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Review

Ruthenium-allenylidene complexes and their specific behaviour

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Contents

Abstract

This review presents recent innovations in the field of stoichiometric transformations of ruthenium-allenylidene systems via synthesis and at the frontier of material science and catalysis. It especially shows new routes to the first bis-allenylidene-ruthenium and diruthenium complexes, trisallenylidene ruthenium triskelia, the use of ruthenium-allenylidene as precursors for alkenylcarbynes and indenylidenes, and the involvement of allenylidenes in the building of dinuclear ruthenium bridges with a C_7 carbon-rich bridge.

Keywords: Allenylidene; Carbyne; Catalysis; C–C bond formation; Carbon-rich metal complexes

1. Introduction

Allenylidene-metal complexes $[M]=C=C=CR_1R_2$ [1] attract interest first for the building of original carbon-rich architectures [2] and material science [3], owing to their rigidity and their one-dimensional nature, and as bridges for electronic communication between a metal site and a remote functionality [4]. Since their first discovery [5], the chemistry of metal-allenylidenes has been rapidly developed especially owing to the discovery by Selegue [6] of a straightforward, very general method of access by simple activation of propargylic alcohols.

Metal-allenylidenes are now currently leading to useful applications in the field of homogeneous catalysis [7] as catalytic intermediates or as catalyst precursors, such

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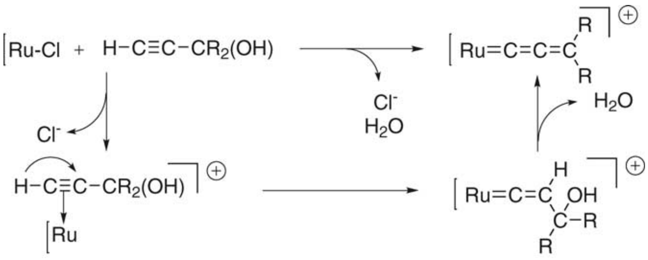


Scheme 1.

as in C–C bond formation [8], alkene metathesis [9], and selective propargylation [10]. It is noteworthy that the later applications have first appeared to be promoted by ruthenium complexes, thus motivating new synthesis and step-by-step modification of ruthenium-allenylidenes.

Elucidation of the reactivity of allenylidene-ruthenium complexes now allows the controlled addition of their carbon-rich chain to unsaturated organometallics with C–C bond formation. This approach constitutes a route to bimetallic systems with carbon-rich bridges.

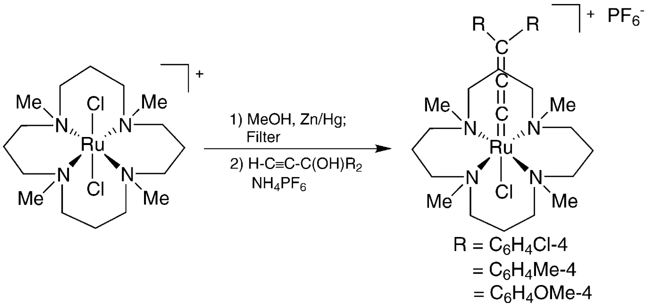
The purpose of this review is to present recent innovations discovered by the Rennes group in the field of ruthenium-allenylidene systems via synthesis and stochiometric transformations at the boundary of material science and catalysis [11].

2. Ruthenium-allenylidene complexes

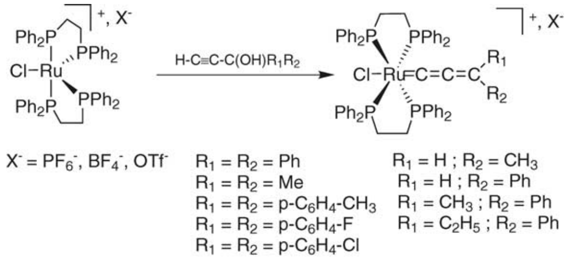
2.1. From propargylic alcohols

The most useful and general method of access to metal-allenylidenes was described by Selegue in 1982 for the preparation of $[Ru(=C=C=CPh_2)(\eta^5C_5H_5)(PMe_3)_2][PF_6]$ [6]. This method is based on the spontaneous dehydration of propargylic alcohol, via the hydroxy vinylidene intermediate after η^2-coordination of the 2-propyn-1-ol to a 16-electron metal centre (Scheme 1).

Allenylidene-ruthenium complexes constitute the most extensive allenylidene family [1a,c]. If a wide range of synthetic investigations have been undertaken, several groups [3,11–20] have used Selegue's method to obtain ruthenium-allenylidenes with various ligands, and substituents such as the η^5-indenyl ruthenium complexes $[Ru(\eta^5C_9H_7)(=C=C=CRR')\ L_2][X]$ (Scheme 2) [12], or very recently the new complexes containing tetradentate macrocyclic tertiary amine ligand (Scheme 3) [13].



Scheme 3.

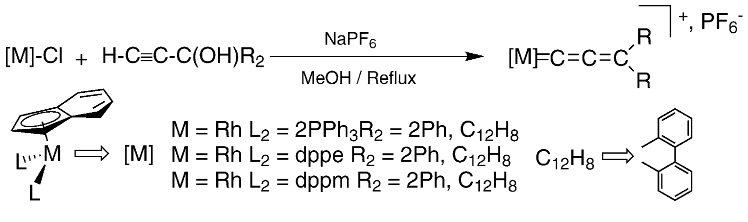


Scheme 4.

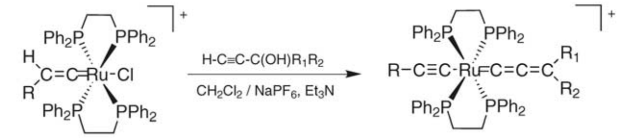
Allenylidene-ruthenium reactivity is highly dependent on the electron-richness of the metal moiety: electrophilic ruthenium complexes lead to highly reactive allenylidenes with electrophilic C_α and C_γ centres while the C_β atom is a nucleophilic site. For example, they easily add alcohol to give an α, β-unsaturated alkoxy carbenes [1c,21]. An increase of the bulkiness and electron-releasing effects of the ligands allow stabilisation of allenylidene with a variety of ruthenium fragments, and their reactivity is then focused on the γ carbon atom [22].

Following our initial work with the $RuCl_2(dppm)_2$ (dppm: 1,2-bis(diphenylphosphino)methane) system [11], a new family of reactive allenylidenes have been obtained starting from $RuCl_2(dppe)_2$ (dppe: 1,2-bis(diphenylphosphino)ethane) or from the 16-electron species $[(dppe)_2RuCl][X]$ ($X = PF_6$, BF_4 or CF_3SO_3), that lead to more stable systems [22] (Scheme 4).

The allenylidene complexes are easily characterised by infrared spectroscopy ($\nu_{(C=C=C)} = 1920$–$1959\ cm^{-1}$). Furthermore ^{31}P and ^{13}C NMR spectra show the equivalency of the four phosphorus nuclei and thus the relative *trans* position of the chlorine atom and of the allenylidene ligand. The low-field ^{13}C signal for the Ru=C carbon nucleus is also characteristic and appears as a quintet around



Scheme 2.



R= H ; $R_1 = R_2$ = Ph
R= nBu ; $R_1 = R_2$ = Ph
R= Ph ; $R_1 = R_2$ = Ph
R= p-C_6H_4-NO_2 ; $R_1 = R_2$ = Ph

R= p-C_6H_4-OCH_3 ; R_1 = H ; R_2 = Ph
R= p-C_6H_4-NO_2 ; R_1 = H ; R_2 = p-C_6H_4-$N(CH_3)_2$
R= H ; R_1 = CH_3 ; R_2 = Ph
R= Ph ; R_1 = C_2H_5 ; R_2 = p-C_6H_4-OCH_3

Scheme 5.

$\delta = 265$–320 ppm with a coupling constant $^2J_{PC} = 14$ Hz. A quintet at $\delta = 169$–237 ppm with a small $^3J_{PC}$ (2–3 Hz) coupling constant for the Ru=C=C carbon nucleus is also observed.

A major advantage of these ruthenium systems with dppe ligands is the possibility of removing the second chloride to introduce a second unsaturated carbon chain in the *trans* position [22]. The synthesis of mixed alkynyl allenylidene complexes from the cationic allenylidene complexes, by displacement of the chloride ligand failed. However, they were made by displacement of the chloride attached to the ruthenium in neutral alkynyl complexes in the presence of a non coordinating salt. With such a route, the 16-electron intermediate was generated, and it activates propargylic alcohols to produce ruthenium mixed alkynyl allenylidene complexes. Nevertheless, the reaction of alkynyl-ruthenium and propargylic alcohols in the presence of $NaPF_6$ led very often, to a mixture of two compounds: the major mixed alkynyl allenylidene complex, and the monosubstitued allenylidene complex. This shows competition between the breaking of Ru–Cl and Ru–C≡C– bonds. The best results were obtained using the strategy described in Scheme 5, starting from the corresponding vinylidene precursor in the presence of a base.

These complexes display two typical IR vibration stretches at 1950–2100 cm^{-1} for $\nu_{C\equiv C}$ (medium) and at 1919–1959 cm^{-1} for $\nu_{(C=C=C)}$ (intense). The ^{13}C NMR spectra show the presence of a low-field quintet signal for the Ru=C carbon nucleus at $\delta = 260$–318 ppm, a signal at $\delta = 163$–216 ppm for Ru=C=C, and a singlet at $\delta = 142$–163 ppm for the Ru=C=C=C carbon nuclei.

It is noteworthy that these allenylidenes are stable toward the addition of methanol on C_α and C_γ carbon atoms in contrast with other systems [1,16,23]. This arises from the steric hindrance of the dppe ligands and the electron-donating capability of the $Ru(dppe)_2$ moiety. However, a stronger nucleophile such as sodium methoxide reacts with ruthenium-allenylidenes and with mixed alkynyl allenylidenes to add selectively to the C_γ electrophilic carbon giving yellow acetylides or mixed diacetylides [22]. The addition of sodium borohydride in THF permits the synthesis of acetylides or diacetylides as the result of hydride addition to the terminal carbon of the allenylidene chain (Scheme 6) [22,24]. Another route to ruthenium acetylide complexes, and more precisely to alkenylacetylides, from allenylidenes consists of the deprotonation of the δ carbon by action of a weak base (Scheme 6) [25].

2.2. *From alkynyl-metal derivatives with an hydrogen atom at C_γ: a new preparation method to metal-allenylidenes*

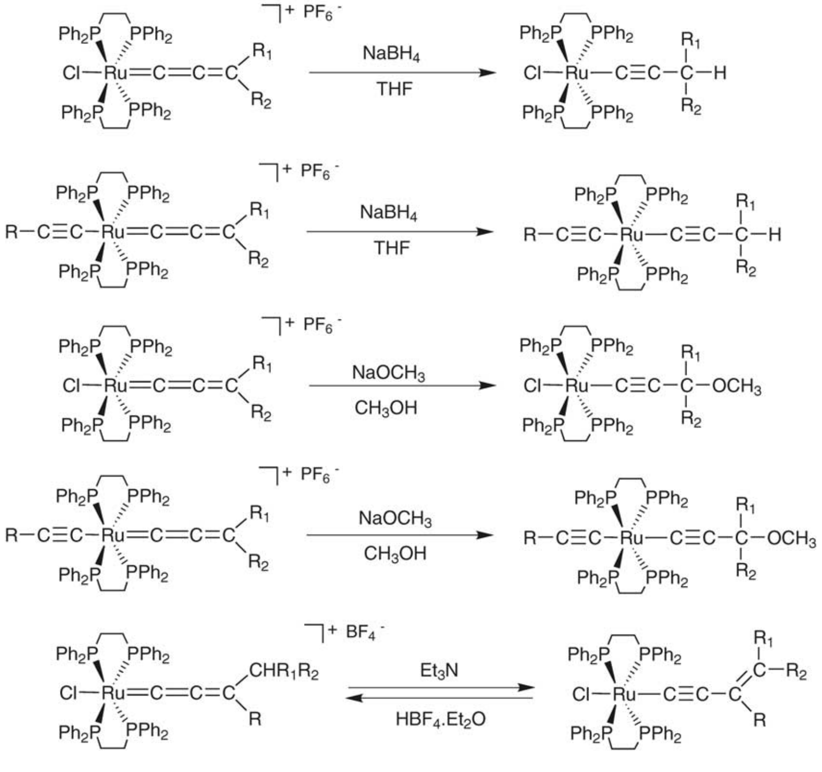
The ruthenium acetylide *trans*-[Cl(dppe)$_2$Ru–C≡C–CHPh$_2$] gives a mixture of the corresponding allenylidene and vinylidene on chemical oxidation with ferricinium salts (Scheme 7) [26]. Interestingly, oxidation of the same complex with the ferricinium salt, but in the presence of pyridine, gives quantitatively *trans*-[Cl(dppe)$_2$Ru=C=C=CPh$_2$] [PF$_6$].

This reaction was rationalized by an one-electron oxidation followed by the γ-elimination of a proton which is able to protonate another molecule of acetylide to form *trans*-[Cl(dppe)$_2$Ru=C=CH-CPh$_2$H]PF$_6$ (Scheme 8). On the other hand, the neutral radical *trans*-[Cl(dppe)$_2$Ru–C≡C–C$^\bullet$Ph$_2$] resulting from the γ-proton elimination is oxidized by ferricinium salt to give the allenylidene *trans*-[Cl(dppe)$_2$Ru=C=C=CPh$_2$]PF$_6$ ($E^\circ = -1.03$ V versus ferrocene). This hypothesis is supported by the observation of a broad ESR signal at $g = 2.0039$, when the reaction was carried out in the ESR cavity at 100 K, that can be attributed to the acetylide radical *trans*-[Cl(dppe)$_2$Ru–C≡C–C$^\bullet$Ph$_2$] (vide supra) [24]. The fact that proton elimination does not occur with *trans*-[Cl(dppe)$_2$Ru–C≡C–CH(CH$_3$)$_2$] or *trans*-[Cl(dppe)$_2$Ru–C≡C–CH$_3$] could be explained in terms of stabilisation of the neutral radical [Cl(dppe)$_2$Ru–C≡C–C$^\bullet$(R)$_2$]. With the phenyl groups, the radical *trans*-[Cl(dppe)$_2$Ru–C≡C–C$^\bullet$Ph$_2$] is highly stabilized by the spin delocalisation over the rings, and proton elimination is preferred. Finally, in the presence of pyridine, the leaving proton can be trapped, and nearly quantitative formation of *trans*-[Cl(dppe)$_2$Ru=C=C=CPh$_2$]PF$_6$ allenylidene is obtained. Two equivalents of [η^5-(C$_5$H$_5$)$_2$Fe][PF$_6$] are necessary to complete the transformation, one for the oxidation of the acetylide complex and one for the oxidation of the neutral radical. This method might be an alternative pathway to obtain allenylidene species from acetylides when propargylic alcohols are not available.

2.3. *Reduction of allenylidene complexes*

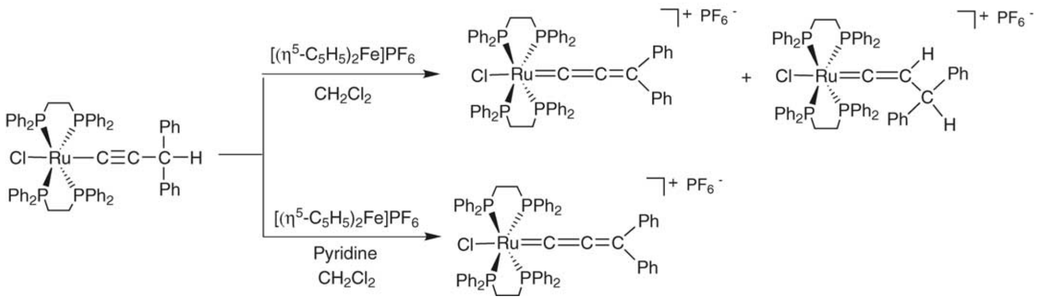
Stimulated by the fact that radical species have been recently proposed as intermediates in metathesis [27], the reduction of some allenylidenes complexes has been recently studied [24].

The first reduced species of complexes *trans*-[Cl(dppe)$_2$ Ru=C=C=CPh$_2$]PF$_6$ ($E^\circ = -1.03$ V versus ferrocene, reversible), and *trans*-[Cl(dppe)$_2$Ru=C=C=C(CH$_3$)$_2$] ($E_{pc} = -1.31$ V, irreversible) were generated in situ with Cp$_2$Co ($E^\circ = -1.33$ V versus ferrocene). At 293 K, ESR experiments exhibit a poorly resolved quintet ($g = 2.0097$, $a_P = 3.0$ G) in a characteristic region for organic radicals for the reduced *trans*-[Cl(dppe)$_2$Ru=C=C=C(CH$_3$)$_2$] complex,



R= Ph ; $R_1 = R_2 = H$
R= CH_3 ; $R_1 = R_2 = H$
R= Ph ; $R_1 = H$; $R_2 = CH_3$
R= Ph ; $R_1 = H$; $R_2 = Ph$

Scheme 6.



Scheme 7.

showing the hyperfine coupling with the four phosphorus nuclei. Reduced *trans*-[Cl(dppe)$_2$Ru=C=C=CPh$_2$]PF$_6$ generated an intense and persistent complex signal ($g = 2.0042$) (Fig. 1) owing to the coupling of the unpaired electron with the four phosphorus nuclei on one hand and further coupling with phenyl hydrogen atoms of the carbon-rich bridge. Addition of Ph$_3$SnH to the radical leads the formation of neutral acetylide compound *trans*-[Cl(dppe)$_2$Ru–C≡C–CHPh$_2$] and *trans*-[Cl(dppe)$_2$Ru–C≡C–CHMe$_2$] demonstrating that radical trapping only occurs at the end of the carbon skeleton (Scheme 9). These ESR data added to the trapping experiments indicate the organic nature of the radicals, and illustrate that significant radical stabilization on the cumu-

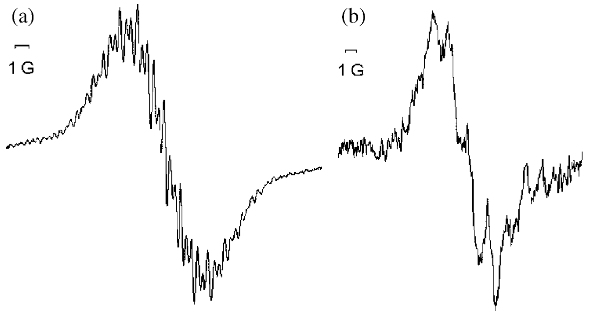
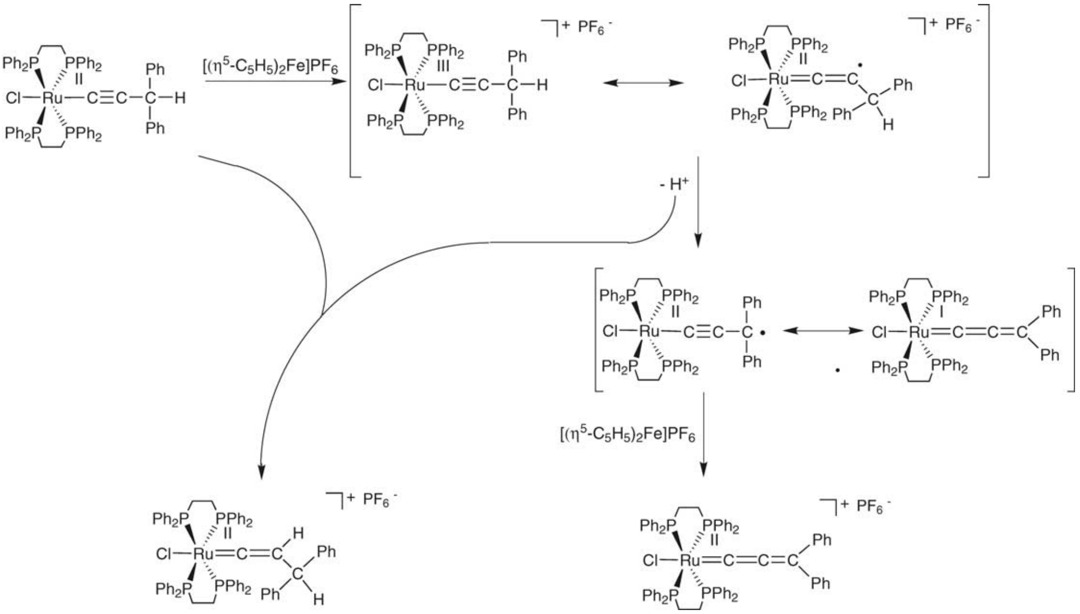


Fig. 1. ESR spectra resulting from reduction of (a) *trans*-[Cl(dppe)$_2$Ru=C=C=CPh$_2$]PF$_6$, $g = 2.0042$; (b) *trans*-[Cl(dppe)$_2$Ru=C=C=CMe$_2$], $g = 2.0097$.



Scheme 8.

lene chain takes place at the trisubstituted carbon atom. These results are consistent with Winter's observations obtained for various allenylidenes systems [20,28].

DFT calculations have been performed on the series $[Cl(PH_3)_4RuC_nH_2]^+$, $Cl(PH_3)_4RuC_nH_2$, and $[Cl(PH_3)_4RuC_nH_2]^-$ ($n = 1$–8) series and are in accord with those findings [29]. The one-electron reduction of the $[Cl(PH_3)_4RuC_nH_2]^+$ compounds leads to neutral species containing linear C_nH_2 chains, with the exception of the $n = 2$ complex, which is bent at C(1). The $Cl(PH_3)_4RuC_nH_2$ compounds are better described as an 18-electron Ru^{II} metal site bonded to the reduced $(C_nH_2)^-$ ligand than 19-electron Ru^I centres. The $[Cl(PH_3)_4RuC_nH_2]^+$ complexes are found to be easier to reduce for odd n rather than for even n. Furthermore, the distribution of the atomic net charges and the localization of the HOMOs and LUMOs indicate that the complexes are subject to nucleophilic attack at odd C atoms, except in the case of C(1). They are subject to electrophilic attack at the even C sites, except for the CH_2 end of the chain. These results are in agreement with previous theoretical studies on ruthenium dppm systems [28b] or on other analogous allenylidenes $[(\eta^5\text{-}C_5H_5)(CO)(PPh_3)Ru{=}C{=}C{=}CH_2]^+$ and $[(\eta^5\text{-}C_9H_7)(PPh_3)_2Ru{=}C{=}C{=}CH_2]^+$ suggesting that the LUMO is strongly located on the cumulenic ligand [16,23].

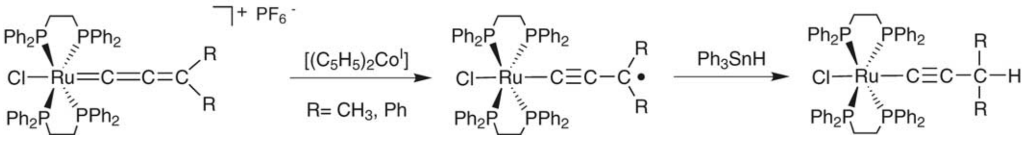
3. Ruthenium bis(allenylidene) complexes

3.1. Bimetallic bis(allenylidene) complexes

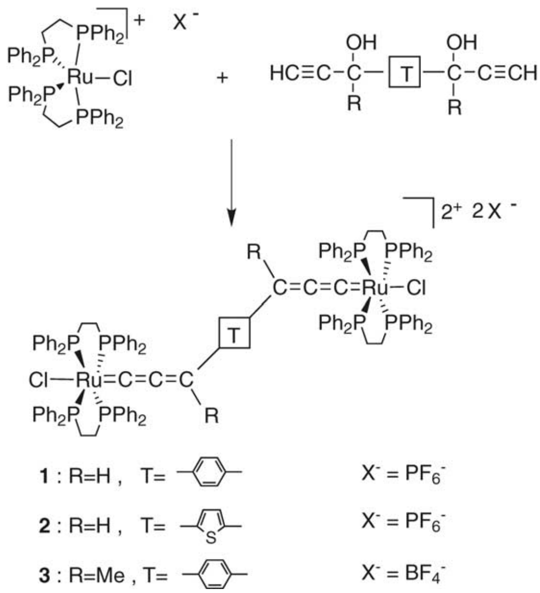
Since bimetallic systems have been made especially from terminal diynes to obtain oxidisable acetylides, mainly of the type $L_nMC_xML_n$ [30], the search for new π-conjugated bridges between two reversible reducible metal moieties was attractive.

Bis-propargylic alcohols separated by a conjugated linker present an interesting possibility for the access to bimetallic complexes with a carbon-rich unsaturated bridge. The synthesis and electrochemical study of new stable bimetallic complexes such as *trans*-$[Cl(dppe)_2Ru{=}C{=}C{=}CH\text{–}p\text{-}C_6H_4\text{–}CH{=}C{=}C{=}Ru(dppe)_2Cl](PF_6)_2$ (Scheme 10) containing two identical metal moieties, and with different bis-allenylidene bridges were obtained via double activation of diynes with $[ClRu(dppe)_2)]PF_6$ [4]. Connecting groups [T] such as thiophene or aryl were used.

This synthesis was then extended from secondary allenylidenes to tertiary allenylidenes with a methyl substituent to obtain *trans*-$[Cl(dppe)_2Ru{=}C{=}C{=}C(CH_3)\text{–}p\text{-}C_6H_4\text{–}C(CH_3){=}C{=}C{=}Ru(dppe)_2Cl](BF_4)_2$. An alkynyl precursor *trans*-$[Cl(dppe)_2Ru\text{–}C{\equiv}C\text{–}p\text{-}C_6H_4\text{–}NO_2]$ was also used to give the rigid rod molecules *trans*-$[NO_2\text{–}p\text{-}C_6H_4\text{–}C{\equiv}$



Scheme 9.



Scheme 10.

C–(dppe)$_2$Ru=C=C=CH–*p*-C_6H_4–CH=C=C=Ru(dppe)$_2$–C≡C–*p*-C_6H_4–NO_2](PF$_6$)$_2$ (**4**) [4].

Electrochemical studies show that the bis-allenylidenes undergo two one-electron reductions at the carbon-rich bridge (Table 1) [24]. The electrochemical behavior of the bis-allenylidene shows two interesting features: (i) the two reversible processes are easily distinguishable, (ii) a significant variation of both reduction potentials indicates that reductions are easier when the two allenylidene moieties are conjugated by comparison with a mono allenylidene such as *trans*-[Cl(dppe)$_2$Ru=C=C=CPh(CH$_3$)]PF$_6$, which displays one reduction wave at -1.094 V versus ferrocene. When two identical redox centers are isolated from each other, the potentials E_1 and E_2 would be expected to be not only identical or of close values, but also very close to the potential of a mononuclear model. Hence, an efficient conjugated path between two equal redox moieties makes the processes easier than for the mononuclear model by stabilization of the electrons along the system. This demonstrates the efficient connection of the allenylidene moieties through the highly conjugated bridges, and the large influence of the bridge with the thiophene as a more efficient linker. The *trans* acetylide groups in **4** significantly favour the reductions processes, showing the influence of the acetylide chains through the ruthenium atoms.

Table 1
Electrochemistry data for bimetallic bis(allenylidene) complexes

	E_1° (mV/Fc)	ΔE (mV)	E_2° (mV/Fc)	ΔE (mV)	$E_2^\circ - E_1^\circ$ (mV)
1	−509	66	−711	81	200
2	−335	71	−606	80	270
3	−640	60	−840	60	200
4	−348	70	−539	110	180

Sample 1 mM; Bu$_4$NPF$_6$ (0.1 M) in CH$_2$Cl$_2$; potential are reported in volt vs. ferrocene.

Recently, a similar dinuclear complex was described by Werner's group with two rhodium centres [Cl(PPh$_3$)$_2$Rh=C=C=C(Ph)-*p*–C$_6$H$_4$–C(Ph)=C=C=Rh(PPh$_3$)$_2$Cl] [31]. These molecules constitute interesting building blocks for the construction of more complex edifices such as molecular wires.

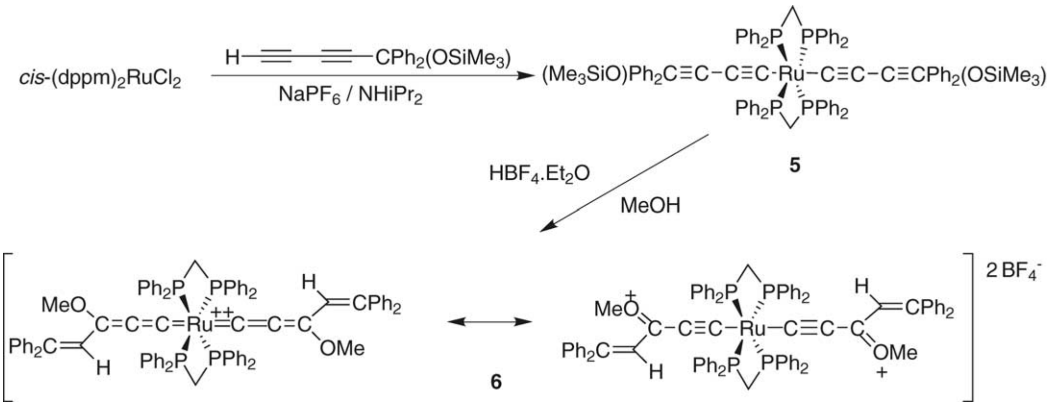
3.2. Monometallic bis(allenylidene) complexes

Much attention is being directed to the preparation of new rod-shaped organometallic compounds containing two unsaturated chains, and bis(alkynyl) metal complexes with Pt, Pd, Hg or Cu have been found to be mostly insulators as they disrupt the π-conjugation between two acetylide chains [32]. By contrast, *trans*-bis(alkynyl) ruthenium systems increase communication between two ferrocene units in an oxidation process [33]. Thus, it appears that an innovative solution to create electronic communication between two carbon-rich chains connected via a metal may arise from the reduction of a bis(allenylidene) metal moiety R$_2$C=C=C=[Ru]$^{2+}$=C=C=CR$_2$.

Attempts to produce a bis(allenylidene) ruthenium derivative from an allenylidene *trans*-[Cl(dppe)$_2$Ru=C=C=CPh$_2$]$^+$ complex using the Selegue method [6] failed since the halide is not labile. However, an interesting method provided the first bis(allenylidene) arrangement via a *trans*-bis (diynyl)ruthenium complex [(dppm)$_2$Ru(–C≡C–C≡C–CPh$_2$ OSiMe$_3$)$_2$] (**5**) [34]. Treatment of the latter in methanol with HBF$_4$·Et$_2$O provided the violet symmetric bis(alkenylallenylidene) ruthenium complex *trans*-[(dppm)$_2$Ru([=C=C=C(OMe)(CH=CPh$_2$)) $_2$](BF$_4$)$_2$ (**6**) by elimination of the two Me$_3$SiO$^-$ groups and methanol addition to the metallacumulene intermediate (Scheme 11).

However, FTIR, ^{13}C NMR spectroscopy ($\nu_{\mathrm{C=C=C}} = 1958\,\mathrm{cm}^{-1}$, C$_\alpha$ resonance is $\delta = 233.7$ ppm) and the crystal structure show that a bis(allenylidene) complex was obtained but with an elevated bis(alkynyl) character owing to the presence of a donor group on the unsaturated chain.

Very recently, the preparation of the first real bis(allenylidene) metal complex *trans*-[Ph$_2$C=C=C=Ru=C=C=CPh$_2$ (dppe)$_2$]$^{2+}$ (**9**) was reported [35] (Scheme 12). The synthetic route is based on the two electron oxidation and deprotonation of *trans*-[(dppe)$_2$Ru–C≡C–CHPh$_2$]PF$_6$ (**7**) (vide infra). Thus, the allenylidene-acetylide *trans*-[Ph$_2$C=C=C=(dppe)$_2$ Ru–C≡C–CHPh$_2$]PF$_6$ (**8**) ($E^\circ = 0.82$ versus ferrocene) was oxidised with Ce$^{\mathrm{IV}}$ ammonium nitrate leading to the elimination of the γ proton to form the bis(allenylidene) complex **9**. The FTIR and ^{13}C NMR spectra ($\nu_{\mathrm{C=C=C}} = 1923\,\mathrm{cm}^{-1}$, C$_\alpha$ resonance is $\delta = 297.6$ ppm) of this complex are characteristic of an allenylidene ligand. Indeed, the C$_\alpha$ carbon atom resonance is consistent with allenylidene species close to that of *trans*-[Cl(dppe)$_2$Ru=C=C=CPh$_2$]$^+$ ($\delta = 308.5$ ppm). Two hydride transfers to the bis(allenylidene) complex confirm the allenylidene structure with nucleophilic addition of two H$^-$ at the C$_\gamma$ atoms (Scheme 12). Furthermore, full DFT ge-

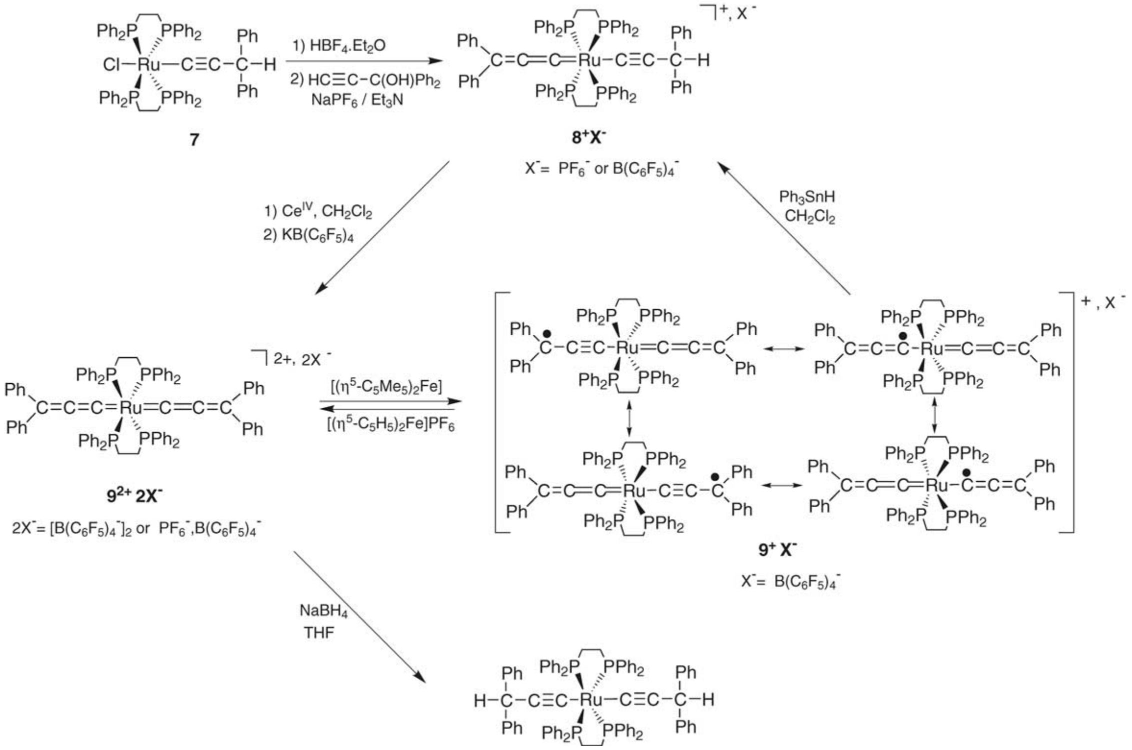


Scheme 11.

ometry optimization without any symmetric constraint of the simplified model *trans*-$[(PH_3)_4Ru(=C=C=CH_2)_2]^{2+}$ ($\mathbf{9'}^{2+}$) leads to the bis(allenylidene) structure shown with consistent allenylidene bond lengths [22,29]. QM(DFT)/MM geometry optimizations of the full complex $\mathbf{9}^{2+}$ lead to a similar structure [35].

Two one-electron reversible reduction waves were observed at $E^{\circ}_1 = -0.30$ V and $E^{\circ}_2 = -0.93$ V versus ferrocene. The singly reduced species was generated in situ with addition of decamethylferrocene ($E^{\circ} = -0.59$ versus ferrocene). Quenching of this radical $\mathbf{9}^{+}$ with Ph_3SnH at the C_γ carbon atom (Scheme 12) supports the localization of the single electron on the trisubstituted carbon atoms. However, the observed ESR quintet for $\mathbf{9}^{+}$ with $g = 1.9972$ with a coupling constant $a_P = 13.5$ G due to the coupling of the single electron with the 4 equiv. phosphorus atoms suggests its localization closer to the metal than in the reduced ruthenium mono(allenylidene). In addition, the IR studies of $\mathbf{9}^{+}$ show the vanishing of the allenylidene band and the formation of a new broad absorption at 1751 cm^{-1}. Thus, all of these results, along with DFT calculations are consistent with a novel symmetric radical with one unpaired electron equally delocalized over both *trans* carbon-rich chains linked by the ruthenium atom.

These studies show the potential of ruthenium bis(allenylidene) systems to mediate electron conduction, which is a key requirement for molecular wires.



Scheme 12.

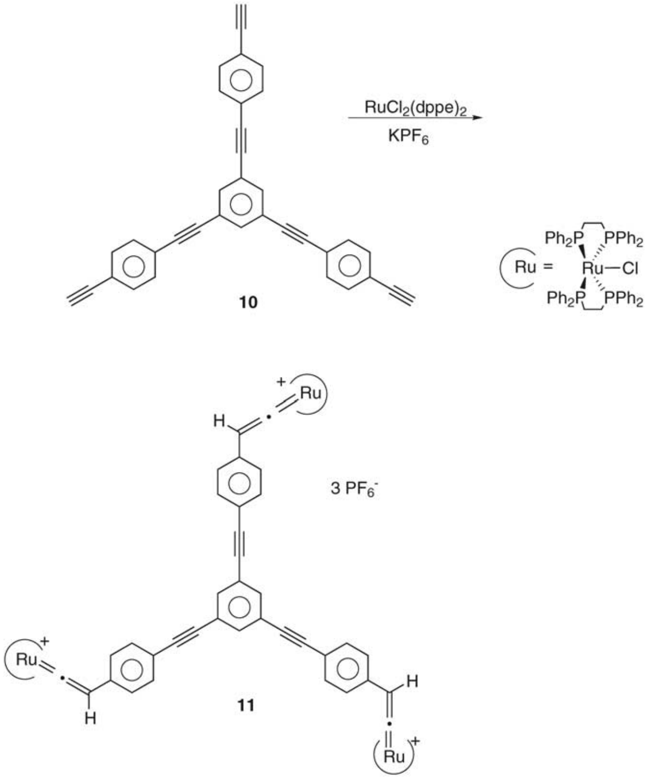
Scheme 13.

4. Trisallenylidene-ruthenium complexes

Star-shaped molecules and dendrimers constitute an emerging field in chemistry for their potential to incorporate guest molecules within their cavities and to bind active molecules or catalysts in their outer sphere [36]. One possible route for an easy access to star macromolecules consists in the building of star alkene metathesis catalysts followed by ROMP polymerisation of cyclic olefins according to Scheme 13.

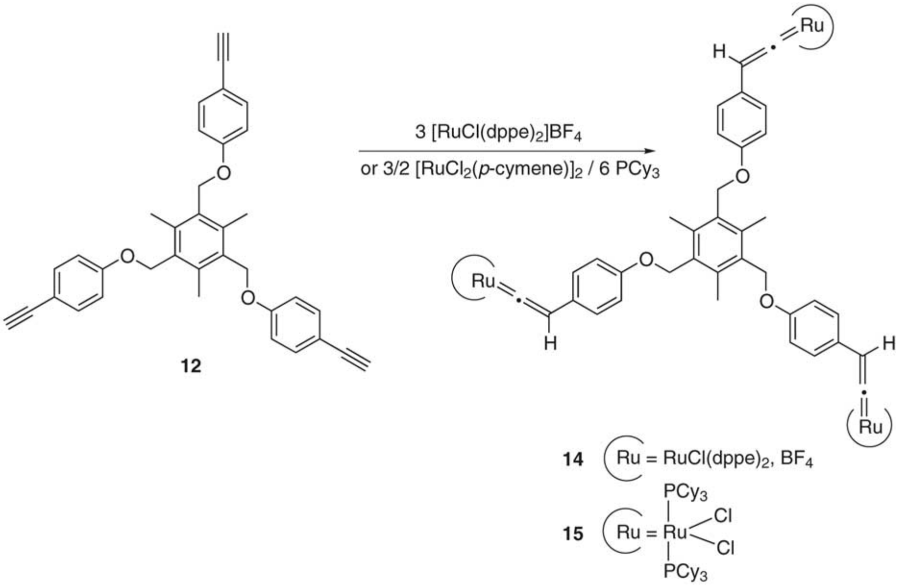
It has been shown that vinylidene [37] and allenylidene [38] ruthenium complexes, easily prepared from terminal alkynes and propargylic alcohols, behave as efficient catalysts for ROMP. Consequently, star polyynes and propargylic alcohols are the target molecules to generate directly star vinylidene-metal and star allenylidene-metal complexes with potential for further ROMP processes and the access to star macromolecules. In this orientation tris(vinylidene)-ruthenium and tris(allenylidene)-ruthenium catalyst models have been designed. The multitopic carbon-rich conjugated triyne **10** has been prepared by multistep catalytic reactions, and the activation of this triyne **10** with the 16-electron ruthenium precursor $RuCl_2(dppe)_2/KPF_6$ has led to the first trisvinylidene-ruthenium complex **11** (Scheme 14) [2a]. This tris(vinylidene) **11** behaves as an acid that is easily deprotonated to give electron-rich, carbon-rich tris alkynyl-ruthenium systems.

The triyne **10** is rigid and conjugated and favours communication between the three ruthenium sites. Flexible non conjugated triyne **12** and trispropargylic alcohol **13** were then prepared. The activation of the triyne **12** with $[RuCl(dppe)_2]BF_4$ and $[RuCl_2(p\text{-cymene})]_2/2PCy_3$ gave the trisvinylidenes **14** and **15**, respectively (Scheme 15) [2b]. The complex **15** is an analog of Grubbs catalyst.

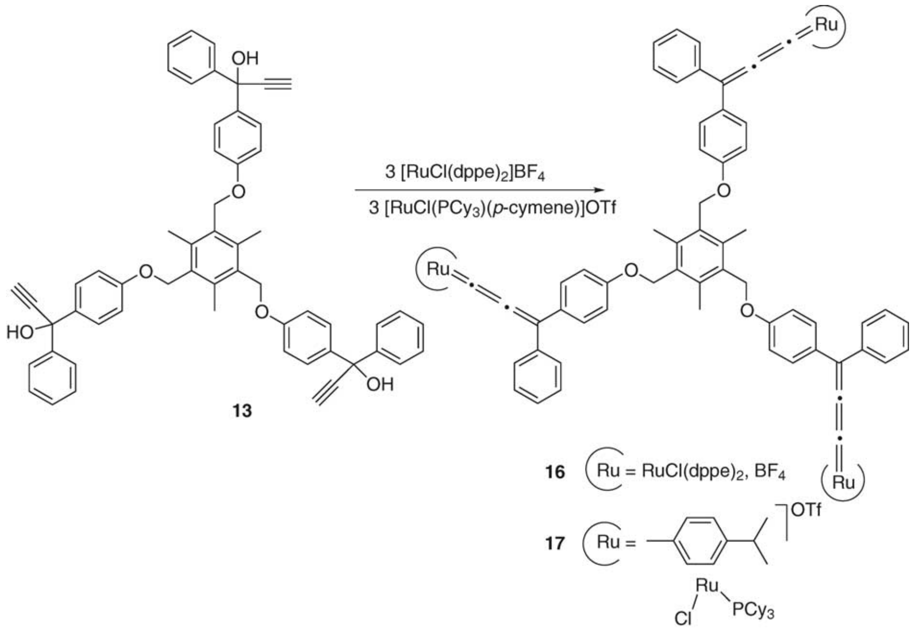


Scheme 14.

The activation of the propargylic alcohol **13** with the 16-electron ruthenium precursors $[RuCl(dppe)_2]BF_4$ and



Scheme 15.



Scheme 16.

$[RuCl(PCy_3)(p\text{-cymene})]OTf$ afforded the first tris(allenylidene)-ruthenium complexes **16** and **17** (Scheme 16) [2b].

The above trisvinylidenes and trisallenylidenes actually display a C_3-symmetry triskel shape [2b].

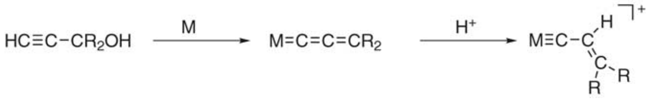
5. Allenylidenes as precursors to carbyne-ruthenium complexes

Metal-carbyne complexes attract interest as possible catalyst precursors for alkyne metathesis [39]. Since the first synthesis of metal-carbyne by modification of metal carbene derivatives by Fischer et al. [40], metal carbenes offer the best direct routes to metal-carbynes [41]. Electrophilic addition to vinylidene-metal derivatives, including protonation, now constitutes an alternative to produce metal-carbynes from simple alkynes [42] (Scheme 17).

A new simple access to metal-carbyne is now emerging from propargylic alcohols trough their metal-allenylidene derivatives. Protonation of the latter appears to be a general method for access to alkenylcarbyne metal complexes (Scheme 18).

$$M + HC{\equiv}CR \longrightarrow M{=}C{=}CHR \xrightarrow{E^+} \left. M{\equiv}C{-}CH(E)R \right]^+$$

Scheme 17.



$$HC{\equiv}C{-}CR_2OH \xrightarrow{M} M{=}C{=}C{=}CR_2 \xrightarrow{H^+} \left. M{\equiv}C{-}C(H){=}CR_2 \right]^+$$

Scheme 18.

5.1. Alkenylcarbynes from osmium allenylidenes

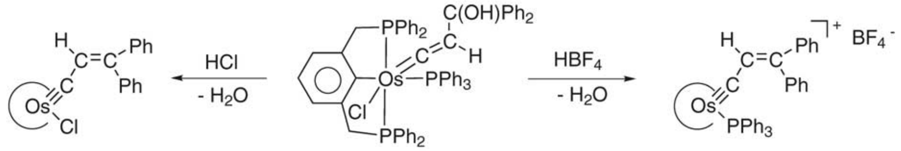
Initially, an alkenylcarbyne-osmium derivative $Os{\equiv}C{-}CH{=}R_2(Cl)_2(H)(PiPr_3)_2$ was prepared by reaction of $OsH_2Cl_2(P^iPr_3)_2$ with propargylic alcohol, through a dihydrogen vinylidene intermediate followed by dehydration, and transfer of a proton from acidic coordinated dihydrogen on the β carbon of the allenylidene [43]. The direct protonation by HPF_6 of $[Os{=}C{=}C{=}CPh_2(\eta^5\text{-}C_5H_5)(PiPr_3)_2]PF_6$ leads to the formation of allenylcarbyne complex $[Os{\equiv}C{-}CH{=}CPh_2(\eta^5\text{-}C_5H_5)(PiPr_3)_2](PF_6)_2$ [44].

Simultaneously, Jia et al. have demonstrated that the neutral osmium-vinylidene $Os{=}C{=}CHC(OH)Ph_2(Cl)_2(PCP)$ (PCP: $2,6\text{-}(Ph_2PCH_2)_2C_6H_3$) arising from propargylic alcohol, thus non dehydrated, on protonation with HCl or HBF_4 leads to neutral and cationic alkenylcarbyne-osmium derivatives, respectively through dehydration and protonation of the β carbon of the unobserved allenylidene intermediate [45] (Scheme 19).

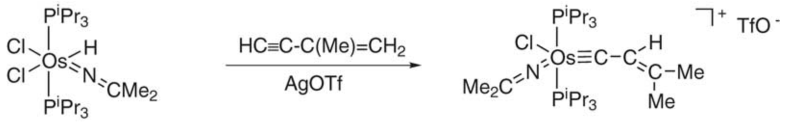
Another example of an alkenylcarbyne-osmium complex arises from the coordination of 2-methyl-1-buten-3-yne to an osmium-hydride derivative [46] (Scheme 20). It likely takes place via the formation of the corresponding allenylidene followed by the transfer of the proton, from the metal, to the β carbon.

5.2. Alkenylcarbynes from ruthenium-allenylidenes

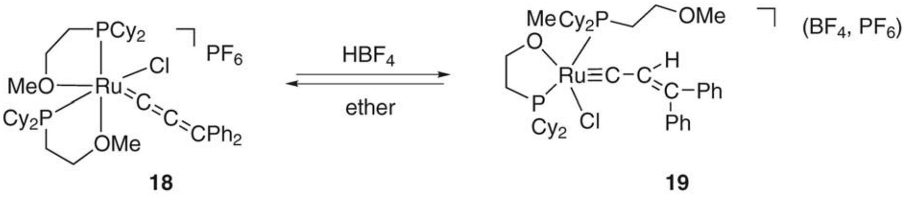
In the ruthenium series, the first observation of an alkenylcarbyne-ruthenium intermediate was recently reported by Werner and co-workers [47]. On protonation of allenylidene-ruthenium complex **18** with HBF_4 the formation of the alkenylcarbyne 19 is observed but not



Scheme 19.



Scheme 20.



Scheme 21.

isolated, as the protonation is reversible (Scheme 21). This reversibility contrasts with the stable and isolable alkenylcarbyne-osmium and the alkenylcarbyne-iridium complex [Ir≡C–CH=C(Ph)R(Cl)(PiPr$_3$)$_2$] X [48], obtained by protonation of the corresponding allenylidene.

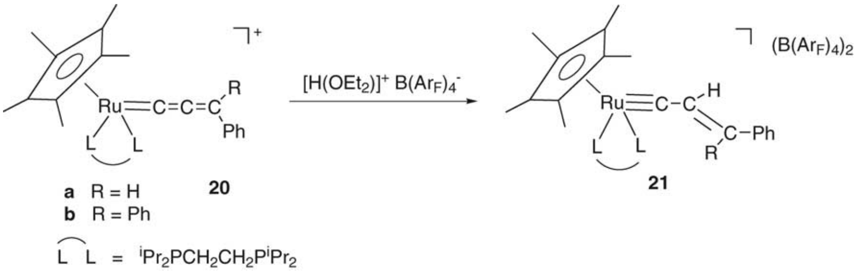
Recently, the nucleophilic addition at the γ carbon atom of the allenylidene-ruthenium **20** was explained by initial activation of the allenylidene ligand by protonation, leading to an alkenylcarbyne intermediate [14]. Indeed, protonation of **20** with $[H(OEt_2)]^+B(Ar_F)_4^-$ ($Ar_F = 3,5\text{-}(CF_3)_2C_6H_3$) led to isolation of the alkenyl carbynes **21a** and **21b** and the X-ray structure of the latter was determined (Scheme 22).

Two major discoveries related to alkenylcarbyne-ruthenium systems have recently been reported by the Rennes group: (i) the evidence that an alkenylcarbyne-ruthenium species rearranges into an indenylidene-ruthenium complex which displays high catalytic activity in alkene metathesis [49] and (ii) the first formation of a conjugated bis(alkenylcarbyne) ruthenium derivative [25].

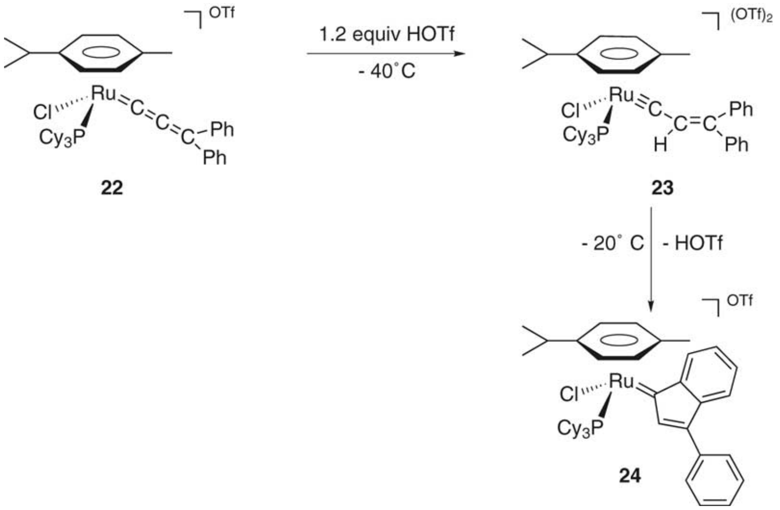
5.2.1. Ruthenium indenylidene catalysts from allenylidene via alkenyl carbynes

The first observed phenomenon arose from the study of the protonation of the allenylidene-ruthenium complex **22**. This complex was shown previously to be a catalyst precursor in alkene metathesis via ring-closing metathesis [9,50] and ROMP polymerisation of cyclic alkenes, but there was no information about the real catalytic species. However, it was observed in the course of kinetic study that the [Ru=C=C=CPh$_2$(Cl)(PCy$_3$)(*p*-cymene)]X **22** was slowly transformed at 50 °C into another species that acted as the catalyst [51]. On the other hand, it was also observed that the addition of a strong acid such as trifluoromethanesulfonic acid to complex **22** led to a dramatic increase of the catalytic activity toward ring-closing metathesis of bis allyltosylamide and in ROMP of cyclooctene.

The addition of 1.2 equiv. of TfOH to complex **22** in CD_2Cl_2 at −40 °C readily led to the formation of the ionic alkenylcarbyne-ruthenium complex **23** (Scheme 23). This



Scheme 22.



Scheme 23.

complex is not stable at $-20\,^{\circ}\mathrm{C}$ and loses 1 equiv. of TfOH to give selectively the indenylidene-ruthenium complex **24**.

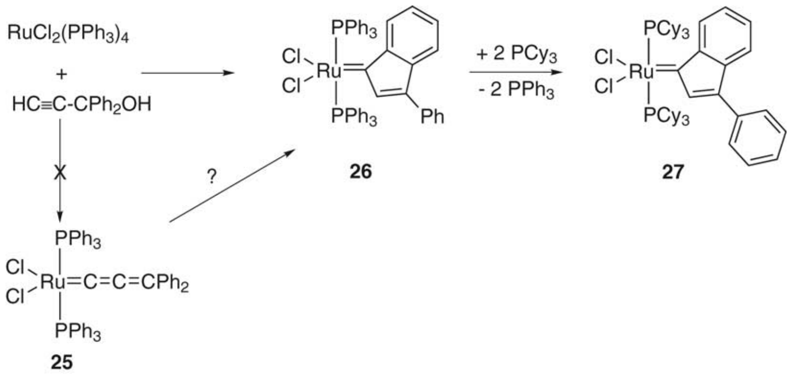
The indenylidene complex **24**, generated in situ appears to be a very efficient catalyst not only for RCM of dienes and also for ROMP of cyclooctene. Thus, for a cyclooctene/**24** ratio of 10^4 after 5 min at $0\,^{\circ}\mathrm{C}$, 97% of polymer were formed (Mn = 387,000; Mw/Mn = 1.5) with a turnover frequency of 116.000. The indenylidene complex **24** also polymerises cyclopentene at room temperature. It is shown that the activity of the catalyst arising from complexes related to **22** is very sensitive to ligand nature, and decreases when PPh_3 or $C{=}C{=}C(C_6H_4{-}OMe)_2$ ligands are introduced in complex **22**.

The observation that the allenylidene complex **22** can be completely transformed into the indenylidene complex **24**, in the presence of a strong acid at low temperature, suggests that the protonation of **22** to give **23** corresponds to an increase of the electrophilicity of the Ru-bonded carbon to undergo electrophilic substitution of the *ortho* proton of the phenyl group.

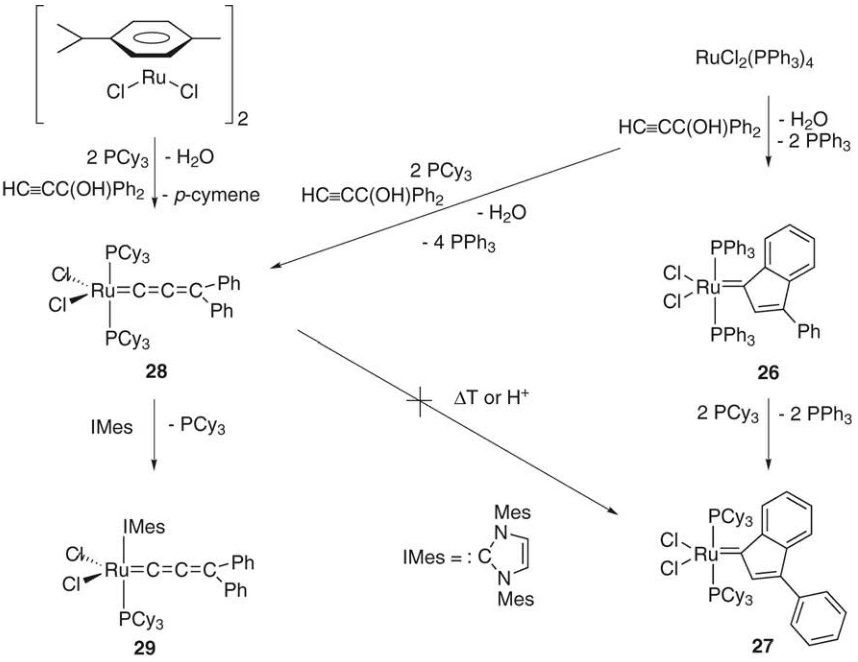
The overall transformation **22** → **23** → **24** corresponds to the first direct observation of the intramolecular transformation of an allenylidene into an indenylidene ligand. Such a rearrangement has been previously postulated. In this reaction of $RuCl_2(PPh_3)_3$ with $HC{\equiv}CCPh_2OH$ the expected allenylidene complex **25** was not obtained [52], although it was believed to be formed [53]. Instead it was found that the indenylidene complex **26** was formed (Scheme 24).

It was therefore suggested, but not observed, that the allenylidene **25** rearranged intramolecularly into **26** [54,55]. The observation of the transformation **22** → **23** → **24** thus supports (i) the reality of rearrangement **25** → **26** and (ii) that the catalytic species thermally formed directly from **22**, in the absence of acid, also corresponds to the indenylidene complex **24**. It is noteworthy that the complex **26** is not active as alkene metathesis catalyst. However, the its related complex **27** containing the bulky, electron-rich PCy_3 ligands appears to be an efficient catalyst for ring-closing metathesis [54,56].

By contrast, the reaction of the classical source of $RuCl_2$ species, $[RuCl_2(p\text{-cymene})]_2$, with $HC{\equiv}C{-}CPh_2OH$ and 2 equiv. of PCy_3 afforded the stable allenylidene complex **28** that was isolated and easily transformed into **29** (Scheme 25) [56]. Complexes **28** and then **29** were also



Scheme 24.



Scheme 25.

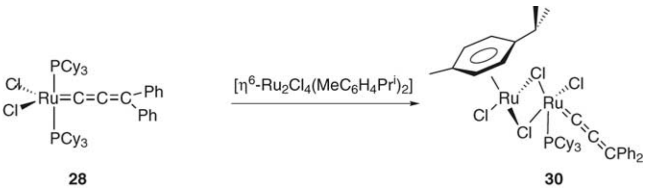
obtained on reaction of $RuCl_2(PPh_3)_2$ with 2 equiv. of PCy_3 and then $HC{\equiv}CCPh_2OH$ [55]. The complexes **28** and **29**, containing electron-releasing ligands with respect to the virtual complex **25**, do not rearrange into indenylidene complex although they promote to some extent catalytic RCM reactions (Scheme 25) [57].

It is noteworthy that complex **28** reacts with $[RuCl_2(p\text{-cymene})]_2$ to give the allenylidene-ruthenium complex **30** [58] (Scheme 26). Complex **30** appears to be an efficient RCM catalyst; however, in that case the likely intramolecular rearrangement into an indenylidene was not observed.

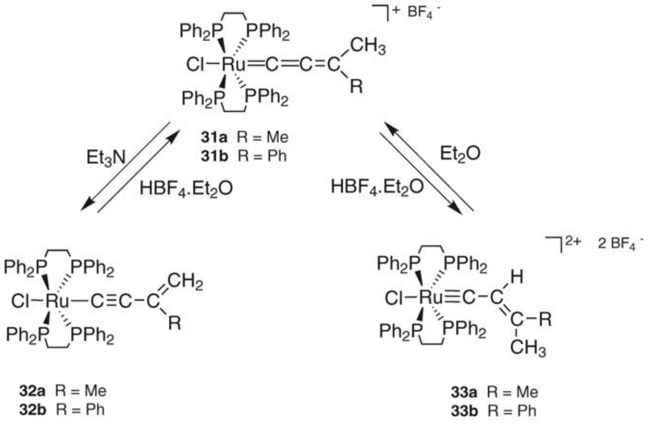
5.2.2. *Bis alkenylcarbyne ligand bridging two metal moieties*

It was surprising that the protonation of the allenylidene-ruthenium complex *trans*-$[RuCl(=C=C=CPh_2)(dppe)_2]PF_6$ was not observed [25]. By contrast the allenylidene complexes **31a**,**b** containing a γ-methyl group show a clear amphoteric character (Scheme 27) [25]. Thus, they are easily deprotonated by NEt_3 to give the alkenylacetylide complexes **32a**,**b** (vide infra). The later are reprotonated into the allenylidenes **31**. The addition of 3 equiv. of HBF_4 to **31a**,**b** leads to the alkenylcarbyne complexes **33a**,**b**. No rearrangement into indenylidene complex was observed for **33a**. These derivatives display characteristic ^{13}C NMR data [**33a**, ^{13}C NMR: δ 307.74 (quint., C_α, $^2J_{PC}$: 13 Hz), 199.65 (s, C_γ), 129.94 (s, C_β)]. In addition, UV–vis spectra show a significant 60 nm shift of the metal to ligand charge transfer band (MLCT) from $\lambda_{max} = 482$ nm for the allenylidene **31b** to $\lambda_{max} = 426$ nm for the carbyne **33b** as a consequence of the conjugation change.

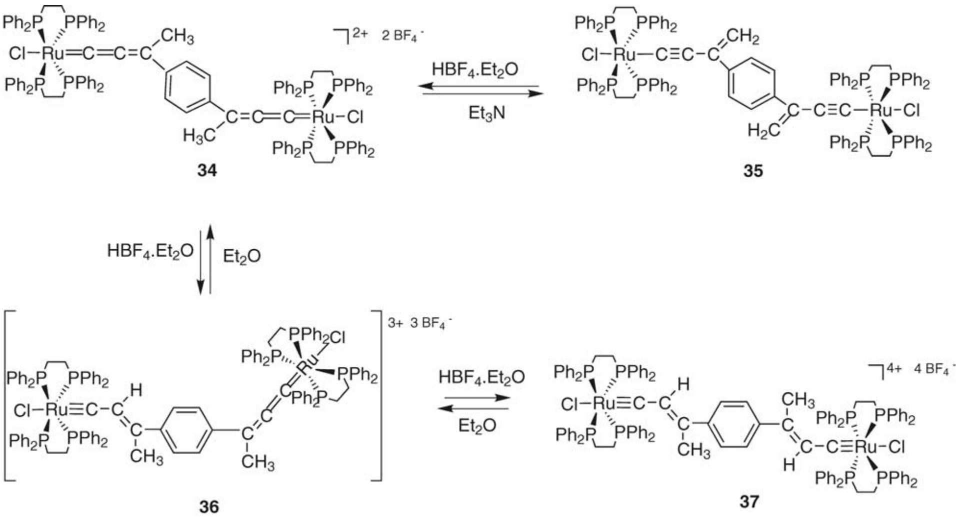
The same concept of reversible deprotonation/protonation was applied to the binuclear complex **34** containing a conjugated bis(allenylidene) bridging ligand owing to the stability of the alkenylcarbyne complex **33**. It was reversibly deprotonated into the conjugated binuclear complex **35** (Scheme 28). The addition of an excess (6 equiv.) of HBF_4 to **34** leads to its complete double protonation and the formation of the first bis alkenylcarbyne-ruthenium complex **37**.



Scheme 26.



Scheme 27.

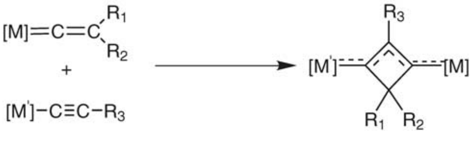


Scheme 28.

The progressive addition of HBF_4 to **34** allows observing by NMR the intermediate formation of the mixed allenylidene/alkenylcarbyne complex **36**. The double protonation of **34** ($\lambda_{max} = 589$ nm) leads to a red shift of the MLCT band, **37** ($\lambda_{max} = 496$ nm). However, whereas complex **37** is stable at room temperature in the presence of an excess of a strong acid, it is very acidic and is easily deprotonated by solvent [25].

6. Bimetallic C_7 systems with delocalized carbon chains

A variety of bimetallic complexes allowing through bridge exchange of electron between the remote metals complexes has been reported [30,59–65] especially with an even number of conjugated carbon atoms spanning metal fragments of various structures such as $L_nMC_xML_n$ [61] or $L_nM(CH)_xML_n$ [62]. By contrast, only a limited number of complexes with an odd numbered linear or cyclic carbon bridge linking the two metal moieties have been described [63–65]. The most general process affords rigid four-membered cyclic bridges with a delocalized C_3 path between metals via the regioselective [2 + 2] cycloaddition between the C=C bond of a vinylidene [M]=C=CHR and the $C_\alpha{\equiv}C_\beta$ bond of a metal acetylide [M]–C≡C–R (Scheme 29) [63]. Interestingly, the C_α–C_β bond is generally the most activated, and when the reaction was applied to an allenylidene [M=C=C=CR_1R_2] complex [63b] or a diyne [M–C≡C–C≡C–R] complex [63c], a similar C_3 conjugated path is formed with an exocyclic double or triple bond inhibiting the access to higher odd numbered carbon-rich bridges.



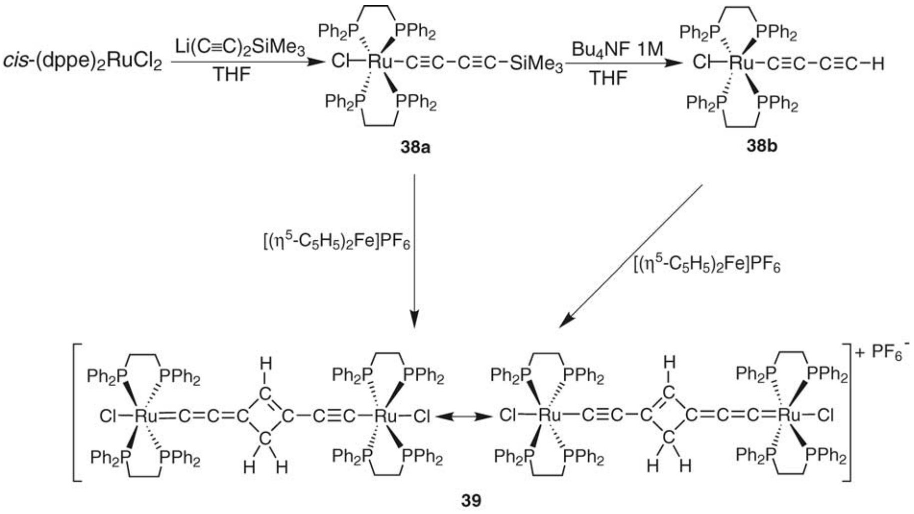
Scheme 29.

Recently, two novel methodologies of C–C bond formation to obtain a new class of carbon-rich homobimetallic complexes with seven conjugated carbons between remote metals and a charge highly delocalized over the extended conjugated structure were discovered [59,60]. The first one consists in an unprecedented radical promoted [2 + 2] coupling reaction occurring on the $C_\gamma{\equiv}C_\delta$ bond of a 1,3-diynylmetal derivative [Ru]–C≡C–C≡CR to lead to a novel complex including a carbon-rich annelated C_8H_3 bridge. The second method describes the coupling between an allenylidene and a metal diyne to provide "W" shaped complexes.

6.1. Binuclear ruthenium with a C_7 bridge based on a radical promoted metal diyne coupling reaction

The complex *trans*-[Cl(dppe)$_2$Ru–(C≡C)$_2$–SiMe$_3$] (**38a**) was prepared using the classical reaction of Li(C≡C)$_2$SiMe$_3$ with the metal halide complex *cis*-[RuCl$_2$(dppe)$_2$] (Scheme 30) [66]. This air stable acetylide is easily further deprotected using Bu_4NF to provide the *trans*-[Cl(dppe)$_2$Ru–(C≡C)$_2$–H] (**38b**). Chemical oxidation of **38a–b** with the addition of half an equivalent of ferricinium hexafluorophosphate leads to the annelated bimetallic complex, via a cycloaddition at the $C_\gamma{\equiv}C_\delta$ triple bond (Scheme 30), with an allenylidene character. The Ru–C_α resonance at $\delta = 247.7$ ppm is downfield compared to that of an alkynyl ($\delta = 105.5$ ppm for *trans*-[Cl(dppe)$_2$Ru–C≡C–CPh$_2$H)]) [24] and upfield to that of an allenylidene complex ($\delta = 308.6$ ppm for *trans*-[Cl(dppe)$_2$Ru=C=C=CPh$_2$]) [22].

The unprecedented regioselectivity observed for the cyclic addition is explained by the steric hindrance, as the $C^\alpha{\equiv}C^\beta$ bond in the diyne complexes is sterically protected



Scheme 30.

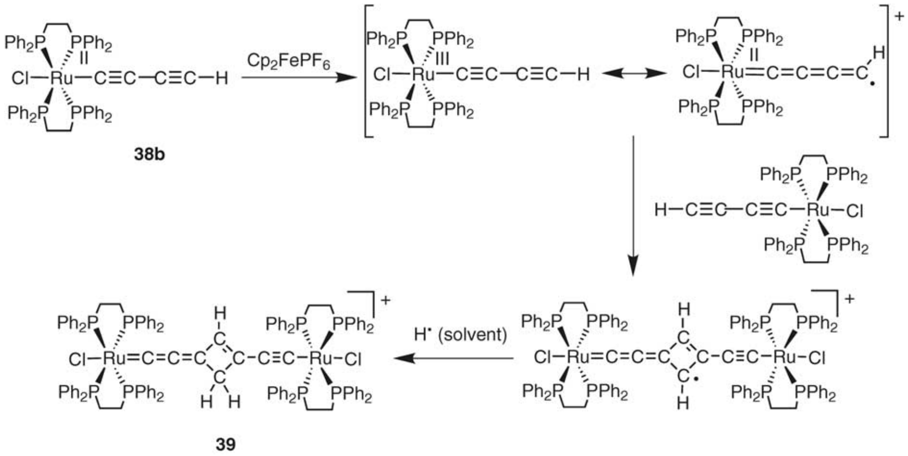
by the bulky ruthenium moieties. It is anticipated that despite the unfavourable potential, the reaction is initiated by an electron transfer between ferricinium cation and **38a** or **38b** generating an electrophilic metallacumulene radical intermediate. The oxidized form should correspond to $Ru^{\bullet +}$–C≡C–C≡CH ↔ Ru^{+}=C=C=C=$C^{\bullet}$H with a significant contribution of the cumulenic form that can react with another molecule of acetylide, followed by further incorporation of a hydrogen atoms from the medium (Scheme 31). In the case of **38a**, desilylation occurs during the process. The isolation of a ruthenium butatrienylidene intermediate has not been yet possible because of its high reactivity. However, such an intermediate has been isolated in an iridium complex [Cl(PiPr$_3$)$_2$Ir=C=C=C=CPh$_2$] [67].

6.2. Binuclear ruthenium with a C_7 bridge based on a metal diyne-metal-allenylidene coupling reaction

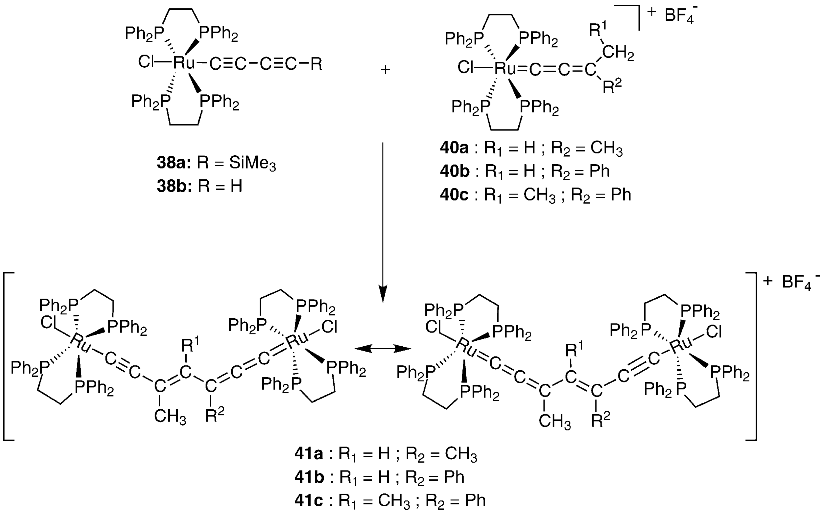
The formation of the annelated bimetallic complex via a possible metallacumulene radical intermediate gave impetus to react metal diyne systems **38a**–**b** with preformed cumulenic species such as allenylidenes (Scheme 32) [60].

The cationic allenylidene complexes **40a**–**c** were allowed to react with the diynyl compound **38b**. The resulting metal assisted C–C forming reaction led to **41a**–**c**. These complexes **41a**–**c** were also obtained when the reaction was performed with the protected diynyl **38a** as desilylation also occurs in the reaction medium. It is noteworthy that the resonances of C_α and C'_α for these compounds (**41a**: $\delta = 224$ ppm) are found downfield from that of an alkynyl and upfield from that of an allenylidene complex. The X-ray structure of **41a** confirmed the nature of the product.

A probable mechanism for this reaction is based on the fact that ruthenium-allenylidenes with a –CH_2R_1 group on C_γ are easily deprotonated into stable ruthenium acetylides (vide infra). This mechanism is depicted on Scheme 33 for **41b**. The first step consists in the transfer of a proton from **40b** to the nucleophilic carbon C_δ of **38b** to form an unstable butatrienylidene complex [A] and the acetylide **42b**. A further fast addition of the nucleophilic C_δ of **42b** on the



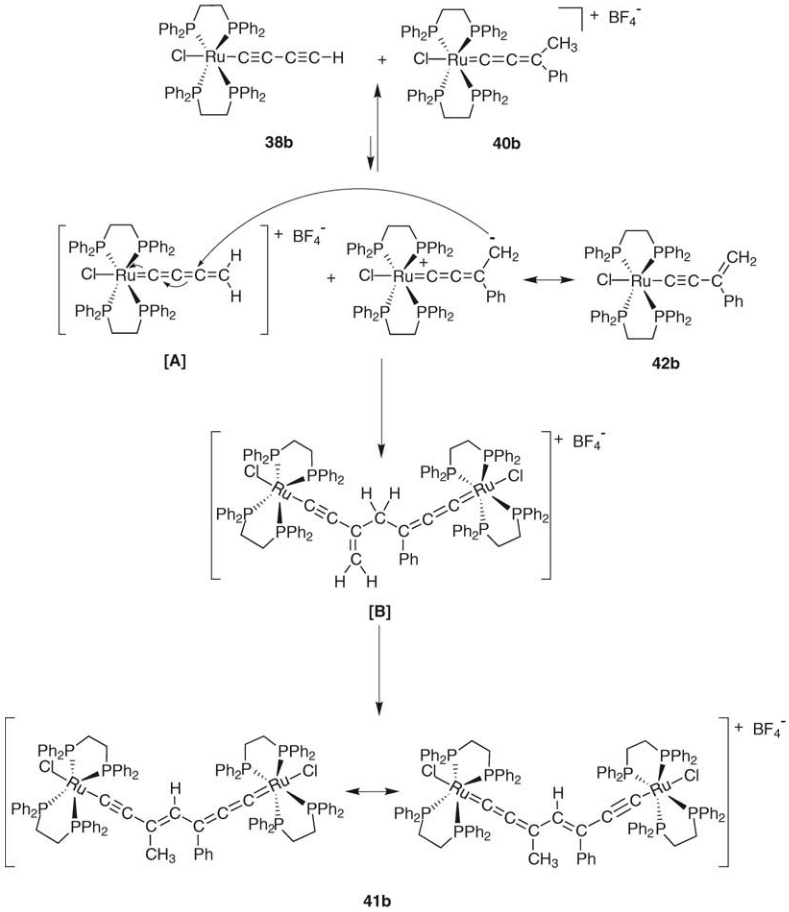
Scheme 31.



Scheme 32.

electrophilic C_γ of [A] leads to the intermediate [B]. The formation of **41b** would then result from an allylic hydrogen transfer.

All compounds show a reversible one-electron reversible oxidation wave followed by an almost reversible or irreversible second oxidation wave. To a first approximation, these two oxidation steps could be viewed as essentially involving the two Ru^{II}/Ru^{III} couples and the large separation of the processes ($E^\circ_{ox1} = 0.32\,V$ versus ferrocene, $E^\circ_{ox2} = 0.97\,V$, $\Delta E^\circ = 650\,mV$ for 41b) is attributable to



Scheme 33.

substantial electronic interaction between the metallic centres. All four complexes also undergo a well-defined one-electron reduction processes ($E^{\circ}_{\mathrm{red}} = -1.38\,\mathrm{V}$ versus ferrocene for **41a**) attributable to the reduction of the unsaturated carbon chain. For example reduction of complexes **39** with cobaltocene allows the observation of an intense and persistent ESR feature at 293 K ($g = 2.009$). This attribution is also supported by the fact that the reduction potential is highly influenced by the introduction of the phenyl group in **41b–c** in comparison with **41a** ($E^{\circ}_{\mathrm{red}} = -1.24\,\mathrm{V}$ versus ferrocene for **41b**). Each complex displays a strong metal to ligand charge transfer band, and the $\lambda_{\max}$ values are influenced by the nature of the bridge. For example, $\lambda_{\max} = 633\,\mathrm{nm}$ and $\lambda_{\max} = 764\,\mathrm{nm}$ for **39** and **41c** respectively.

These unique annelated and “W” shaped C_7 bridge arrangement, obtained under very mild conditions, display remarkable stabilities. The structural variation in the C_7 bridge largely influence the electrochemical and optical properties and this could be related to the efficiency of the delocalized path. These observations support the necessity to tune a general system to find the best physical properties.

7. Conclusion

This review shows that the selective activation of a variety of functional prop-2-yne-1-ols allows the formation of a wide range of carbon-rich allenylidenes for catalysis, and with potential for material science. Ruthenium-allenylidene complexes have brought specific behaviour in transition metal chemistry.

Ruthenium-allenylidenes are precursors for the synthesis of new bimetallic complexes with carbyne ligands via protonation, or with odd numbered carbon chains via original C–C bond coupling reactions. The preparation of a bis(allenylidene) metal complex and its one-electron reduction showed the possibility of electronic communication between two carbon-rich chains through a ruthenium atom, which is a crucial issue for the development of molecular wires.

At the same time, the chemistry of ruthenium-allenylidenes has reached such a state of development that they now become a powerful tool in modern synthesis. Their use as precatalysts in catalytic olefin metathesis is at this time under control. These first steps in catalysis should lead to the development of catalysts for new processes for fine chemical and polymer production.

Acknowledgements

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