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Allenylidenes: their multifaceted chemistry at rhodium

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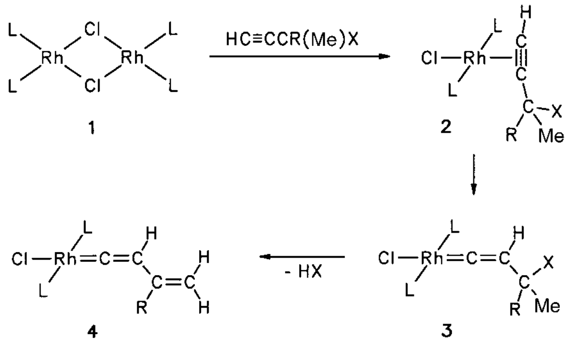
Rhodium allenylidenes, which represent a class of ‘flat’ metallabutatrienes, are useful tools for the generation of metal-bound species that are hardly accessible (sometimes not accessible at all) by other synthetic routes. In contrast to various *octahedral* allenylidene metal complexes, *e.g.* of Cr^0, Mn^I or Ru^{II}, the square-planar rhodium compounds *trans*-[RhX(=C=C=CRR′)(PPr$^i_3$)$_2$] are attacked by both nucleophiles and electrophiles. Moreover, non-polar substrates such as H$_2$ or Cl$_2$ react cleanly with the title complexes to give products in which the allenylidene unit is preserved as part of a newly formed ligand. Attempts to prepare a square-planar cationic metallaheptahexaene, *trans*-[Rh(=C=C=CRR′)$_2$(PPr$^i_3$)$_2$]$^+$, unexpectedly led to the formation of two isomeric hexapentaenerhodium(I) complexes of which the isomer having the polyene coordinated in an unsymmetrical fashion is the thermodynamically more stable. C–C coupling reactions also occur on treatment of *trans*-[RhCl(=C=C=CPh$_2$)(PPr$^i_3$)$_2$] with vinyl Grignard reagents or phenylacetylene leading to highly unsaturated RhC$_5$ and RhC$_5$P frameworks from which vinylallenes and phosphacumuleneylides are obtained.

Introduction

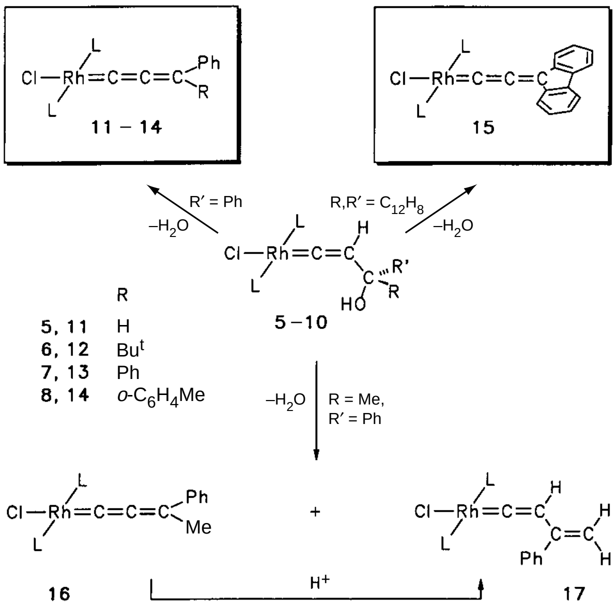
One of the most exciting areas in chemical research which emerged in the last decades undoubtedly is that of transition-metal carbene chemistry. Numerous compounds of general composition [M(=CRR′)L$_n$] (L = non-carbene ligands) have been prepared, structurally characterized and used particularly in organic synthesis and homogeneous catalysis.[1] Regarding the date of the landmark report on the isolation of the first carbenemetal complex (1964),[2] and the furious development which started almost immediately thereafter,[3] the chemistry of related metal compounds containing *unsaturated* carbenes as ligands has much more hesitantly explored. As far as *allenylidenes* are concerned, the breakthrough came in 1982 with the paper by Selegue which illustrated that propargylic alcohols HC≡CCRR′OH can be converted quite smoothly into a C=C=CRR′ unit in the coordination sphere of an electron-rich transition-metal centre by elimination of water.[4] Since this report, a variety of allenylidene–metal complexes have been prepared, the elements of the chromium, manganese and iron triads thereby playing a dominant role.[5]

As part of our work on *vinylidene* complexes [M(=C=CRR′)L$_n$] (M = Ru, Os, Rh, Ir),[6] we recently observed that γ-functionalized alkynes HC≡CCR(Me)X (R = H, Me; X = OH, NH$_2$) react with [RhCl(PPr$^i_3$)$_2$]$_2$ **1** to give, *via* the alkyne rhodium derivatives **2** as intermediates (Scheme 1), the square-planar compounds **3** which on treatment with Al$_2$O$_3$ or traces of acid undergo elimination of HX to afford the rhodium vinylvinylidenes **4** in excellent yield.[7] If, however, instead of HC≡CCH(Me)OH or HC≡CC(Me)$_2$OH the corresponding phenyl-substituted alkynols HC≡CCR(Ph)OH (R = H, Bu^t, Ph, *o*-C$_6$H$_4$Me) or the fluorenone-derived species HC≡CC(C$_{12}$H$_8$)OH are used, the four-coordinate allenylidene complexes **11–15** (Scheme 2) are exclusively obtained.[8,9] They are formed from the initially generated rhodium vinylidenes **5–9** (**9**: R, R′ = C$_{12}$H$_8$) by abstraction of water. The reaction of **10** (R = Me, R′ = Ph) with neutral alumina gives a mixture of **16** and **17** (ratio *ca.* 1 : 9) which can be converted quantitatively into **17** by treatment with an excess of acidic Al$_2$O$_3$ in benzene at room temperature.[8] With regard to the studies described in this paper it should be mentioned that the allenylidene complexes **11–15** are crystalline, only moderately air-sensitive solids which are quite easy to handle and can be stored under argon for weeks.

The aim of the present article is to illustrate that compounds of composition *trans*-[RhCl(=C=C=CRR′)(PPr$^i_3$)$_2$] are not only interesting as far as their synthesis and molecular structure are concerned but that they also offer new insights into the reactivity of metal-containing cumulenes. It will be shown that the behaviour in some respects is different to that of the analogous metal vinylidenes *trans*-[RhCl(=C=CRR′)(PPr$^i_3$)$_2$] which is not unexpected insofar as the stereochemistry of the



Scheme 1 L = PPr$^i_3$; R = H, Me; X = OH, NH$_2$



Scheme 2 L = PPr$^i_3$

latter corresponds to that of *allenes* while the complexes **11–15** are relatives of *butatrienes* (Fig. 1).

Ligand substitution reactions of the metallabutatrienes: Part I

Since allenylidenes like carbon monoxide, isocyanides and vinylidenes (*i.e.* strictly isoelectronic species CX if X is O, NH or CH_2) are good π-acceptor ligands,[10] we had anticipated that in square-planar complexes of general composition *trans*-$[RhX(=C=C=CRR')(PPr^i_3)_2]$ the allenylidene unit would exert a strong influence on the ligand in the *trans* position. Substitution of the chloride in complexes **11–15** should therefore be favoured and this has been confirmed with various nucleophiles. While it is not surprising that on treatment of **12**, **13** or **14** with KI or NaC_5H_5 products such as **18**, **19** or **20**, **21** are formed, the preparation of the hydroxo derivatives **22–24** (Scheme 3) constitutes a more interesting example. This is due to the fact that hydroxo complexes of platinum group metals are not only quite rare,[11] but that compounds **22–24** open the gate to a variety of other square-planar rhodium allenylidenes *trans*-$[RhX\{=C=C=C(Ph)R\}(PPr^i_3)_2]$ (see Scheme 4) which are not accessible *via* any other route.

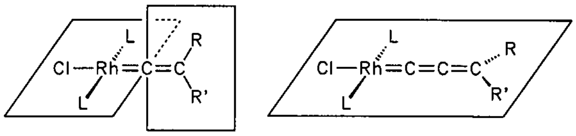
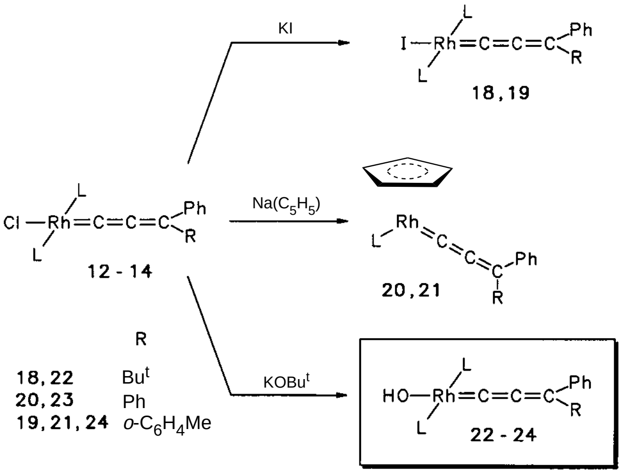


Fig. 1 Different stereochemistry of rhodium vinylidenes ('metallaallenes') and rhodium allenylidenes ('metallabutatrienes'); L = PPr^i_3



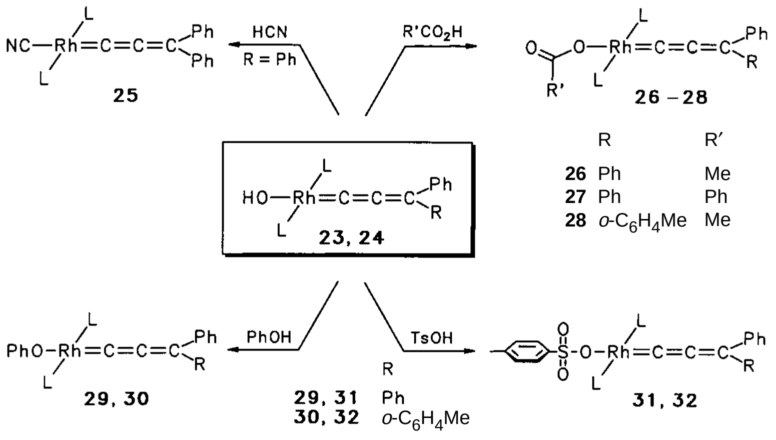
Scheme 3 L = PPr^i_3

In contrast to the tosylato compounds **31** and **32**, which on treatment with carbon monoxide lose the allenylidene unit to give **33** (Scheme 5), the acetato and phenolato derivatives **26**, **28** and **29**, **30** react with CO to yield the 1 : 1 adducts **34–37** almost quantitatively.[12] As the X-ray crystal structure analysis of **36** reveals, a migration of the phenolato ligand to the γ-carbon atom of the allenylidene moiety has taken place and a new functionalized alkynyl unit is formed. The Rh–C^1 distance [2.037(4) Å] is significantly longer than in complex **14** [1.855(5) Å][8] and nearly identical to the Rh–C bond lengths in the five-coordinate bis(alkynyl)hydrido rhodium(iii) compound $[RhH(C{\equiv}CCPr^i_2OH)_2(PPr^i_3)_2]$ (**57**, see Scheme 13 later).[13] The Rh–C–C–C chain in **36** is almost linear while the two phenyl substituents at C^3 are orthogonal to each other, thus presumably minimizing the repulsion between the C–H units.

For the elucidation of the mechanism of the migratory insertion process leading to **34–37** some crossover experiments with **26** and **30** as starting materials were performed. Unfortunately, they did not give a conclusive answer. We found that the Rh–O bond in the acetato and phenolato allenylidene complexes is extremely labile and thus, before CO was passed through the solution of **26** and **30** in benzene, a random exchange took place and a mixture of **26**, **28**, **29** and **30** was formed. The observation, however, that the reaction of **29** with CO in the presence of acetate ions exclusively yields **36** (and not a mixture of **34** and **36**) indicates that the formation of the alkynyl complexes **34–37** occurs intramolecularly and does not involve a heterolytic cleavage of the Rh–OR bond. The formal 1,4-shift of the acetato or phenolato group may take place stepwise *via* an OR-substituted allenylmetal intermediate which rapidly rearranges to the final product. Since the reaction of *trans*-$[Rh(OMe)(CO)(PPr^i_3)_2]$ with CO yields *trans*-$[Rh(CO_2Me)(CO)(PPr^i_3)_2]$,[14] it should be noted that on treatment of **29** and **30** with carbon monoxide no insertion into the Rh–OR bond takes place.

Ligand substitution reactions of the metallabutatrienes: Part II

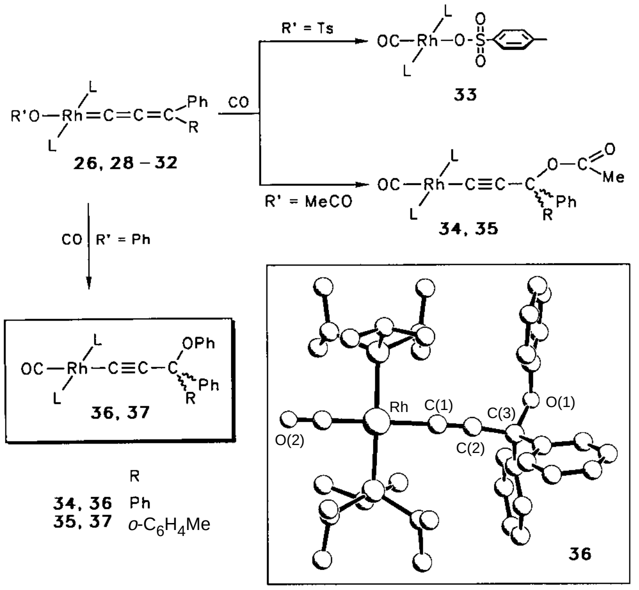
Attempts to replace the halide ligand in the diphenylallenylidene complex **13** by C-nucleophiles such as alkyls, aryls or vinyls led to a surprising result. While the reaction of **13** with MeMgI or PhMgBr gives a mixture of products among which the anticipated species *trans*-$[Rh(R)(=C=C=CPh_2)(PPr^i_3)_2]$ (R = Me, Ph) could not be unequivocally identified,[15] on treatment of **13** with $CH_2{=}CHMgBr$ in toluene–thf both the substitution of chloride by vinyl *and* the coupling of the C-nucleophile and the allenylidene ligand occurs.[16] To explain the formation of the π-allylic complex **38** (Scheme 6), we assume that initially a four-coordinate intermediate **A** is generated which rearranges by migratory insertion of the allenylidene unit into the Rh–CH=CH_2 bond to give **38**. In this context, it is remarkable that the rhodium vinylidenes *trans*-



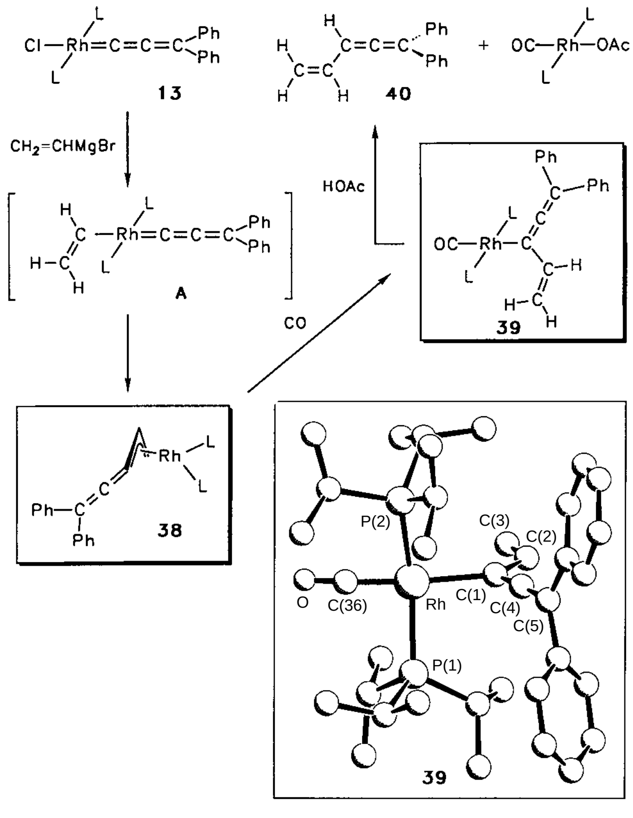
Scheme 4 L = PPr^i_3

$[\mathrm{RhCl(=C=CHR)(PPr^i_3)_2}]$ (R = H, Bu^t, Ph) react with $\mathrm{CH_2{=}CHMgBr}$ to give the *isolable* complexes *trans*-$[\mathrm{Rh(CH{=}CH_2)(=C=CHR)(PPr^i_3)_2}]$ which upon heating to 45–50 °C in benzene slowly isomerize to give the allylic C–C coupling products $[\mathrm{Rh(\eta^3\text{-}\mathit{C}H_2\mathit{C}H\mathit{C}{=}CHR)(PPr^i_3)_2}]$.[17]

Compound **38** reacts with CO even below room temperature almost instantaneously to give the yellow crystalline 1 : 1 adduct **39** in excellent yield.[16] The addition of CO to the metal centre is accompanied by a π–σ conversion of the $\mathrm{C_5}$ ligand, possibly *via* an 18-electron intermediate $[\mathrm{Rh(\eta^3\text{-}\mathit{C}H_2\mathit{C}H\mathit{C}{=}C{=}CPh_2)(CO)(PPr^i_3)_2}]$. As shown in Scheme 6, the X-ray crystal structure analysis of **39** confirmed a square-planar coordination sphere around rhodium and a nearly linear $\mathrm{C^1}$–$\mathrm{C^4}$–$\mathrm{C^5}$ chain with the vinyl carbon atoms $\mathrm{C^2}$ and $\mathrm{C^3}$ lying in the same plane as Rh, $\mathrm{C^1}$, $\mathrm{C^4}$ and $\mathrm{C^5}$. The cleavage of the Rh–C σ bond in **39** by an equimolar amount of acetic acid proceeds smoothly and affords the new vinylallene **40** quantitatively.[16]



Scheme 5 L = $\mathrm{PPr^i_3}$

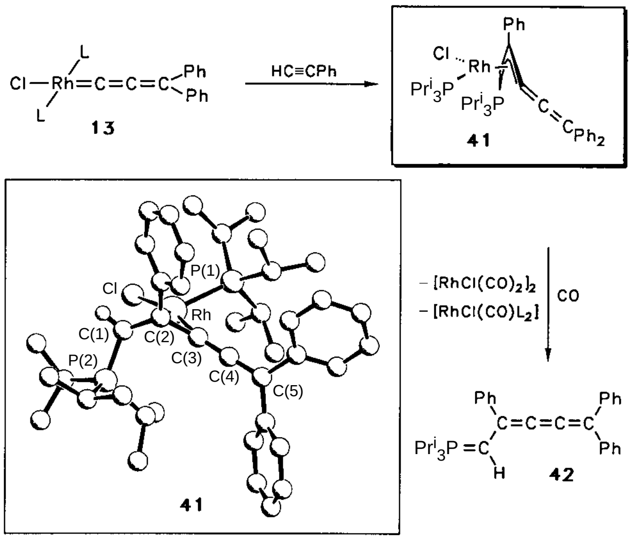


Scheme 6 L = $\mathrm{PPr^i_3}$

A second $[\mathrm{C_2 + C_3}]$ coupling reaction which involves one of the phosphine ligands of **13** is even more exceptional. Upon treatment of a solution of **13** in benzene with phenylacetylene at 10 °C, a gradual change of colour occurred and a light-red crystalline product **41**, formally corresponding to a 1 : 1 adduct of the allenylidene complex and the alkyne, was isolated in practically quantitative yield.[16] The ^{31}P NMR spectrum of **41** already showed the presence of two distinctly different $\mathrm{PPr^i_3}$ groups, and the X-ray structural analysis finally confirmed that only one of the phosphines is still coordinated to the metal centre. The other is part of a π-bonded ylide which is formed from the allenylidene, the alkyne and the second phosphine unit. While the $\mathrm{PC_5}$ ligand in **41** is coordinated in a π-allylic fashion (see Scheme 7), the distances between the rhodium and the carbon atoms $\mathrm{C^1}$, $\mathrm{C^2}$ and $\mathrm{C^3}$ differ by *ca.* 0.15 Å, probably due to the different hybridization at $\mathrm{C^3}$ compared with $\mathrm{C^1}$ and $\mathrm{C^2}$ and to the different influence of the ligands $\mathrm{Cl^-}$ and $\mathrm{PPr^i_3}$ in *trans* positions. Although the carbon atoms of the $\mathrm{=C=CPh_2}$ unit are not coplanar with the allylic fragment, the $\mathrm{C^3}$–$\mathrm{C^4}$–$\mathrm{C^5}$ chain in **41** is almost linear with $\mathrm{C^3}$–$\mathrm{C^4}$ and $\mathrm{C^4}$–$\mathrm{C^5}$ distances that are comparable to those in the allenylidene complex **14** and in **39**. The free ylide **42**, formerly unknown, was generated from **41** on treatment with CO and characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy.[16]

Addition reactions of the metallabutatrienes: the unexpected products

Following the idea that the bonding capabilities of CO and unsaturated carbenes are similar,[10,19] we had anticipated that in analogy to the carbonyl derivative *trans*-$[\mathrm{RhCl(CO)(PPr^i_3)_2}]$[20] also the Rh-containing metallabutatrienes would react with substrates such as HCl, MeI and $\mathrm{H_2}$ by oxidative addition and formation of octahedral rhodium(III) complexes. This, however, is not the case. Compound **13** (which was chosen for these studies as an easily accessible starting material) adds 1 equiv. of HCl quite rapidly but instead of the six-coordinate hydridorhodium complex $[\mathrm{RhHCl_2(=C=C=CPh_2)(PPr^i_3)_2}]$ the five-coordinate allenyl compound **43** (Scheme 8) is quantitatively formed.[15] To explain the course of this unexpected reaction, we assume that initially the electrophile attacks the Lewis-basic metal centre to give the salt-like intermediate $[\mathrm{RhHCl(=C=C=CPh_2)(PPr^i_3)_2}]^+\mathrm{Cl^-}$,[21] which by 1,2-H shift from rhodium to the α-carbon atom of the allenylidene unit, accom-

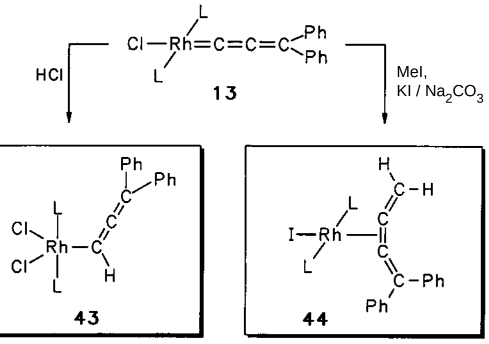


Scheme 7 L = $\mathrm{PPr^i_3}$

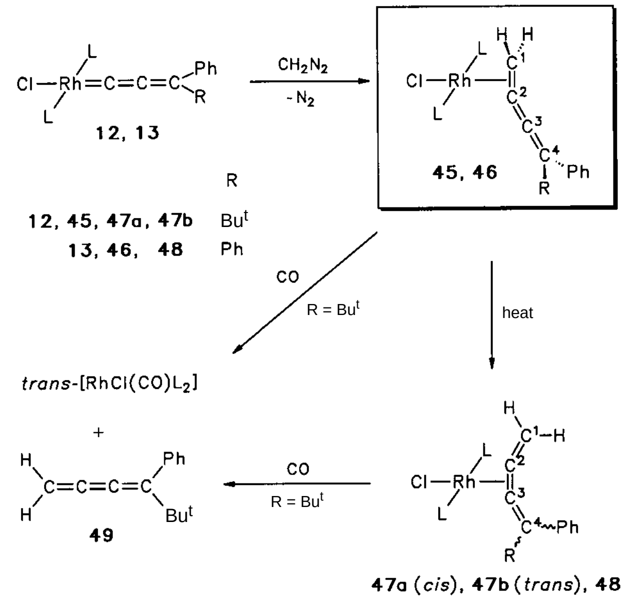
panied by nucleophilic addition of Cl$^-$ to the metal, yields the final product. We note that the *octahedral* metallabutatriene complex [RuCl$_2$(=C=C=CPh$_2$){Pr$^i_2$PCH$_2$C(OMe)=O-κ*P*}{Pr$^i_2$PCH$_2$C(OMe)=O-κ^2*P*,*O*}] reacts with HCl by attack of the electrophile to the C$_\alpha$–C$_\beta$ and not to the Ru–C$_\alpha$ double bond and attribute this difference to the 18-electron configuration of the metal centre.[22]

Methyl iodide, which we used as a counterpart to HCl in the course of the investigations into the reactivity of **13**, also reacts in an unexpected way with **13**. While in the absence of a basic substrate the reaction of **13** with MeI proceeds very slowly and gives a mixture of products, the novel 1,1-diphenylbutatriene complex **44** is formed as the major species besides **47** (see below) in the presence of Na$_2$CO$_3$. Subsequent treatment of the reaction mixture with KI yields **44** almost quantitatively.[23] As far as the mechanism of formation of **44** is concerned, we assume that in the initial step the expected oxidative addition of MeI at the rhodium centre takes place which is followed by an insertion of the allenylidene unit into the Rh–Me bond. The intermediate containing the allene-type RhC(Me)=C=CPh$_2$ moiety then reacts by a β-H shift to give a butatriene(hydrido)-diiodorhodium(iii) compound that upon reductive elimination of HI (facilitated by Na$_2$CO$_3$) generates the final product. Analogous to the first two steps is the formation of [IrCl(I){C(Me)=CH$_2$}(PPr$^i_3$)$_2$] and [IrI{C(Me)=CH$_2$}{N(SiMe$_2$CH$_2$PPh$_2$-κ^3*N*,*P*,*P*)$_2$}] from the corresponding vinylidene complexes and methyl iodide.[24] In this case, however, a subsequent β-H shift does not occur.

There is also a second route to convert a metal-bonded allenylidene unit into a butatriene ligand (Scheme 9). Both compounds **12** and **13** react with excess diazomethane at room temperature to afford the butatriene complexes **45** and **46** in excellent yield.[23] The coordination of the C$_4$ cumulenes *via* the C=CH$_2$ bond is not only supported by the ^{1}H and ^{13}C NMR spectra, but also confirmed by the X-ray structure analysis of **46**. This reveals a distorted square-planar geometry around the metal centre with the Cl, Rh and C^1–C^4 atoms lying in one plane. Although the C=CH$_2$ unit is bonded unsymmetrically to the metal (as is shown by the linearity of the Cl–Rh–C^2 axis), the distances Rh–C^1 and Rh–C^2 are nearly identical and quite similar to the Rh–C bond lengths in structurally related allene rhodium(i) compounds.[25] The P–Rh–P axis in **46** deviates somewhat from linearity which is probably due to the steric requirements of the bulky phosphine ligands.



Scheme 8 L = PPr$^i_3$

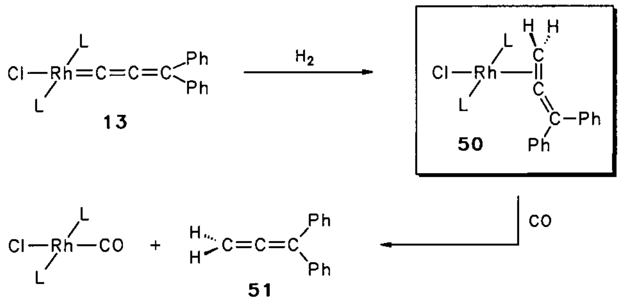


Scheme 9 L = PPr$^i_3$

Both **45** and **46** are thermally labile and upon heating in toluene at 80–90 °C rearrange to the thermodynamically more stable complexes **47** and **48**. For **47**, a mixture of two isomers **47a,b** (see Scheme 9) is formed which differ in the relative positions of the phenyl and *tert*-butyl groups to the rhodium centre. Although isomer **47a** is the dominating and probably preferred species, even after heating the mixture of **47a,b** in toluene at 90 °C for 10 h a complete conversion of **47b** to **47a** does not occur. Nevertheless, complex **47a** could be isolated analytically pure upon fractional crystallization and, by comparison of the NMR data with those of **47b**, identified as the isomer in which the Bu^t group at C^4 is directed towards the metal. In all of the previously described 1,1,4,4-tetrasubstituted butatrienerhodium(i) compounds *trans*-[RhCl(η^2-R$_2$C=C=C=CR$_2$)(PPh$_3$)$_2$], which were prepared from [RhCl(PPh$_3$)$_3$] and butatrienes,[26] the *central* C=C bond is linked to the metal. The coordination of a *terminal* R$_2$C=C bond, as it has been observed for **45** and **46**, was only recently reported by White and Stang for platinum(0) as the central atom.[27] The two isomeric forms **45** and **47a,b** as well as **46** and **48** rapidly react with CO to yield *trans*-[RhCl(CO)(PPr$^i_3$)$_2$] by ligand exchange. Of the butatrienes formed in these conversions, the one with CPh$_2$ as the terminal unit is quite labile undergoing secondary reactions whereas the hitherto unknown cumulene **49** has been characterized by GC–MS and spectroscopic techniques.[23]

The allenylidene ligand of **13** can be converted not only to a butatriene but also to an allene. The reaction of **13** with H$_2$ in benzene at room temperature is rather slow but after 40 h, by cleavage of the Rh=C double bond, the square-planar rhodium(i) complex **50** (Scheme 10) is quantitatively formed.[15,23] Remarkably, under the chosen conditions no hydrogenation of the allene ligand occurs. Since the ^{1}H NMR spectrum of **50** displays only one signal for the CH$_2$ protons, there is no doubt that it is the *unsubstituted* double bond of the allene which is bonded to the metal. On treatment of **50** with CO, the alkenic ligand is readily displaced and together with the allene **51** the carbonyl complex *trans*-[RhCl(CO)(PPr$^i_3$)$_2$] is formed.

The reaction of **13** with a solution of chlorine in thf–hexane yields a 1 : 1 adduct **52** by oxidative addition which, however, does not have the expected octahedral geometry. The ^{1}H, ^{13}C and ^{31}P NMR spectra display two completely different sets of signals for the hydrogen, carbon and phosphorus atoms of the PPr$^i_3$ groups and, since only one of the ^{31}P NMR resonances



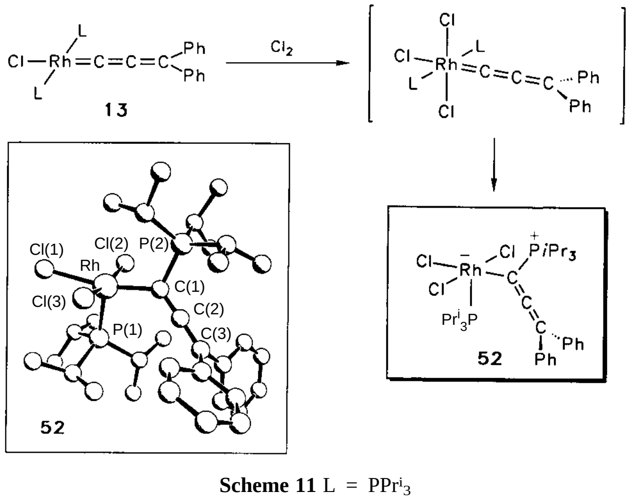
Scheme 10 L = PPr$^i_3$

shows a strong Rh–P coupling, it is clear that one of the phosphines is not linked to rhodium. The X-ray crystal structure analysis of **52** (Scheme 11) indeed reveals that a five-coordinate rhodium(iii) complex has been formed which contains in addition to one phosphine and three chlorides the phosphacumuleneylide $\mathrm{Pr^i_3P{=}C{=}C{=}CPh_2}$ as an η^1-bonded ligand. The geometry around the metal centre is best described as square-pyramidal with the triisopropylphosphine in the apical position. The two planes containing the substituents at $\mathrm{C^1}$ (Rh and $\mathrm{P^2}$) and $\mathrm{C^3}$ (*ipso*-carbons of $\mathrm{C_6H_5}$) are orthogonal to each other, in agreement with the allene-type structure of the molecule.[28] Related phosphacumuleneylide ligands to that found in **52** are known from $[\mathrm{(C_5H_5)Mn\{C(PPh_3){=}C{=}CPh_2\}(CO)_2}]$ and $[\mathrm{Cr\{C(PPh_3){=}C{=}CPr^i_2\}(CO)_5}]$, but have been generated by attack of free triphenylphosphine on allenylidene complexes.[29]

[C$_3$ + C$_3$] coupling reactions: are metallabutatrienes involved?

When we considered proceeding one step further in the investigation of rhodium-containing metallacumulenes, the question arose whether it would be possible to generate a cation like **II** (Fig. 2) which would be structurally comparable to the dicarbonyl species **I** recently prepared in our laboratory.[30] For this purpose we attempted to apply a methodology which by using the η^3-benzyl complex **53** as starting material led to the formation of alkynyl rhodium vinylidenes **54** and, on further reaction with HCl and CO, finally to enynes and butatrienes (Scheme 12).[31]

With the reactivity of compound **53** towards terminal alkynes such as $\mathrm{HC{\equiv}CPh}$ or $\mathrm{HC{\equiv}CBu^t}$ in mind, we were not surprised that on treatment of **53** with 2 equiv. of $\mathrm{HC{\equiv}CCR_2OH}$ (R = Me, Ph, $\mathrm{Pr^i}$) a rapid reaction occurred that led to the formation of crystalline, only slightly air-sensitive solids **55**–**57** in *ca.* 70% yield.[13] The IR and NMR spectra of the products illustrated quite clearly that instead of the expected alkynyl(vinylidene)-rhodium(i) complexes *trans*-$[\mathrm{Rh(C{\equiv}CCR_2OH)({=}C{=}CHCR_2OH)(PPr^i_3)_2}]$ the bis(alkynyl)hydridorhodium(iii) isomers $[\mathrm{RhH(C{\equiv}CCR_2OH)_2(PPr^i_3)_2}]$ were formed. These five-coordinate compounds possess a square- pyramidal and not trigonal-bipyramidal configuration, as was confirmed by the crystal structure analysis of **57**.[13] The SCHAKAL diagram, which is included in Scheme 13, shows that the basal plane of the pyramid consists of an exactly linear P–Rh–P and an almost linear C–C–Rh–C–C arrangement with Rh–C bond lengths that are nearly identical to those of the octahedral bis(alkynyl)-hydrido complex $[\mathrm{RhH(C{\equiv}CPh)_2(PMe_3)_3}]$.[32] The structure of **57** found in the crystal is most probably also preserved in solution since the ^{1}H NMR spectrum (like the spectra of **55** and **56**) displays a doublet of triplets at δ −30.5 which together with a Rh–H coupling constant of 50 Hz is most typical for five-coordinate hydridorhodium(iii) species.[33]



Scheme 11 L = $\mathrm{PPr^i_3}$

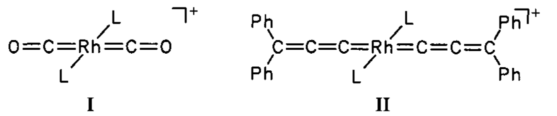
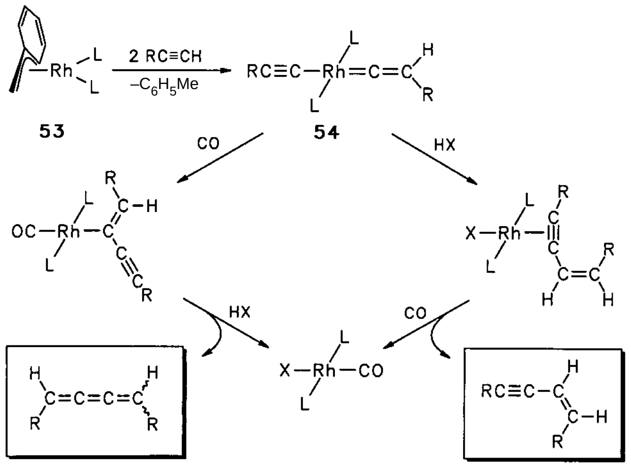
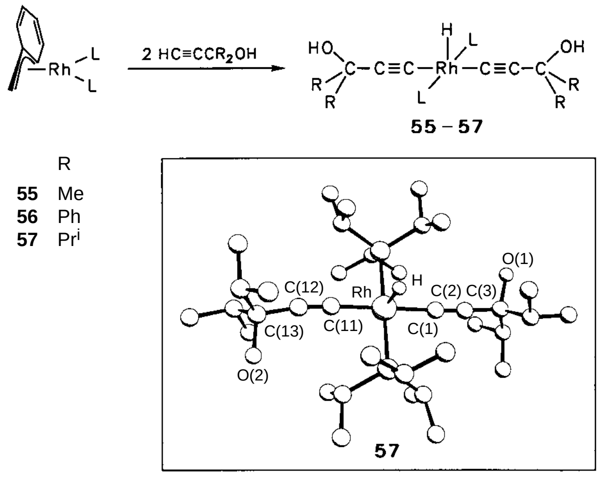


Fig. 2 Formal relation between the cationic dicarbonylrhodium and bis(allenylidene)rhodium complexes **I** and **II**; L = $\mathrm{PPr^i_3}$

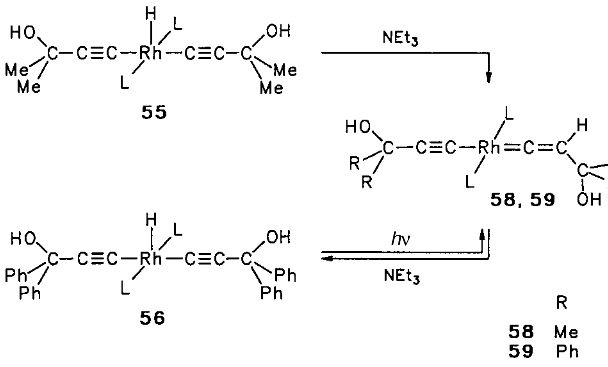
Compound **55** is not completely inert in benzene solution and at room temperature reacts slowly to give the OH-functionalized alkynyl(vinylidene)rhodium(i) derivative **58** (Scheme 14) in good yield.[13] The formation of this complex (which is structurally related to the species **54** shown in Scheme 12) is



Scheme 12 L = $\mathrm{PPr^i_3}$



Scheme 13 L = $\mathrm{PPr^i_3}$



Scheme 14 L = $\mathrm{PPr^i_3}$

significantly facilitated by addition of NEt_3, probably due to a weakening interaction of the amine with the Rh–H bond. A complete rearrangement of **56** to the isomer **59** does not proceed under thermal conditions but takes place on irradiation of the bis(alkynyl)hydrido compound in benzene. Unlike **58**, the analogous complex **59** is not stable in benzene or toluene solution and, particularly in the presence of NEt_3, partly rearranges to the isomer **56** until an equilibrium of **56** : **59** = 30 : 70 is reached. No isomerization of compound **57** occurs, neither thermally nor photochemically, which could be due to the efficient shielding of the β-carbon atom of the alkynyl ligands by the bulky isopropyl groups.[13]

While the reactions of **56** and **59** with CO followed established routes and gave by addition and (in the case of **59**) by migratory insertion the carbonyl complexes $[RhH(C{\equiv}CCPh_2OH)_2(CO)(PPr^i_3)_2]$ and *trans*-$[Rh\{\eta^1$-(Z)-$C(C{\equiv}CCPh_2OH){=}CHCPh_2OH\}CO)(PPr^i_3)_2]$, respectively, treatment of **56** and **59** with acidic Al_2O_3 in the presence of chloride ions led to a completely unexpected result. In analogy to the preparation of **13** from **7** (see Scheme 2) we anticipated the formation of *trans*-$[Rh(C{\equiv}CCPh_2OH)({=}C{=}C{=}CPh_2)(PPr^i_3)_2]$ or, hopefully, of a salt of the bis(allenylidene)rhodium(i) cation *trans*-$[Rh({=}C{=}C{=}CPh_2)_2(PPr^i_3)_2]^+$. However, we isolated (besides small amounts of **13**) the novel hexapentaene complex **60** (Scheme 15) in 70% yield.[13] If the time for the interaction of **56** or **59** with $Al_2O_3/H^+/Cl^-$ is not sufficient, an isomeric mixture of **60** and **61** is formed which, however, can be quantitatively converted to **60** by stirring a solution of **60**/**61** in benzene at room temperature. The assumption that **61** is the kinetically preferred and **60** the thermodynamically preferred isomer could be confirmed by stepwise synthesis of the two compounds from dimer **1**. The more symmetrical complex **61** was exclusively obtained from **1** and the hexapentaene $Ph_2C{=}C{=}C{=}C{=}C{=}CPh_2$ **62** in toluene at −30 °C, provided that the solution was worked up quickly at low temperature. The further rearrangement of **61** to **60** proceeded at 25 °C. Both compounds **60** and **61** smoothly react with carbon monoxide by ligand displacement to give *trans*-$[RhCl(CO)(PPr^i_3)_2]$ and the cumulene **62**. With regard to the structure of the more stable isomer **60**, the X-ray analysis showed that the C_6 chain is bent, possessing C–C–C angles which are similar to those found in related butatrienerhodium(i) complexes.[23,26] The plane of the carbon atoms C^1–C^6 is exactly perpendicular to the plane containing the metal, the chloride and the phosphorus atoms, the dihedral angle being 89.8(1)°.

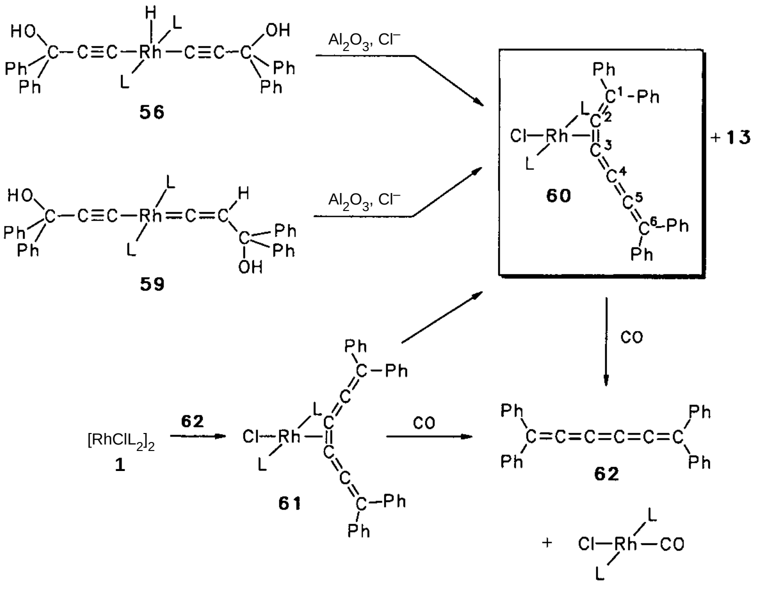
The proposed mechanism of formation of **60** and **61** is outlined in Scheme 16. We assume that in analogy with the preparation of **13** from **7** and Al_2O_3 an alkynyl(allenylidene)rhodium(i) intermediate **B** is generated initially which can be converted either by proton attack (and elimination of water) to the bis(allenylidene)metal cation **C** or, alternatively, by solvent-assisted migration of the alkynyl ligand to the α-carbon atom of the allenylidene unit to give **D**. Coupling of the two C_3 fragments of **C** or acid-initiated abstraction of OH^- from **D** could then generate the hexapentaene ligand and, on addition of Cl^-, afford complex **61**. There is precedent for the linkage of two allenylidene moieties to give a tetrasubstituted hexapentaene insofar as on heating of $[(C_5H_5)Mn(CO)_2({=}C{=}C{=}CBu^t_2)]$ small quantities of $Bu^t_2C{=}C{=}C{=}C{=}C{=}CBu^t_2$ are formed.[34]

Why rhodium?

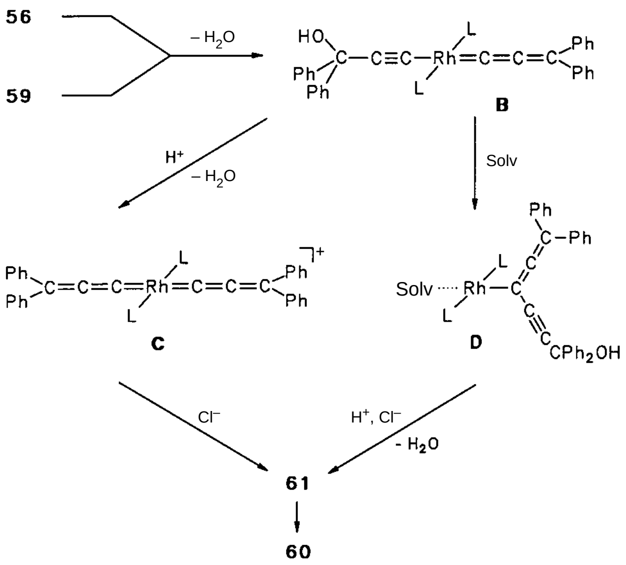
In summarizing the results shown in Schemes 3–16, the question certainly arises whether the square-planar rhodium allenylidenes are unique as far as their reactivity is concerned. Although a conclusive answer is as yet not possible, a few trends emerge which can be described as follows.

(*i*) The allenylideneiridium(I) compound **65** (Scheme 17), which is prepared from the dihydridoiridium(iii) derivative **63** and $HC{\equiv}CCPh_2OH$ *via* **64** as intermediate, reacts rapidly with H_2 in dichloromethane at room temperature to give the allene complex **66** in excellent yield.[35] In this respect, compound **65** behaves in an exactly analogous manner to the rhodium counterpart **13** (see Scheme 10). However, in contrast to **13** the iridium allenylidene **65** is rather inert towards HCl and CH_3I which is probably due to the increased kinetic stability of Ir=C compared with Rh=C double bond systems.

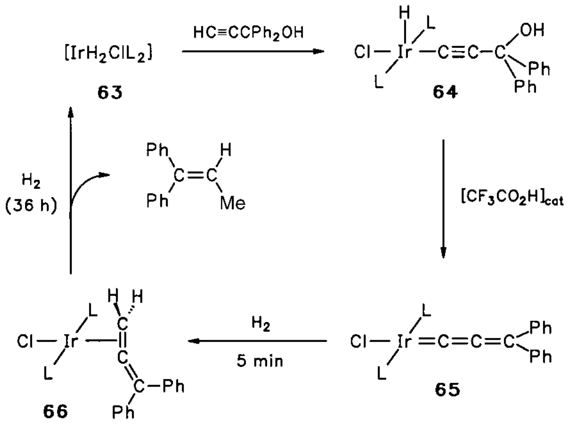
(*ii*) Allenylideneruthenium(ii) complexes, which since the first studies in this field constitute the largest group of compounds containing an M=C=C=CRR′ unit,[5] are quite reactive towards *nucleophiles*. Work by Dixneuf and coworkers[36] and more recently by Gimeno and coworkers[37] has shown that in particular *cationic* compounds such as **67** and **69** (Scheme 18) are easily attacked by alcohols, alcoholates and also acetylides. The reaction of **69** with NaOMe affords a functionalized alkynyl ligand which is related to the rhodium-bound $C{\equiv}CCPh_2(OPh)$ unit generated on treatment of the neutral allenylidene rhodium complex **29** with CO (see Scheme 5).



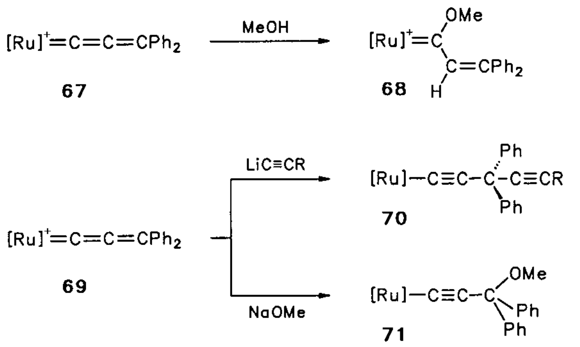
Scheme 15 L = PPr^i_3



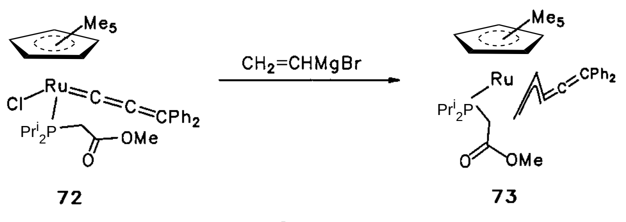
Scheme 16 L = PPr^i_3



Scheme 17 L = PPr^i_3



Scheme 18 For **67**, **68**: [Ru] = $(C_6Me_6)RuCl(PMe_3)$; for **69**–**71**: [Ru] = $(C_9H_7)Ru(PPh_3)_2$



Scheme 19

Attempts to attack the allenylidene ligand in the *neutral* ruthenabutatrienes $[RuCl_2(=C=C=CPh_2)\{Pr^i_2PCH_2C(OMe)=O\text{-}\kappa P\}\{Pr^i_2PCH_2C(OMe)=O\text{-}\kappa^2 P,O\}]$[22] and $[(C_5Me_5)RuCl(=C=C=CPh_2)\{Pr^i_2PCH_2C(OMe)=O\text{-}\kappa P\}]$ **72**[38] by methanol or dimethylamine failed. The half-sandwich type compound **72**, however, cleanly reacts with $CH_2=CHMgBr$ in C_6H_6–thf to give the η^3-3,4,5-pentatrienyl complex **73** (Scheme 19) in good yield.[38] We were really surprised that this reaction occurred smoothly even at room temperature since compared with rhodium in the square-planar compound **13** (see Scheme 6) the ruthenium centre in **72** is more effectively shielded and thus a nucleophile attack of the Grignard reagent should be more hindered. For the success of the C–C coupling reaction leading to **73** it could be important that the two C-bonded ligands in the supposed intermediate $[(C_5Me_5)Ru(CH=CH_2)(=C=C=CPh_2)\{Pr^i_2PCH_2C(OMe)=O\text{-}\kappa P\}]$ are *cis* disposed since this should favour the migration of the vinyl group to the α-carbon atom of the allenylidene unit forming the pentatrienyl moiety.

Conclusion

It is shown in this article that square-planar rhodium allenylidenes of general composition *trans*-$[RhX(=C=C=CRR')(PPr^i_3)_2]$, which are easily accessible from $[RhCl(PPr^i_3)_2]_2$ and propargylic alcohols, react with both nucleophiles and electrophiles. They are also attacked by phenylacetylene as well as by non-polar substrates such as H_2 or Cl_2 to give products in which the allenylidene unit is preserved as part of a newly formed ligand. In this respect, compounds having a metallabutatriene framework $Rh=C=C=CRR'$ behave quite differently to those containing a related metallaallene type unit $Rh=C=CRR'$.

Current work in our laboratory is aimed *inter alia* at the use of the rhodium allenylidenes also for catalytic purposes. The focus will be on reaction conditions which allow the conversion, *e.g.* of the butatriene complexes **45**–**48** upon treatment with $HC\equiv CCPh_2OH$ to the starting materials **12** and **13** and free butatrienes. Moreover, the exploration of new C–C coupling reactions using compounds such as **12**–**14** and **22**–**28** as starting materials will be on the agenda for further investigations.

Acknowledgements

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Helmut Werner's research interests are in the field of synthetic and mechanistic organometallic chemistry, ranging from triple-decker sandwich complexes to C–H activation and C–C coupling reactions. After obtaining his Diploma degree with Franz Hein at Jena, he escaped from East Germany and went to Munich to work for his PhD with Ernst Otto Fischer. Following postdoctoral work at Caltech (Pasadena) and finishing his Habilitation at the Technische Universität in Munich, he joined the Faculty at the University of Zurich, Switzerland, where he became Professor of Inorganic Chemistry in 1970. He returned to Germany at the end of 1975 to take up the chair of Inorganic Chemistry at the University of Würzburg. He has been honoured by the awards of the Pacific West Coast Inorganic Lectureship (1987) by the American Chemical Society, the Alfred-Stock-Gedächtnispreis by the German Chemical Society (1988), the Centenary Lectureship by the Royal Society of Chemistry (1993), the Max-Planck-Forschungspreis (1994), the

Paolo-Chini-Memorial Lectureship by the Italian Chemical Society (1995) and most recently by the Alexander-von-Humboldt/J. C. Mutis Award. Since 1988, he has been a fellow of the Deutsche Akademie der Naturforscher Leopoldina.

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