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A new class of carbon-rich organometallics. The C_3, C_4 and C_5 metallacumulenes $Ru{=}(C{=})_nCR_2$

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Contents

Abstract

This review article profiles the advances in ruthenium chemistry for the synthesis of a new class of organometallic complexes containing conjugated carbon-rich chains. The preparation and reactivity of recently described metallacumulenes complexes, or reactive intermediates, of general formula $L_nRu{=}(C{=})_nCR_2$ ($n=2,3,4$), are presented. They are shown to be produced, under very mild conditions, *via* the activation of propargyl alcohols derivatives $HC{\equiv}C\text{-}CR_2OR$, conjugated diynes $HC{\equiv}C\text{-}C{\equiv}C\text{-}R$ and pentadiynes $HC{\equiv}C\text{-}C{\equiv}C\text{-}CR_2(Y)$ by Ruthenium(II) precursors of type $RuCl_2(PR_3)(arene)$ and $RuCl_2(Ph_2P(CH_2)_nPPh_2)_2$ ($n=1,2$) in the presence of a non coordinating salt. © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

The use of vinylidene–metal intermediates $M{=}C{=}CR_2$ in catalysis is now well recognized [1–16]. It has only been developed during the last decade, though the

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first vinylidene complex was discovered as early as 1972 [17–21]. Their recent involvement in catalysis is obviously as a result of their direct formation upon activation of terminal alkynes by 16 electron metal intermediates, especially those generated from ruthenium(II) precursors [3–16].

Their closely related homologs, the allenylidene–metal, or prop-1,2-dienylidene–metal complexes, $M{=}C{=}C{=}CR_2$ have been known for 20 years [22,23]. However, they have hardly been involved in catalysis or in stoichiometric reactions leading to the displacement from the metal of the carbon-rich ligand. One catalytic reaction involving an allenylidene-ruthenium species permitted the one step synthesis of unsaturated α,β-unsaturated ketones [24]. More recently the allenylidene ligand has been displaced from Rhodium complexes [25] by diazoalkanes to produce buta-1,2,3-trienes [26] or via C–C bond formation to generate vinylallenes or cumulenes [27,28]. Allenyl phosphorus ylids have also been obtained from allenylidene derivatives [27].

The present lack of uses of allenylidene–metal intermediates or complexes in stoichiometric organic reactions or catalysis is likely due to the absence, in their early days, of a general method of formation, and at the same time easy to perform from accessible substrates. The first examples were made by modification of unsaturated, functional carbene complexes by E.O. Fischer et al. [22] or by addition of C_3-skeleton anion to metal carbonyl complexes by Berke et al. [23]. The door leading directly to allenylidene complexes was actually unbolted by Selegue in 1982 [29] with the activation of a propargylic alcohol with $RuCl(PMe_3)_2C_5Me_5$ in the presence of NH_4PF_6. The reaction led to the formation of the allenylidene-ruthenium(II) derivative as in Eq. (1) [29]. However, the analogous reactions performed with different prop-2-yn-1-ols or ruthenium precursors afforded unstable allenylidene intermediates leading to new complexes [30–32].

$$(C_5H_5)(Me_3P)_2RuCl + HC{\equiv}C-CPh_2OH \xrightarrow{NH_4PF_6}$$

$$(C_5H_5)(Me_3P)_2Ru{=}C{=}C{=}CPh_2]PF_6 + H_2O + NH_4Cl \qquad (1)$$

This reaction (Eq. (1)), showing in addition the stability of the $Ru{=}C{=}C{=}CR_2$ moiety toward the released water, has indeed initiated the development into a general method of access to a variety of metal–allenylidene complexes. We have participated in this adventure and introduced the graft leading to higher cumulenes $M{=}(C{=})_4CR_2$.

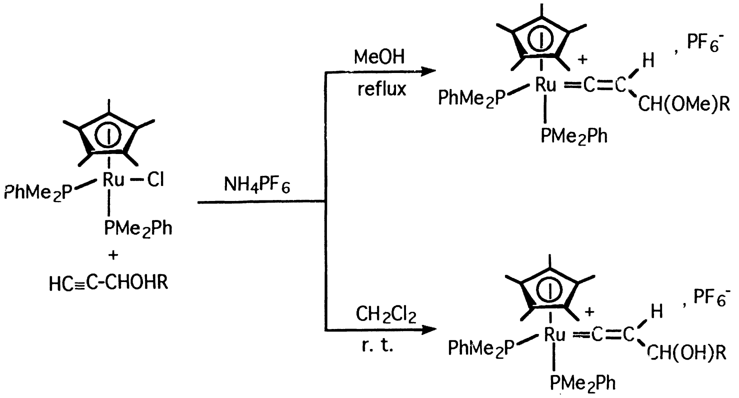
The objective of this review is to present the selective activation of a variety of functional prop-2-yn-1-ols oriented toward the formation of carbon-rich, allenylidene-ruthenium derivatives, and study the required criteria for the ruthenium moiety to allow the control of the reaction. The design of bimetallic complexes containing *bis*-allenylidene bridging ligands and the access to higher metallacumulenes will also be discussed (for previous reviews on the activation of alkynes with ruthenium complexes see [33,34].

2. Preparation of allenylidene ruthenium complexes

The direct activation of propargylic alcohols by ruthenium complexes greatly depends on the electrophilicity or electron-richness of the *in situ* generated 16 electron species. It will be shown that it is now possible to selectively orient this activation of prop-2-yn-1-ols by dehydration toward stable allenylidenes. The use of very electron-rich ruthenium complexes leading to stable vinylidene metal derivatives, thus preventing the allenylidene ligand formation, must be avoided. On the other hand the promoted activation by electrophilic ruthenium moieties leads to very electrophilic allenylidene complexes, thus too reactive to be isolated.

2.1. *Electron-rich ruthenium precursors*

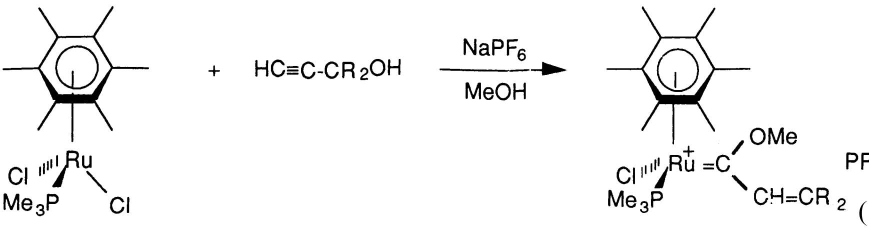
The activation of prop-2-yn-1-ols $HC{\equiv}CCR_2OH$ or $HC{\equiv}C\text{-}CHROH$ by complex $RuCl(PMe_2Ph)_2C_5Me_5$, which oxidizes at low potential ($E^0 = +0.15\ V_{SCE}$), in the presence of a non coordinating salt allows the formation of the stable vinylidene derivatives that can not be dehydrated into allenylidene derivatives [35] (Eq. (2)).



(2)

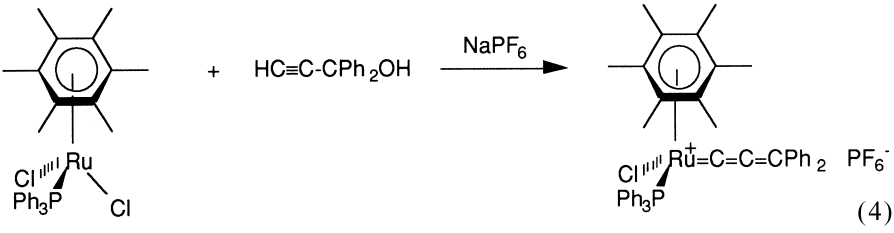
2.2. *Electrophilic ruthenium precursors*

Our initial study of the activation of prop-2-yn-1-ols was performed with $RuCl_2(PR_3)$(arene) precursors which were known to provide activation of terminal alkynes and the formation of very electrophilic vinylidene intermediates [33,34,36]. These precursors actually led to the new transformation of the prop-2-yn-1-ol molecule into alkenylcarbene derivatives in the presence of alcohol [37,38] (Eq. (3)). This reaction has been used for the stereoselective access to chiral carbene-ruthenium complexes and mixed chromium–ruthenium systems [37,38].



(3)

This formation of an electrophilic Ru=C=C=CR$_2$ moiety and nucleophilic addition at the Ru=C carbon accounts for the reaction. Indeed the RuCl$_2$(L)(C$_6$Me$_6$) precursors oxidize at much higher potential ($E° = +0.77\ V_{SCE}$; L=PMe$_3$). However, the allenylidene intermediate could be isolated with a bulky phosphorus group (L=PPh$_3$) (Eq. (4)) or when the prop-2-yn-1-ol had a ferrocenyl electron donating group at carbon C3 (Eq. (5)) [37,38].



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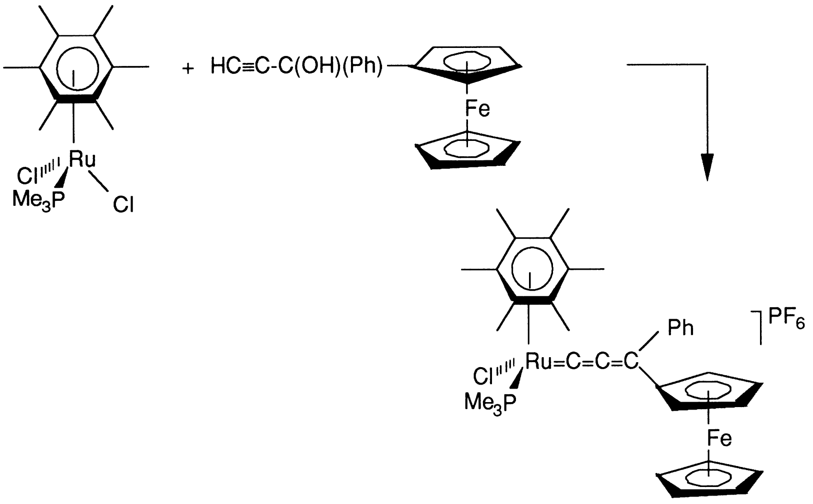
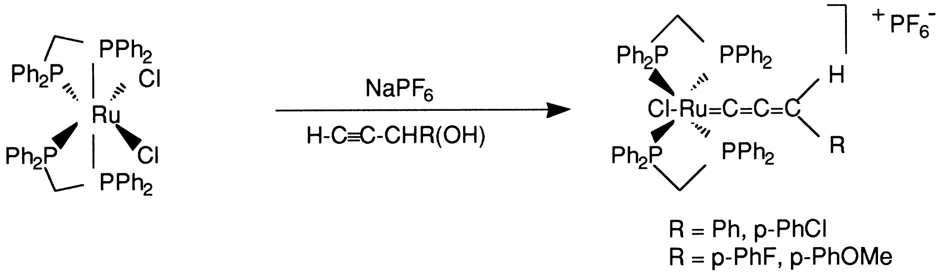


(5)

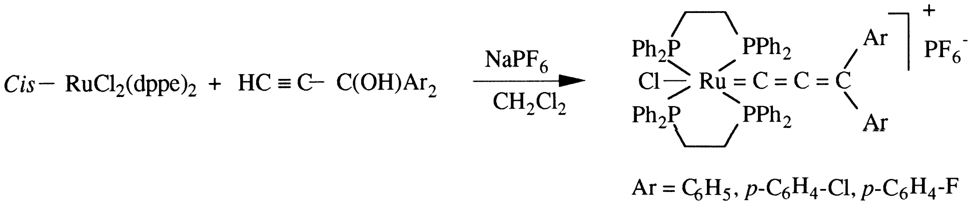
2.3. Suitable precursors of allenylidene-ruthenium derivatives

The ruthenium(II) precursors that have an intermediate oxidation potential between these two sets of electrophilic and electron-rich ruthenium(II) complexes activate prop-2-yn-1-ols and lead to stable allenylidene metal derivatives. This activation proceeds smoothly at room temperature, on the condition that the precursor possesses a labile ligand. Thus from the *cis*-RuCl$_2$(dppm)$_2$ precursor (dppm=Ph$_2$PCH$_2$PPh$_2$) a variety of stable *trans*-Cl-Ru=C=C=CR$_2$ complexes were isolated (Eq. (6)) [39–41].



(6)

Analogously, the precursors *cis*-$RuCl_2(dppe)_2$ (dppe=$Ph_2PCH_2CH_2Ph_2$) and $RuCl_2[N(CH_2CH_2PPh_2)_3]$ ($E°_{1/2}$= +0.60 V_{SCE}) allows the formation of stable allenylidene complexes (Eq. (7) D. Touchard, unpublished results; Eq. (8) [42]). The *trans*-Ru-Cl_2(dppe)$_2$ precursors oxidize at $E°_{1/2}$= +0.47 V_{SCE} and $E°_{1/2}$= +0.51 V_{SCE} respectively.



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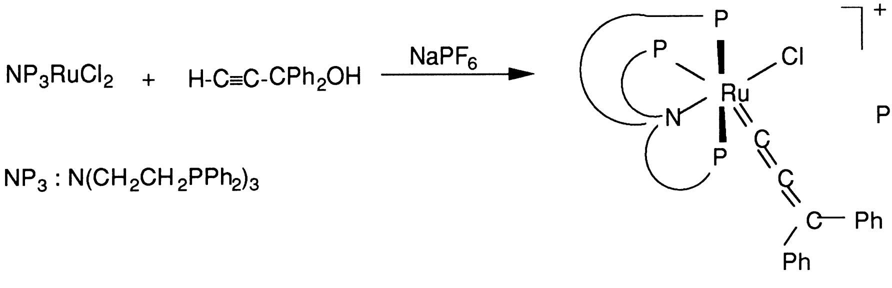
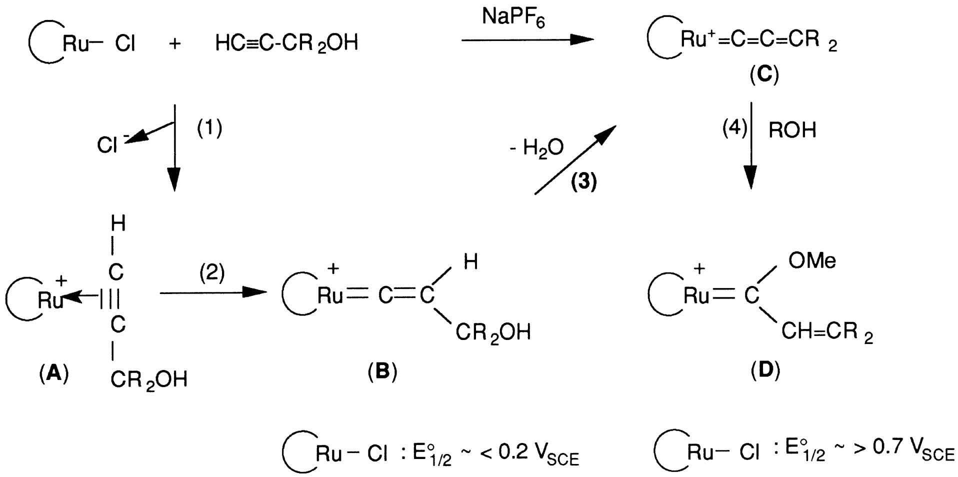


(8)

The overall activation of prop-2-yn-1-ols can be summarized according to the Scheme 1. Electron-rich precursors stop the activation at step 2 (B) and electron-deficient precursors continue the activation up to the step 4 (D) whereas allenylidenes (C) are isolable in a range of potentials E°: 0.3–0.6 V_{SCE}. However, the steric hindrance around the ruthenium site plays an important role: increase of the steric hindrance of the ancillary ligands allow stabilization of allenylidene complexes with precursors having a higher oxidation potential.

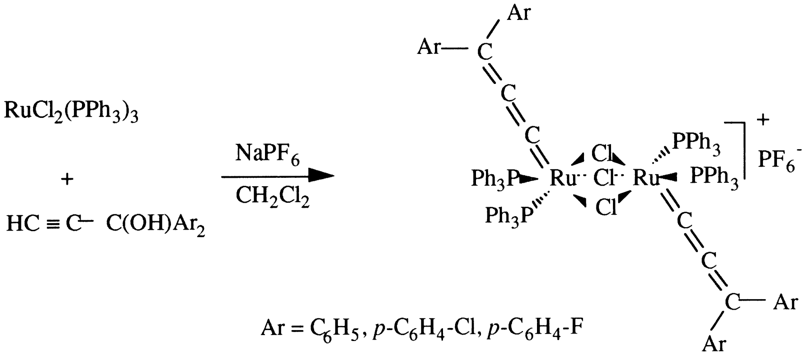
A variety of allenylidene ruthenium(II) complexes have now been prepared on



Scheme 1.

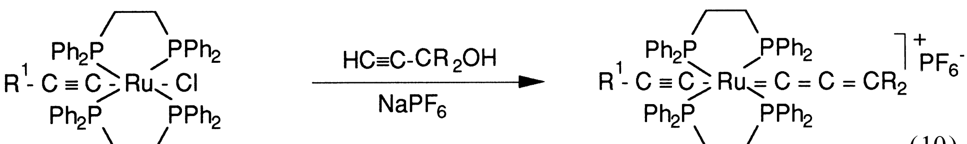
the basis of the activation of prop-2-yn-1-ols with $(C_5H_5)(PR_3)_2RuCl$ precursors by Bruce [19–21,43,44] and Tamm [45] and with $(Indenyl)(PR_3)_2RuCl$ by Gimeno et al. [46–52]. Metal carbonyl precursors were used by E. O. Fischer [22], Berke [23,53,54], H. Fischer [55–58], and de Meijere [59], to produce derivatives of type $(OC)_5M{=}C{=}C{=}CR_2$ (M represents Cr, W or Mn). In the field of Ru, Rh and Ir derivatives containing bulky phosphines important developments were brought by Werner [25,60–64] and Esteruelas [65] in the synthesis and reactivity of allenylidene–metal derivatives.

The benefit of the activation of prop-2-yn-1-ols was used recently for the access to a new generation of bis allenylidene binuclear derivatives. Thus $RuCl_2(PPh_3)_3$ reacts with propargylic alcohols to generate the new complexes containing two $Ru{=}C{=}C{=}CR_2$ moieties (Eq. (9)) [66].



(9)

The Ph_3P phosphines of these binuclear complexes can be displaced by other ligands such as dppe to afford the allenylidene derivatives such as in Eq. (7).

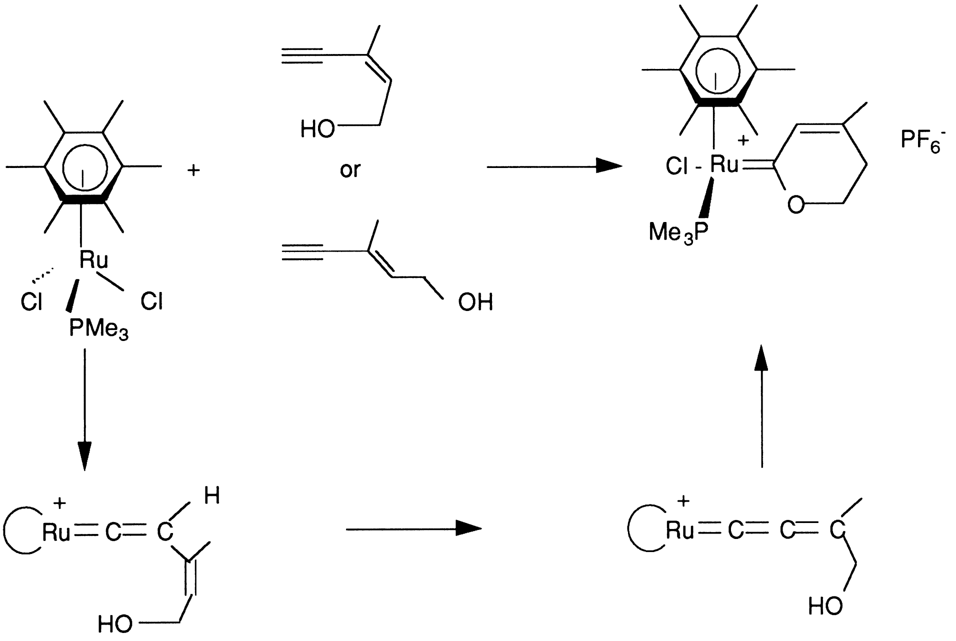


(10)

Stable mixed alkynyl allenylidene complexes have been built from alkynyl–ruthenium complexes that also promote the activation of propargylic alcohols [67,68] (Eq. (10)). Electrophilic, transient allenylidene metal intermediates are especially the key species in the stoichiometric activation of conjugated Z and E-enynols leading to cyclic α, β-unsaturated carbenes [69] (Scheme 2).

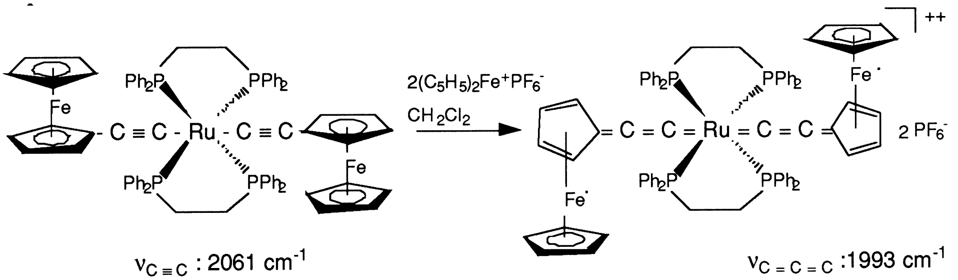
On the other hand, bis-allenylidene ruthenium moieties have been suggested, on the basis of spectroscopic studies, in order to explain that ruthenium(II) derivatives are able to communicate electronic effects. Thus the controlled synthesis of *trans*-bis-alkynylruthenium derivatives has led to the building of the linear Fc-C≡C-Ru-C≡C-Fc arrangement.

Oxidation of the corresponding complex shows that both ferrocenyl groups do not oxidize at the same potential but that on the contrary the oxidation of the first group significantly influences — through the ruthenium moiety — the second ferrocenyl group. The formation of the bis-allenylidene intermediate ($\nu_{C=C=C}$ = 1993 cm^{-1}) accounts for this communication process in which the ruthenium(II) moiety surprisingly appears as an electron-providing system [70]



Scheme 2.

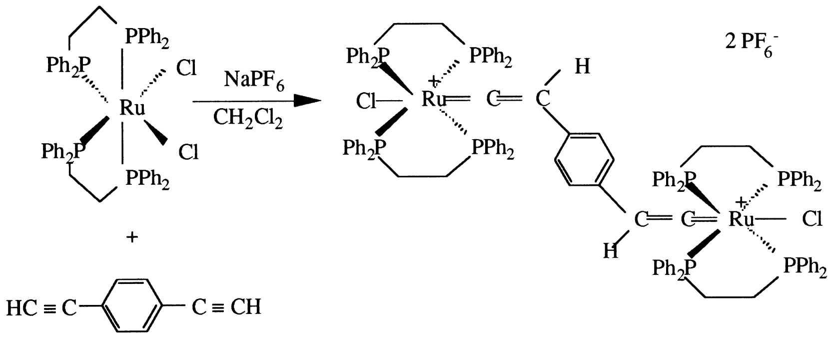
(Eq. (11)).



$E°_1 = -364$; $E°_2 = -159$; $E°_3(Ru^{II}/Ru^{III}) = +534$ mV_{SCE} (11)

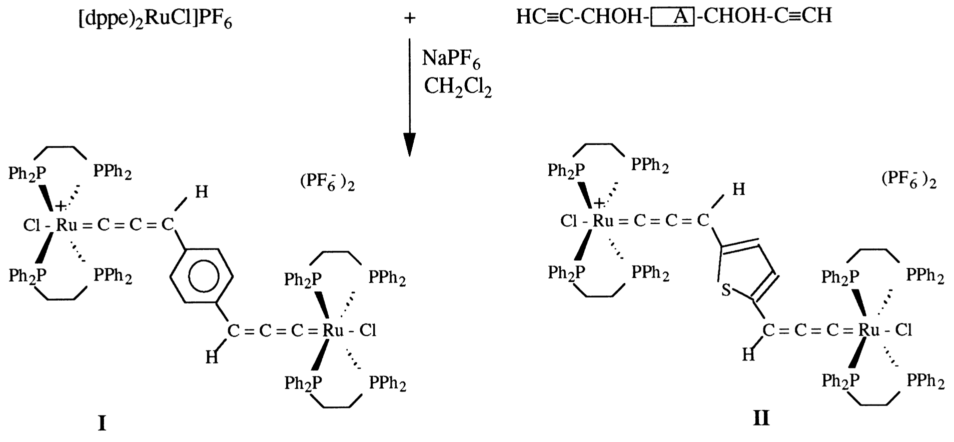
3. Diruthenium complexes with carbon-rich bis-allenylidene bridges

The metal activation of organic molecules containing two terminal alkyne or prop-2-yn-ol functionalities has potential for the access of bimetallic systems with carbon-rich, unsaturated bridge. We have first shown that the diyne $HC{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}CH$ can be activated by the $RuCl_2(dppe)_2$ precursor to generate a bis-vinylidene diruthenium derivatives [71] (Eq. (12)).

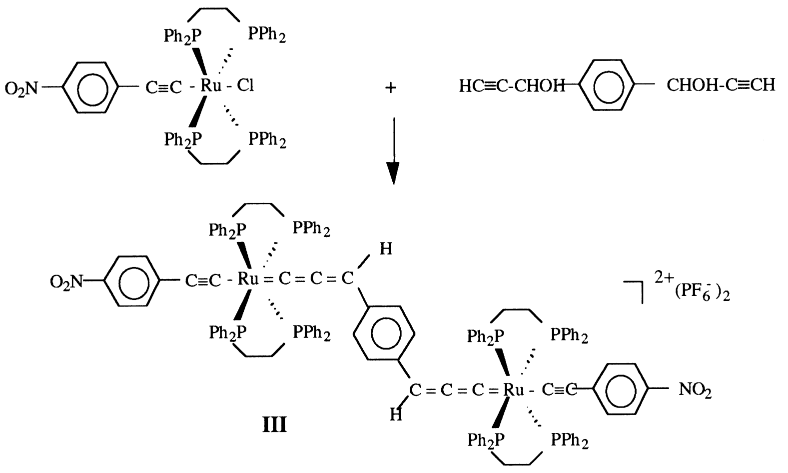


(12)

The double activation of molecules containing two terminal propargylic alcohol functional groups offer access to bis-allenylidene groups bridging two identical metal moieties. Thus the 16 electron moieties $[RuCl(dppe)_2]PF_6$ activate such molecules to generate carbon-rich, highly unsaturated orgnometallics [71] (Eq. (13)). The bis allenylidene bridges with a connecting group A: $\text{-}1,4\text{-}C_6H_4\text{-}$ (I) or $\text{-}2,5\text{-}C_4H_2S\text{-}$ (II) have been built in this way. Alkynyl–ruthenium precursors can be used to activate bis-prop-2-yn-1-ols and for instance $RuCl(C{\equiv}C\text{-}C_6H_4NO_2)(dppe)_2$ has led to the formation of the rigid, rod-like bimetallic molecule III [71] (Eq. (14)).



(13)



(14)

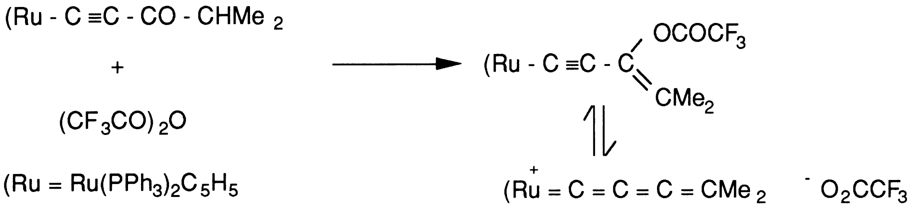
The resulting bimetallic complexes I–III can be reversibly reduced at different potentials as shown by cyclic voltammetry. $E_{1/2} = -79$ and -281 m v_{SCE} for I, $E_{1/2} = +95$ and -176 m v_{SCE} for II and $E_{1/2} = +82$ and -74 m v_{SCE} for III. The simple cyclic voltammetry study of complexes I–III shows that (i) the carbon-rich bridge allows the differentiation of both identical ruthenium moieties: e.g. the highly conjugated bridge communicate to the second ruthenium moiety that the first one has been reduced, (ii) the 2,5-thiophendiyl group is the most efficient group for this communication as D $(E_{1/2}) = 271$ mn (*versus* 202 mn for the 1,4-C_6H_4 group in I) and (iii) that an electron-withdrawing group attached to the ruthenium atom (-C≡C-C_6H_4-NO_2) favours the reduction of both ruthenium moieties [71].

There is no doubt that these rigid molecules constitute new freestones for the building of unsaturated metal containing monomers and polymers.

It is noteworthy that a bis allenylidene complex has been made by activation of a bis propargylic alcohol derivative of ferrocene with the dimolybdenum carbonyl complex $Cp_2Mo_2(CO)_4$ [72,73] in which the allenylidene group is directly linked to one metal and π-coordinated to the other metal. Recently G. Jia has also been able to generate, *via* activation of H-C≡C-CHOH-C≡CH, new bimetallic systems with carbon-rich bridges such as the conjugated linear C_5H_5 group bridging two $Ru(PPh_3)_2(CO)Cl(X)$ moieties (Ru=CH-CH=CH-CH=CH-Ru) [74] and the mixed vinylidene-allenylidene or alkynyl allenylidene in complex $[(dppe)(C_5Me_5)Ru\text{-}C{\equiv}C\text{-}CH{=}C{=}C{=}Ru(C_5Me_5)(dppe)]$ [75,76].

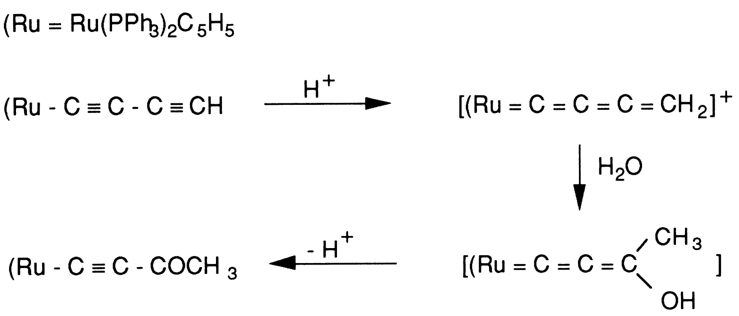
4. Toward the formation of C_4 metallacumulenes $Ru{=}(C{=})_3CR_2$

Several attempts have been made to generate C_4 metallacumulenes $M{=}(C{=})_3CR_2$. However, metallacumulenes with an even number of carbon have the tendency to reach a canonical form closely related to an alkynyl–metal complex such as $^-M\text{-}C{\equiv}C\text{-}C^+{=}CR_2$. All attempts to produce C_4 metallacumulenes have actually led to allenylidene intermediates by nucleophilic addition at the electrophilic carbon C(3). The first evidence was given by Selegue on the reversible trifluoroacetate elimination at C(3) according to Eq. (15) [77].



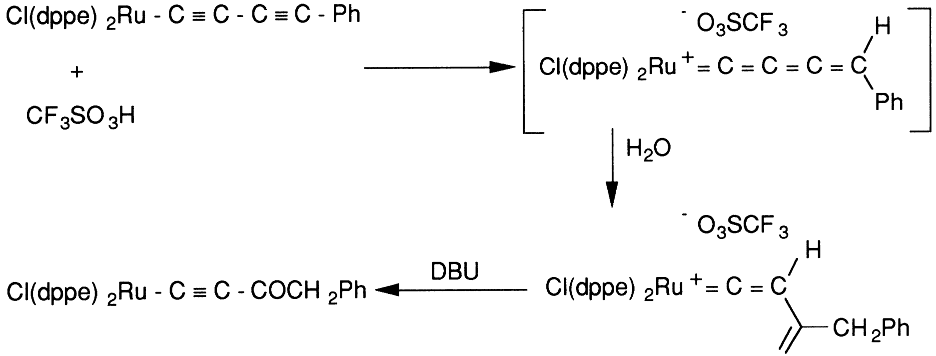
(15)

The protonation of a diynyl–ruthenium complex is expected to occur at C(4) and generate a $[Ru{=}(C{=})_3CH_2]^+$ intermediate as supported by the reaction of this intermediate with water to give an acetylethynyl ligand (Eq. (16)) [78].



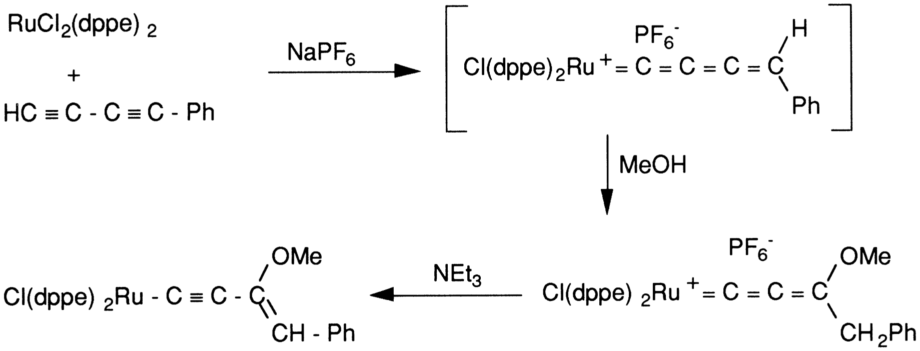
(16)

We have shown that the protonation of a Ru-C≡C-C≡C-Ph complex with trifluorosulfonique acid produced a 3-oxo-vinylidene ruthenium complex, for which the X-ray structure has been determined. Its formation is expected to take place *via* addition of water to the electrophilic carbon C(3) of the resulting $[Ru{=}(C{=})_3CHPh]^+$ cumulene and the vinylidene is easy deprotonated (Eq. (17)) [79,80].



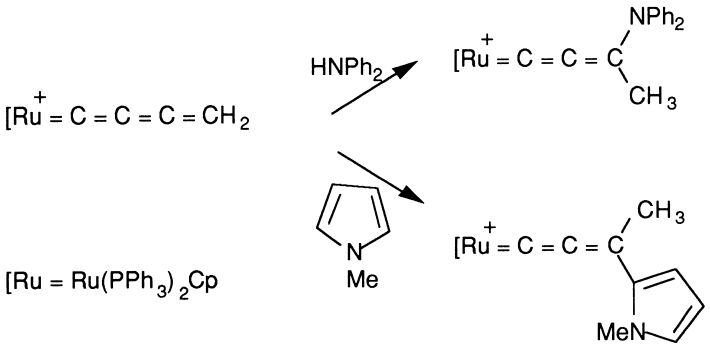
(17)

The direct activation of the diyne PhC≡C-C≡CH with the 16 electron species $[RuCl(dppe)_2]PF_6$, generated from the reaction of $RuCl_2(dppe)_2$ and $NaPF_6$, in methanol promoted the formation of a methoxy allenylidene derivative, by addition of methanol to the electrophilic carbon C(3) of the expected, but not isolated, metallacumulene $[Ru{=}(C{=})_3CHPh]^+$ (Eq. (18)) [79,80].



(18)

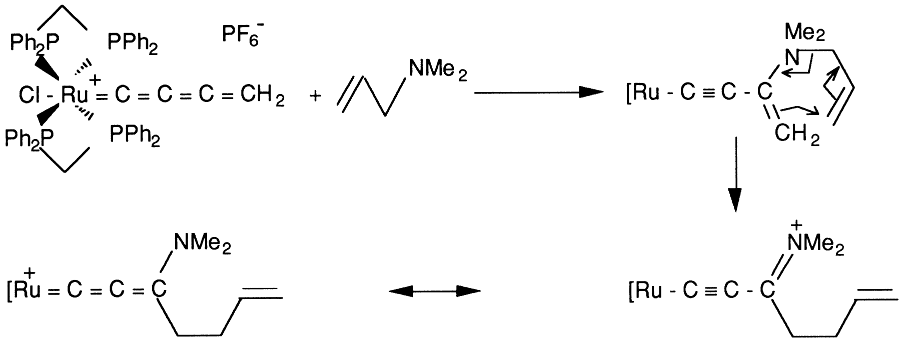
In recent work, Bruce *et al.* have developed the chemistry of the *in situ* generated intermediate $[Cp(PPh_3)_2Ru{=}C{=}C{=}C{=}CH_2]^+$ which adds nucleophiles at C(3) to generate functional allenylidenes (Eq. (19)) [81].



(19)

This reaction has been extended to the addition of imines as a unique way to produce 4-ethynylquinoline and 1-azabuta-1,3-diene complexes (Scheme 3) [82].

The addition of allylamine to a $[Ru{=}(C{=})_3CH_2]^+$ intermediate leads by contrast to the aza-Cope rearrangement and to new functional allenylidenes (Eq. (20)) [83].



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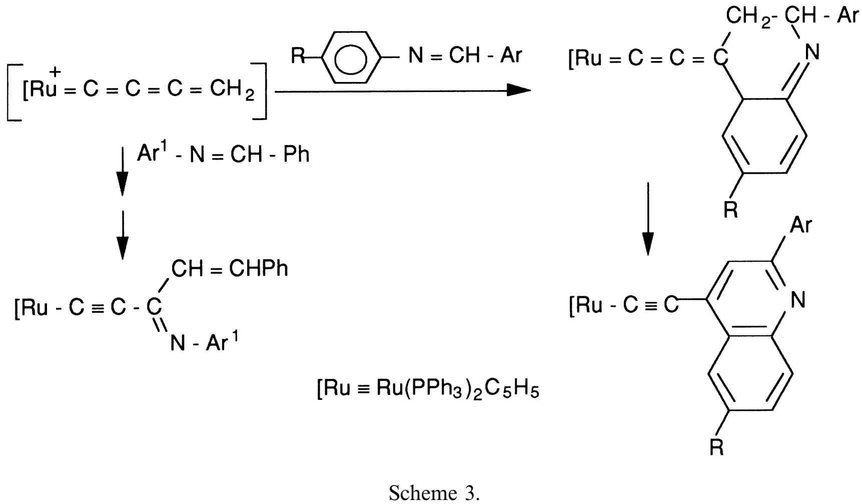


Scheme 3.

The above reactions show that the $[Ru{=}C{=}C{=}C{=}CHR]^+$ intermediates, either from protonation at C(4) of a diynylmetal complex or by direct activation of a terminal diyne $HC{\equiv}C\text{-}C{\equiv}C\text{-}R$, are too electrophilic and reactive to be isolated or characterized, but at the same time they offer a new way to reach novel functional allenylidenes by nucleophilic addition at C(3).

5. Activation of diynes and formation of $\mathbf{M{=}(C{=})_4CR_2}$ intermediates and $\mathbf{M{=}(C{=})_2C(Y)CH{=}CR_2}$ complexes.

As is now well established that the direct activation of prop-2-yn-1-ols by metal complexes can produce metal allenylidene intermediates, we have focused our search for the higher cumulenes $M{=}(C{=})_4CR_2$. The direct activation of penta-1,3-diynes could be expected to promote the migration of terminal $(HC{\equiv}C)$ hydrogen to C(2) (vinylidene) and to C(4) (buta-1,2,3-trienylidene) and favor the elimination of a leaving group at C(5) (Eq. (21)).

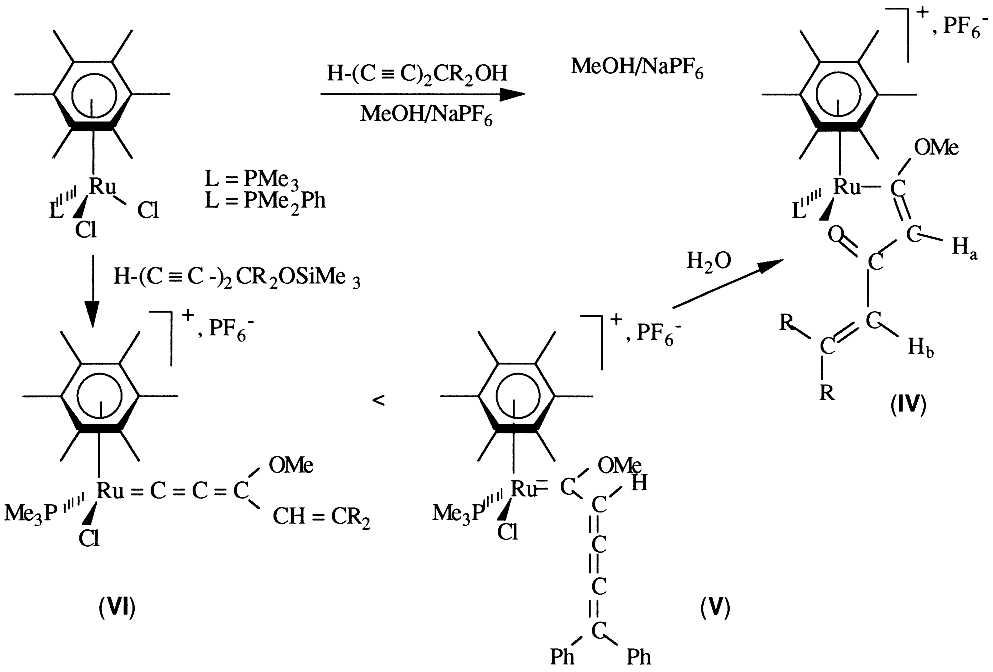
$$[Ru-Cl \quad + \quad HC\equiv C-CR_2OH \xrightarrow[\substack{(-\,NaCl)\\ -\,H_2O}]{NaPF_6} [\overset{+}{Ru}=C=C=CR_2$$

$$[Ru-Cl \quad + \quad HC\equiv C-C\equiv C-CR_2OY \xrightarrow[\substack{-\,NaCl\\ -\,HOY}]{NaPF_6} [\overset{+}{Ru}=C=C=C=C=CR_2 \qquad (21)$$

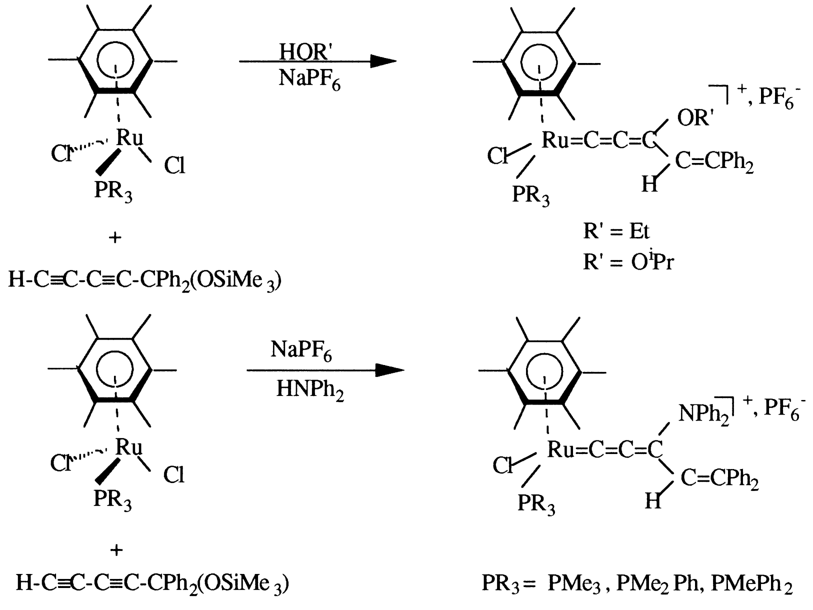
Our first attempt in this direction led us to consider the direct activation of the 5-hydroxy diynes $H(C{\equiv}C)_2CR_2OH$ with the electrophilic $RuCl_2(PR_3)$(arene) precursors. The reaction actually led to the isolation of metallacycles IV. The formation of IV could be explained *via* the initial formation of the expected $Ru{=}(C{=})_4CR_2$ moiety by water elimination followed by addition of methanol, followed by that of water (Scheme 4) [84,85].

The activation of the diyne $H\text{-}(C{\equiv}C\text{-})CR_2OSiMe_3$ in methanol, but in the absence of water, afforded by contrast the buta-1,2,3,4-tetraenyl carbene derivative V as the major product and a trace of alkenyl allenylidene complex VI. Both of them arise from the $Ru{=}(C{=})_4CR_2$ intermediate *via* addition of the methanol at carbon C(1) and carbon C(3), respectively. The derivative V was shown to produce the metallacycle IV on addition of water (Scheme 4) [84,85].

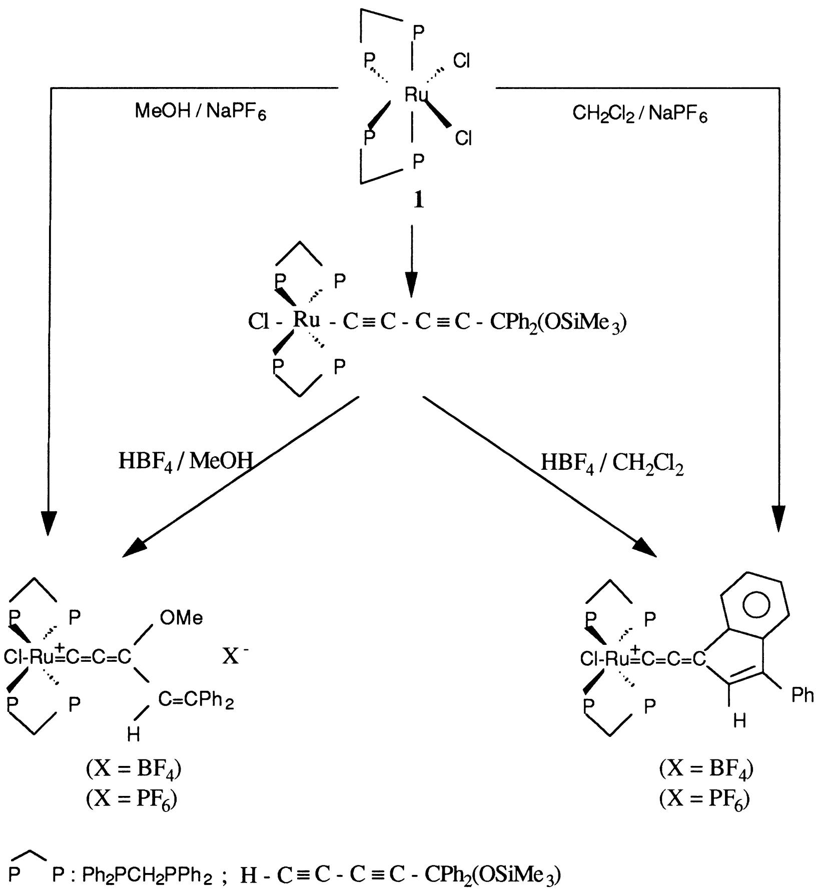
The activation of closely related diynes $H(C{\equiv}C)_2CR_2OSiMe_3$ by a variety of bulkier $RuCl_2(PR_3)$(arene) complexes in the presence of ethanol, isopropanol or amine (Eq. (22)) [86,87] or more electron-rich precursors of type $RuCl_2(dppm)_2$ (Eq. (23)) [88] has actually allowed to develop a general route to 3-alkenyl allenylidene ruthenium complexes *via* addition to carbon C(3) of the non isolated $Ru{=}(C{=})_4CR_2$ intermediate.


H-(C ≡ C)2CR2OH
MeOH/NaPF6
MeOH/NaPF6
L = PMe3
L = PMe2Ph
H-(C ≡ C -)2 CR2OSiMe 3
H2O
+, PF6-
OMe
Ha
Hb
(IV)
(V)
(VI)
Ru = C = C = C
CH = CR2
Me3P
Ph
Ph
<

Scheme 4.


HOR'
NaPF6
+, PF6-
OR'
Ru=C=C=C
C=CPh2
PR3
R' = Et
R' = OiPr
+
H-C≡C-C≡C-CPh2(OSiMe3)
NaPF6
HNPh2
NPh2
PR3 = PMe3, PMe2Ph, PMePh2

(22)

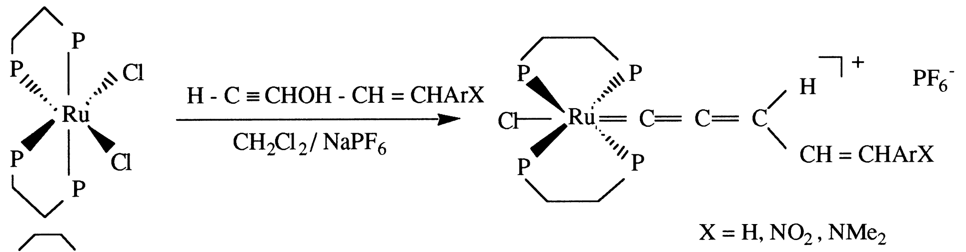


(23)

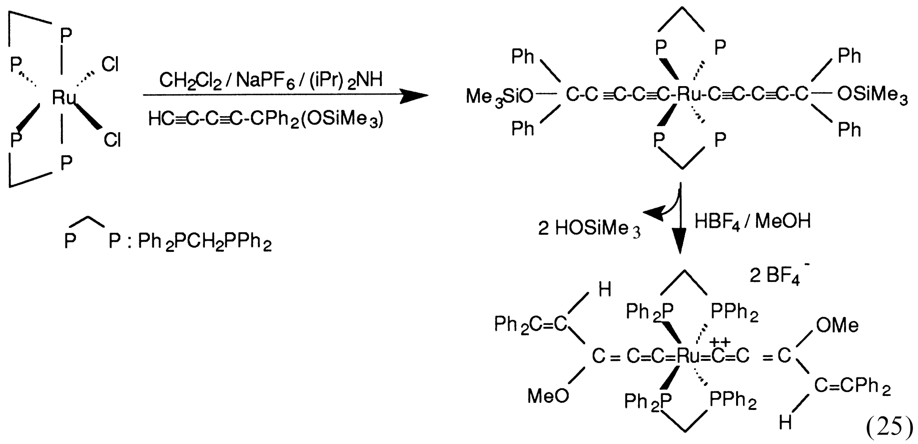
In the absence of a nucleophile (methanol) the production of the intermediate $(Ru{=}(C{=})_4CPh_2$ leads to the formation of a new type of allenylidene *via* electrophilic ortho proton substitution of a phenyl group by the very electrophilic carbon atom C(3) (Eq. (23)) [87].

The reaction of the alkyne H-C≡C-CHOHCH=CHArX with $RuCl_2(dppe)_2$ constituted another direct formation of 3-alkenyl allenylidene without any stabilizing heteroatom group at carbon C(3) (Eq. (24)) [89].

The diyne activation has been put in action in order to produce *trans*-bis allenylidene complexes from *trans*-bis diynyl-ruthenium derivatives. The protonation of the $OSiMe_3$ leads to the $Ru{=}(C{=})_4CR_2$ moiety which readily adds the nucleophile at C(3) (Eq. (25)) [87].



(24)



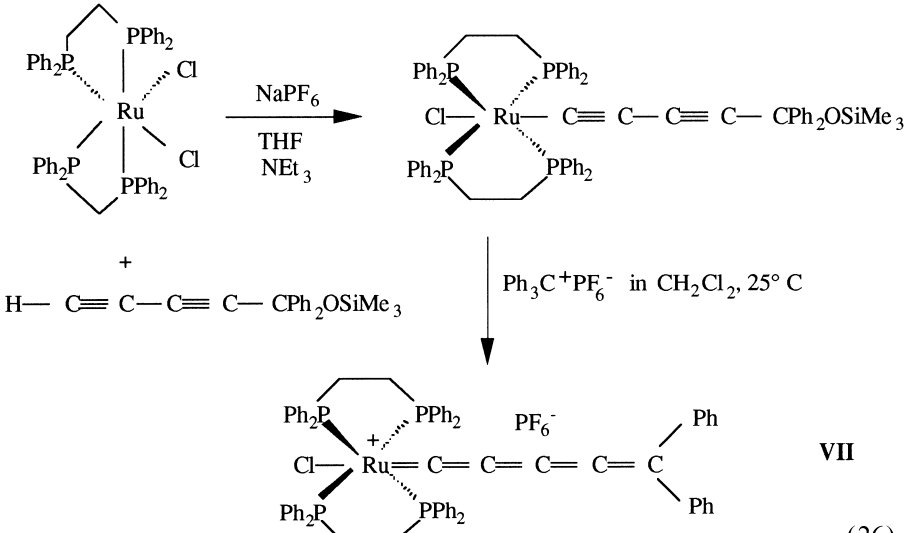
(25)

6. The penta-1,2,3,4-tetraenylidene complexes M=(C=)$_4$CR$_2$

The above attempts to generate and isolate the (Ru=C=C=C=C=CR$_2$ complexes taught us that the cumulenylidene ligand was too electrophilic to be isolated in a complex. Our objective was thus to introduce electron-donating groups in the cumulenylidene ligand or to select a more electron-releasing organometallic moiety for the activation.

The activation of the diyne derivative containing electron-releasing groups at C(5) $Me_3SiC{\equiv}C\text{-}C{\equiv}C\text{-}C(OSiMe_3)(C_6H_4NMe_2)_2$ was first attempted with $RuCl_2(PMe_3)(C_6Me_6)$ in methanol. The reaction led to the isolation of the deep blue C$_5$ cumulene (Scheme 5) [90]. The spectroscopic analysis showed that cumulene was closer to the canonical forms B and C than A. Indeed the infrared absorptions at $\nu = 2085$ and 1996 cm^{-1} were higher than expected for a C=C=C arrangement but close to the C≡C absorption wavenumber. The (Ru=C)^{13}C carbon *nucleus* resonance occurred at δ 180.10 ppm, at much higher field than expected for a (Ru=C=) carbon *nucleus*.

The second approach consisted in generating a less electron-deficient Ru-C≡C-C≡C-CR$_2$ (OSiMe$_3$) moiety and displacing the leaving group at carbon C(5) under mild conditions. Thus the Cl(dppe)$_2$Ru-C≡C-C≡C-CPh$_2$(OSiMe$_3$) was produced and reacted with $Ph_3C^+BF_4^-$ in order to eliminate the Me_3SiO^- group at C(5). This reaction led to the first real penta-1,2,3,4-tetraenylidene metal complex VII (Eq. (26)) [91]. The latter absorbs in the infrared at $\nu_{(C=C=C)}=2024$ and 1918 cm^{-1} and the $(Ru{=}C)^{13}C$ resonance occurs at $\delta=316.35$ ppm. The X-ray diffraction study of VII show the linear arrangement of Ru-C(1)-C(2)-C(3)-C(4)-C(5) with Ru-C(1) = 1.891(9) Å; C(1)-C(2) = 1.25 (1) Å; C(2)-C(3) = 1.30 (1) Å [91].

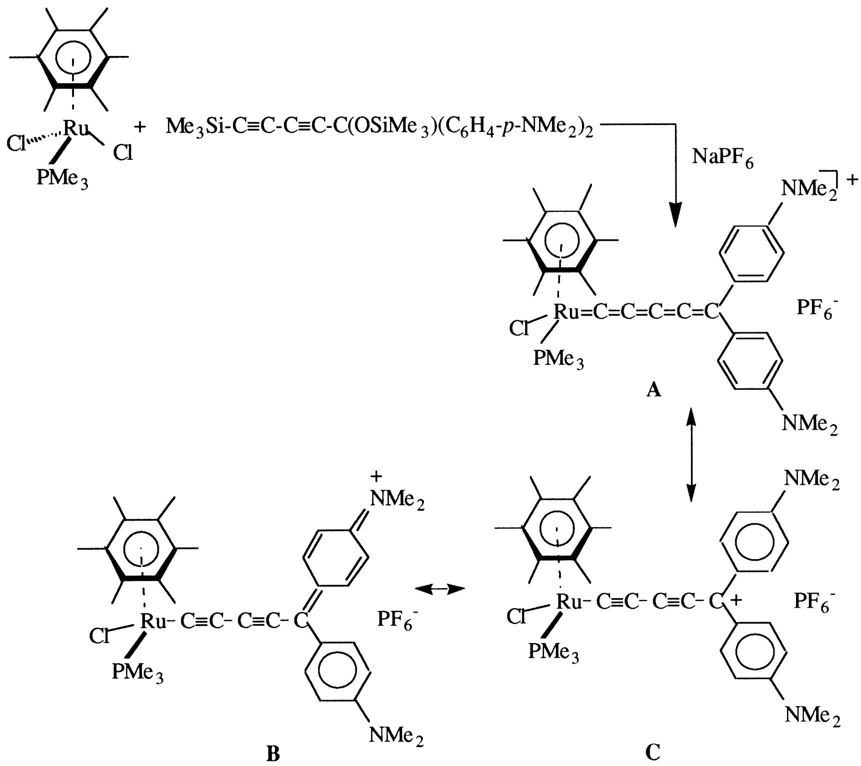


VII

(26)

The full characterization of the first $M{=}(C{=})_4CR_2$ isolated complex allowed us to demonstrate its chemistry. Complex VII reacts with methanol and secondary amine to give access to 3-methoxy and the 3-amino 3-alkenyl allenylidene derivatives VIII and IX (Scheme 6) [91].

In the absence of a nucleophile the C5 metallacumulene led us to the allenylidene X which produced by electrophilic substitution with the electrophilic C(3) carbon atom (Scheme 6). Such a cyclization was observed with a similar non-isolated intermediate (Eq. (23)) [88]. The reactivity of complex VII actually confirmed the mechanisms that were suggested before, for the activation of $H(C{\equiv}C)_2CR_2OSiMe_3$ without the isolation of the $Ru{=}(C{=})_4CR_2$ intermediate (Eq. (22), 23). Since the report of this first $M{=}(C{=})_4CR_2$ complex VII in 1994 [91] four new penta-1,2,3,4-tetraenylydene metal complexes were prepared and characterized. First H. Werner *et al.* reported the formation of the neutral cumulene *trans*-$(Cl)Ir{=}(C{=})_4CPh_2(P^iPr_3)_2$ *via* the reaction of $Ir(Cl)(H)(C{\equiv}C\text{-}C{\equiv}C\text{-}CPh_2OH)(P^iPr_3)_2$ with $(CF_3SO_2)_2O$ [92]. H. Fischer's group succeeded in the preparation of complexes $(OC)_5M{=}(C{=})_4C(NMe_2)_2$ (M represents Cr or W) on reaction of the anion $[(OC)_5M\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}C(NMe_2)_3]^-$ with $BF_3.OEt_2$ [93]. Recently, an attempt to reach the $M{=}(C{=})_6C(NMe_2)_2$ complex failed, but the formation of a new 5-alkenyl pentatetraenylidene was produced

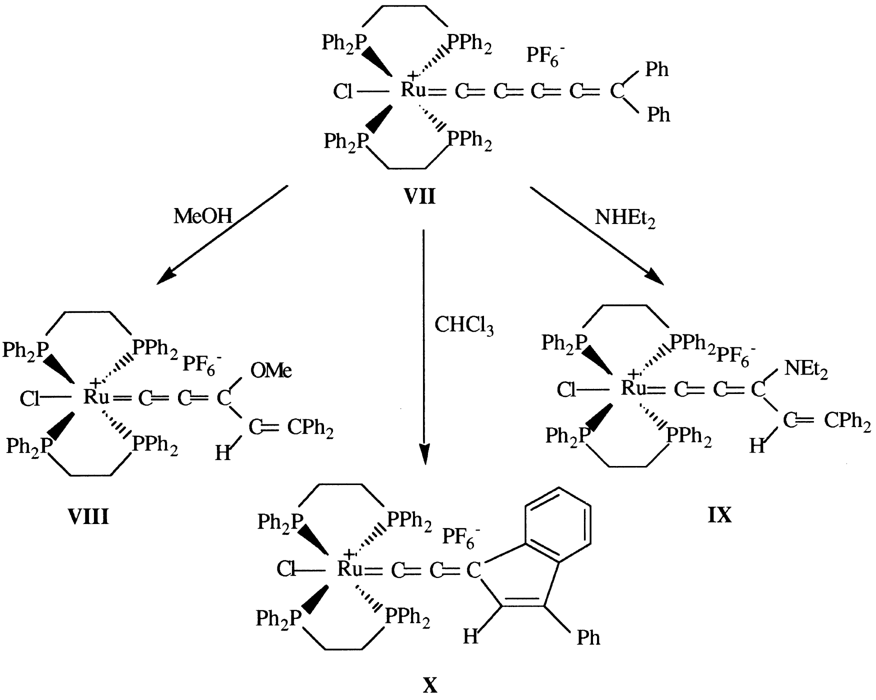


Scheme 5.

$(OC)_5W{=}(C{=})_4C(NMe_2)(CH{=}C(NMe_2)_2)$ from the reaction $(OC)_5W(THF)$ with $Li(C{\equiv}C)_3C(NMe_2)_3$ and then $BF_3.OEt_2$ [94].

7. Conclusion

The step to step access to allenylidene–, butatrienylidene– and pentatetraenylidene–metal complexes is now under control even if we learned that the C_4 metallacumulenes are too reactive to be isolated yet. These controlled preparations raise two questions: will it be possible to increase the length of the cumulene chain? The answer is expected to be yes if one succeeds to gather at the same time bulky and electron-releasing metal moieties. The second question concerns the possibility to use the metallacumulenes. They have already been involved in stoichiometric reactions with release of the cumulene ligand from the metal. The use of allenylidene complexes to promote catalytic reactions remains to be done. The chemistry has taught us that when chemists are able to control the synthesis and the reactivity of one type of metal complexes — this is the case at least for allenylidene–metal complexes — the application in catalysis is close.



Scheme 6.

Acknowledgements

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