm)$_2$]$^+$, generated by treatment of *cis*-[RuCl$_2$(dppm)$_2$] with an excess of butadiyne (HC≡CC≡CH) in the presence of a halide-abstracting reagent (NaPF$_6$ or NaSbF$_6$), could also be trapped in situ by addition of a variety of nucleophiles (alcohols, amines, thiols, selenols, pyrroles, furans, thiophene, or selenophene) at C_γ to yield stable allenylidenes [RuCl{=C=C=C(Nu)Me}(dppm)$_2$]$^+$ (if a Nu−H bond is present) or *σ*-enynyl derivatives [RuCl{C≡CC(Nu)=CH$_2$}(dppm)$_2$]$^+$ (if no Nu−H bond is present).[58,111−115,246] The reaction of *trans*-[RuCl(=C=C=C=CH$_2$)(dppm)$_2$]$^+$ with ferrocenylmethyldimethylamine merits to be highlighted since, in this case, the initially generated 2-ammoniobutenynyl derivative [RuCl{C≡CC(NMe$_2$CH$_2$Fc)=CH$_2$}(dppm)$_2$]$^+$ **182** evolved into the iminiumalkynyl complex **183** through the migration of the resonance-stabilized ferrocenylcarbenium ion from the quaternary nitrogen atom to the neighboring nucleophilic C_δ (Scheme 49).[110] Synthesis of the thio−allenylidene derivatives [RuCl{=C=C=C(SCH$_2$CH=CH$_2$)(CH$_2$CH$_2$CH=CH$_2$)}(dppm)$_2$]$^+$ and [RuCl{=C=C=C(SMe)(CH$_2$CH$_2$CH=CH$_2$)}(dppm)$_2$]$^+$ from the in situ generated butatrienylidene *trans*-[RuCl(=C=C=C=CH$_2$)(dppm)$_2$]$^+$ and diallyl sulfide or allyl methyl sulfide, respectively, has also been described.[111]

The reactivity of the highly reactive butatrienylidene [RuCp(=C=C=C=CH$_2$)(PPh$_3$)$_2$][PF$_6$], prepared in situ by reacting a THF solution of [RuClCp(PPh$_3$)$_2$] with buta-1,3-diyne and AgPF$_6$ has also been reported.[113,247] Thus, complexes [RuCp{C≡CC(PPh$_3$)=CH$_2$}(PPh$_3$)$_2$][PF$_6$], [RuCp{=C=C=C(NPh$_2$)Me}(PPh$_3$)$_2$][PF$_6$], [RuCp{C≡CC(=O)Me}(PPh$_3$)$_2$], and [RuCp{=C=C=C(−2-MeC$_4$H$_3$N)Me}(PPh$_3$)$_2$][PF$_6$] were prepared by trapping this cumulenylidene derivative with triphenylphosphine, diphenylamine, water, and *N*-methylpyrrole, respectively.[113] In addition, a wide series of functionalized alkynyl derivatives containing either quinoline **184** or 1-azabuta-1,3-diene fragments **185** could be obtained when the in situ formed complexes [RuCp(=C=C=C=CH$_2$)(PR$_3$)$_2$][PF$_6$] (PR$_3$ = PPh$_3$, P(OMe)$_3$) were treated with an excess of aromatic imines (Scheme 50).[247]

As commented previously, an analogous butatrienylidene cationic intermediate [RuCp*(=C=C=C=CH$_2$)(dppe)]$^+$ was also responsible for the formation of the binuclear butenynylallenylidene [{RuCp*(dppe)}$_2${*μ*-C≡CC(OMe)=C(H)C-(Me)=C=C=C}][PF$_6$].[143]

Isolation of iridium(I)−butatrienylidene complexes *trans*-[IrX(=C=C=C=CPh$_2$)(P^{i}Pr$_3$)$_2$] (**84** in Chart 17) has allowed a systematic study of their reactivity including the following (Scheme 51):[193]

(i) CO-promoted migratory insertion of the carbene moiety into the Ir−Me bond to give *trans*-[Ir{C(=CPh$_2$)C≡CMe}(CO)(P^{i}Pr$_3$)$_2$] (**186**). Similarly, insertion into the Ir−N$_3$ bond gave initially *trans*-[Ir{C≡CC(N$_3$)=CPh$_2$}(CO)(P^{i}Pr$_3$)$_2$] (**187**), which rearranged slowly to give the stable butatrienyl species *trans*-[Ir{C(N$_3$)=C=C=CPh$_2$}(CO)(P^{i}Pr$_3$)$_2$] (**188**).

(ii) Oxidative addition of HCl to afford the butadienyl−Ir(III) complex *trans*-[IrCl$_2${CH=CHC(Cl)=CPh$_2$}(P^{i}Pr$_3$)$_2$] (**189**), involving probably the vinylidene intermediate *trans*-[IrCl{=C=C(H)C(Cl)=CPh$_2$}(P^{i}Pr$_3$)$_2$].

(iii) The addition of CF$_3$CO$_2$H across the C_β=C_γ bond to give the vinylvinylidene *trans*-[IrCl{=C=CHC(O$_2$CCF$_3$)=CPh$_2$}(P^{i}Pr$_3$)$_2$] (**190**).

(iv) The transformation of the hydroxo complex *trans*-[Ir(OH)(=C=C=C=CPh$_2$)(P^{i}Pr$_3$)$_2$] into the butatrienyl iridium(III) derivative [IrH$_2$(CH=C=C=CPh$_2$)(CO)(P^{i}Pr$_3$)$_2$] (**191**) upon treatment with carbon monoxide in methanol.

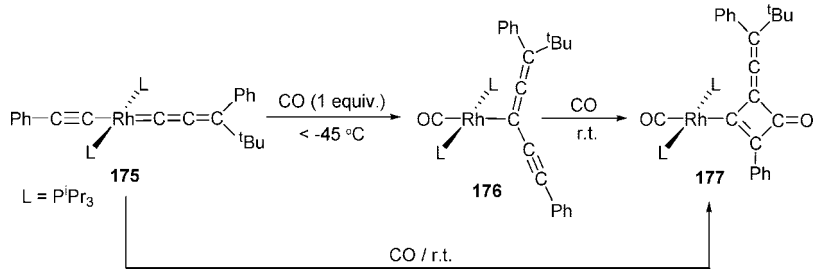
6.2. Reactions of Pentatetraenylidene Complexes

After the early studies on the reactivity of Group 6, ruthenium, and rhodium pentatetraenylidene complexes toward alcohols and secondary amines,[37] further developments are very scarce. In this context, it has been reported that the bimetallic complex [Cp*(PPh$_3$)(NO)Re=C=C=C=C=C=Mn(CO)$_2$(*η*^{5}-C$_5$Cl$_5$)][BF$_4$], obtained by treatment of [Cp*(PPh$_3$)(NO)ReC≡CC≡CC(OMe)=Mn(CO)$_2$(*η*^{5}-C$_5$Cl$_5$)] with an excess of BF$_3$ gas,[248] is stable toward dimethyl sulfide, ethylene, or tetracyanoethylene but readily reacts with trimethylphosphine, even at −80 °C, to afford complicated mixtures of products that have not been identified.

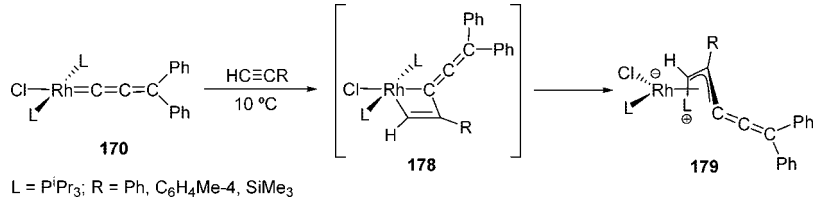
7. Catalytic Reactions Involving Allenylidene Complexes

Although the involvement of transition-metal allenylidenes in homogeneous catalysis was reported for the first time in 1992,[249] it has been only recently that these metallacumulenes have really emerged as useful catalyst precursors or catalyst intermediates in organic synthesis. In particular, significant advances have been made in the field of alkene metathesis

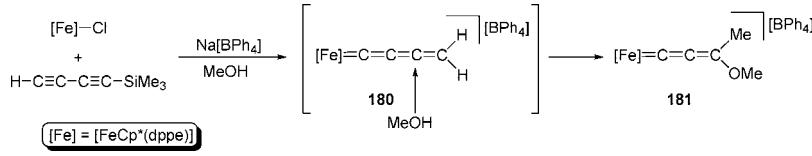
Scheme 46



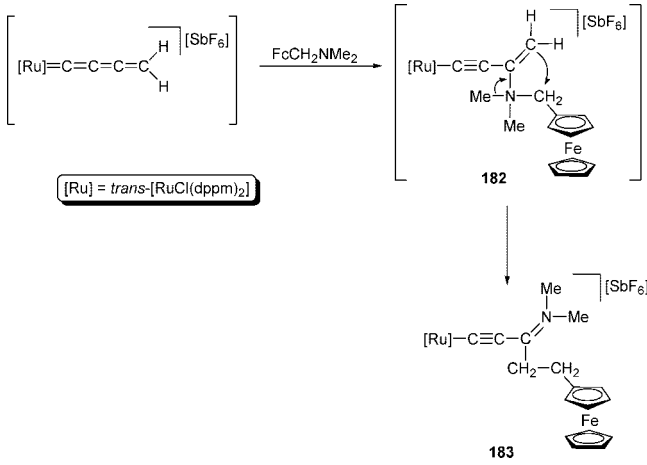
Scheme 47



Scheme 48



Scheme 49



and propargylation reactions using mainly ruthenium complexes. In this section, a survey of this chemistry is presented.

7.1. Reactions Involving Allenylidene Complexes as Catalyst Precursors

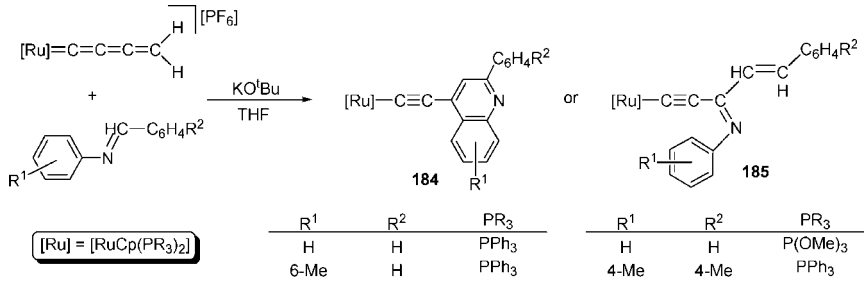
7.1.1. Olefin Metathesis

7.1.1.1. RCM Reactions. Owing to the great functional group tolerance of well-defined ruthenium−alkylidene complexes [L$_n$Ru]=CHR (the Grubbs catalysts family), alkene metathesis has recently known a real breakthrough, becoming a powerful synthetic tool in organic, material, and polymer chemistry.[250] Despite the tremendous profit brought by these catalysts, efforts are still needed to find more accessible and active carbene-type complexes. In this context, ruthenium−allenylidene complexes, easy to prepare and to handle, have been revealed as a valid alternative. Reviews covering the specific contribution of allenylidene catalysts in olefin metathesis have been published.[17,22,26]

The first catalytic application of allenylidene complexes in alkene metathesis was described in 1998 by Dixneuf's and Fürstner's groups.[158−160] Thus, using the RCM of *N*,*N*-diallyltosylamide **192** into *N*-tosyldihydropyrrole **193** as the model reaction (Scheme 52), they evaluated the catalytic potential of several well-defined 18-electron ruthenium−allenylidene complexes [RuCl(=C=C=CR$_2$)(η^6-*p*-cymene)(PR$_3$)][X] (**101**). The following general trends were observed: (i) The activity increases with the electron richness and size of the phosphine ligand in the order PCy$_3$ > P^{i}Pr$_3$ ≫ PPh$_3$. (ii) The nature of the counteranion of these ionic precursors has a dramatic influence on the catalytic activity, which increases with the sequence TfO$^-$ ≫ PF$_6^-$ ≈ BPh$_4^-$ ≫ BF$_4^-$. (iii) Several 3,3-diarylallenylidene ligands were shown to be efficient, but the most simple 3,3-diphenylallenylidene−ruthenium derivatives led to the best performances, showing an activity similar to that of [RuCl$_2$(=CHPh)(PCy$_3$)$_2$]. As an illustrative example, using 2.5 mol% of complex [RuCl(=C=C=CPh$_2$)(η^6-*p*-cymene)(PCy$_3$)][PF$_6$] (**101a**) diene **192** was quantitatively (GC) converted into **193** (83% isolated yield) after heating a toluene solution for 4 h at 80 °C.[158,160] Enhancement of the catalytic activity of **101a** was observed upon photochemical activation, which favors decomplexation of the coordinated *p*-cymene ligand, generating vacant sites on the metal for substrate activation.[160] Thus, when the RCM reaction of *N*,*N*-diallyltosylamide **192** was performed under constant irradiation with UV light (300 nm), *N*-tosyldihydropyrrole **193** was formed in 81% after only 5 h at r.t.

Complex **101a** was successfully applied in the RCM of several representative diene substrates, allowing the synthesis of essentially all ring sizes greater than four, including mono- and bicyclic compounds, in good-to-excellent yields.[158−160] As expected, the formation of medium-sized rings required particularly long reaction times (up to 100 h) and high dilute conditions, while decomposition of the catalytically active species seemed to occur with a rate similar to that of the

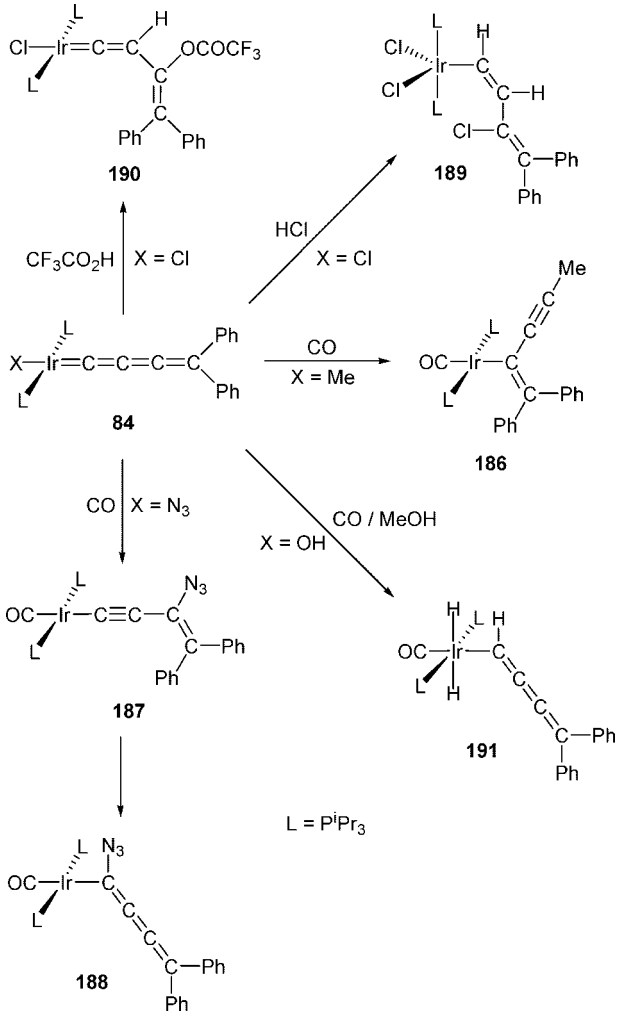
Scheme 50



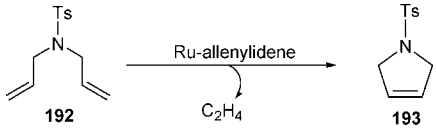
R^1	R^2	PR_3
H	H	PPh_3
6-Me	H	PPh_3
H	4-NO_2	PPh_3
H	4-NO_2	$P(OMe)_3$
H	3-NO_2	PPh_3
H	4-CO_2Me	$P(OMe)_3$
6-OMe	4-NO_2	PPh_3
6-OMe	4-NO_2	PPh_3
5-Cl	H	PPh_3
7-Cl	H	PPh_3
benzo	H	PPh_3

R^1	R^2	PR_3
H	H	$P(OMe)_3$
4-Me	4-Me	PPh_3
4-Me	4-Me	$P(OMe)_3$
4-OMe	4-OMe	PPh_3
4-OMe	4-OMe	$P(OMe)_3$
4-NO_2	H	PPh_3
3-NO_2	H	PPh_3
H	4-CO_2Me	PPh_3
4-NO_2	4-CO_2Me	PPh_3
4-NO_2	4-CO_2Me	PPh_3
4-CO_2Et	H	PPh_3
H	benzo	PPh_3

Scheme 51



Scheme 52



productive RCM. Despite these inherent inconveniences, complex **101a** showed a great synthetic utility, allowing the efficient synthesis of a set of uncommon macrocyclic compounds. For example, it promotes smooth cyclization of dienes **194**, **196**, and **198** to yield, respectively, **195**, a precursor of Exaltolide that is a valuable perfume ingredient;[158,160] **197**, which under deprotection affords a potent insect repellent; and **199**,[160] an advanced intermediate to the carcinostatic resin tricolorin A (Scheme 53).[158,160,251] Fluorinated α-aminophosphonates **200**, which exhibit high potential as antibacterial agents, are also cyclized in **201** in good yields, using as catalyst the triflate salt of allenylidene **101a**.[252]

The ionic nature of these ruthenium−allenylidene complexes makes them soluble in ionic liquids, and, taking advantage of this property, it was demonstrated that complex **101a** is able to promote RCM of dienes using imidazolium salts, containing triflate or hexafluorophosphate anions, as solvents at 80 °C.[253] Although the activity in this medium was slower than in classical organic solvents, the catalyst could be recycled twice owing to its moderate stability. A method to heterogenize the allenylidene catalyst, allowing also its recovery and reuse, was described using the benzene rings of polystyrene (complex **71** in Scheme 14). Although catalytic conditions with this polymer-supported version of **101a** were rather drastic (20 mol % of Ru; 12 h under ^{i}PrOH/hexane reflux), good activity was still observed after the third recycling.[165] The catalytic activity of complex **101a** in RCM of dienes was also explored under controlled microwave irradiation.[254] In this case, the results obtained (61−98% yield after 20 min in dichlomethane at 100 °C) compared very favorably with classical thermal protocols (dichloromethane at 40 °C) where reaction times of 16 h were necessary to achieve similar conversions.

In an attempt to improve the catalytic performance of arene−allenylidene−ruthenium complexes **101**, replacement of the ancillary phosphine ligands by a higher electron-releasing *N*-heterocyclic carbene was carried out. The resulting complex, i.e., [RuCl(=C=C=CPh_2)(η^6-*p*-cymene-)(IMes)][PF_6] (**74**), was found to be active in the RCM of diethyl diallylmalonate, but its activity did not reach that of **101a**.[169] As just mentioned, the stability of **101a** was found to be the limiting factor in applications to the synthesis of medium-sized rings. A way to increase the stability of ruthenium−allenylidene complexes was investigated by the use of chelating arene ligands containing a pendant phosphine or NHC group (Chart 24).

Scheme 53

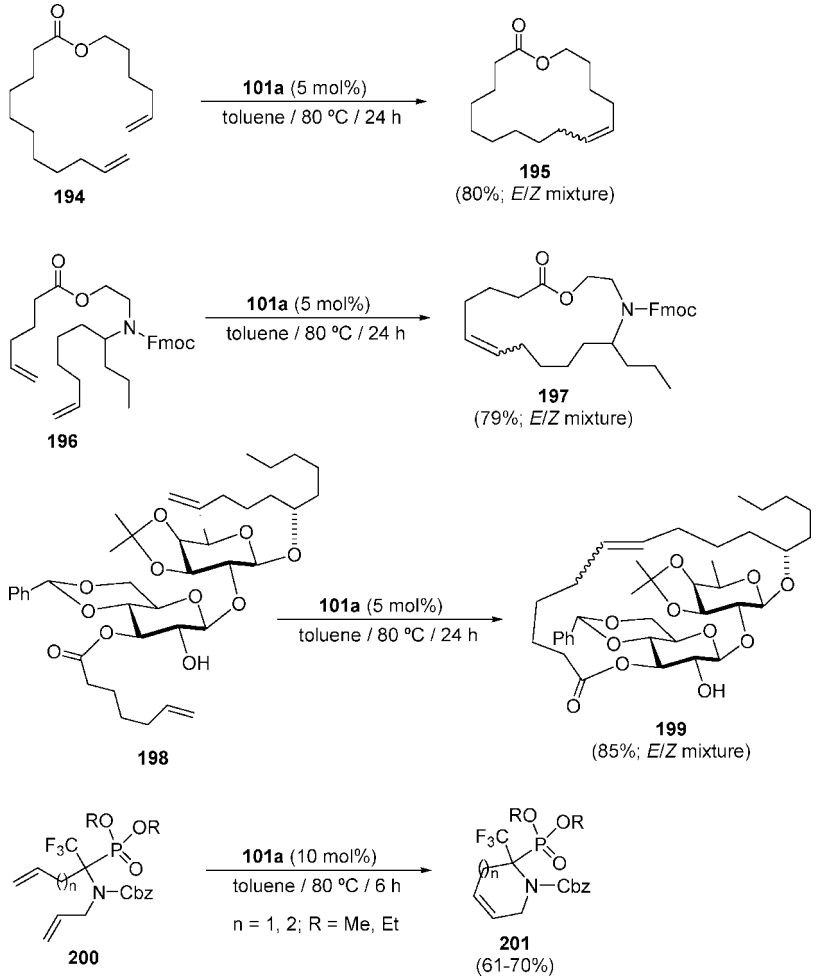
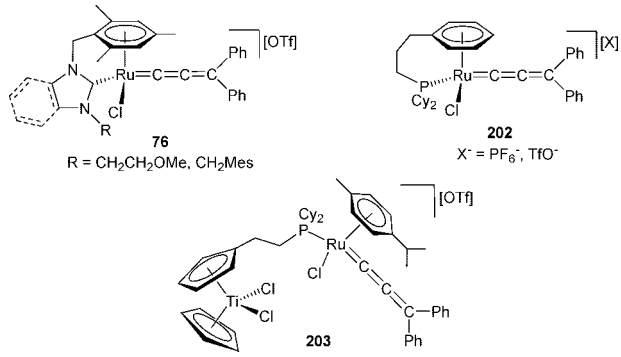


Chart 24



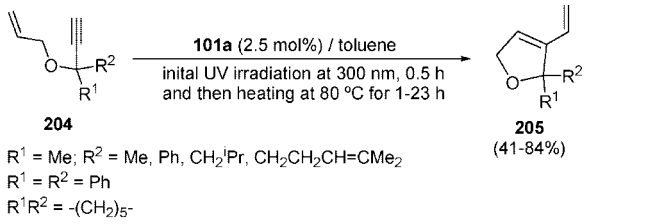
However, none of the reported examples improved the performances of their nonchelated analogue **101a**. Thus, complex **202** gave satisfactory results in RCM of a representative set of substrates, but rates were in all cases lower than those of **101a**.[160] Concerning complexes **76**, the reaction pattern of RCM reactions was rather complex due to competitive transformation of the dienes through alkene metathesis or cycloisomerization. The nature of the substrate and the solvent dramatically influenced both activity and selectivity, but the activity was always lower than that of the nonchelating arene complex **101a**.[176] In order to evidence a possible cooperative effect, the catalytic activity of allenylidene complex **203**, containing in the same molecule both early and late metal centers, was checked in the RCM of dienes **192**, **194**, and dimethyl diallylmalonate.[162] The catalytic activity shown by this complex was similar to that of the monometallic species **101a**.

RCM of enynes is one of the most powerful methods presently available for generating conjugated alkenyl cycloolefins with atom economy.[255] This cycloisomerization reaction is also promoted by allenylidene−ruthenium precursors. Thus, the straightforward synthesis of 3-vinyl-2,5-dihydrofurans **205** from enynes **204** could be achieved using catalytic amounts of [RuCl(=C=C=CPh_2)(η^6-*p*-cymene)(PCy_3)][PF_6] (**101a**) after initial UV activation of the catalyst (Scheme 54).[256] Complex **101a**, as its triflate salt, was also applied in the modification of the terpenoid derivatives **206** and **208**, with the corresponding spirocyclic dienes **207** and **209** being generated in quantitative yield (GC) after heating at 80 °C for 24 h, prior to photochemical activation of the catalyst.[257]

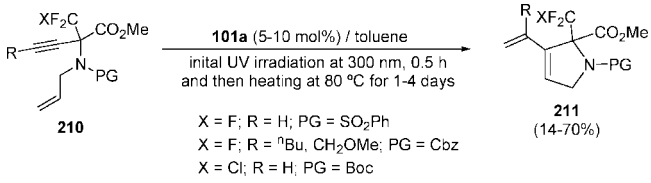
Allenylidene **101a** (as the TfO^- salt) also gave access to a variety of vinyl cyclic amino acid derivatives **211** by RCM of fluorinated amino esters **210** with the enyne structure (Scheme 55).[258] However, compared to the precedent cases, extremely long reactions times and higher catalyst loadings were required in this case.

On the basis of kinetic studies and stoichiometric reactions,[161,163,164] it could be demonstrated that the real active catalytic species involved in the RCM reactions promoted by complex [RuCl(=C=C=CPh_2)(η^6-*p*-cymene)(PCy_3)][X] (**101a**) is the corresponding indenylidene derivative **103**, whose formation is favored in acidic media via intramolecular rearrangement of the dicationic alkenylcarbyne intermedi-

Scheme 54



Scheme 55



ate **102** (Scheme 27). Indeed, addition of HBF_4 or HOTf to **101a** revealed a significant increase in catalyst activity in the RCM reaction of dienes and enynes. As an example, in the presence of 5 equiv of HOTf, **101a** (0.02 mol %) was able to transform quantitatively *N*,*N*-diallyltosylamide **192** into *N*-tosyldihydropyrrole **193** after only 30 min at 0 °C.[161,164] Apparently, once **103** is formed, the stronger steric interaction between the indenylidene group and the arene ligand forces the decoordination of the latter, thus generating the required vacant sites for substrate binding. The utility of the isolated indenylidene complex **103** in RCM, as well as ring-opening metathesis polymerization (ROMP) reactions, was explored in detail by Dixneuf and co-workers.[161,164] In this context, it must be noted that other indenylidene−ruthenium(II) complexes, generated by rearrangement of transient allenylidenes, are presently well-recognized and widely used initiators in olefin metathesis.[259]

In addition to half-sandwich arene complexes, other ruthenium allenylidenes have been tested as catalyst precursors in RCM reactions of dienes. Reported examples include (Chart 25) (i) the cationic 18-electron complex **212** containing a hemilabile phosphine,[97] (ii) the neutral 18-electron NHC-based derivative **213**,[260] and (iii) the 16-electron derivatives **214**−**217**.[109,260] Moderate activity was observed in all cases.

7.1.1.2. ROMP Reactions. The ring-opening metathesis polymerization (ROMP) of cyclic olefins constitutes an excellent method to synthesize linear polymers with regularly disposed CH=CH bonds.[250] In this context, it was demonstrated that the allenylidene complex [RuCl(=C=C=CPh_2)(η^6-*p*-cymene)(PCy_3)][OTf] (**101a**) promotes, at room temperature, the ROMP of norbornene much faster than the precursor [$RuCl_2$(η^6-*p*-cymene)(PCy_3)]. Thus, using 0.1 mol % of **101a**, polynorbornene with high molecular weight (M_n = 198 000 g/mol) and low polydispersity (M_w/M_n = 1.8) was generated in 90% yield after only 5 min at r.t.[261] Complex **101a** was also active in the polymerization of the less-strained cyclooctene. However, previous activation of the catalyst, either thermally or by UV irradiation, was in this case necessary to achieve good conversions at room temperature.[261] ROMP of norbornene with **101a** was also carried out in a biphasic medium consisting of the ionic liquid [bdmim][PF_6] (bdmim = 1-butyl-2,3-dimethylimidazolium) and toluene.[262] Good catalytic activity was maintained within four consecutive cycles (96−99% yields after 30 min at 40 °C using 0.3 mol % of **101a**), without significant influence on the M_n (113 800−206 700 g/mol) and M_w/M_n (1.8−1.9) values after each successive run. Moreover, probably because of its ionic nature, complex **101a** showed better recycling ability than neutral standard Grubbs-type first- and second-generation catalysts [$RuCl_2$(=CHPh)(PCy_3)$_2$] and [$RuCl_2$(=CHPh)(PCy_3)(H_2IMes)] (H_2IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene), respectively. It is also worth noting that, as observed in the RCM reactions of dienes and enynes, the rate of polymerization can be dramatically accelerated by adding a strong acid to the initiator **101a** (in situ formation of the active indenylidene species **103**). Thus, impressive TOF values of 1 096 000 and 44 444 h^{-1} could be reached in the room-temperature ROMP of cyclooctene and cyclopentene.[161]

Several arene-free ruthenium−allenylidene complexes, such as **212**,[97] **215**−**217**,[260] [$RuCl_2$(=C=C=CPh_2)(PCy_3)$_2$(DMSO)],[83] [$RuCl_2$(=C=C=CPh_2)(PCy_3)(DMSO)$_2$],[83] [RuCl(=C=C=CPh_2)(PCy_3)(DMSO)$_2$][OTf],[83] and [RuCl(=C=C=CPh_2)(PCy_3)$_2$(DMSO)$_2$][OTf],[83] were also tested in the ROMP of cyclic olefins, but their efficiencies were found to be lower than that of **101a**.[263]

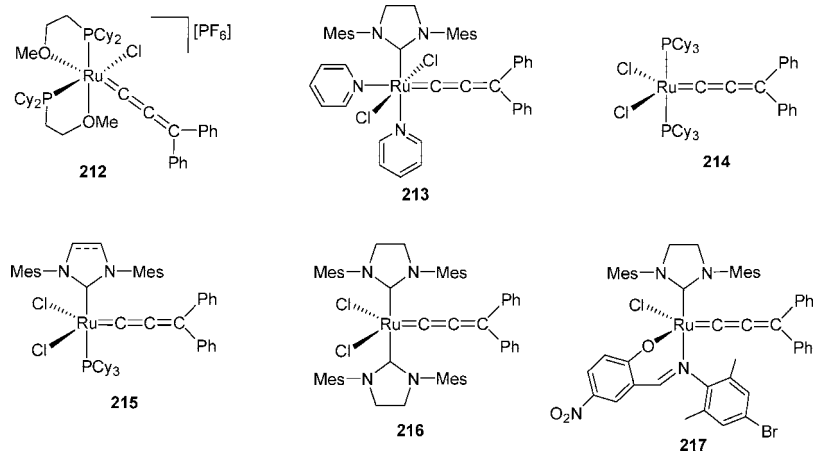
7.1.1.3. Cross-Olefin Metathesis and Acyclic Diene Metathesis Reactions. Cross-olefin metathesis of cyclopentene with methyl acrylate using as catalyst the water-soluble allenylidene−ruthenium(II) complex [{RuCl(μ-Cl)(=C=C=CPh_2)(TPPMS)$_2$}$_2$] (**41** in Chart 9), bearing the water-soluble sulfonated phosphine TPPMS, has been described (Scheme 56).[120] The nature of the resulting polyunsaturated ester was found to be dependent on the solvent employed. Thus, while the selective formation of ester **218** (56% yield after 2 h) occurred under monophasic conditions (MeOH), a 1:12 mixture of **218** and **219** was formed in the biphasic system Et_2O/H_2O (42% yield after 2 h).

Acyclic diene metathesis (ADMET) polymerization of decadiene could be efficiently performed with allenylidene **101a** after activation with HOTf (Scheme 57).[161]

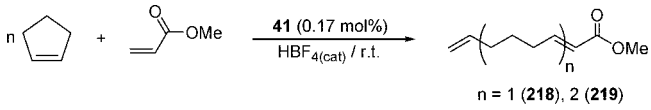
7.1.2. Other Catalytic Reactions

Several cationic mononuclear Ru(II)−allenylidenes of general composition [RuCp{=C=C=C(Ar)Ph}(PMe_3)$_2$][PF_6] (**57** in Chart 13) were found to catalyze the hydrogenative dimerization of tributyltin hydride, in acetonitrile or dichloromethane solution, under nitrogen or air atmosphere.[130] Best results in terms of activity were observed using 1.4 mol% of [RuCp{=C=C=C(2-C_6H_4C≡CMe)Ph}(PMe_3)$_2$][PF_6], which led to the quantitative formation of (^{n}Bu_3Sn)$_2$ after only 5 min at r.t. in air. Oxidative addition of the tin hydride across the allenylidene unit, with concomitant release of PMe_3, makes available the 16-electron Ru(IV) intermediate **220** (Scheme 58), considered by the authors to be the real active species. Then, a sequence of

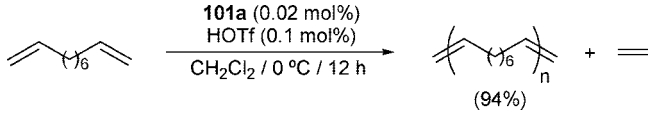
Chart 25



Scheme 56



Scheme 57



classical σ-bond metathesis steps generates the corresponding Sn−Sn and H−H bonds of the products.

In the presence of an appropriate initiator (ethyl 2-bromo-2-methylpropionate, methyl 2-bromopropionate, or (1-bromoethyl)benzene), cationic allenylidenes [RuCl(=C=C=CPh_2)(η^6-*p*-cymene)(L)] (L = PCy_3, 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene (**75**)) implemented the controlled atom transfer polymerization of vinyl monomers such as styrene, methyl methacrylate, methyl acrylate, and isobutyl methacrylate.[170] The reactions, which were performed in toluene at 85−110 °C using a 800:1:2 [monomer]/[Ru]/[initiator] ratio, delivered the corresponding polymers (up to 80% yield after 16 h) with high molecular weights (M_w = (10.0 × 10^3)−(167 × 10^3)) and a narrow polydispersity (M_w/M_n = 1.18−1.56). Improvements on the activity were observed by adding additives or transforming the allenylidene entity into a Fischer-type carbene.

Selective transetherifications of linear and cyclic vinyl ethers under nonacidic conditions using the water-soluble ruthenium allenylidene **41** (5 mol%; see Chart 9) have been described.[264] The reactions performed in methanol afforded acetals, while the corresponding aldehydes or ketones were obtained in a $CHCl_3/H_2O$ mixture.

As commented previously, the diphenylallenylidene complex [MnCp(=C=C=CPh_2)$(CO)_2$] was shown to catalyze the reduction of protons from HBF_4 into dihydrogen in acetonitrile at −0.84 V.[202] This working potential is the lowest reported to date for protonic acids reduction in nonaqueous media. The catalytic cycle involves C_β-protonation of the allenylidene unit to form the cationic carbyne [MnCp{≡CC(H)=CPh_2}$(CO)_2$]$^+$, followed by its reduction to the corresponding 19-electron radical [MnCp{≡CC(H)=CPh_2}$(CO)_2$]$^\bullet$. This radical undergoes a rapid homolytic cleavage of the C_β−H bond generating an H-radical, which produces the molecular hydrogen, with concomitant recovery of the neutral metallacumulene.

Despite the known ability of allenylidene−ruthenium(II) complexes to perform RCM of diolefins, allenylidene complexes generated in situ by treatment of [$RuCl_2$(η^6-arene)(L)] (L = *N*-substituted imidazolines or benzimidazoles) with AgOTf and HC≡$CCPh_2$(OH) were found to catalyze selectively the cycloisomerization of *N*,*N*-diallyltosylamide **192** to *N*-tosylpyrrolidine **221**, without formation of the expected *N*-tosyl-2,5-dihydropyrrole **193** (Scheme 59).[171] No involvement of the allenylidene moiety in the catalytic cycle was proposed by the authors, with displacement of the arene ligand being solely responsible for the observed reactivity.

7.2. Reactions Involving Allenylidene Complexes as Intermediates

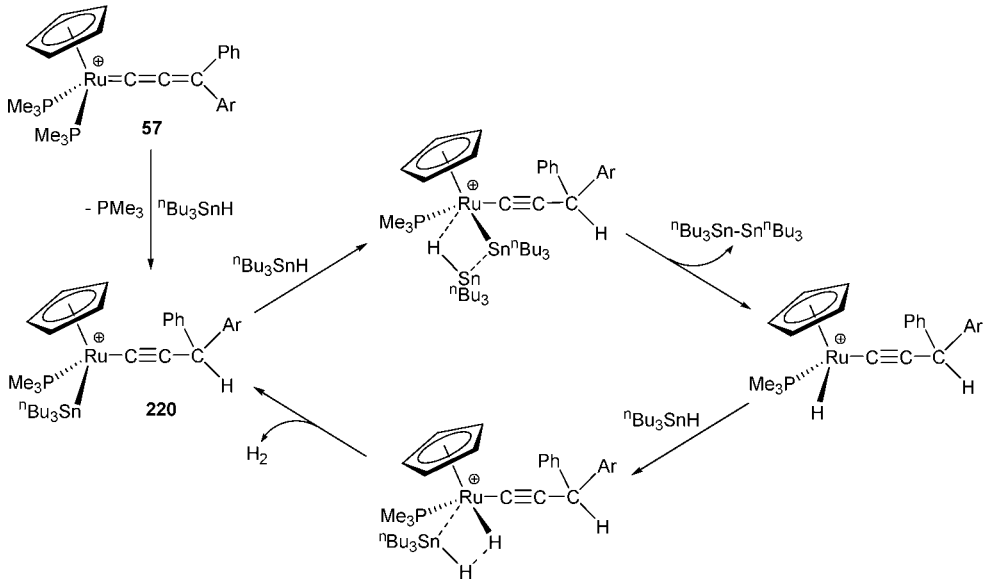
7.2.1. Propargylic Substitution Reactions

7.2.1.1. Propargylic Substitutions With Heteroatom-Centered Nucleophiles. In sharp contrast to the widely studied metal-catalyzed substitution reactions of allylic substrates,[265] related transformations involving propargylic derivatives have not been studied in much detail until recently.[266] In this context, the ability shown by transition-metal allenylidenes to undergo nucleophilic additions at the C_γ atom of the cumulenic chain has allowed the development of efficient catalytic processes for the direct substitution of the hydroxyl group in propargylic alcohols.[267] These transformations represent an appealing alternative to the well-known and extensively investigated Nicholas reaction, in which stoichiometric amounts of [$Co_2(CO)_8$] are employed.[268]

Studies of propargylic substitution reactions, through metal allenylidene intermediates, were initiated in 2000 by the collaborative work of Nishibayashi, Hidai, and Uemura, using as catalyst precursors the thiolate-bridged diruthenium(III) complexes [{Cp*RuCl(μ-SR)}$_2$] (R = Me (**222a**), Et (**222b**), ^{n}Pr (**222c**), ^{i}Pr (**222d**)) and [Cp*RuCl(μ-SR)$_2$-RuCp*(OH_2)][OTf] (R = Me (**223a**), ^{i}Pr (**223b**)) (Chart 26).[267]

Thus, as shown in Scheme 60, in the presence of catalytic amounts of complex **222a** and NH_4BF_4, reactions of propargylic alcohols bearing a terminal C≡C unit with a variety of heteroatom-centered nucleophiles, such as alcohols, amines, amides, and diphenylphosphine oxide, gave the corresponding propargylic-substituted products **224**−**227** in moderate-to-high yields with complete selectivity.[151,269] The nature of the bridging thiolate ligands or the replacement of

Scheme 58



Scheme 59

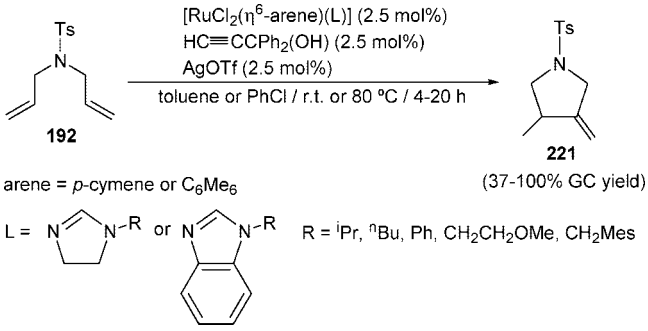
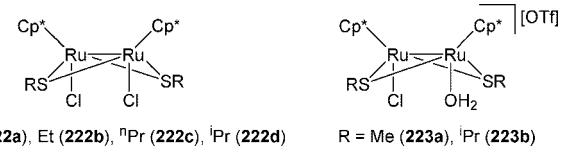


Chart 26



R = Me (**222a**), Et (**222b**), ^{n}Pr (**222c**), ^{i}Pr (**222d**) R = Me (**223a**), ^{i}Pr (**223b**)

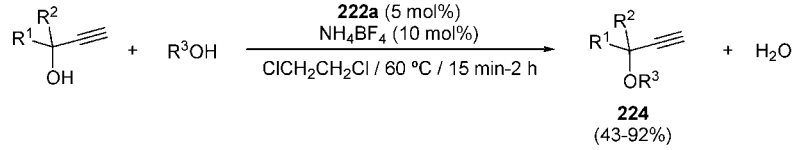
a terminal chloride ligand by water did not have much effect on the catalytic activity, with complexes **222b**−**d** and **223a**−**b** also being operative in these transformations. In contrast, conventional monometallic ruthenium derivatives, as well as diruthenium complexes having no Ru−Ru bond, did not work at all.[270] Concerning the scope of the process, when alcohols and amines were used as nucleophiles, propargylic alcohols bearing not only aryl but also alkyl substituents are tolerated, with substitution with alcohols being especially rapid. In contrast, with amides or diphenylphosphine oxide, only propargylic alcohols bearing aryl moieties reacted to give the corresponding propargylic substituted products **226**−**227**. In general, the reactions proceeded faster with secondary versus tertiary alkynols.

The proposed catalytic cycle for these reactions is shown in Scheme 61. Initially, a hydroxy−vinylidene complex **228** is formed in the reaction of the diruthenium complex with the propargylic alcohol. Dehydration of **228** leads to an allenylidene intermediate **229**, which undergoes selective addition of the heteroatom−hydrogen bond of the nucleophile across the C_γ=C_β double bond. Then, the resulting vinylidene complex **230** evolves into its η^2-coordinated propargyl tautomer **231**, which liberates the final product by the reaction with a second propargylic alcohol molecule and regenerates complex **228**. Stoichiometric reactions of isolated allenylidenes such as [Cp*RuCl(μ-SMe)Ru{=C=C=C(H)Ph}Cp*][BF_4]or[Cp*RuCl(μ-SMe)Ru{=C=C=C(C_6H_4Me-4)$_2$}Cp*][BF_4], prepared by treatment of **222a** with propargylic alcohols in the presence of NH_4BF_4, gave the corresponding propargylic-substituted products, confirming the proposed reaction pathway.[151,269] It is worth noting that, although complexes **222a** and **223a** are also able to promote propargylic substitutions using thiols as nucleophiles, the results obtained from stoichiometric reactions suggest that Ru-coordinated propargylic cations, instead of the corresponding allenylidene intermediates, are now involved in the catalytic cycle. Accordingly, the process was also operative with propargylic alcohols bearing internal C≡C bonds.[271]

The reason why only the diruthenium complexes are effective catalysts for these reactions is believed to be governed by the ruthenium moiety not involved in the allenylidene formation. To this regard, it was established that this ruthenium partner acts as an electron pool, facilitating the exchange of the coordinated propargylic-substituted product by the incoming propargylic alcohol in intermediate **231** (Scheme 62).[269] In order to prove the occurrence of such a synergistic effect, a series of chalcogenolate (S, Se, Te)-bridged diruthenium complexes, as well as hybrid phosphido/thiolato-bridged species, were prepared, their catalytic activity toward propargylic substitution reactions checked, and their electronic properties investigated by means of cyclic voltammetry. The results obtained showed that the easiness of the charge transfer from one Ru atom to the other (Ru^{III}−Ru^{III} → Ru^{II}−Ru^{IV}) is a key factor in promoting the ligand-exchange step.[152,153] Theoretical studies on the catalytic cycle using density functional calculations (B3LYP) also support this proposal.[128]

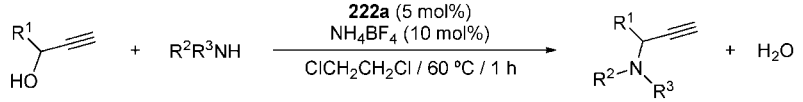
As shown in Scheme 63, the intramolecular version of these propargylic-substitution processes could be developed starting from appropriate propargylic alcohols bearing an additional hydroxyl group located at a suitable position on the molecule.[269] Moreover, the successful application of this methodology for the construction of rotaxanes **232** (Chart 27) has also been described starting from an ammonium-

Scheme 60



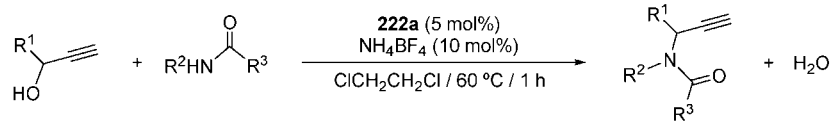
224
(43-92%)

R^1 = H; R^2 = Ph; R^3 = Et, Me, ^{i}Pr, Ph, CH_2CH_2Cl, $CH_2C(Cl)=CH_2$, $CH_2CH=CHPh$, $CH_2C{\equiv}CMe$
R^1 = H; R^2 = Ph; R^3 = (*S*)-$CH_2CH(Me)Et$, (*S*)-$CH_2CH(Me)Ph$, (*S*)-CH(Me)Et, (*S*)-CH(Me)Ph
R^1 = H; R^2 = Fc, *n*-C_5H_{11}; R^3 = Et
R^1 = R^2 = Ph, C_6H_4Me-4; R^3 = Et
R^1R^2 = -$CH_2(CH_2)_nCH_2$- (n = 2, 3); R^3 = Et



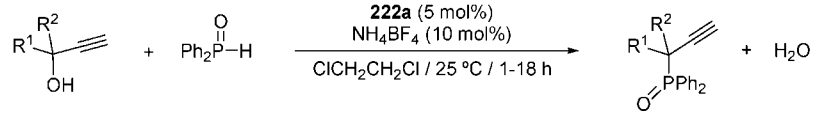
225
(16-88%)

R^1 = Ph, C_6H_4Me-4, C_6H_4OMe-4, C_6H_4F-4, C_6H_4F-4, 1-Napht, Cy; R^2 = H; R^3 = Ph
R^1 = Ph; R^2 = H; R^3 = $C_6H_4CF_3$-2, $C_6H_4CO_2Me$-2, $C_6H_4NO_2$-4, C_6H_4Me-4
R^1 = Ph; R^2 = Me; R^3 = Ph
R^1 = Ph; R^2R^3 = 2,2′-biphenyl



226
(18-78%)

R^1 = Ph, C_6H_4Me-4, C_6H_4OMe-4, C_6H_4F-4, C_6H_4Cl-4, 1-Napht, $CH=CPh_2$; R^2 = H; R^3 = Me
R^1 = Ph; R^2 = H; R^3 = ^{i}Pr, Cy, $CH=CH_2$, Ph, C_6H_4Me-4, C_6H_4Cl-4
R^1 = Ph; R^2 = Me; R^3 = Me, Ph
R^1 = Ph; R^2R^3 = -$CH_2(CH_2)_nCH_2$- (n = 0, 1, 2)



227
(67-96%)

R^1 = H; R^2 = Ph, C_6H_4Me-4, C_6H_4Me-3, C_6H_4Me-2, C_6H_4OMe-4, C_6H_4F-4, C_6H_4Cl-4, 1-Napht, $CH=CPh_2$
R^1 = R^2 = Ph, C_6H_4Me-4

functionalized alkynol and several heteroatom-centered nucleophiles, by performing the catalytic reactions with **222a** in the presence of dibenzo[24]crown8.[272]

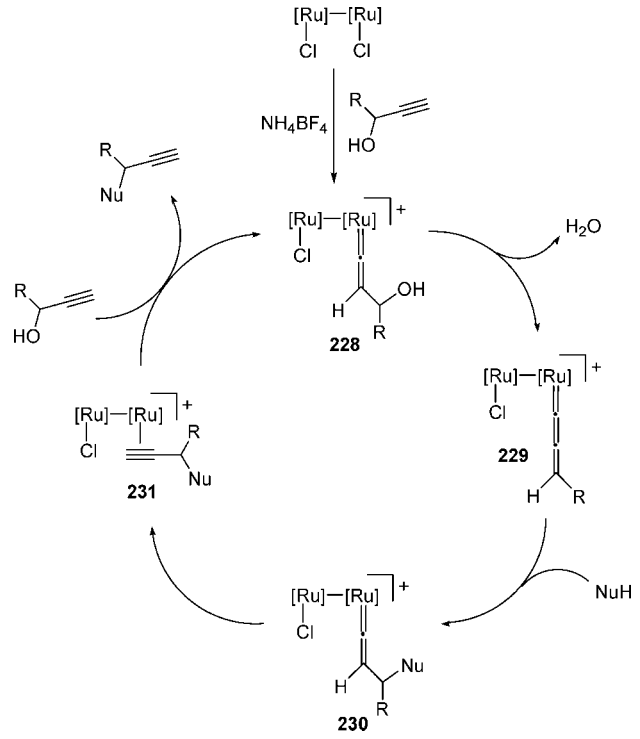
Interestingly, when the propargylation reactions with diphenylphosphine oxide were performed at 60 °C, instead of 25 °C, double phosphinylation of the alkynols occurred, giving the corresponding 2,3-bis(diphenylphosphinyl)-1-propenes **235** in high yields with a complete selectivity (Scheme 64).[273] Detailed investigation of the reaction pathway indicated the involvement of an allenyldiphenylphosphine oxide intermediate **234**, which results from a Ru-catalyzed tautomerization of the initially formed propargylic-substituted products **233**. Subsequent addition of $Ph_2P(O)H$ to **234** also catalyzed by **222a** generates the 2,3-bis(diphenylphosphinyl)-1-propenes **235**.

The unexpected and highly efficient formation of aryl(diphenyl)phosphine oxides **237** was observed when 1,1-diaryl-1-pentene-4-yn-3-ols **236** were treated with $Ph_2P(O)H$ in the presence of **222a** (Scheme 65).[274] As in the precedent case, the process involves the formation of an allenyl intermediate that now evolves into the final products by intramolecular cyclization and aromatization.

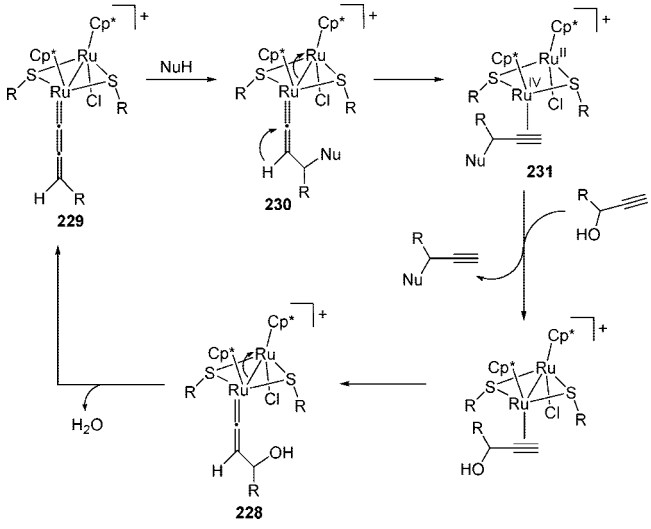
An elegant and straightforward route for the synthesis of oxazoles **240** starting from secondary alkynols and amides by the sequential action of complex **222a** and $AuCl_3$ has also been described (Scheme 66).[275] In this transformation, the corresponding propargylic amides **238** are initially formed by the action of **222a**. Then, an $AuCl_3$-catalyzed isomerization of **238** into allenamides **239** occurs, which is followed by a final intramolecular cyclization step, also promoted by $AuCl_3$, to give the substituted oxazoles **240**.

7.2.1.2. Propargylic Substitutions With Carbon-Centered Nucleophiles. Propargylic substitutions catalyzed by the thiolate-bridged diruthenium complexes **222a**−**d** and **223a**−**b** also take place with carbon-centered nucleophiles. Thus, reactions of secondary propargylic alcohols with acetone (used as solvent) in the presence of **222a** proceeded quite smoothly to give the corresponding alkylated products **241** in high yields (Scheme 67).[276] This C−C bond-forming reaction proceeds through the nucleophilic attack of the

Scheme 61



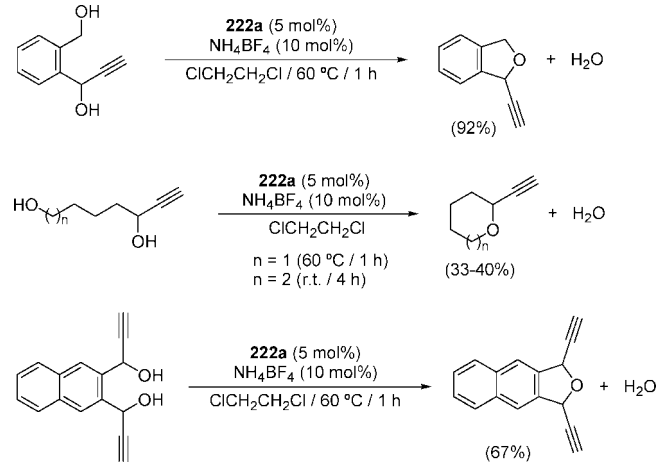
Scheme 62



acetone enol tautomer on the corresponding Ru−allenylidene intermediate. Other simple ketones such as diethyl ketone, cyclopentanone, and cyclohexanone, as well as silyl enol ethers, also afforded the corresponding γ-keto-alkynes with complete selectivity. A striking regioselectivity was observed when unsymmetrical ketones were used as substrates, with the propargylic alkylation occurring at the more encumbered α-site of the ketones (compounds **242** and **243**).

Asymmetric approaches to γ-keto-alkynes **241**, through the incorporation of a bridging chiral thiolate ligand into the diruthenium catalyst, have been investigated.[277] In particular, among the different catalysts designed, the best enantioselectivities (62−82% ee) were obtained with complex **222e** (Chart 28). The chiral induction of the process is believed to be determined by $\pi-\pi$ interactions between one of the aromatic rings of the thiolate ligand and the aryl substituent of the alkynol in the corresponding allenylidene intermediate. Unfortunately, the asymmetric reaction only worked for

Scheme 63



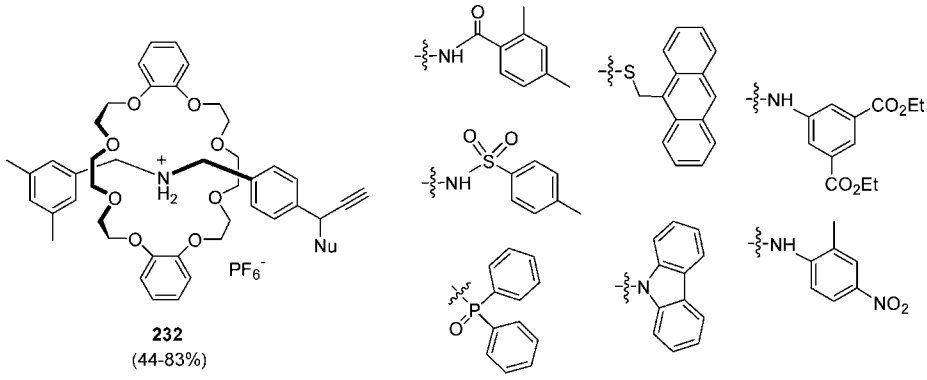
acetone; other simple ketones such as 2-butanone proceeded very sluggishly.

On the basis of this alkylation process of alkynols with acetone, an original synthetic route to furans was developed, via ruthenium- and platinum-promoted sequential reactions (Scheme 68).[278] The process, which proceeds in a one-pot manner, involves the initial formation of the γ-ketoalkyne **241**, by the aid of **222a**, which subsequently undergoes a regioselective catalytic hydration of the C≡C bond promoted by $PtCl_2$. Then, the resulting 1,4-diketone **244** evolves into the final trisubstituted furan **245** through a Pt-catalyzed Paal−Knorr cyclocondensation. As shown in Scheme 67, several secondary alkynols could be transformed into the corresponding furans **245** in moderate-to-good yields (24−74%), employing acetone by itself as solvent under refluxing conditions. The generality of this sequential transformation was confirmed by using other enolizable ketones such as 2-butanone, 3-pentanone, cyclohexanone, and cycloheptanone. Moreover, by introducing anilines ($ArNH_2$) in the reaction media, *N*-aryl pyrroles **246** could be selectively synthesized (Chart 29).[278] In this case, the reaction was considered to proceed through the platinum-catalyzed hydroamination of the C≡C bond of **241**, followed by Paal−Knorr cyclocondensation of the resulting imines.

The diruthenium complexes **222a**−**d** also catalyze the substitution reactions of terminal secondary alkynols with simple alkenes and 1,3-conjugated dienes, leading to the selective formation of 1,5-enynes **247** and dienynes **248**−**249** (Scheme 69).[279] Although these catalytic transformations were initially considered to proceed through a concerted allenylidene-ene mechanism,[279] recent DFT calculations pointed out that nucleophilic attack of the olefinic π-electrons on a carbocationic ruthenium−alkynyl [Ru]−C≡C−C^+HR complex, a resonance structure of the allenylidene intermediate $[Ru]^+$=C=C=CHR, is really involved in the catalytic cycle.[280] It should be noted also that, by changing the reaction solvent from 1,2-dichloroethane to simple alcohols, oxypropargylation of the alkene was observed.[281]

The intramolecular version of these C−C bond-forming reactions has also been described. Thus, in the presence of catalytic amounts of complexes **222a**−**d**, propargylic alcohols **250** were cleanly converted into the substituted chromanes **251**, which were isolated as a mixture of two diastereoisomers, with the *syn* isomer being in all cases the major product (Scheme 70). The steric demand of the thiolate ligands in the diruthenium catalysts was found to affect

Chart 27



Scheme 64

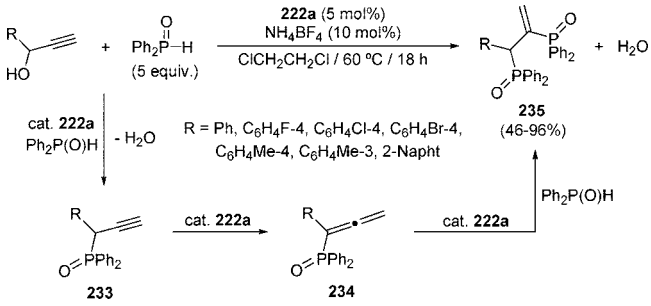
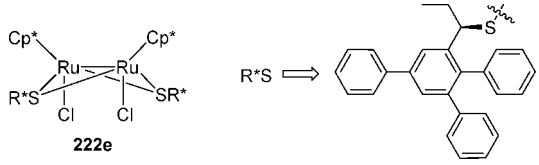


Chart 28

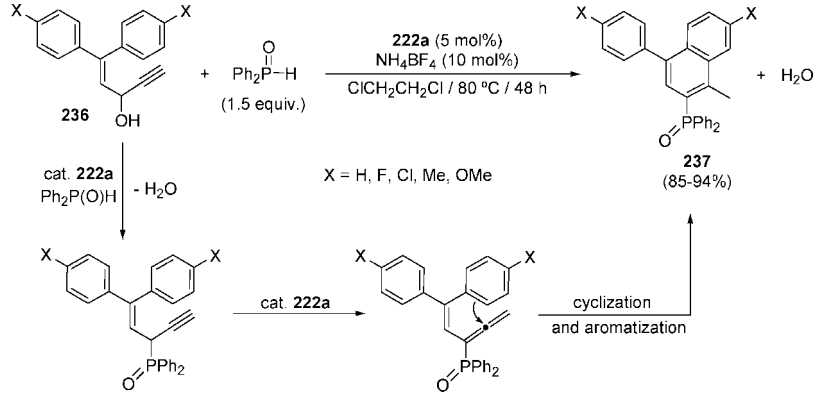


considerably the diasteroselectivity of the process, with the best results being achieved with complex [{Cp*RuCl(μ-S^{i}Pr)}$_2$] (**222d**), which contains the bulkier thiolates.[279a] It is worth noting that, by means of a classical Nicholas protocol, the diastereoselectivity of the produced chromanes is completely the reverse of that observed with **222a**−**d**.[282] As an extension of this work, quite recently, related enantioselective intramolecular cyclizations were reported using suitable chiral diruthenium complexes.[283] Moreover, when the cyclizations of propargylic alcohols **250** were performed in the presence of both **222d** and $PtCl_2$, the fused polycyclic compounds **252**, containing a bicyclo[3,1,0]hex-2-ene framework (Chart 30), could be synthesized in good-to-excellent yields via a Pt-catalyzed cycloisomerization of the in situ generated chromenes **251**.[284]

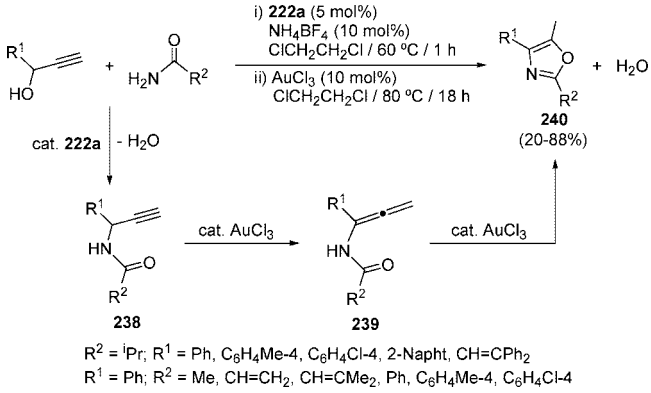
Propargylation of aromatic compounds can also be performed with Nishibayashi's catalysts.[285] Thus, as shown in Scheme 71, reactions of secondary propargylic alcohols with heteroaromatic compounds such as furans, thiophenes, pyrroles, and indoles in the presence of **222a** proceeded smoothly to afford the corresponding propargylated products **253** and **254** in high yields with complete regioselectivity. Viewed from the side of the aromatic compounds, the reaction can be considered as a typical electrophilic aromatic substitution. In agreement, the propargylation occurred in all cases selectively at the α-position of the heterocyclic rings, while the β-propargylated indole **254** was obtained in the reaction with indole. Intramolecular cyclization reactions starting from alkynols **255** were also operative, leading to the tricyclic species **256** (Scheme 72).[285b] Once again, the involvement of allenylidene intermediates was demonstrated through the stoichiometric reaction of isolated [Cp*RuCl(μ-SMe)Ru{=C=C=C(H)Ph}Cp*][BF_4] with 2-methylfuran, which led to the expected propargylated species 2-methyl-5-(1-phenyl-2-propynyl)furan as the sole reaction product.[285,286]

Not only heteroaromatic compounds but also electron-rich arenes, such as anilines, 1,3,5-trimethoxybenzene, 3,5-dimethylacetanilide, and azulene, could be propargylated using **222a**, with the corresponding aromatic products **257**−**259** being generated in moderate yields (Chart 31).[285] It is also worth noting that the asymmetric version of these reactions, using as catalyst the chiral diruthenium complex **222e** (Chart 28), has also been described (up to 95% ee).[287]

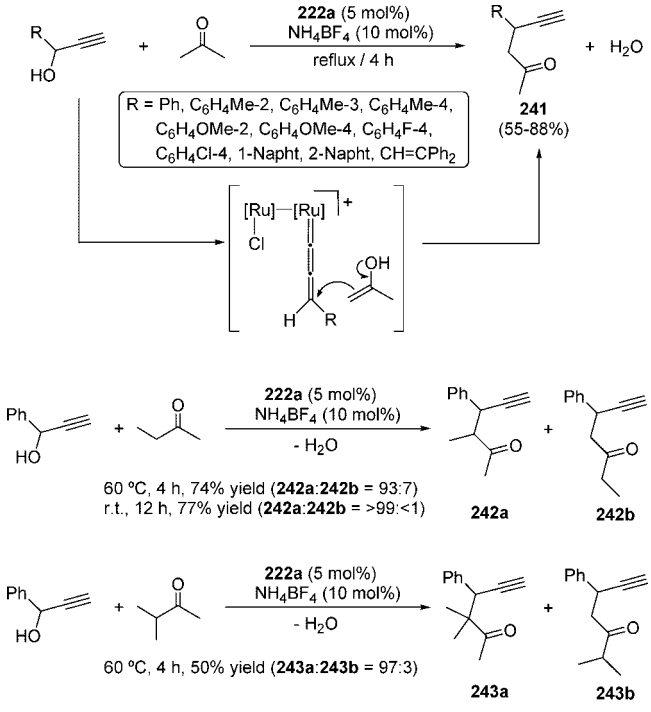
Scheme 65



Scheme 66



Scheme 67



Scheme 68

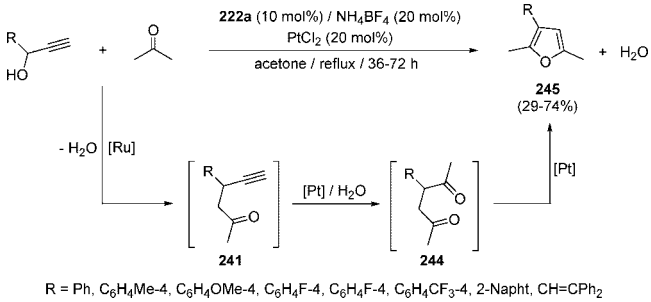
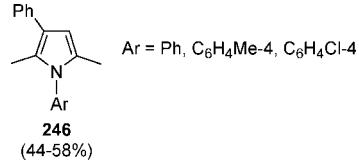


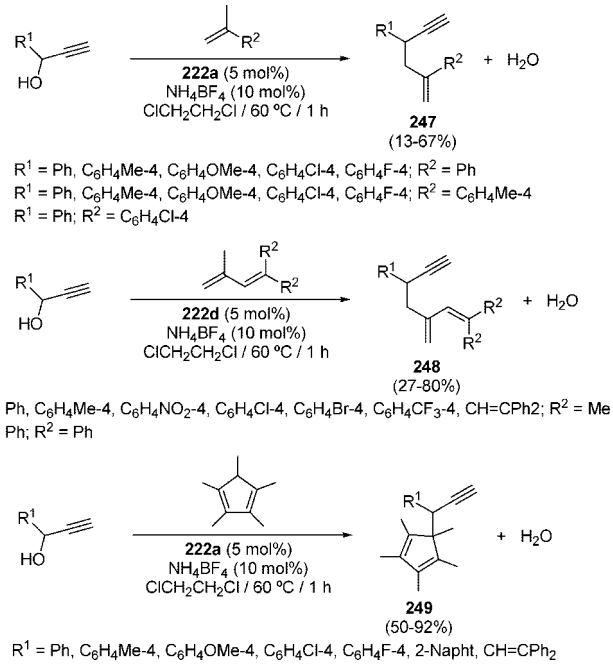
Chart 29



7.2.2. Cycloaddition Reactions

In sharp contrast to the alkylation reactions of propargylic alcohols with simple ketones catalyzed by **222a** (Scheme 67), related reactions with six- and five-membered cyclic 1,3-diketones led to the unexpected formation of chromenone and pyranone derivatives **260** and **261**, respectively (Scheme 73).[288] Similarly, starting from cyclic β-keto esters cycloaddition, products **262** and **263** were synthesized in excellent yields. The stoichiometric reaction of isolated allenylidene complex [Cp*RuCl(μ-SMe)Ru{=C=C=C(H)Ph}Cp*][BF_4] with 1,3-cyclohexanedione gave the corresponding chromenone **260**, confirming the involvement of the cumulenic species in this cycloaddition process. A reaction sequence consisting of the initial nucleophilic attack of the dicarbonyl compound to the C_γ atom of the allenylidene intermediate **229** to give vinylidene **264**, which evolves into **265** by intramolecular nucleophilic attack of the enol unit to the C_α atom of **264**, was proposed by the authors. Interestingly, this process is highly sensitive to the nature of the 1,3-dicarbonyl compound, the use of acyclic 1,3-diketones and β-keto esters, and even seven-membered ring cyclic 1,3-diketones, leading to the exclusive formation of the corresponding alkylated propargylic products.

Scheme 69



Cycloaddition reactions of secondary alkynols with 2-naphthols and phenols bearing electron-donating groups to afford the corresponding 1*H*-naphtho[2,1-*b*]pyrans **266** and 4*H*-1-benzopyrans **267**, respectively, catalyzed by **222a** have also been described (Scheme 74).[289] Two independent reaction pathways, where either the aromatic carbon (path A) or the oxygen (path B) atom of the phenolic substrates may work as nucleophile, were proposed for this coupling process. The first one (path A) involves the initial nucleophilic attack of the carbon at 1-position of phenols or 2-naphthols to the C_γ atom of the allenylidene intermediate **229** to give vinylidene **268**, which subsequently evolves into an alkenyl complex **269** by nucleophilic attack of the alcohol functionality to the electrophilic carbenic C_α atom of **268**. Alternatively (path B), initial addition of the alcohol group across the C_α=C_β of allenylidene **229** can occur, leading to an α,β-unsaturated carbene **270**, which rearranges into **268** via a Claisen-type process.

Scheme 70

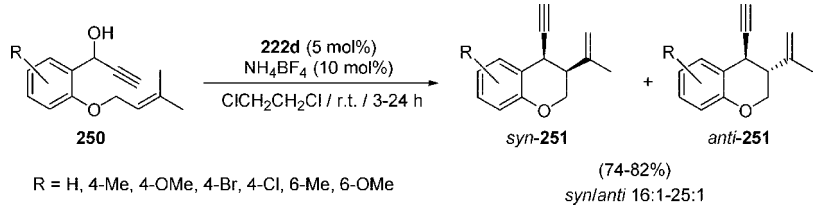
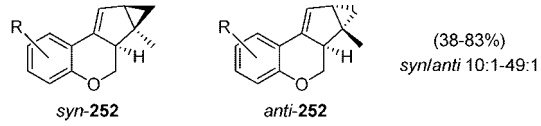
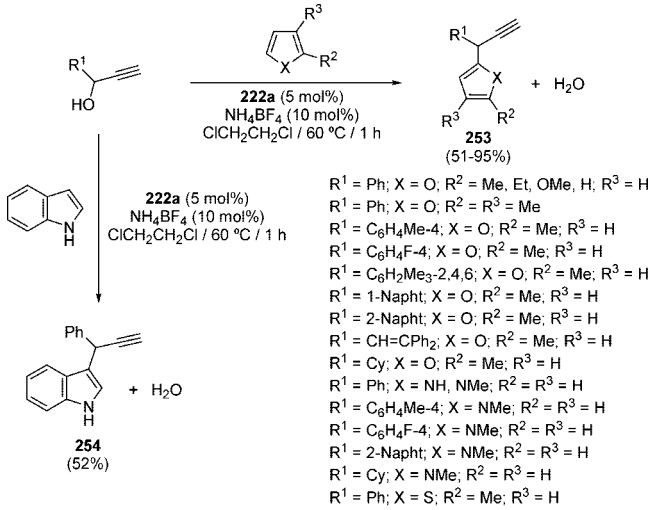


Chart 30



Scheme 71



Scheme 72

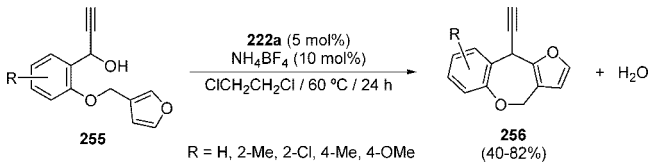
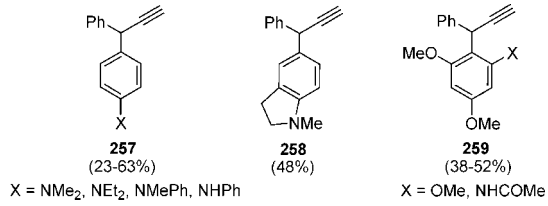


Chart 31



7.2.3. Meyer−Schuster Rearrangements

The Meyer−Schuster- and Rupe-type rearrangements of propargylic alcohols to α,β-unsaturated carbonyl compounds are useful transformations in synthetic organic chemistry (Scheme 75).[290] These textbook reactions are generally carried out at elevated temperatures in acidic medium or by using transition metal oxides as catalysts, which often give rise to nonregioselective transformations.[290] The exceptional ability shown by ruthenium catalysts to activate carbon−carbon triple bonds has recently created new opportunities for developing much milder and selective reactions, with Ru−allenylidene species being proposed as key intermediates in some cases.

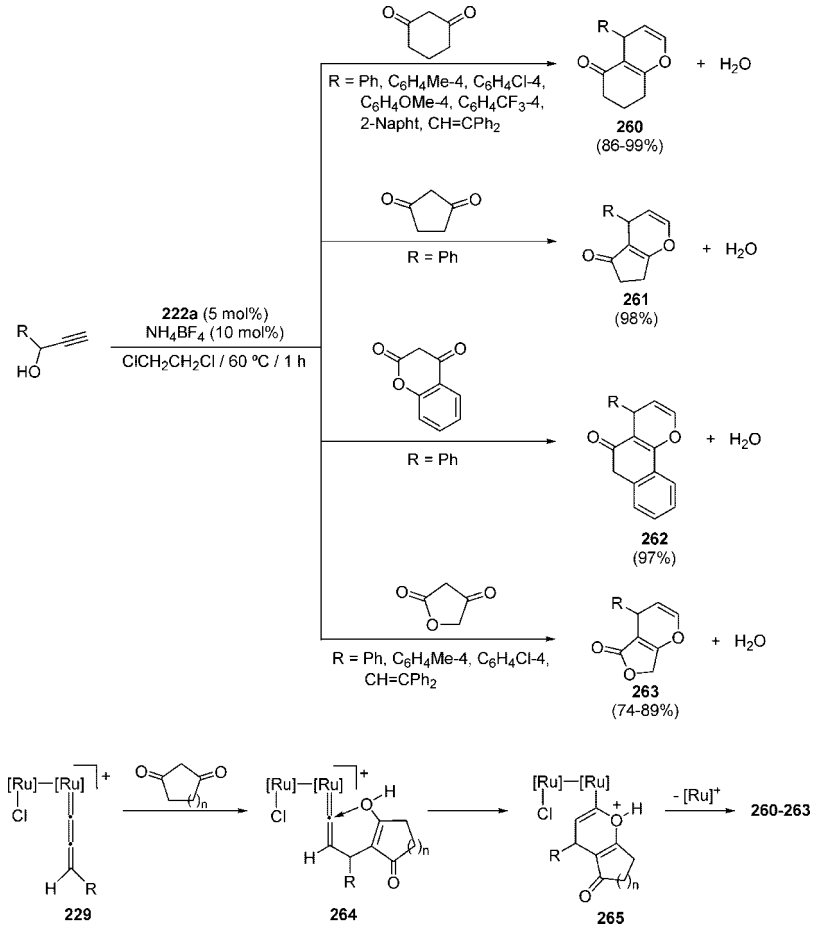
Thus, as shown in Scheme 76, Meyer−Schuster rearrangement of several monosubstituted propargylic alcohols could be achieved under neutral conditions employing catalytic amounts of [RuClCp(PMe_3)$_2$], with the corresponding enals **271** being isolated in high yields as mixtures of the corresponding *E* and *Z* isomers.[291] An *anti*-Markovnikov hydration of the alkyne moiety with concomitant dehydration of the original OH group has been proposed by the authors as a possible reaction pathway. Moreover, they have also suggested that nucleophilic addition of water to the electrophilic C_α of the hydride−ruthenium(IV) allenylidene **272** or hydroxy−vinylidene **273** could be involved in the hydration step. Although this transformation was found to be remarkably clean and proceeds under neutral conditions, it presents an important limitation concerning the nature of the alkynol, since tertiary propargylic alcohols remain completely unreacted under these conditions.

The 16e$^-$ (η^3-allyl)−ruthenium(II) derivative [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (**274**; dppf = 1,1′-bis(diphenylphosphino)ferrocene) was also found to catalyze efficiently the isomerization of both tertiary and secondary terminal propargylic alcohols into the corresponding enals **271** (Scheme 77).[270,292] The catalytic reactions were performed in THF at 75 °C, employing 5 mol% of complex **274** and 10 mol% of trifluoroacetic acid (TFA) as cocatalyst. Although in the absence of TFA complex **274** by itself is also able to catalyze these transformations, the introduction of TFA reduces drastically the reaction times. As an example, the total conversion of 1,1-diphenyl-2-propyn-1-ol into 3,3-diphenyl-2-propenal, in the absence of TFA, required 1.5 h, whereas it only required 0.2 h in the presence of TFA. A remarkable feature of catalyst **274** is that it is able to completely control the stereochemistry of the C=C bond formed. Thus, when secondary propargylic alcohols were employed as substrates, the resulting enals were exclusively formed as the thermodynamically more stable *E*-isomers.

The extremely sensitive nature of **274** toward the propargylic alcohols substituents merits being highlighted, since the catalytic isomerization of alkynols bearing a C−H bond in the β-position with respect to the alcohol group proceeded in a different way, affording selectively α,β-unsaturated methyl ketones **275** instead of the expected enals (representative examples are shown in Scheme 78).[292] These enones are the result of a formal Rupe-type rearrangement of the alkynol.

Scheme 79 shows the proposed mechanisms for the formation of enals **271** and enones **275**, respectively, catalyzed by complex **274**. The key intermediate in these isomerization reactions is, in both cases, a hydroxyvinylidene complex [Ru]$^+$=C=C(H)C(OH)R^1R^2 (**276**). The proposed formation of hydroxyvinylidene **276** is in agreement with the absence of catalytic activity observed when internal propargylic alcohols were used as substrates (i.e.,

Scheme 73



MeC≡CCH$_2$(OH) or (HO)MeHCC≡CCHMe(OH)), since they are not able to undergo the required tautomerization into a vinylidene species. Then, the fate of the catalytic cycle is dependent on the nature of the propargylic alcohol substituents. Thus, if no C−H bonds are present in the β-position with respect to the alcohol group (R^1 and $R^2 \neq CHR^3R^4$), dehydration of **276** generates an allenylidene complex **277**. The electrophilicity of the C_α carbon of the unsaturated chain in **277** favors the stereoselective *E* readdition of water to give the hydroxy−carbene derivative **278**. Finally, the demetallation of carbene **278** takes place, via the acyl intermediate **279**, affording the corresponding *E*-enals **271** and regenerating the catalytically active ruthenium species. In contrast, if a C−H bond is present ($R^2 = CHR^3R^4$), dehydration of hydroxyvinylidene **276** leads to the alkenyl−vinylidene **280**, instead of the allenylidene tautomer **277**, which is in equilibrium with its π-enyne isomer **281**. Then, Markovnikov addition of water to the coordinated C≡C bond in **281** occurs, affording the corresponding enones **275** via intermediates **282** and **283**.

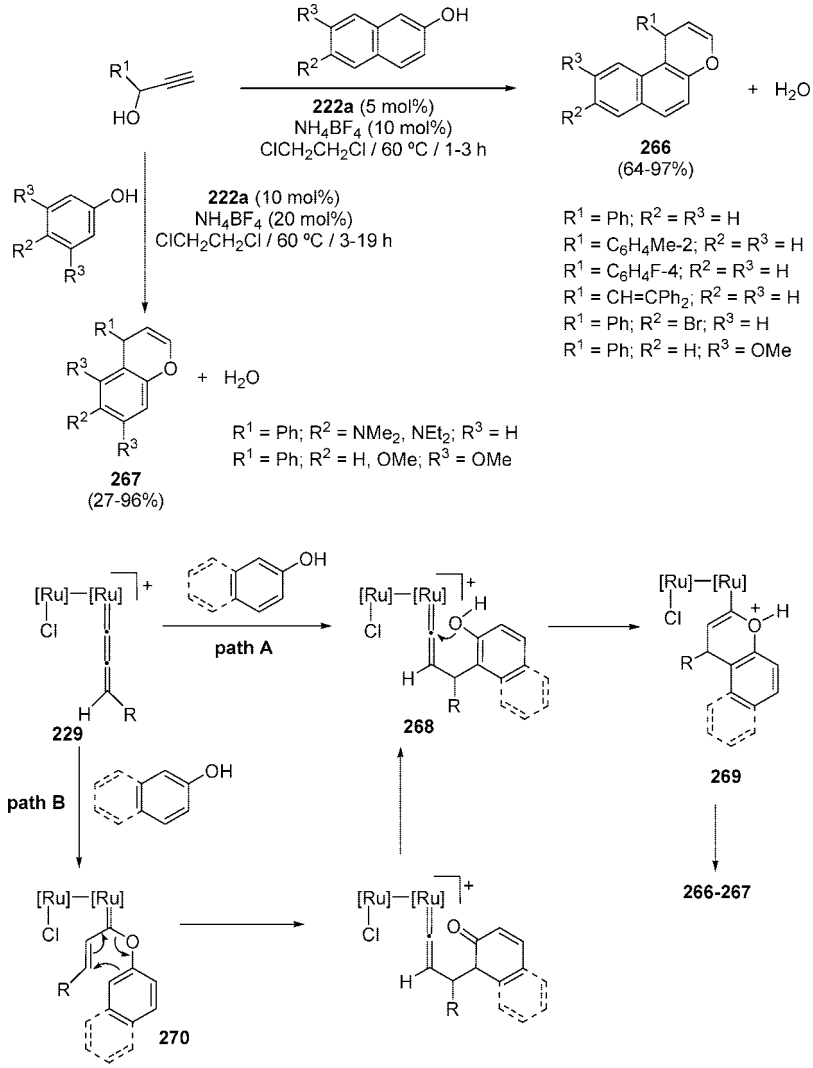
Taking advantage of the ability shown by complex **274** to promote Meyer−Schuster rearrangements, a general and efficient synthetic approach to 3,5-hexadien-2-ones **284** was developed starting from appropriate 1,1-diaryl- and 1-aryl-substituted propargylic alcohols and enolizable ketones (Scheme 80).[293] These highly unsaturated species result from the initial Meyer−Schuster rearrangement of the propargylic alcohol into the corresponding enal, which subsequently undergoes an aldol-type condensation with the ketone. The reactions proceeded with complete control on the stereoselectivity, with dienones **284** being obtained, in all cases, as the thermodynamically more stable *E* or *EE* isomers. Related coupling reactions of terminal alkynols with acetone were also described using the dicationic thiolate-bridged diruthenium(III) complex [Cp*Ru(μ-SMe)$_2$RuCp*(OH$_2$)][OTf]$_2$.[294] However, using this catalyst, the corresponding 3,5-hexadien-2-ones were isolated in low yields (<54%) after longer reaction times (ca. 70 h).

β-Dicarbonyl compounds were also operative in this coupling process. Thus, starting from 1,3-diketones and tertiary aryl-substituted propargylic alcohols, a variety of conjugated diene−diones **285** could be stereoselectively (*E*-isomers) prepared in excellent yields using the catalytic system **274**/TFA (Scheme 81).[293]

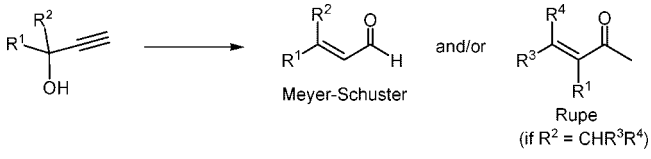
7.2.4. Other Catalytic Reactions

In addition to the propargylic substitution and cycloaddition processes discussed above, the thiolate-bridged diruthenium(III) complexes **222a**−**d** and **223a**−**b** (Chart 26) were found to promote other catalytic transformations of alkynols via ruthenium−allenylidenes as key intermediates. Thus, when monoaryl-substituted propargylic alcohols were treated with pinacolborane (H-Bpin) in the presence of a catalytic amount of **222a**/NH_4BF_4, selective formation of the corresponding 1,5-hexadiynes **286** (*dl* and *meso* isomers) was observed (Scheme 82).[295] Hydroboration of the initially produced allenylidene complex **229** at the C_β=C_γ double bond has been proposed as the key step in this reductive homocoupling process. Then, the resulting β-boravinylidene **287** is converted into the cationic radical complex **288** through radical fission assisted by adventitious molecular

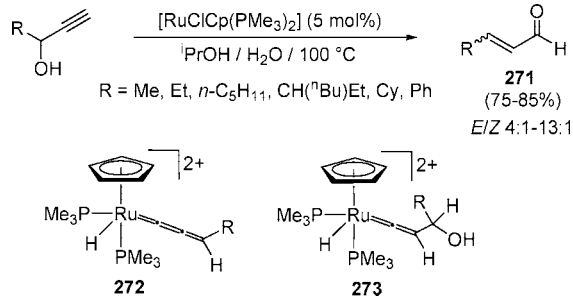
Scheme 74



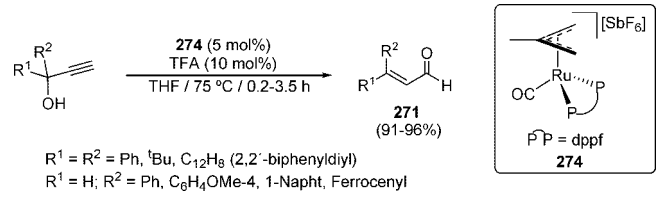
Scheme 75



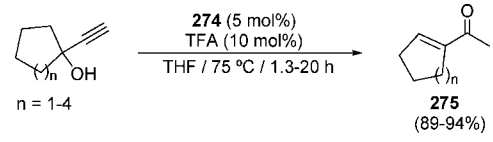
Scheme 76



Scheme 77



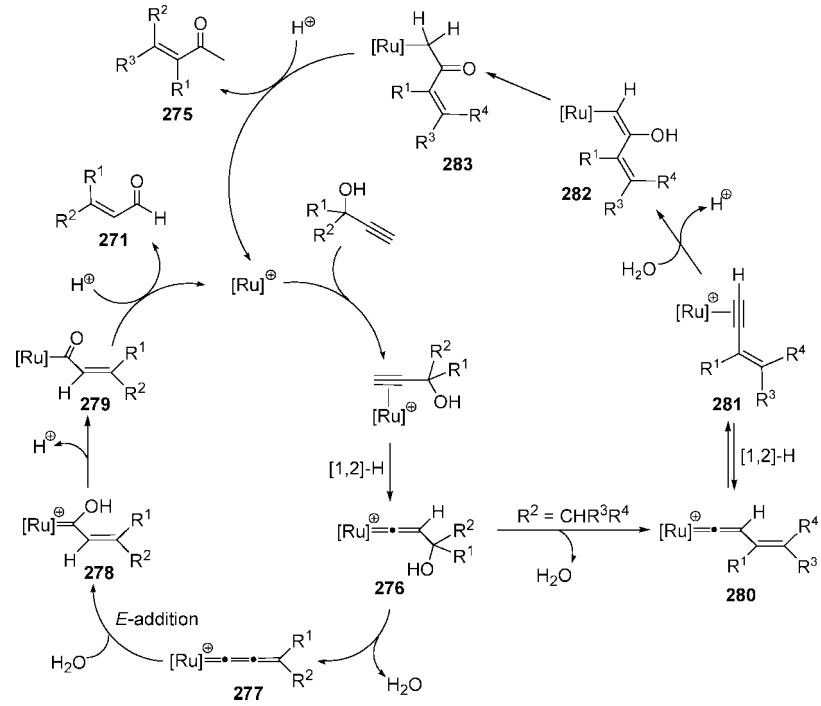
Scheme 78



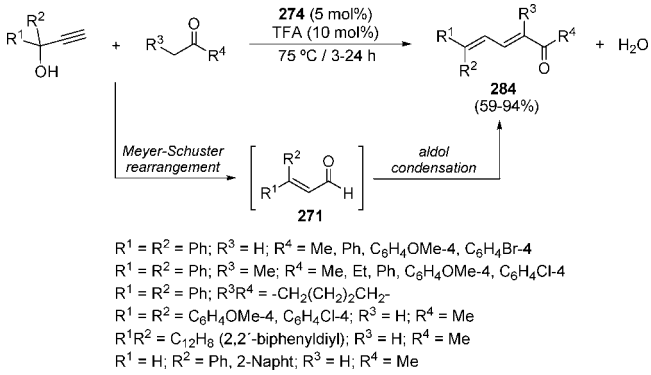
oxygen. Elimination of a proton at C_γ and radical migration from C_β to C_γ leads to the neutral complex **289**, in which the radical is stabilized by spin delocalization over the aryl group. Finally, intermolecular coupling between two radical species results in the formation of the final products.

Reactions of tertiary alkynols **290**, bearing a cyclopropyl group at the propargylic position, with nitrogen- and oxygen-centered nucleophiles, such as anilines or water, catalyzed by complex **223a** (or **222a** in the presence of NH_4BF_4) did not give the expected propargylic-substituted products. Instead, the conjugated enynes **294** were stereoselectively formed (*E*-isomers) in high yields (Scheme 83).[296] The proposed mechanism for this transformation, which was corroborated by DFT calculations and isolation of one of the key allenylidene intermediates, involves the direct attack of the nucleophile on the activated cyclopropane ring in intermediate **291**. This is followed by proton transfer from the nucleophile to the alkynyl moiety in **292** to give the

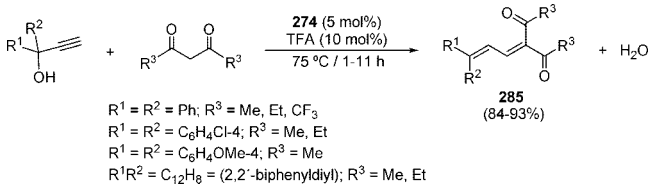
Scheme 79



Scheme 80



Scheme 81



corresponding vinylidene complex **293**, which, through a classical demetallation process, liberates the enyne.

Intramolecular cyclization of 3-butyne-1,2-diols **295** catalyzed by complex **222a** has been reported to yield the corresponding substituted furans **299** in good-to-excellent yields (Scheme 84).[297] Initial formation of allenylidene **296**, which tautomerizes into the vinyl−vinylidene **297**, followed by intramolecular nucleophilic attack of the hydroxyl group at the electrophilic Ru=C_α (intermediate **298**), has been proposed as a possible reaction pathway. Cyclization of 1-amino-1-phenyl-3-butyn-2-ol to afford 2-phenylpyrrole, catalyzed by [Cp*RuCl(μ-SMe)$_2$RuCp*(OH_2)][OTf] (**223a**), has also been described.[297]

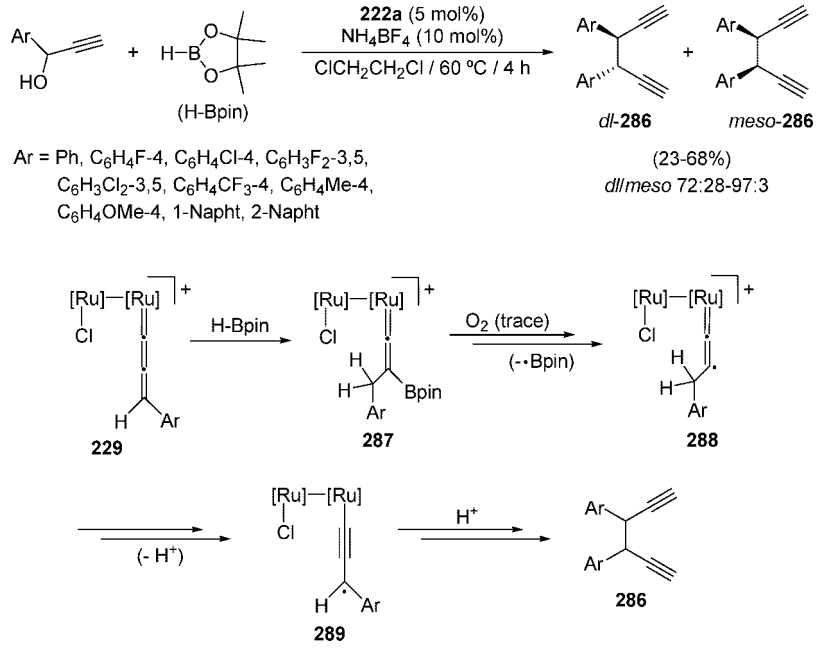
Catalytic activation of functionalized terminal alkynes using the cationic Ru(II) complex [RuTp(PPh_3)($NCMe)_2$][PF_6] (Tp = tris(1-pyrazolyl)borate) has been extensively explored by Liu and co-workers, with some of the reported examples involving the formation of highly reactive allenylidene intermediates.[298] Thus, in the presence of a catalytic amount of this complex and LiOTf, propargylic alcohols **300** were split into alkenes **301** and carbon monoxide (Scheme 85).[299] This C≡C bond-cleavage reaction seems to proceed via a cationic ruthenium−allenylidene intermediate, which traps the formed water molecule at C_α to generate an acyl complex that decomposes through decarbonylation. This catalyst was further employed for the catalytic fragmentation of propargylic ethers **302** into ketones **303**, ethylene, carbon monoxide, and hydrogen. Formation of a ruthenium−allenylidene intermediate with cleavage of the ether bond followed by nucleophilic attack of the free alcohol at the allenylidene C_α atom, hydrogen transfer to the metal, and substitution by water generates the ketone and an acyl complex that, as in the precedent case, undergoes decarbonylation.[300]

Complex [RuTp(PPh_3)($NCMe)_2$][PF_6] also promoted the conversion of 3-benzyl but-1-ynyl ethers **304** into 1,3-dienes **305** and benzaldehyde (Scheme 86).[301] The proposed mechanism entails again the initial formation of an allenylidene intermediate via cleavage of the ether bond.

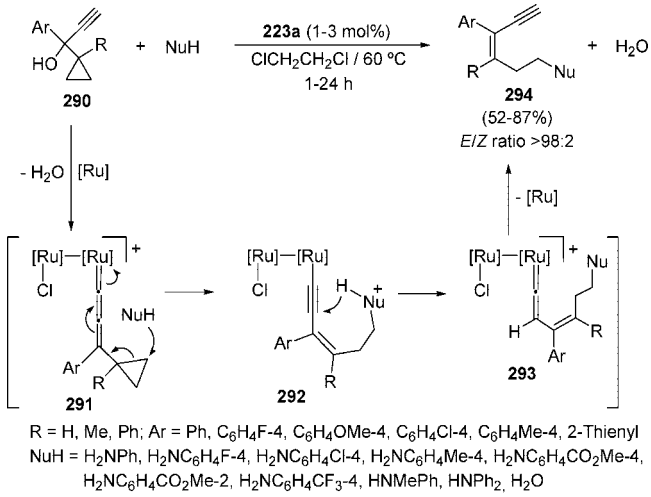
8. Catalytic Reactions Involving Higher Cumulenylidene Complexes

Implication of higher cumulenylidene complexes in catalytic processes is so far limited only to the vinylic substitution of trifluoromethanesulfonates **306** with 1,3-diketones and alcohols to give the vinylic ethers **307** and **308**, respectively (Scheme 87).[302] The latter are also accessible starting from α-ketoacetylenes **309**. These reactions, which are catalyzed by the diruthenium(III) complexes [{Cp*RuCl(μ-SR)}$_2$] (R = Me (**222a**), Et (**222b**)) and [Cp*RuCl(μ-SMe)$_2$RuCp*(OH_2)][OTf] (**223a**), are believed to proceed via a ruthenium−butatrienylidene complex as key intermediate, which under-

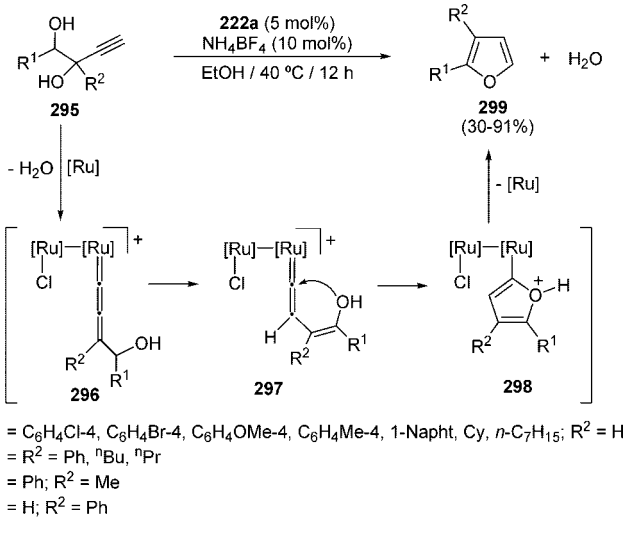
Scheme 82



Scheme 83



Scheme 84



goes O−H bond addition of the nucleophiles across the $C_\gamma=C_\beta$ double bond.

9. Conclusions

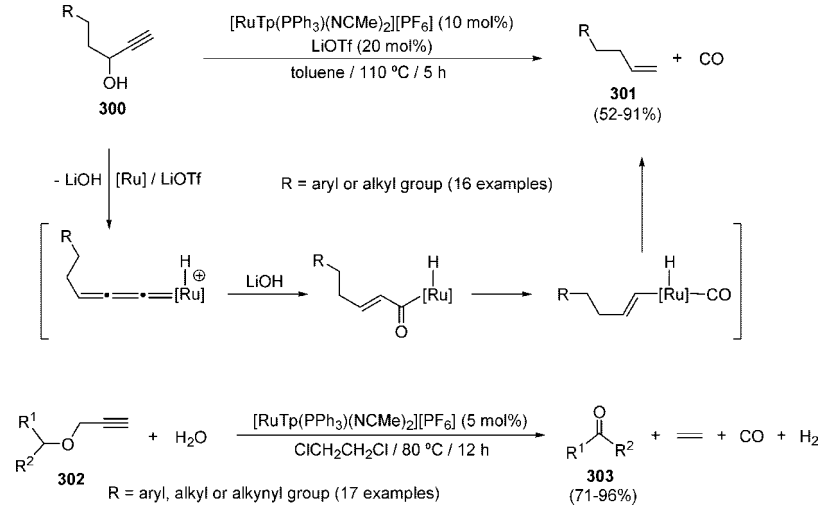
This review presents an updated "state of the art" of the chemistry of allenylidene and higher cumulenylidene complexes. Since the appearance of the last general review on this topic 10 years ago, very significant advances have been reported. This chemistry has grown in such a way that numerous brief accounts, specific surveys, and a book have appeared meanwhile. These facts reveal that these unsaturated carbene species readily accessible from propargylic alcohols and related terminal alkynes have received continuous interest during the past decade.

The growth of this chemistry stems mainly from the versatile reactivity due to the presence of unsaturated carbon chains, mostly bearing other functional groups, that provide multifaceted reactive sites (nucleophilic and electrophilic) of interest in organic synthesis. The steric and electronic influence on the reactivity, modulated by the transition-metal fragments, has also continued being used to favor selective processes. Nowadays, theoretical studies supported by the application of modern computational means (mainly DFT studies) have disclosed fundamental understanding of the structural and electronic features, providing a very useful rationalization of the experimental behavior.

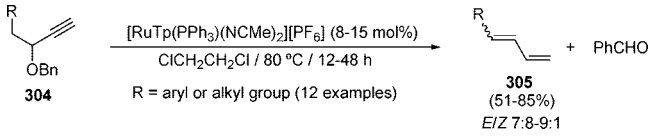
The remarkable developments on the utility of metal allenylidenes as catalytic precursors or as intermediates in transformations of propargylic alcohols (mainly OH-substitution reactions) and other multifunctional alkynes, as well as in metathesis of olefins, have triggered the increasing importance of metal allenylidenes. In this sense, taking advantage of the simultaneous presence of electrophilic and nucleophilic sites within the allenylidene chain, a huge number of new atom-economical processes have been designed.

Although the basic milestones of the chemistry of allenylidenes have been well-established, both experimentally and theoretically, the search for higher cumulenylidenes was an appealing goal, but it still remains as a matter of difficult accessibility. In this regard, it is worth mentioning the isolation of the first heptahexaenylidene complexes $[M\{=C=C=C=C=C=C=C(NMe_2)_2\}(CO)_5]$ (M = Cr, W),

Scheme 85



Scheme 86



albeit in low yield, exhibiting the longest cumulenylidene chain to date.[9]

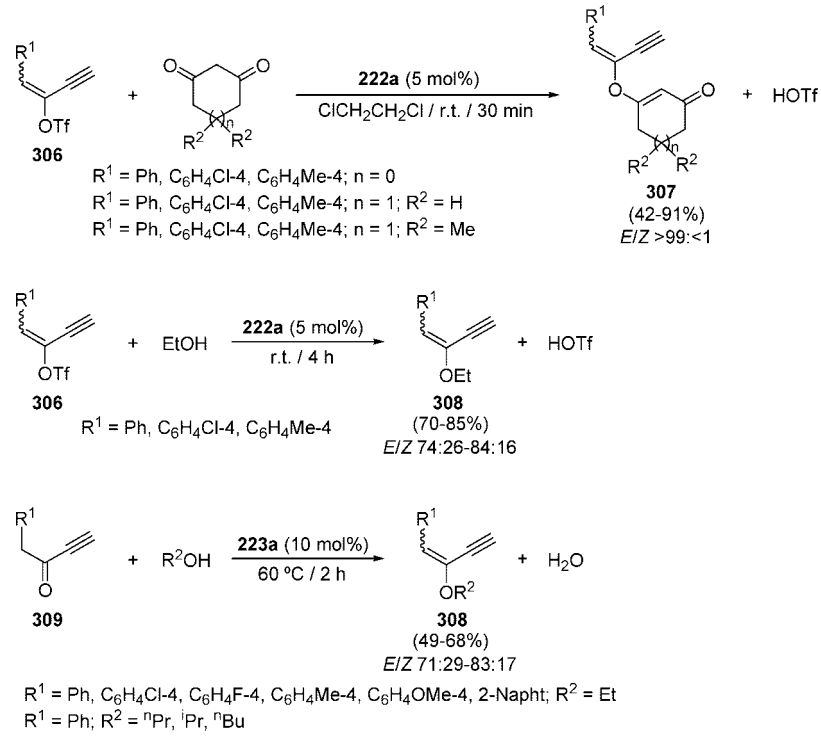
Despite all these numerous achievements, the chemistry of allenylidenes shows several aspects still unexplored. Among others, the following is noteworthy: (i) Besides the titanium complex $[TiCp_2(=C=C=CPh_2)(PMe_3)]$,[11] no further representations of early transition-metal complexes have been prepared, including d^6 Group 6 metal derivatives. (ii) In spite of the fact that the chemistry of rhodium and iridium allenylidenes is widely documented, no cobalt derivative has been prepared to date. (iii) Only one series of Group 10 metal complexes, $[PdBr\{=C=C=C(OR)NR_2\}(PR_3)_2][X]$, recently reported, is known.[12] No Group 11 metal allenylidenes have been isolated to date.[10]

Overall, this review shows that the chemistry of metal allenylidenes and higher cumulenylidenes not only has reached a remarkable level of conceptual and experimental knowledge but also has brought to light new perspectives with potential synthetic utility. It is apparent that these achievements would enhance the rapid growth of new developments, challenging the interest of those working in metal-promoted organic synthesis.

10. Acknowledgments

Current financial support by the Ministerio de Educación y Ciencia (MEC) of Spain (Projects CTQ2006-08485/BQU and Consolider Ingenio 2010 (CSD2007-00006)) and the

Scheme 87



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