Unsaturated carbene and allenylidene ruthenium complexes from alkynes

*Hubert Le Bozec and Pierre H. Dixneuf**

Laboratoire de Chimie de Coordination Organique, URA CNRS 415, Campus de Beaulieu
Université de Rennes, 35042 Rennes, France.
Fax: 10 (33) 99 28 6939. E-mail: dixneuf@univ-rennes1.fr

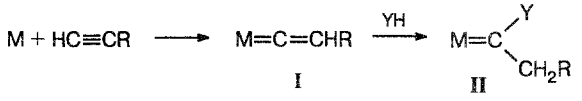
The author's studies aimed at activation of terminal alkynes by metal complexes and reactivity patterns and selective preparations of unsaturated carbene, allenylidene, and cumulenylidene derivatives of (arene)ruthenium complexes are reviewed.

Key words: activation of terminal alkynes, 2-propyn-1-ols, enynes, diynes and diynylsilanes with (arene)ruthenium(II) complexes; ruthenium(II) carbene complexes *via* vinylidene intermediates; polyenylcarbenes *via* allenylidene species; selective preparation of allenylidene, diynyl, and pentatetraenylidene ruthenium complexes.

Organometallics containing carbon-rich and conjugated chains attract interest because of their intrinsic properties[1] and because they can be used as molecular material precursors,[2] especialy for polymerization.[3] They are also interesting from the poit of view of non-linear optics.[4] Those containing a M=C bond can also be used as building blocks for access to unusual organic molecules,[5] due to the powerful synthetic properties of carbene complexes,[6] or for alkyne polymerization[7] and cyclic olefin metathesis.[8]

Vinylidene metal complexes (**I**) have the simplest unsaturated chain linked to a metal *via* a M=C bond. They are used to obtain a variety of carbene complexes (**II**)[9,10] and carbynes[11] (Scheme 1). More importantly they are related to the activation of *terminal* alkynes, as the initial transient $M(\eta^2\text{-}HC{\equiv}CR)$ intermediate readily leads to the vinylidene $M(\eta^1\text{-}C{=}CHR)$ complex, which is its more stable tautomer.[9,12] Such vinylidenes have been shown to be key intermediates in the selective catalytic transformations of terminal alkynes into fine chemicals by ruthenium complexes.[13,14] The activation of terminal alkynes leading to stable ruthenium vinylidene complexes was first performed with *electron-rich* ruthenium precursors $RuX(PR_3)_2Cp$.[9,15–18] By contrast, whereas the $RuX(PR_3)_2Cp$ complexes are inactive, the isoelectronic arene ruthenium(II) complexes $RuX_2(PR_3)(arene)$[19,20] were shown to provide electrophilic catalytic activation of terminal alkynes giving a variety of products of regioselective addition to the C≡C bond.[13,21–23] This difference in the behavior of *"electrophilic"* $RuX_2(PR_3)(arene)$[1] complexes with respect to *"electron rich"* $RuX(PR_3)_2Cp$ ruthenium(II) precursors is useful for the investigation of the generation and uses of vinylidenes by means of activation of *terminal* alkynes by electrophilic complexes.

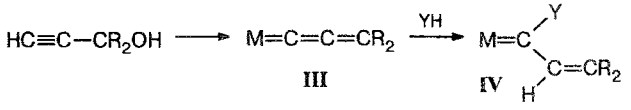
Scheme 1



I II

Propargyl alcohol derivatives consitute a class of easily available terminal alkynes, and $HC{\equiv}CCPh_2OH$ has been shown to react with $RuCl(PMe_3)_2Cp$ to give the first allenylidene ruthenium compound[24] of type **III** (Scheme 2). Its stability motivated the search for reactive allenylidenes that allow nucleophilic addition reactions as a step to complexes of type **IV** and to organometallics containing a polyenylidene chain. It could be expected that *electrophilic* complexes would generate electrophilic allenylidenes.

Scheme 2



III IV

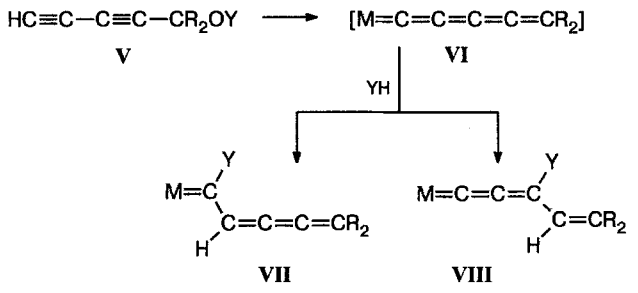
The principle of activation of propargyl alcohol derivatives into allenylidene moieties (see Scheme 2) suggested that, by homologation, the activation of diynes of type **V** would constitute an elegant way to generate higher cumulenes **VI** that could be used for the synthesis of unsaturated chain-containing organometallics **VII** and **VIII** (Scheme 3).

* The review is based on the lecture given at Workshop «Modern Problems of Organometallic Chemistry» (May 1994).

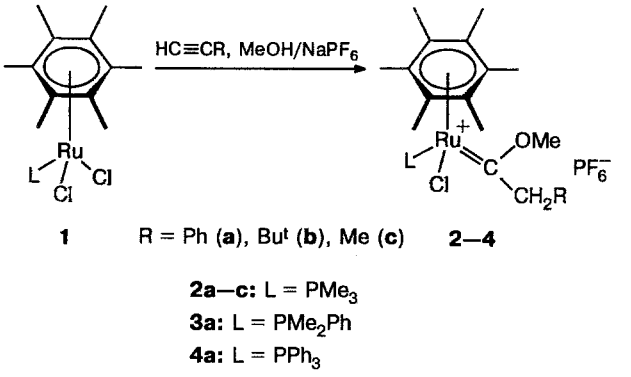
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 827—838, May, 1995.

1066-5285/95/4405-0801 $12.50

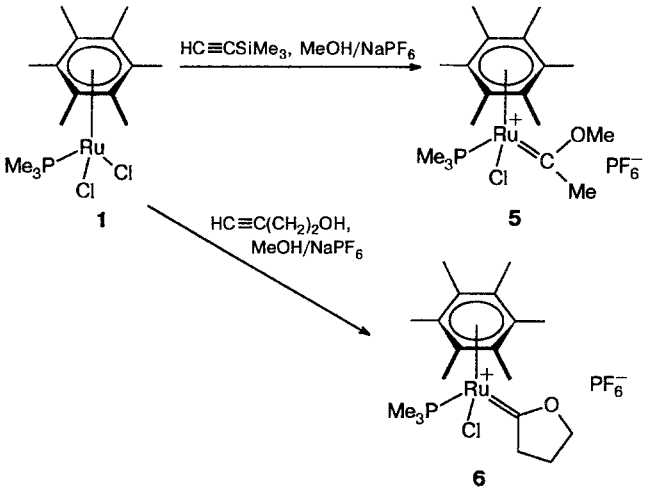
Scheme 3



Scheme 4



Scheme 5



The aim of this review is to describe the use of the activation of *terminal* alkynes, propargylic derivatives, and diynes by electrophilic (arene)ruthenium(II) precursors in attempts to control the selective synthesis of vinylidene, functional carbene, allenylidene, or cumulenylidene ruthenium derivatives as key steps in the preparation of unsaturated chain organometallics. The following aspects will be studied successively:

1) the preparation of (arene)ruthenium carbene complexes *via* activation of terminal alkynes and *vinylidene* intermediates;

2) the building of polyenylidene derivatives *via allenylidene* intermediates;

3) the activation of diynes and formation of diynyl and functional allenylidene complexes.

Preparation of carbene derivatives of (arene)ruthenium(II) complexes *via* activation of alkynes

Access to alkoxy alkyl carbene ruthenium complexes

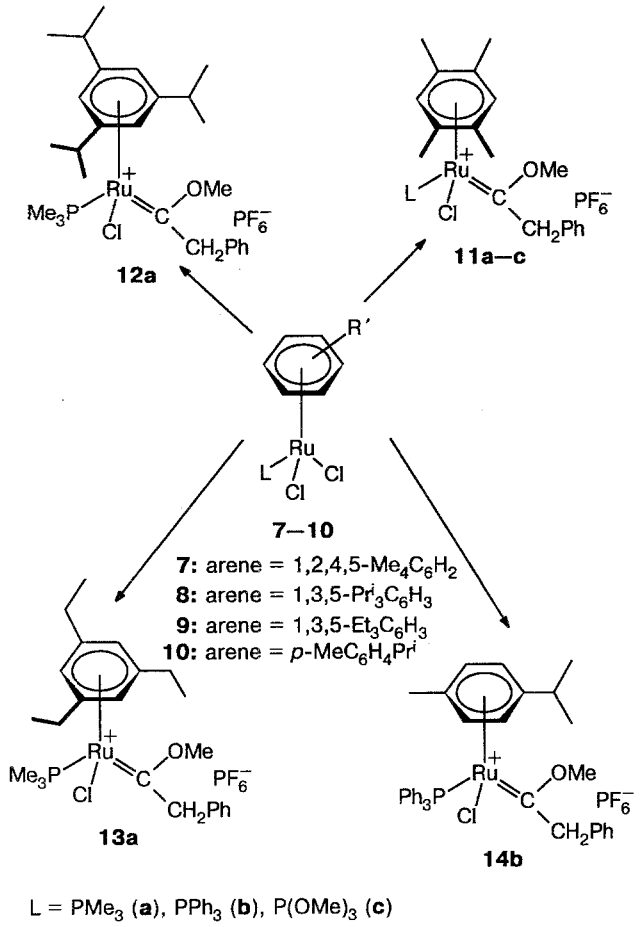
The reaction of hexamethylbenzene ruthenium(II) complexes **1** (L = PMe_3, PMe_2Ph, PPh_3) with phenylacetylene in methanol and in the presence of $NaPF_6$ affords the methoxy carbene derivatives **2—4** in 60—80 % yields (Scheme 4).[20] When treated with $Bu^tC{\equiv}CH$ and $MeC{\equiv}CH$ complexes **1** give the corresponding carbene complexes **2b** and **2c**. However, the reaction of complex **1** (L = PMe_3) with $Me_3SiC{\equiv}CH$ in methanol leads to the carbene derivative **5** indicating that, in the presence of **1**, the C—Si bond is cleaved in methanol. The reaction of but-3-yn-1-ol with **1** (L = PMe_3) affords the oxacyclopentylidene compound **6** in methanol, which shows that the intramolecular addition of the hydroxy group is favored over the addition of methanol (Scheme 5).[20]

Arene ruthenium(II) complexes $RuCl_2(L)$(arene) (**7—10**) containing a variety of arene ligands L = PR_3 also react with phenylacetylene in methanol to give the methoxybenzyl carbenes **11—14** (Scheme 6).[25] The study shows that the reaction is very slow with the weak electron donor ligand L = $P(OMe)_3$ (**7c** → **11c**) and does not proceed at all with the electron withdrawing ligand (L = CO). The electron donating capability of PR_3 groups is essential for the reaction to take place but it is not a criteria for the stability of the ruthenium carbene complex. Indeed, **10a** does not give a stable carbene complex, whereas **10b**, which contains the bulky PPh_3 group, affords **14b**. The stability of carbene complexes is due to the simultaneous presence of sterically hindered arene and phosphine ligands.[25]

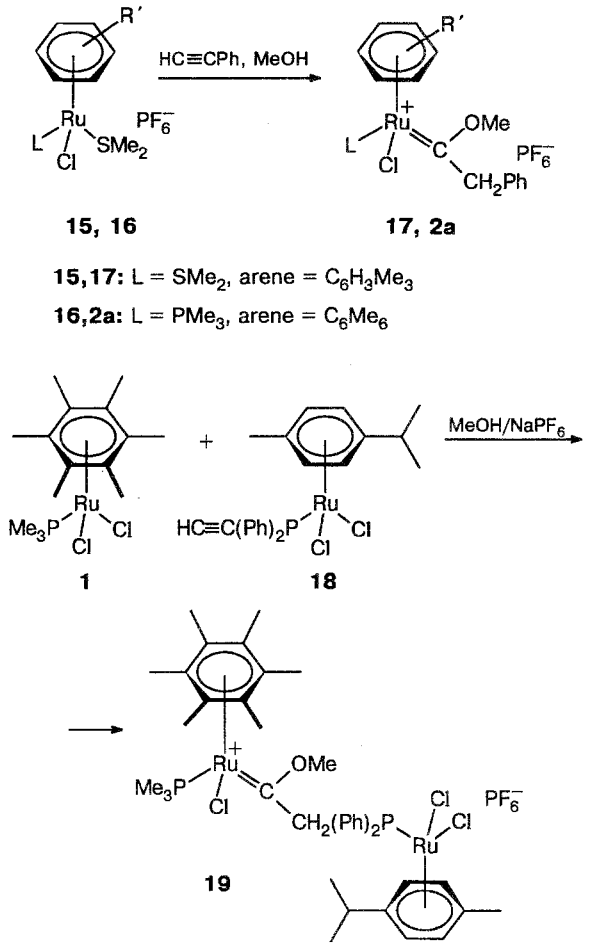
Methoxy carbene ruthenium **2a** and **17** (L = SMe_2) complexes were also made by displacement of the coordinated SMe_2 by phenyl acetylene (Scheme 7).[26] Coordinated phosphinoalkyne **18** can also be activated by arene ruthenium(II) complex **1** (L = PMe_3) to give the mixed phosphine carbene bridged binuclear complex **19** (see Scheme 7).[27]

The synthesized carbene ruthenium complexes were identified on the basis of a low fieid ^{13}C NMR chemical shift ($\delta > 320$ and $^2J_{P,C} \approx 20$ Hz). The chirality of the ruthenium derivative is reflected in the AB resonance signal of the diastereotopic methylene protons.[19,20,25]

Scheme 6



Scheme 7



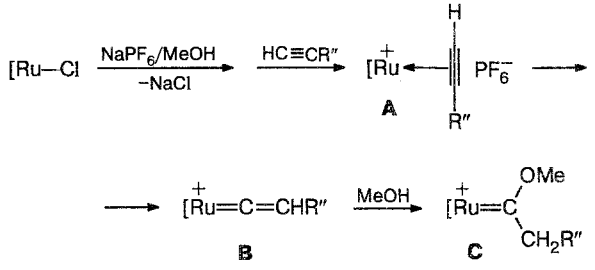
Evidence for a ruthenium vinylidene intermediate and mechanism

Arene ruthenium carbenes **C** are formed *via* vinylidene intermediates **B**, tautomers of Ru(η^2-alkyne) complexes **A** (Scheme 8).

However, while $[(PR_3)_2CpRu{=}C{=}CHR"]PF_6$ complexes are stable even in refluxing methanol,[16] the corresponding vinylidene derivatives $[Cl(PR_3)(C_6R'_6)Ru{=}C{=}CHR"]PF_6$ could not be directly isolated due to their high reactivity toward weak nucleophiles such as alcohols.[20] The first vinylidene ruthenium arene complex **21** was isolated,[20] *via* an indirect approach, by protonation of the σ-acetylide precursor **20**. Vinylidene **21** can be characterized spectroscopically by its ^{13}C NMR, which shows a doublet at low field (δ 360, $^2J_{P,C}$ = 20.6 Hz) for the Ru=C carbon nucleus. The addition of methanol to a CD_2Cl_2 solution of **21** affords the carbene complex **2a** (Scheme 9) within a few minutes[20].

Vinylidene ruthenium complexes stable toward the addition of nucleophiles have been obtained recently from electron-rich $RuCl_2(Ph_2PCH_2PPh_2)_2$ [28] and $RuCl_2(Ph_2PCH_2CH_2PPh_2)_2$.[29] When treated with

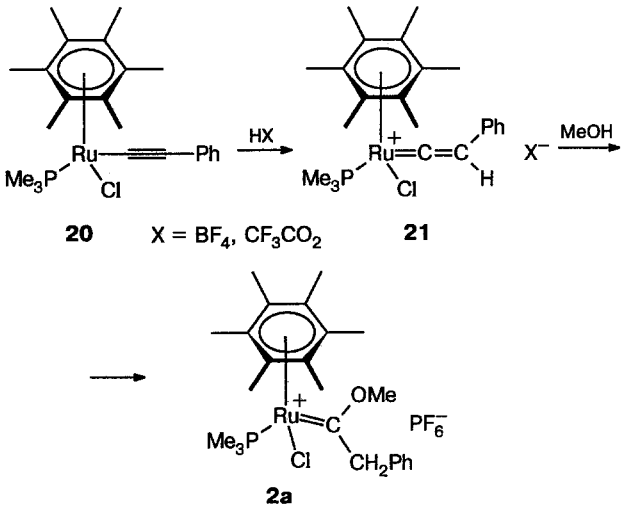
Scheme 8



[Ru–Cl = (arene)(PR_3)ClRu–Cl

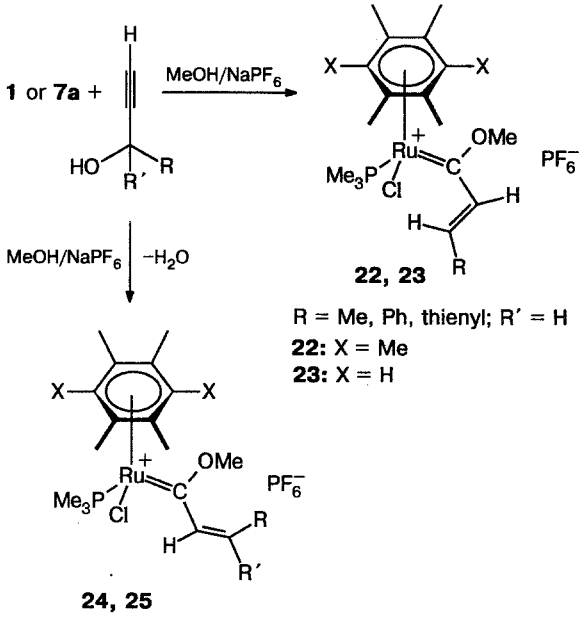
terminal alkynes in the presence of a non-coordinating anion salt ($NaPF_6$), they provide *trans*-$[(Ph_2P(CH_2)_nPPh_2)_2(Cl)Ru{=}C{=}CHR]PF_6$, which can be easily deprotonated to give ruthenium acetylides. This two step reaction is the best way to prepare acetylides directly from alkynes without the help of classical organometallic (Li, MgX, and Cu) acetylides. Stable vinylidenes have also been obtained with functional phosphine-containing ruthenium(II) derivatives $RuCl_2(Ph_2PCH_2CH_2OMe)_2$ and

Scheme 9



20 X = BF_4, CF_3CO_2 **21** **2a**

Scheme 10



22, 23

R = Me, Ph, thienyl; R' = H
22: X = Me
23: X = H

24, 25

R,R' = Me,Me; Ph,Ph; *cyclo*-C_6H_{11}
24: X = Me
25: X = H

$RuCl_2(Ph_2PCH_2CO_2Me)_2$.[30] The C_5Me_5-containing electron releasing complex $RuCl(PMe_2Ph)_2C_5Me_5$ is also suitable precursor for forming stable vinylidenes from terminal alkynes, especially from propargyl alcohol derivatives such as $[(C_5Me_5)(PhMe_2P)_2Ru{=}C{=}CH{-}CH(OMe)Me]PF_6$, which has been structurally characterized.[31]

Synthesis of unsaturated carbene complexes *via* allenylidene intermediates

Activation of prop-2-yn-1-ol derivatives

Access to alkenyl carbene ruthenium(II) complexes. Prop-2-yn-1-ol derivatives are readily dehydrated by **1** and **7a** in the presence of methanol and $NaPF_6$ to afford the new methoxyalkenylcarbene complexes **22** and **23** (Scheme 10).[32] The reaction is stereospecific, giving only the (*E*)-isomers as determined by the large vicinal coupling constants ($^3J_{H,H} \approx 15$ Hz). Moreover, NOE experiments have established the *s-cis* conformation for the alkenylcarbene ruthenium moieties. The same reaction occurs with dimethyl and diphenyl propargyl alcohols, except that the carbene ruthenium moiety in **24** and **25** adopts the *s-trans* conformation (Scheme 10).[32] The alternative *s-cis* conformation may be unfavorable because of steric interaction of the R, R' groups with the phosphine ligand.

The ease of obtaining propargyl alcohols from aldehydes and lithium acetylide has made possible the preparation of new polyunsaturated carbenes. Dienyl **26a** and trienyl **27b** carbene ruthenium complexes can be prepared in 70—90 % yield, in one step from $RuCl_2(PMe_3)(C_6Me_4H_2)$ (**7a**) and unsaturated prop-2-yn-1-ol derivatives containing either a propenyl, styryl, or dienyl substituent (Scheme 11).[32,33]

These reactions gives the *all-trans* geometry for the dienyl and trienyl substituents. The ^{13}C NMR spectra show characteristic doublet resonances at low field (δ 295—299), due to the carbene carbon nucleus. These shifts are found at higher field than those observed for the carbene complexes **23** and **25** (δ 303—310), and are consistent with an increased electron density at the carbene carbon atom.

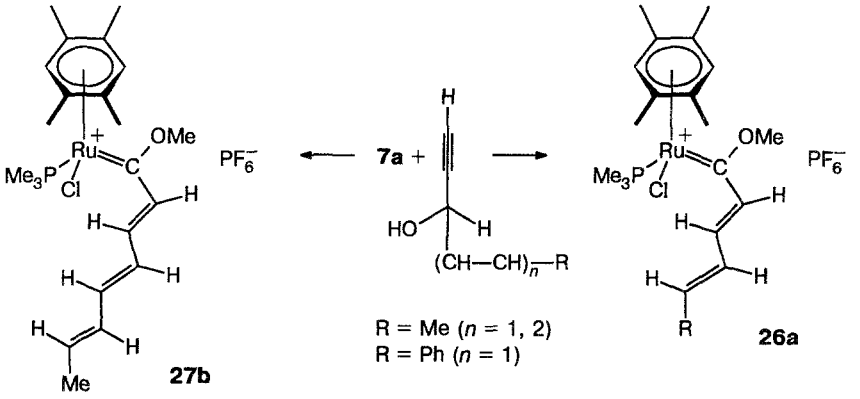
The reaction of **1** (L = PMe_3) with an unsubstituted propargyl alcohol in methanol takes a different route and affords the methoxy(methoxyethyl)carbene complex **28**.[32] This compound formally results from the dehydration of the coordinated alkyne and the double addition of methanol (Scheme 12).

Synthesis of allenylidene ruthenium complexes and mechanism of the reaction. The reaction of **1** with 1,1-diphenyl prop-2-yn-1-ol in methanol is slow, making it possible to isolate the violet, unstable diphenylallenylidene ruthenium complex **29**. The replacement of PMe_3 by the bulkier PPh_3 ligand leads to the stabilization of the ruthenium diphenylallenylidene moiety in **30** (Scheme 13).[32]

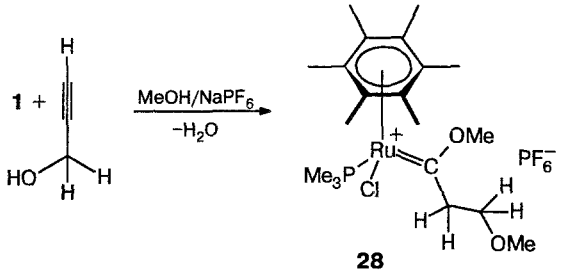
The allenylidene ligand is characterized by strong IR absorption for ν(C=C=C) stretching vibrations at *ca.* 1950 cm^{-1}, and by three resonances in the ^{13}C NMR spectrum at δ 288, 191 and 167 corresponding to the C(1) (carbene), C(2), and C(3) chemical shifts, respectively.

The more stable bimetallic ferrocenyl phenylallenylidene ruthenium complex **31** has been prepared by the activation of a propargyl alcohol containing an electron releasing ferrocenyl group. This complex is totally unreactive toward the addition of methanol. This stability can be explained by the important contribution

Scheme 11



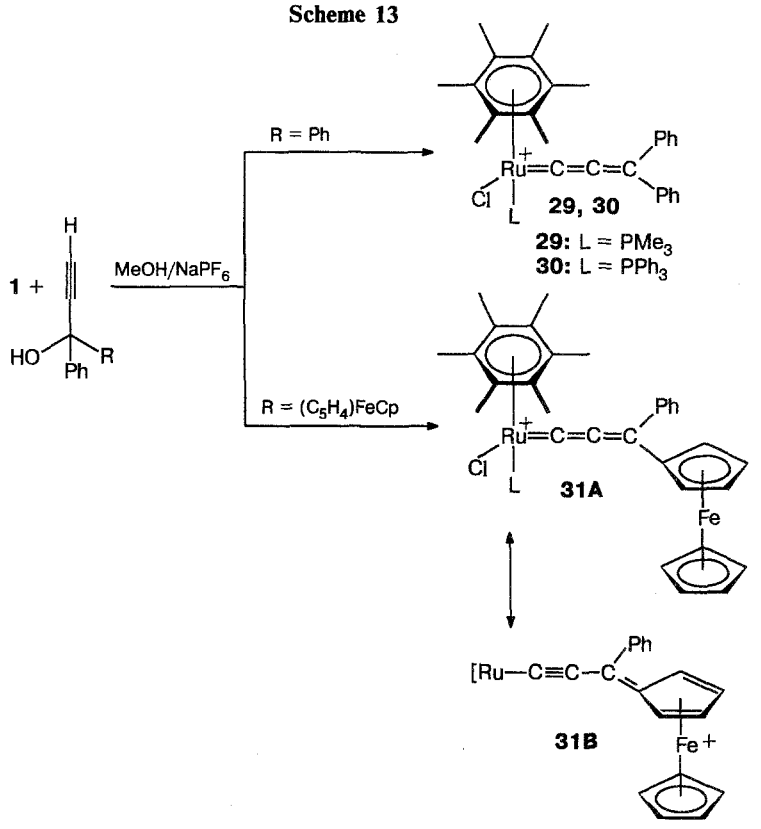
Scheme 12



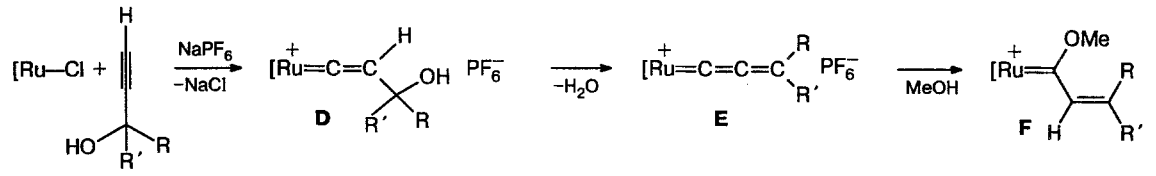
of the mesomeric acetylide structure **31B**, which is supported by strong shielding of the C(1) (δ 243), C(2) (δ 170), and C(3) (δ 155) carbon nuclei in the ^{13}C NMR spectrum.

The mechanism of the formation of methoxyalkenyl carbene ruthenium complexes involves η^1-hydroxyvinylidene ruthenium (**D**) which readily dehydrates to form allenylidene ruthenium (**E**).[32,33] The last step is probably nucleophilic attack by methanol on the electrophilic C(1) carbon atom of the allenylidene ligand to give **F** (Scheme 14). This mechanism is also consistent with that proposed by Selegue[24,34] to explain the forma-

Scheme 13



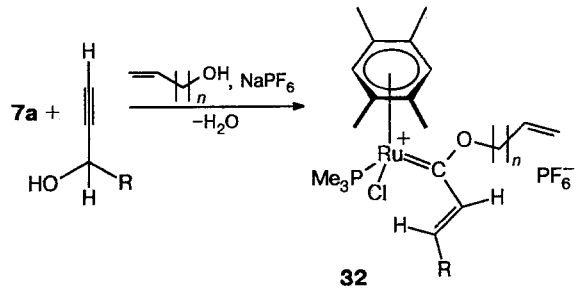
Scheme 14



tion of $[Cp(PMe_3)_2Ru{=}C{=}C{=}CPh_2]PF_6$. While complexes **29** and **30** slowly add methanol, the isoelectronic cyclopentadienyl complex seems inert toward the addition of ethanol. This difference in reactivity again results from the fact that $[RuCl(PR_3)(arene)]^+$ is more electron deficient than $[Ru(PR_3)_2Cp]^+$.

Activation of prop-2-yn-1-ol derivatives in ethylenic alcohols. The reaction of mono substituted propargyl derivatives with **7a** in the presence of ethylenic alcohols affords alkenyloxyalkenyl carbenes **32** in 50—70 % yield (Scheme 15).

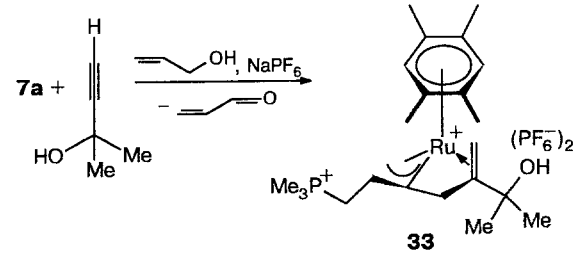
Scheme 15



R = Me, Ph, thienyl, CH=CHMe, CH=CH–CH=CHMe

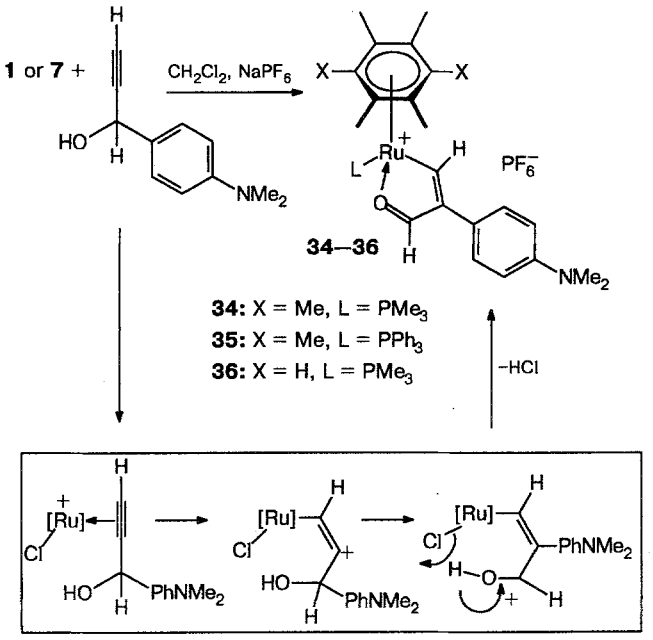
By contrast, the reaction of **7a** with $HC{\equiv}C{-}C(OH)Me_2$ and allyl alcohol leads to a novel η^5-allylalkene ruthenium complex **33**, which has been characterized by X-ray crystal structural analysis (Scheme 16).[35] This ligand can be viewed as resulting from carbon—carbon coupling between two alkyne molecules, with the following transformations: dehydration, proton shift, and migration of trimethylphosphine from the metal to the ligand. Allyl alcohol is used as the hydrogen source and is dehydrogenated to propenal during the reaction.

Scheme 16



Ruthenium(II) oxametallacycles. The reaction of **1** or **7a** with $HC{\equiv}CC(H)(OH)(p\text{-}NMe_2{-}C_6H_4)$ in dichloromethane results in the formation of new oxametallacyclic ruthenium(II) complexes **34—36** *via* the unprecedented 1,2-migration of the aryl substituent.[36] This reaction suggests that the mechanism of the reaction involves the rearrangement of an η^2-alkyne intermediate to its η^1-isomer, which is σ-bonded to Ru. The electron-releasing dialkylamino substituent in the *para* position of the phenyl ring must favor 1,2-aryl migration to give a vinylidene intermediate over hydrogen transfer (Scheme 17).

Scheme 17

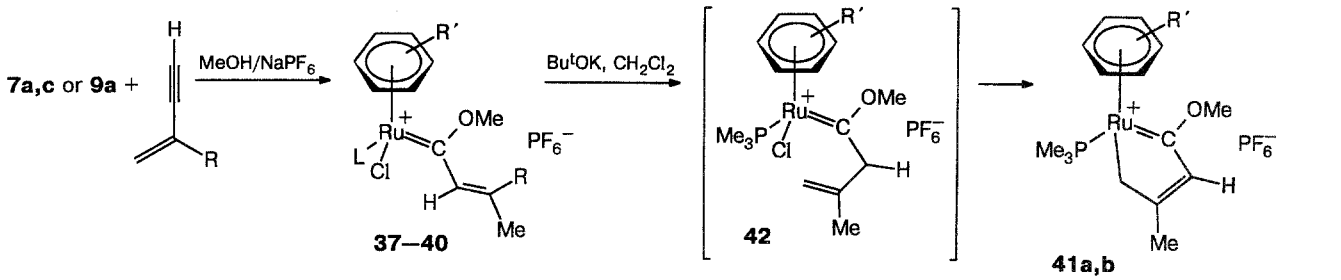


34: X = Me, L = PMe_3
35: X = Me, L = PPh_3
36: X = H, L = PMe_3

Activation of alkenylacetylenes

The activation of vinylacetylene and isopropenylacetylene by arene ruthenium(II) complexes $RuCl_2(L)$(arene) (**7a,c** or **9a**) in methanol directly affords alkenylcarbene derivatives **37** (72 %), **38** (80 %), **39** (78 %), and **40** (65 %), respectively (Scheme 18).[37] The formation of the expected allylcarbenes has never been observed.

Scheme 18



7a, 37, 38: arene = 1,2,4,5-$Me_4C_6H_2$, L = PMe_3

9a, 39: arene = 1,3,5-$Et_3C_6H_3$, L = PMe_3

7c, 40: arene = 1,2,4,5-$Me_4C_6H_2$, L = PPh_3

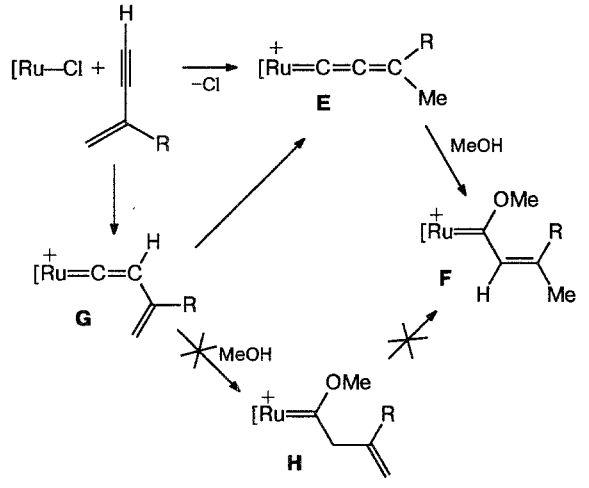
R = H (**37**), Me (**38**, **39**, **40**)

arene = $C_6H_2Me_4$ (**a**), $C_6H_3Et_3$ (**b**)

The deprotonation of **38** and **39** with Bu^{t}OK in dichloromethane leads to the formation of a new type of cyclic unsaturated carbenes, **41a** (65 %) and **41b** (68 %) as a result of deprotonation of one methyl group to give the neutral dienylruthenium intermediate **42,** which undergoes chloride substitution (see Scheme 18).

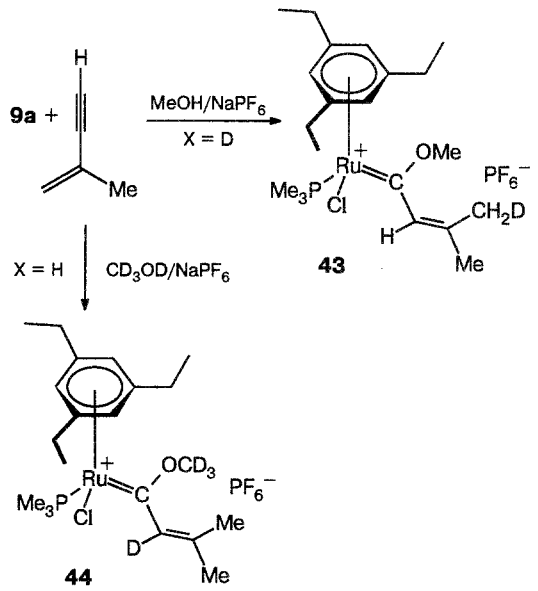
The formation of alkenylcarbenes **37**—**40** of type **F** (Scheme 19) from alkenyl acetylene takes place through the formation of an allenylidene intermediate **E**, *via* 1,2-migration of the terminal H atom to give the vinylidene **G**, which then undergoes 2,4-migration of the hydrogen atom to form **E**. The addition of methanol to the electrophilic C(1) carbon atom in **E** gives **F**. The formation of the allylcarbene intermediate (**H**) can be ruled out.

Scheme 19



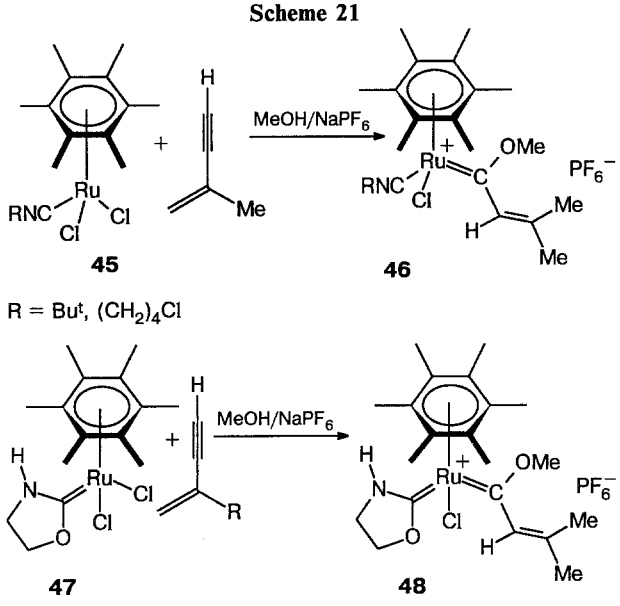
This was shown by experiments with labelled atoms (Scheme 20).[37] Activation of DC≡CC(=CH_2)Me by complex **9a** in MeOH affords complex **43** with deuterium at the C(4) carbon atom, whereas complex **44**, formed from HC≡CC(=CH_2)Me in CD_3OD, does not contain deuterium at the C(4) carbon atom, but hydrogen from the HC≡C group. This observation indicates the absence of exchange between the alkyne hydrogen and the deuterium of CD_3OD. The formation of **43** and **44** excludes the reaction of an allyl carbene intermediate of type **H** as a precursor of the moiety **F** (see Scheme 19).

Scheme 20



The activation of alkenylacetylenes by electrophilic or electron-rich ruthenium(II) complexes is apparently a general reaction. It has been performed with arene ruthenium(II) containing isonitrile ligands, which are less electron releasing than phosphine. For instance, isonitrile complexes **45** activate isopropenyl acetylene[38] to give alkenyl carbene derivatives **46**. The ruthenium complex **47** is also able to perform the same activation

Scheme 21



to form complex **48**, which contains two different carbene ligands, one of which is cyclic and electron releasing, and the other of which is an electron withdrawing group (Scheme 21). Recently,[39] the electron-rich complex $RuCl_2(Ph_2PCH_2PPh_2)_2$ activated isopropenyl acetylene to give the stable allenylidene complex *trans*-$[(Ph_2PCH_2PPh_2)_2(Cl)Ru{=}C{=}C{=}CMe_2]PF_6$.

Electron-rich ruthenium(II) precursors are also able to activate tertiary prop-2-yn-1-ols to give stable allenylidenes such as $[Cp(PMe_3)_2Ru{=}C{=}C{=}CPh_2]PF_6$,[24] $[(Ph_2P(CH_2)_nPPh_2)_2(Cl)Ru{=}C{=}C{=}CR_2]PF_6$ (n = 1 [39] or 2 [40]) or $[N(CH_2CH_2PPh_2)_3(Cl)Ru{=}C{=}C{=}CR_2]PF_6$ (see Ref. 41).

Recently allenylidene ruthenium complexes have been obtained by activation of propargyl alcohol derivatives by binuclear ruthenium complex $Ru_2(\mu\text{-}SPr^i)_2(Cl)_2(C_5Me_5)$ [42] or $(\eta^5\text{-}C_9H_7)Ru(PR_3)_2Cl$.[43] Secondary prop-2-yn-1-ols have been activated to afford[40] the first stable monosubstituted allenylidene $[(Ph_2P{-}CH_2CH_2{-}PPh_2)_2(Cl)Ru{=}C{=}C{=}CHR]PF_6$, whereas with more electron releasing $RuCl(PMe_2Ph)_2{-}(C_5Me_5)$ complexes stable vinylidenes containing the (Ru=C=CHCHOHR) moiety were isolated that were inert toward dehydration, and thus to the formation of allenylidenes.[31]

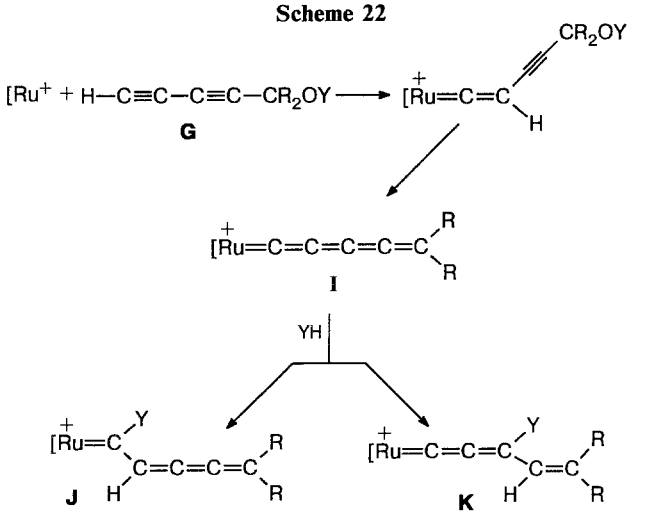
Activation of diynes and formation of diynyl and allenylidene ruthenium complexes

The complexes $RuCl_2(PR_3)$(arene) were found to be suitable for dehydrating tertiary propargyl alcohol derivatives to give ruthenium allenylidene derivatives of type **E**, which then undergo nucleophilic addition to form alkenyl carbenes **F** (see Scheme 14). The homologation of this reaction could be expected. Then the activation of type **G** diynes having one additional C≡C bond with respect to prop-2-yn-1-ols could lead to new penta-1,2,3,4-tetraenylidene intermediates of type **I**, possibly *via* the vinylidene **H**, which is analogous to **D**. Such cumulenes **I** could be expected to be reactive electrophiles and lead to organometallics containing unsaturated chains such as **J** or **K** (Scheme 22).

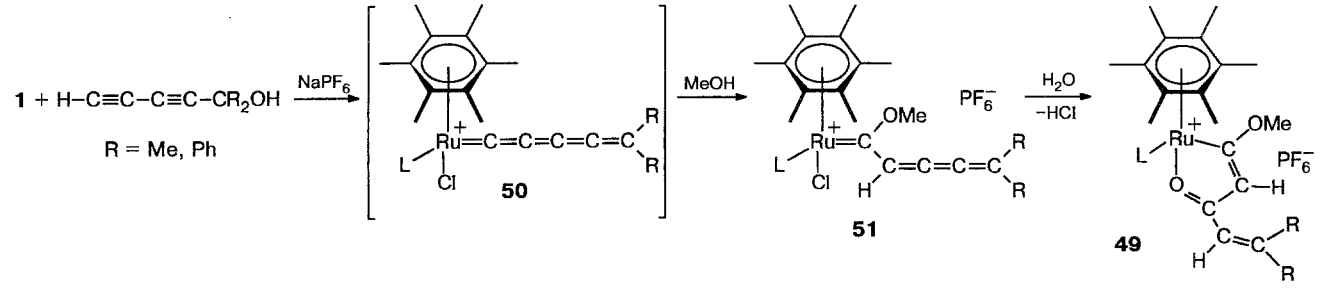
The reaction of HC≡C—C≡C—CR_2OH with arene ruthenium complex **1** in methanol actually led to the 3-oxo-1,4-pentadienyl ruthenium complex **49**. However, this complex was likely the result of the following transformations: dehydration to give cumulene intermediate **50**, which adds methanol to give the unsaturated carbene **51**, which then adds back the released water to give **49** (Scheme 23).[44]

To avoid the presence of water the activation of HC≡C—C≡C—$CPh_2(OSiMe_3)$ (**52**) by complex **1** was

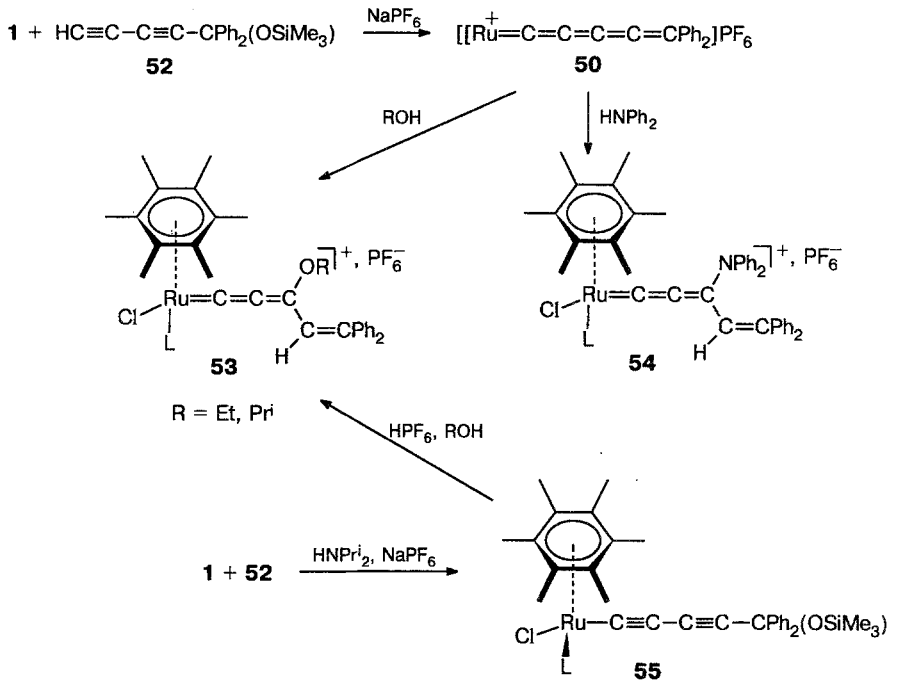
Scheme 22



Scheme 23



Scheme 24



undertaken and complex **51** was isolated in 40 % yield. It has been shown[44] that in the presence of water complex **51** is transformed into metallacycle **49**.

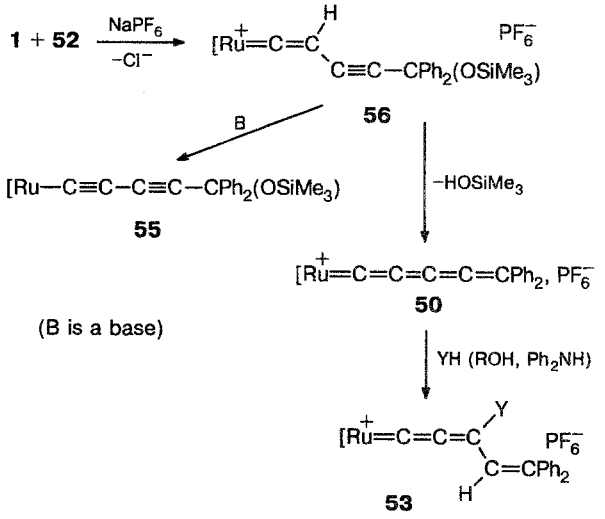
The activation of diyne **52** by **1** in the presence of $NaPF_6$ and alcohols (EtOH, Pr^iOH)[45] leads to the formation of alkenylallenylidenes **53** as a result of the addition of alcohol to the C(3) carbon atom (Scheme 24). Analogously, the very weak base $HNPh_2$ gives the allenylidene **54**. But when a strong base is used ($HNPr^i_2$ or NEt_3) the diynylruthenium derivatives **55** are obtained. The X-ray structure of one of these compounds (L = PMe_3) has been determined.[45] During protonation complexes **55** loose the Me_3SiO^- group and in the presence of alcohol the allenylidenes **53** are formed (see Scheme 24).[45]

It is noteworthy that the formation of diynyl derivatives requires the presence of $NaPF_6$. This is not a simple replacement of the chloride in **1** by a deprotonated diyne. The role of $NaPF_6$ is to stabilize the 16-electron ruthenium species resulting from the dissociation of the Ru—Cl bond in **1**. It is likely that the terminal HC≡C bond coordinates to the ruthenium to give a vinylidene **56**, which is deprotonated to give **55** in the presence of a strong base. It is now established that the best way to produce an alkynyl ruthenium complex from a terminal alkyne is to generate a vinylidene intermediate under deprotonation conditions.[28] In the absence of a strong base, elimination of $HOSiMe_3$ takes place, and the metallacumulene intermediate **50** adds alcohol to give **53** (Scheme 25).

This strategy of generating alkenylallenylidenes by activating diynes of type **52** has been applied to various $RuCl_2[(Ph_2PCH_2CH_2)_3N]$ [41] and $RuCl_2(Ph_2PCH_2PPh_2)_2$ systems. The first bis-allenylidene system, *viz. trans*-$[Y(MeO)C=C=C=Ru=C=C=C(OMe)Y](Ph_2PCH_2PPh_2)_2(PF_6)_2$ (Y = $Ph_2C=CH$) was built from the latter.[46]

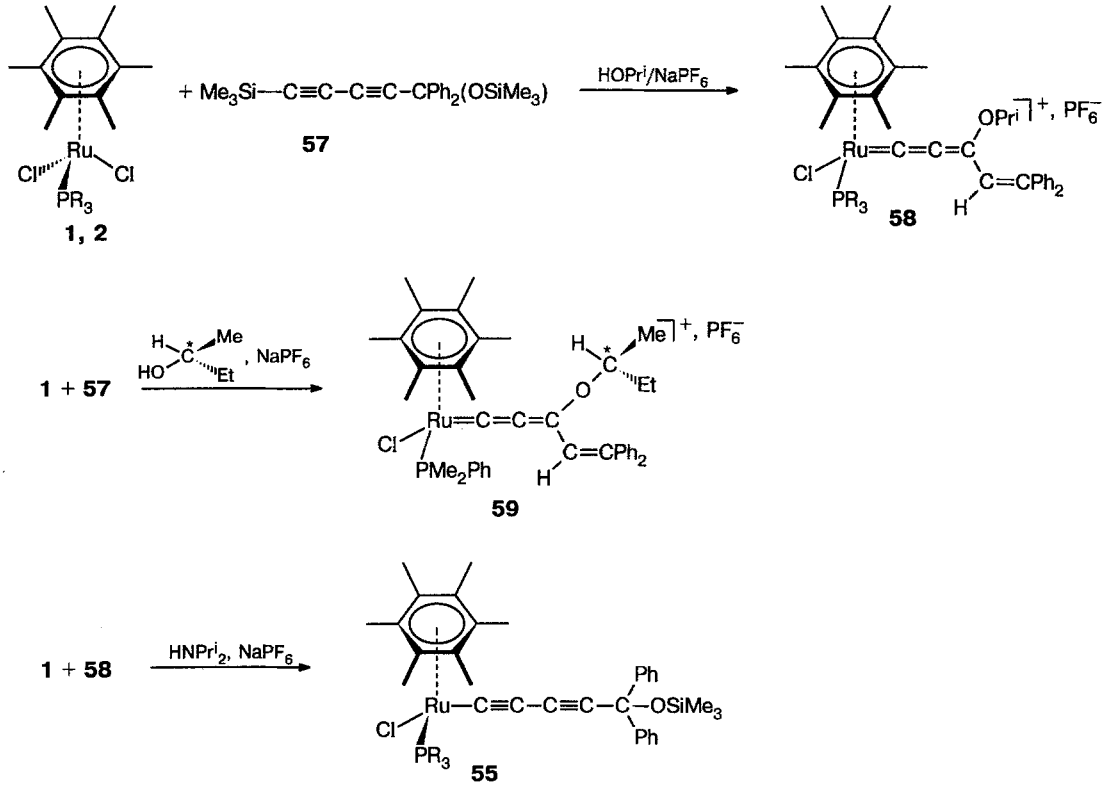
Desilylation of diynylsilanes: the route to the first penta-1,2,3,4-tetraenylidene metal complex. The activation of silylacetylenes has been shown to be a way to generate M=C bonds by 1,2-migration of the silyl group to produce a vinylidene intermediate.[47] As the activation of diyne **52** did not allow the isolation of complexes containing the $[Ru=C=C=C=CR_2]$ moiety, the pos-

Scheme 25

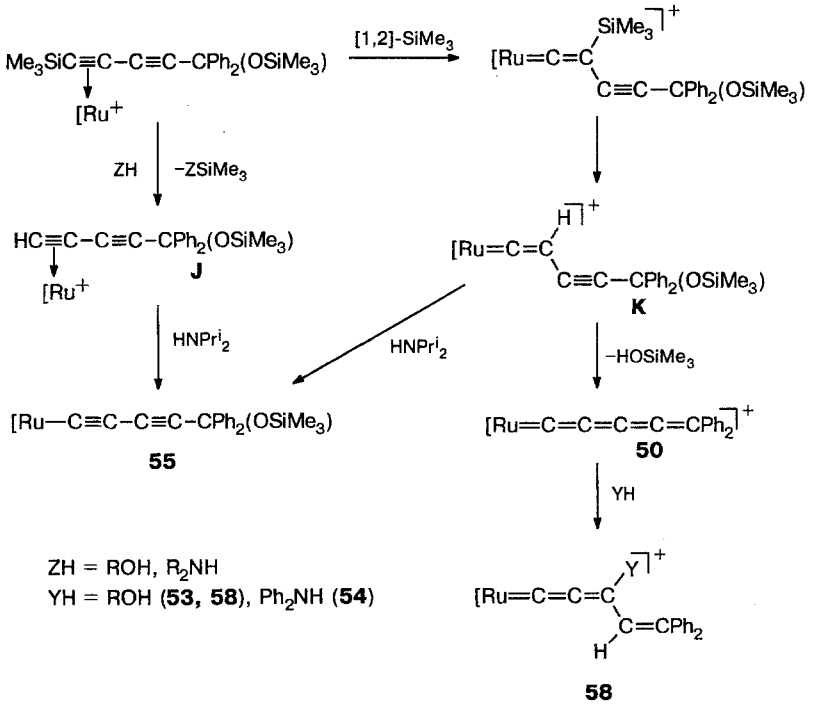


sibility of activating diynyltrimethyl silane **57** was considered. Diyne **57** was activated by complexes **1**, **2** in the presence of alcohols and $NaPF_6$ to afford[48] the allenylidenes **58**. Thus **57** behaves similarly to diyne **52**. However, it could be used, *via* its desilylation process, for the synthesis of chiral allenylidenes **59** *via* the addi-

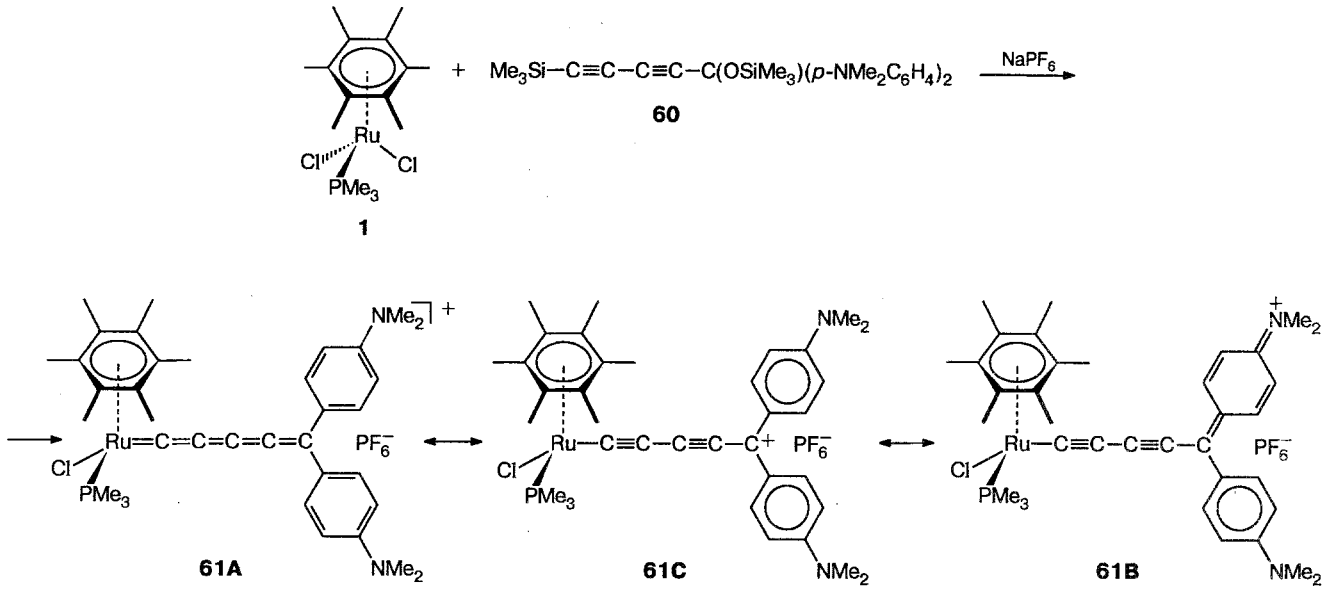
Scheme 26



Scheme 27



Scheme 28



tion of an optically active alcohol to the C(3) carbon atom of the cumulene intermediate **50** (Scheme 26).[48]

When the reaction was performed in the presence of a base (*e.g.*, an amine) the diynyl ruthenium complexes **55** were obtained. This observation indicates that the first step of the activation of diyne **57** is not the elimination of $Me_3SiOSiMe_3$ to generate the cumulene. Activation involves a desilylation reaction. Scheme 27 accounts for the formation of complexes **58**, **59**, and **55** *via* the key intermediates **J** or **K**, which can be easily deprotonated to give **55** or, in the absence of a base, the cumulene species **50** *via* $HOSiMe_3$ elimination.[48]

The instability of metallacumulene **50** is probably due to the electrophilicity of the $[RuCl(PR_3)(arene)]^+$ moiety. In an attempt to isolate this species, the activation of diyne **60**, which contains electron donating aryl groups, by complex **1** was studied. The blue pentatetraenylidene complex **61** was isolated.[48] Actually, its spectroscopic data indicated that complex **61** is best described as consisting of several canonical forms **A**, **B**, and **C** (Scheme 28).

* * *

The electrophilic activation of terminal alkynes by (arene)ruthenium(II) complexes appears to be quite different from activation promoted by isoelectronic electron releasing complexes, especially $RuCl(L)_2Cp$ complexes. It allows the generation of reactive vinylidenes, allenylidenes, and pentatetraenylidenes, which are useful for the formation of unsaturated, rod-like, chain-containing organometallics.

References

1. P. J. Stang, A. K. Datta, V. Dixit, and L. G. Wistrand, *Organometallics*, 1989, **8**, 1020, 1024; H. Lang, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 547; W. Weng, J. A. Ramsden, A. M. Arif, and J. A. Gladysz, *J. Am. Chem. Soc.*, 1993, **115**, 3824; J. W. Seyler, W. Weng, Y. Zhou, and J. A. Gladysz, *Organometallics*, 1993, **12**, 3802.
2. N. Hagihara, K. Sonogashira, and S. Takahashi, *Adv. Polym. Sci.*, 1981, **41**, 149; M. Bourgault, C. Mountassir, H. Le Bozec, I. Ledoux, G. Pucetti, and J. Zyss, *J. Chem. Soc., Chem. Commun.*, 1993, 1623; F. Diederich and Y. Gubin, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1101; S. Takahashi, Y. Takai, H. Morimoto, and K. Sonogashira, *J. Chem. Soc., Chem. Commun.*, 1984, 3; H. B. Fyfe, M. Mlekuz, D. Zargarian, N. J. Taylor, and T. B. Marder, *J. Chem. Soc., Chem. Commun.*, 1991, 188.
3. J. E. Carraher, Jr and C. E. Pittman, Jr, *Metal-Containing Polymeric Systems*, Plenum, New York, 1985; N. Hagihara, K. Sonogashira, and K. Takahashi, *Adv. Polym. Sci.*, 1980, **41**, 150; S. Takahashi, H. Morimoto, F. Murata, S. Kataobe, K. Sonogashira, and N. J. Hagihara, *Polym. Sci., Polym. Chem. Ed.*, 1982, **20**, 562; J. L. Brefort, R. J. Corriu, P. Gerbier, C. Guérin, B. J. L. Henner, A. Jean, and Th. Kuhlmann, *Organometallics*, 1992, **11**, 2500.
4. Z. Yuan, G. Stringer, I. R. Jobe, D. Kreller, K. Scott, L. Koch, and T. B. Marder, *J. Organomet. Chem.*, 1993, **452**, 115; H. S. Nalwa, *Appl. Organomet. Chem.*, 1991, **5**, 349; S. R. Marder, in *Inorganic Materials*, Eds. D. W. Bruce and D. O'Hare, Wiley, Chichester, 1992, 115.
5. M. Iyoda, M. Oda, Y. Kai, N. Kanekisa, and N. Kasai, *Chem. Lett.*, 1990, 2149; M. Iyoda, Y. Kuwatani, and M. Oda, *J. Chem. Soc., Chem. Commun.*, 1992, 399.
6. W. D. Wulff, W. E. Bauta, R. W. Käsler, P. J. Lankford, R. A. Miller, C. K. Murray, and D. C. Yang, *J. Am.*

Chem. Soc., 1990, **112**, 3642; B. A. Anderson, W. D. Wulff, T. S. Powers, S. Tribitt, and A. L. Rheingold, *J. Am. Chem. Soc.*, 1992, **114**, 10784; K. H. Dötz, T. Schäfer, F. Kroll, and K. Harms, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1236; H. Le Bozec, C. Cosset, and P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.*, 1991, 881.

7. S. J. Landon, P. M. Schulman, and G. L. Geoffroy, *J. Am. Chem. Soc.*, 1985, **107**, 673; T. J. Katz and S. J. Lee, *J. Am. Chem. Soc.*, 1980, **102**, 422.
8. R. R. Schrock, *Acc. Chem. Res.*, 1980, **23**, 158; S. T. Nguyen, L. K. Johnson, and R. H. Grubbs, *J. Am. Chem. Soc.*, 1992, **114**, 3974; S. T. Nguyen, R. H. Grubbs, and J. W. Ziller, *J. Am. Chem. Soc.*, 1993, **115**, 9858.
9. M. I. Bruce and A. G. Swincer, *Adv. Organomet. Chem.*, 1983, **22**, 59; M. I. Bruce, *Chem. Rev.*, 1991, **91**, 197.
10. A. B. Antonova, and A. B. Ioganson, *Usp. Khim.*, 1989, **58**, 1197 [*Russ. Chem. Rev.*, 1989, **58**, 693 (Engl. Transl.)].
11. H. P. Kim and R. J. Angelici, *Adv. Organomet. Chem.*, 1987, **27**, 51.
12. J. Silvestre and R. Hoffmann, *Helv. Chim. Acta.*, 1985, **68**, 1461.
13. R. Mahé, P. H. Dixneuf, and S. Lécolier, *Tetrahedron Lett.*, 1986, 633; R. Mah , Y. Sasaki, C. Bruneau, and P. H. Dixneuf, *J. Organomet. Chem.*, 1989, **54**, 1518.
14. B. M. Trost, G. Dyker, and R. J. Kulawiec, *J. Am. Chem. Soc.*, 1990, **112**, 7809; B. M. Trost and R. J. Kulawiec, *J. Am. Chem. Soc.*, 1992, **114**, 5579; B. M. Trost and J. A. Flygare, *J. Org. Chem.*, 1994, **59**, 1078.
15. S. G. Davies, J. P. Mc Nally, and A. J. Smallridge, *Adv. Organomet. Chem.*, 1990, **30**,K1.
16. M. I. Bruce, F. S. Wong, B. W. Skelton, and A. H. White, *Austr. J. Chem.*, 1979, **32**, 1471; M. I. Bruce and A. G. Swincer, *Austr. J. Chem.*, 1980, **33**, 1471; M. I. Bruce, F. S. Wong, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1982, 2203.
17. G. Consiglio, F. Morandini, G. F. Ciani, and A. Sironi, *Organometallics*, 1986, **5**, 1976.
18. R. M. J. Bullock, *J. Chem. Soc., Chem. Commun.*, 1989, 165.
19. H. Le Bozec, D. Touchard, and P. H. Dixneuf, *Adv. Organomet. Chem.*, 1989, **29**, 163.
20. H. Le Bozec, K. Ouzzine, and P. H. Dixneuf, *Organometallics*, 1991, **10**, 2768.
21. C. Bruneau, M. Neveux, Z. Kabouche, C. Ruppin, and P. H. Dixneuf, *Synlett*, 1991, 755; H. Doucet, J. Höfer, C. Bruneau, and P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.*, 1993, 850.
22. D. Devanne, C. Ruppin, and P. H. Dixneuf, *J. Org. Chem.*, 1988, **53**, 925; C. Darcel, C. Bruneau, P. H. Dixneuf, and G. Neef, *J. Chem. Soc., Chem. Commun.*, 1994, 333.
23. C. Bruneau and P. H. Dixneuf, *J. Mol. Catal*, 1992, **74**, 97; J. Höfer, H. Doucet, C. Bruneau, and P. H. Dixneuf, *Tetrahedron Lett.*, 1991, **32**, 7409.
24. J. P. Selegue, *Organometallics*, 1982, **1**, 217.
25. D. Devanne and P. H. Dixneuf, *J. Organomet. Chem.*, 1990, **390**, 371.
26. M. Gaye, B. Demerseman, and P. H. Dixneuf, *J. Organomet. Chem.*, 1991, **411**, 263.
27. M. Gaye, B. Demerseman, and P. H. Dixneuf, *J. Organomet. Chem.*, 1992, **424**, 65.
28. D. Touchard, P. Haquette, N. Pirio, L. Toupet, and P. H. Dixneuf, *Organometallics*, 1993, **12**, 3132.
29. D. Touchard, C. Morice, V. Cadierno, P. Haquette, L. Toupet, and P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.*, 1994, 859.
30. H. Werner, A. Stark, M. Shulz, and J. Wolf, *Organometallics*, 1992, **11**, 1126.
31. R. Le Lagadec, E. Roman, L. Toupet, U. Müller, and P. H. Dixneuf, *Organometallics*, 1994, **13**.
32. D. Pilette, K. Ouzzine, H. Le Bozec, and P. H. Dixneuf, *Organometallics*, 1992, **11**, 809.
33. H. Le Bozec, D. Pilette, and P. H. Dixneuf, *New. J. Chem.*, 1990, **14**, 793.
34. J. P. Selegue, B. A. Young, and S. L. Logan, *Organometallics*, 1991, **10**, 1972.
35. D. Pilette, H. Le Bozec, A. Romero, and P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.*, 1992, 1220.
36. D. Pilette, S. Moreau, H. Le Bozec, P. H. Dixneuf, J. Corrigan, and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 1994, 409.
37. D. Devanne and P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.*, 1990, 642.
38. R. Dussel, D. Pilette, P. H. Dixneuf, and W. P. Fehlhammer, *Organometallics*, 1991, **10**, 3287.
39. N. Pirio, D. Touchard, L. Toupet, and P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.*, 1991, 980.
40. N. Pirio, D. Touchard, and P. H. Dixneuf, *J. Organomet. Chem.*, 1993, **462**, C18.
41. A. Wolinska, D. Touchard, P. H. Dixneuf, and A. Romero, *J. Organomet. Chem.*, 1991, **420**, 217.
42. H. Matsuzaka, Y. Takagi, and M. Hidai, *Organometallics*, 1994, **13**, 13; M. Hidai, Y. Mizobe, and H. Matsuzaka, *J. Organomet. Chem.*, 1994, **473**,K1.
43. V. Cadierno, M. P. Gamasa, J. Gimeno, and E. Lastra, *J. Organomet. Chem.*, 1994, **474**, C27; V. Cadierno, M. P. Gamasa, J. Gimeno, E. Lastra, J. Borge, and S. Garcia-Granda, *Organometallics*, 1994, **13**, 745.
44. A. Romero, A. Vegas, and P. H. Dixneuf, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 215.
45. A. Romero, D. Péron, and P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.*, 1990, 1410.
46. N. Pirio, D. Touchard, P. H. Dixneuf, M. Fettouhi, and L. Ouahab, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 651.
47. H. Sakurai, Y. Nakadaira, A. Hosomi, Y. Eriyama, K. Hirama, and C. Kabuto, *J. Am. Chem. Soc.*, 1984, **106**, 8315; H. Sakurai, T. Fujii, and K. Sakamoto, *Chem. Lett.*, 1992, 339; D. Schneider and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1991, **20**, 700; H. Werner, M. Baum, D. Schneider, and B. Windmüller, *Organometallics*, 1993, **13**, 1089; N. G. Connely, A. G. Orpen, A. L. Rieger, P. H. Rieger, C. J. Scott, and G. M. Rosair, *J. Chem. Soc., Chem. Commun.*, 1992, 1293.
48. D. Péron, A. Romero, and P. H. Dixneuf, *Gazz. Chim. Ital.*, 1994.

Received September 18, 1994