Journal of Organometallic Chemistry, 475 (1994) 45–55

Invited Lecture

Organometallic chemistry of alkenes and alkynes *

Helmut Werner

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg (Deutschland)

(Received January 18, 1994)

Abstract

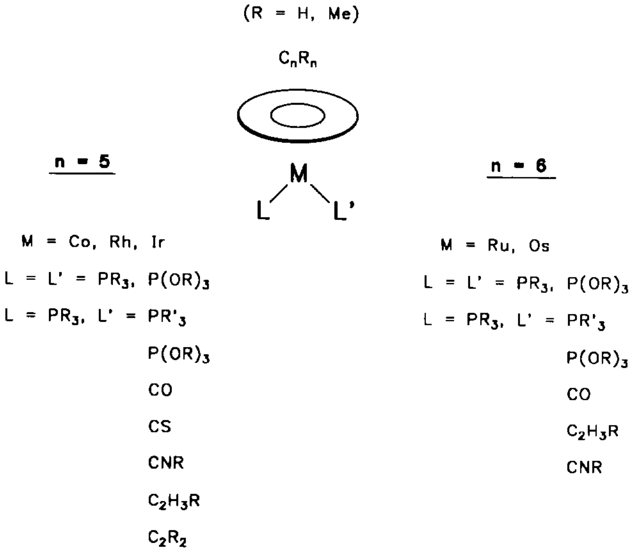
During the last decade, the chemistry of transition-metal complexes containing unsaturated carbenes such as :C=CRR′ (vinylidenes) and :C=C=RR′ (allenylidenes) as ligands has attracted a great deal of attention. Using rhodium as an example of an electron-rich metal centre, this paper describes preparative routes for the conversion of terminal alkynes to vinylidenes and allenylidenes and briefly discusses the mechanism of these reactions. Rhodium complexes which contain a linear RC≡C–Rh=C=CHR′ chain have been prepared from $[(\eta^3\text{-}C_3H_5)RhL_2]$ or $[(\eta^3\text{-}CH_2C_6H_5)RhL_2]$ ($L = P^iPr_3$) and terminal alkynes and have been used as starting materials for the coupling of C_2 units to either enynes or butatrienes. In the course of attempts to obtain square-planar carbene rhodium derivatives regarded as the missing link in the series of double bond systems $[Rh]{=}C({=}C)_nRR'$, where [Rh] is $[RhCl(P^iPr_3)_2]$ and n is 0, 1 and 2, a new catalytic reaction of ethene and diazoalkanes to give trisubstituted olefins has been discovered. Studies aimed at elucidating the mechanism of this process have led to a whole series of novel carbene rhodium complexes which not only react with ethene to give substituted olefins but also have a great potential as precursors for organic and other organometallic compounds.

Key words: Alkene; Alkyne; Cumulene; Rhodium; Carbene; Vinylidene

1. Introduction

One major activity of our group in the 1970s and early 1980s was concerned with the chemistry of half-sandwich type complexes of general composition $[(C_nR_n)MLL']$ (see Scheme 1) [1]. The most characteristic feature of these compounds, which all contain a d^8 metal centre, is that they behave like Lewis bases and react with a variety of electrophiles to form products with a new metal–element bond. The Lewis basicity ("metal basicity" [2]) is mainly determined by the donor properties of the ligands C_nR_n, L and L′ which explains why the bis(trimethylphosphine)metal complexes $[C_5H_5M(PMe_3)_2]$ (M = Co, Rh) are more nucleophilic than $[C_5H_5M(CO)_2]$ or $[C_5H_5M(CO)(PMe_3)]$ and the pentamethylcyclopentadienyl or hexamethylbenzene metal compounds are more nucleophilic than their cyclopentadienyl or benzene counterparts [1].

After we had prepared the complexes $[C_5H_5Rh(PMe_3)_2]$ [3], $[C_5H_5Rh(CO)(PMe_3)]$ [4], $[C_5H_5Rh(CS)(PMe_3)]$ [5] as well as the olefin derivatives

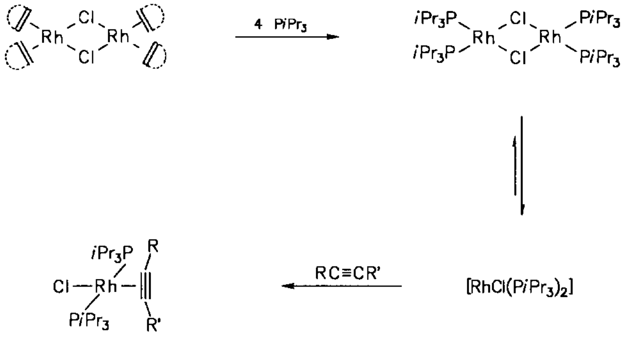


Scheme 1.

---

* Presented at the First Journal of Organometallic Chemistry Conference, Munich, November 4–5, 1993, in honour of Professor Ernst Otto Fischer, one of the great pioneers of modern organometallic chemistry.

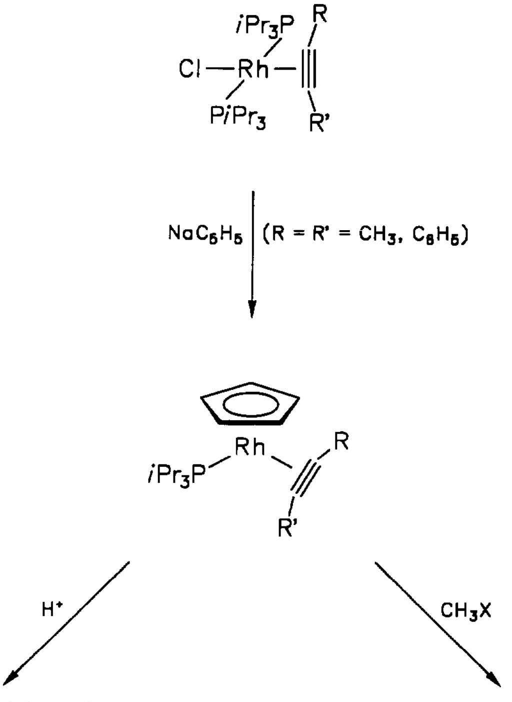
0022-328X/94/$7.00
SSDI 0022-328X(94)24515-K



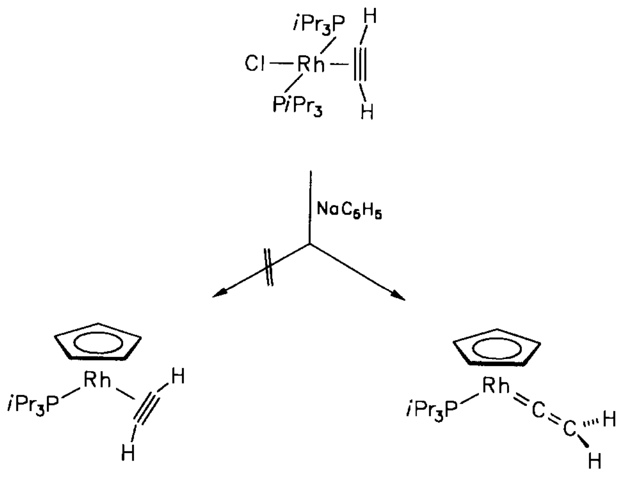
R/R' = H, CH_3, C_6H_5, $SiMe_3$, CO_2R

Scheme 2.

$[C_5H_5Rh(CH_2{=}CHR)(PMe_3)]$ (R = H, Me, Ph) [6], we were interested to know whether the corresponding alkyne-(phosphine) compounds were also accessible. Some preliminary, not very successful attempts [7] led us to believe that in contrast to our earlier investigations, PMe_3 was not the ligand of choice and therefore we used P^iPr_3 as the donor source. Following the work by Busetto *et al.* [8], the synthesis of the square-planar complexes *trans*-$[RhCl(RC{\equiv}CR')(P^iPr_3)_2]$ was straightforward (Scheme 2) [9] and from the ^{13}C NMR spectroscopic data, there was no doubt that the alkyne, even for R = R' = H, coordinates via the C≡C triple bond. The reaction of *trans*-$[RhCl(MeC{\equiv}CMe)(P^iPr_3)_2]$ and



Scheme 3.



Scheme 4.

trans-$[RhCl(PhC{\equiv}CPh)(P^iPr_3)_2]$ with NaC_5H_5 gave, as expected, the half-sandwiches $[C_5H_5Rh(RC{\equiv}CR)(P^iPr_3)]$ (R = Me, Ph) in good yield [9] and these compounds in analogy to the olefin derivatives $[C_5H_5Rh(CH_2{=}CHR)(PMe_3)]$, indeed behave like Lewis bases (Scheme 3). The protonation in particular led to some surprising results which provided a new entry into the chemistry of π-allyl and rhoda-heterocyclic complexes [9,10].

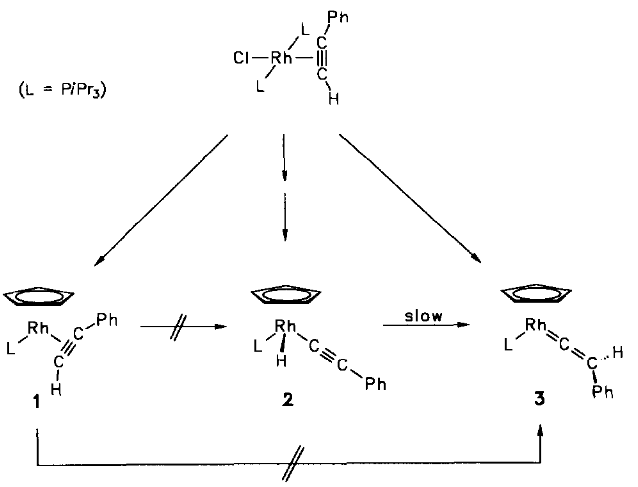
2. The formation of rhodium vinylidenes and allenylidenes from terminal alkynes

A surprising observation was made, however, when the parent acetylenerhodium compound *trans*-$[RhCl(HC{\equiv}CH)(P^iPr_3)_2]$ was treated with NaC_5H_5. Instead of the alkyne complex $[C_5H_5Rh(HC{\equiv}CH)(P^iPr_3)]$ the vinylidene isomer $[C_5H_5Rh({=}C{=}CH_2)(P^iPr_3)]$ (Scheme 4) was obtained [11] and even by altering the reaction conditions, the result remained unchanged. By using PhC≡CH as the acetylenic starting material, we not only succeeded in the isolation of all three isomeric alkyne, alkynyl(hydrido) and vinylidene compounds **1**–**3** (Scheme 5) but also confirmed that under the conditions of the synthesis of **3**, the isomers **1** and **2** are quite inert and do not, or only slowly rearrange to give **3** [11].

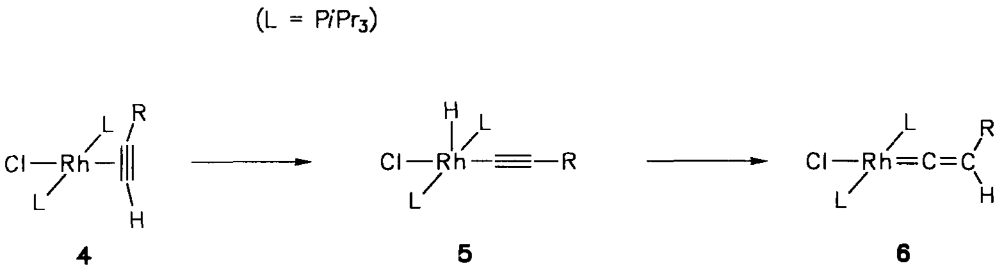
During extensive attempts to elucidate the mechanism of the formation of **3** and various analogous complexes $[C_5H_5Rh({=}C{=}CHR)(P^iPr_3)]$, we observed that the starting materials *trans*-$[RhCl(RC{\equiv}CH)(P^iPr_3)_2]$ on warming to 50°C in hexane become rather labile and rearrange to give the isomeric vinylidene compounds *trans*-$[RhCl({=}C{=}CHR)(P^iPr_3)_2]$ (**6a**–**e**) [12]. Only for R = Ph and ^tBu was it possible to isolate and characterize the five-coordinate intermediates

$[RhH(C{\equiv}CR)Cl(P^iPr_3)_2]$ (**5c,d**) (Scheme 6) for which a square-pyramidal structure with the hydrido ligand in the apical position has been proposed. The conversion of the alkyne to the alkynyl(hydrido) and finally to the vinylidene isomers also occurs in the iridium series [12a,13] and thus there is no doubt that the rearrangement of the square-planar compounds *trans*-$[MCl(RC{\equiv}CH)(P^iPr_3)_2]$ proceeds stepwise.

When we extended the type of terminal alkynes $RC{\equiv}CH$ which we had used for the synthesis of the isomers **4**, **5** and **6** (see Scheme 6) to those having as the substituent R an alkynyl and alkenyl group, we found that the order of stability can be changed significantly. The most simple diyne $HC{\equiv}C{-}C{\equiv}CH$ reacts with $[RhCl(P^iPr_3)_2]_n$ in pentane at −78°C to give the (diyndiyl)dihydrido complex **7** (Scheme 7) and we were

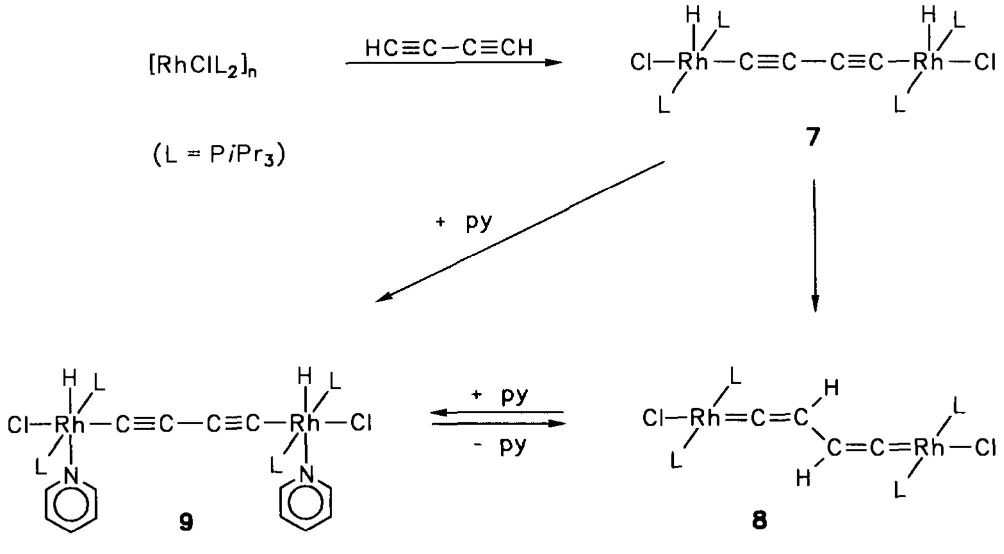


Scheme 5.

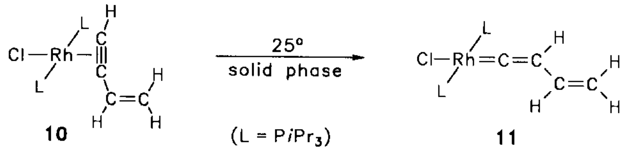


R = H (**a**), CH_3 (**b**), tC_4H_9 (**c**), C_6H_5 (**d**), CO_2Me (**e**)

Scheme 6.



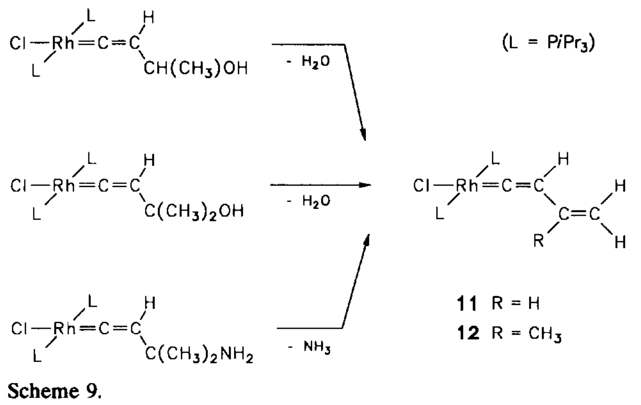
Scheme 7.



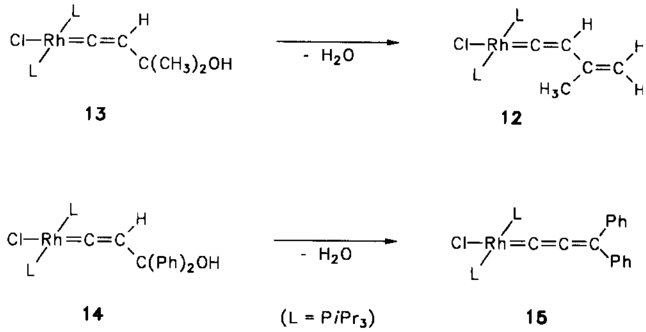
Scheme 8.

unable to detect, even by using dilute solutions of the starting materials, the expected initial formation of the dinuclear diyne derivative [14]. On warming to 45°C, compound **7** rearranges almost quantitatively to give the isomer **8** which in turn regenerates the HRh–C≡C–C≡C–RhH unit upon treatment with pyridine (see **9**). It is interesting to note that the bis-silylated derivative $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ if treated with $[RhCl(P^iPr_3)_2]_n$ behaves differently from HC≡C–C≡CH and yields a mononuclear product in which only one C≡C triple bond is coordinated to rhodium [14].

In some cases the formation of the remarkably stable four-coordinate vinylidenerhodium(I) complexes *trans*-$[RhCl({=}C{=}CHR)(P^iPr_3)_2]$ is favored to such an extent that it even proceeds in the solid state. The parent enyne compound **10** (Scheme 8), which was originally prepared from $[RhCl(P^iPr_3)_2]_n$ and $HC{\equiv}C{-}CH{=}CH_2$ in pentane at −78°C [15] and which is a yellow solid, rearranges in a sealed tube under argon in 2 days to give the dark green isomer **11** [16]. The methyl derivative *trans*-$[RhCl({=}C{=}CHC(CH_3){=}CH_2)(P^iPr_3)_2]$ is obtained likewise in the solid state from *trans*-$[RhCl({=}C{=}CHC(CH_3)_2NH_2)(P^iPr_3)_2]$ by elimination of NH_3 [16]. Because the enynes $HC{\equiv}C{-}C(R){=}CH_2$ ($R = H, CH_3$) are quite sensitive with regard to polymerization, the synthesis of both complexes **11** and **12** is best achieved by using the OH- and NH_2-functionalized vinylidene-precursors (see Scheme 9) which are accessible from $[RhCl(P^iPr_3)_2]_n$ and the corresponding alkyne $HC{\equiv}C{-}CR(CH_3)X$ ($R = H, CH_3$; $X = OH, NH_2$) [15,17].



Scheme 9.



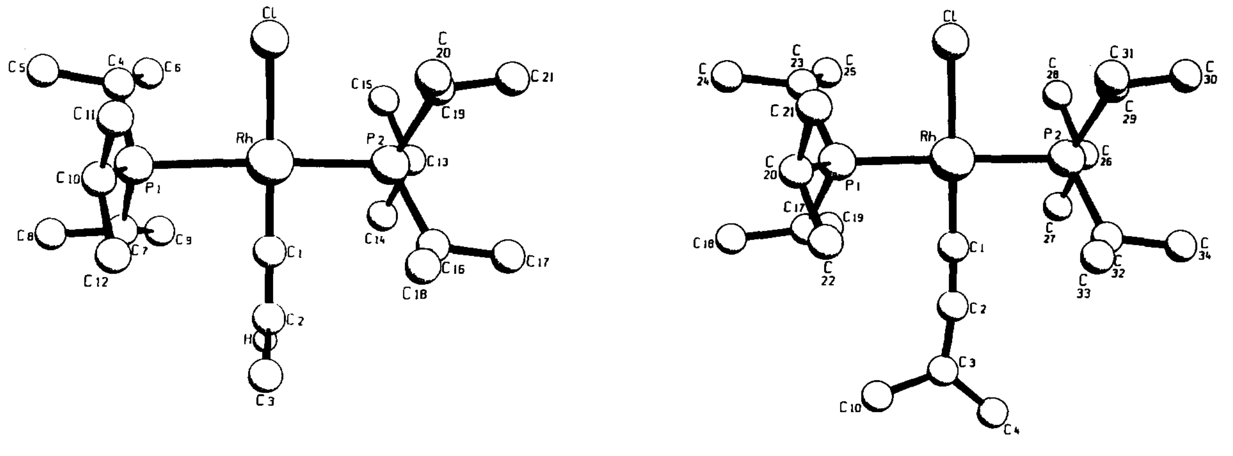
Scheme 10.

If the two alkyl substituents at the C_γ atom of the vinylidene complex **13** are replaced by aryls, water elimination is only possible between the OH group and the vinylidene hydrogen atom and thus diarylallenylidenerhodium(I) compounds such as **15** (Scheme 10) are formed [17,18]. This procedure with $HC{\equiv}C{-}C(Ph)_2OH$ as starting material had already been used by Selegue [19] and more recently also by Dixneuf [20] to prepare ruthenium complexes with $Ru{=}C{=}C{=}CPh_2$ as a molecular unit. The X-ray structural analysis of *trans*-$[RhCl({=}C{=}C{=}C(o\text{-}Tol)Ph)(P^iPr_3)_2]$ reveals that in contrast to the vinylidene compounds (*e.g.* **6b**, Scheme 11) which stereochemically resemble allenes [21], in the corresponding allenylidenes the *ipso*-carbon atoms of the aryl groups on C_γ are in the same plane as the phosphorus, the rhodium and the C_α, C_β and C_γ allenylidene carbon atoms and therefore a similarity to butatrienes exists.

With the methyl(phenyl) derivative **16**, a structurally related analogue to compounds **13** and **14**, we succeeded for the first time in directing the course of the elimination of H_2O either to the allenylidenerhodium complex **17** or to the vinylvinylidene isomer **18** (Scheme 12). Compound **18** seems to be thermodynamically preferred because in the presence of trace amounts of CF_3CO_2H or of acidic Al_2O_3, a quantitative isomerization of **17** to **18** takes place [17,18].

3. Coupling reactions of σ-bonded organyl groups and vinylidene ligands

The gate to alkynyl(vinylidene)rhodium(I) complexes was opened after we found that η^3-allylrhodium compounds are excellent precursors for the coordination of two C_2 units to the metal centre. The η^3-benzyl compounds **19** and **20**, which are prepared from $[RhCl(P^iPr_3)_2]_n$ and the corresponding Grignard reagent



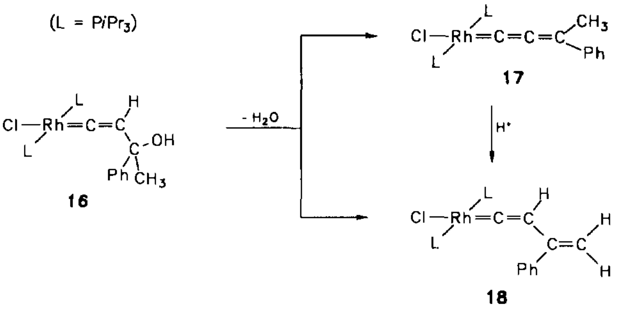
trans-[RhCl(=C=CHCH$_3$)(P*i*Pr$_3$)$_2$] [12b] **trans-[RhCl(=C=C=C(*o*-Tol)Ph)(P*i*Pr$_3$)$_2$]** [18]

Scheme 11.

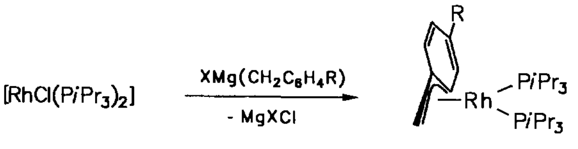
(Scheme 13) [22], are even more suitable than the η^3-allyl derivatives $[Rh(\eta^3\text{-}2\text{-}RC_3H_4)(P^iPr_3)_2]$ for which two synthetic routes are known [23]. The reason for the enhanced reactivity of **19** and **20** towards terminal alkynes and other acidic substrates probably is that the η^3-benzyl is coordinated to rhodium in a highly unsymmetrical mode (see Scheme 14) which is best illustrated by the distances Rh–C1 and Rh–C3 of 2.125(9) and 2.41(1) Å [22]. This difference also explains why the complexes **19** and **20** are fluxional in solution. At room temperature, an antarafacial (π-σ-π) as well as a suprafacial rearrangement occurs, the first of which is frozen out at 263 K. On cooling to 193 K, the faster process (equally designated as a metallotropic shift) is also slowed down and the rigid structure of **19** and **20** is observed.

The η^3-benzyl compound **19** reacts smoothly with two equivalents of a terminal alkyne RC≡CH to give the square-planar complexes **23a–c** in 70–80% yield [24]. If the reaction is not carried out at 30–40°C but at 20°C (R = ^{t}Bu) or below (R = Me, Ph), the intermediarily formed alkyne(alkynyl)rhodium(I) and bis(alkynyl)hydridorhodium(III) compounds **21a,c** and **22b** (Scheme 15) can be isolated. Since they rearrange quantitatively to yield **23a–c**, there is no doubt that in this case as well as in the synthesis of **6** (see Scheme 6), the generation of the vinylidene unit proceeds stepwise and not according to an alkyne-vinylidene "slippage" as proposed by MO calculations [25].

Surprisingly, the reaction of **23c** with a solution of HCl in benzene at room temperature does not cause the elimination of phenylacetylene but gives the enyne complex **25** in about 50% yield. If **23c** is treated in ether at −40°C with gaseous HCl, instead of **25**, the alkynyl(vinyl) compound **24** is formed quantitatively (Scheme 16). Presumably, in the initial step, an oxidative addition of HCl to the metal centre takes place, followed by the migration of the hydride ligand to the α-carbon atom of the vinylidene unit. Because the reaction of **23c** with HCl to produce **24** is both regio- and stereoselective, we conclude that the exclusive formation of the *Z* isomer is due to the kinetically

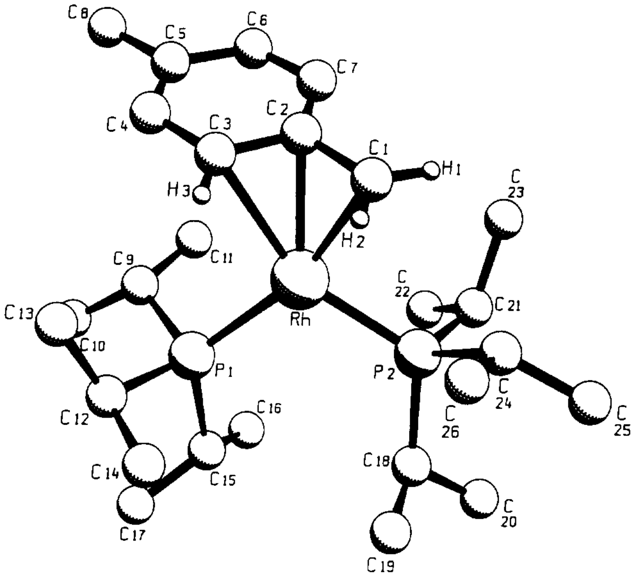


Scheme 12.

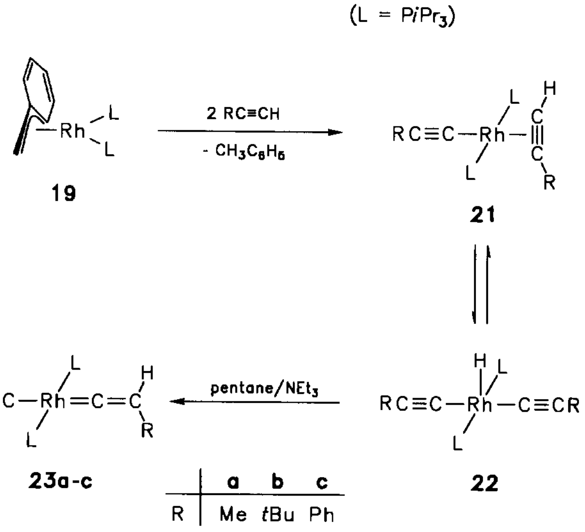


19: R = H
20: R = CH$_3$

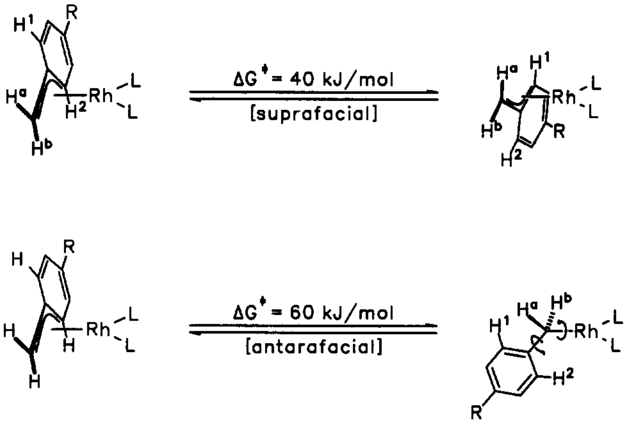
Scheme 13.



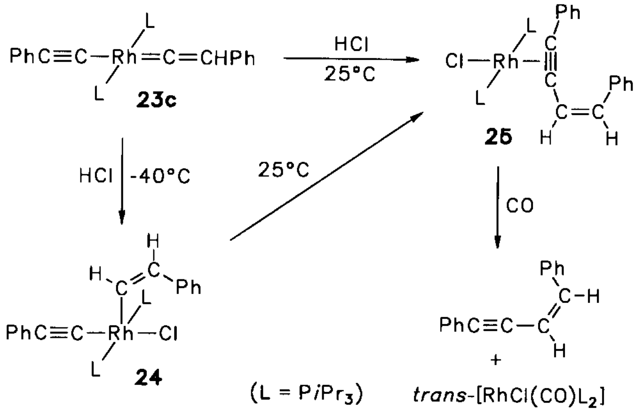
20



Scheme 15.



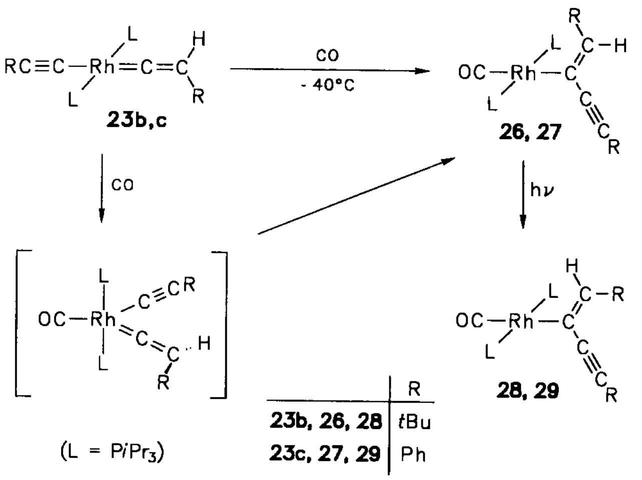
Scheme 14.



Scheme 16.

preferred transfer of the hydride from the side opposite to the phenyl group. The rearrangement of **24** to **25** occurs quantitatively in benzene at room temperature and is equally selective; only the isomer containing the enyne in the *Z* configuration is formed [26]. Upon treatment of **25** with CO, a ligand displacement takes place to give the *Z* enyne and the square-planar carbonyl complex *trans*-[RhCl(CO)(P^{i}Pr$_3$)$_2$].

Coupling of the C$_2$ units of **23c** (and also of the corresponding t-butyl derivative **23b**) occurs in a different way if the sequence of the addition of acid HX and CO is reversed. Both alkynyl(vinylidene) complexes react with CO in pentane at −40°C to give exclusively the *Z* isomers of the enynylrhodium compounds **26** and **27** in about 80% yield (Scheme 17). We assume that initially the carbon monoxide adds to the metal

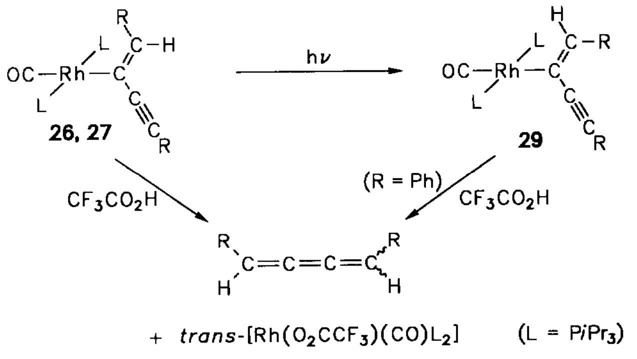


Scheme 17.

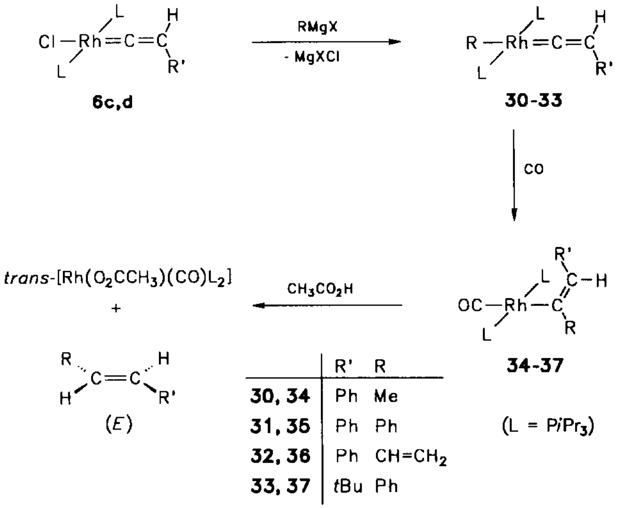
centre, thus generating a five-coordinate intermediate, which after migration of the alkynyl ligand to the α-carbon atom of the vinylidene unit is transformed to the isolated product. The X-ray structural analysis of an analogue of **26** or **27** with R = CO_2Me, which has been prepared from $[Rh(\eta^2\text{-}O_2CCH_3)(P^iPr_3)_2]$ and $HC{\equiv}CCO_2Me$ in the presence of Na_2CO_3 [24a], reveals that the enynyl unit is perpendicular to the [CO, Rh, P1, P2] plane and that there is no additional interaction between the C≡C triple bond or the cisoid ester group with the rhodium atom. Photolysis of a solution of **26** or **27** in benzene leads to an isomerization which affords the thermodynamically preferred compounds **28** and **29** [26].

In contrast to what we had expected, the cleavage of the enynyl–metal bond in **26**, **27** and **29** by CF_3CO_2H in acetone or benzene gives the butatrienes RCH=C=C=CHR in 90–95% yield as well as small amounts of the corresponding enyne (Scheme 18). Whereas compound **27** is inert towards acetic acid, the reaction of **26** with CH_3CO_2H leads to a 2:3 mixture of E-$^tBuC{\equiv}CCH{=}CH^tBu$ and E,Z-$^tBuCH{=}C{=}C{=}CH^tBu$, and that of **29** with CH_3CO_2H gives Z-PhC≡CCH=CHPh. Both the product distribution and the isomer ratio of the E/Z-butatrienes indicate that, with a strong proton donor such as CF_3CO_2H, the attack of the acid does not occur at the Lewis basic metal centre but directly at the triple bond of the enynyl ligand. Presumably, a cationic butatrienerhodium complex is formed as an intermediate (*cf.* ref. 14), from which the cumulene is displaced by the carboxylate anion [26].

Migration of a σ-bonded organyl group from rhodium to a vinylidene ligand has not only been observed during the formation of **26** and **27** but has also recently been achieved with alkyl, aryl and vinyl units [27]. The chloro derivatives **6c,d** react with an equimolar amount of CH_3MgI, C_6H_5MgBr or $CH_2{=}CHMgBr$ in ether/toluene or ether/THF at −30°C to give the alkyl, aryl and vinyl complexes **30**–**33** in 80–90% yield (Scheme 19). These compounds, like the rhodium alkynyls **23b,c** are highly reactive towards carbon monoxide and afford the carbonyl complexes **34**–**37** almost quantitatively. Both the NMR spectroscopic data of **34**–**37** and the X-ray crystal structure analysis of **36** provide evidence that only the Z isomers having the substituents R and R′ in a *trans* orientation at the C=C double bond are formed. The reactions of **30** and **31** with CN^tBu also occur selectively and give the compounds *trans*-$[Rh(CR{=}CHR')(CN^tBu)(P^iPr_3)_2]$ in about 80% yield [27].



Scheme 18.



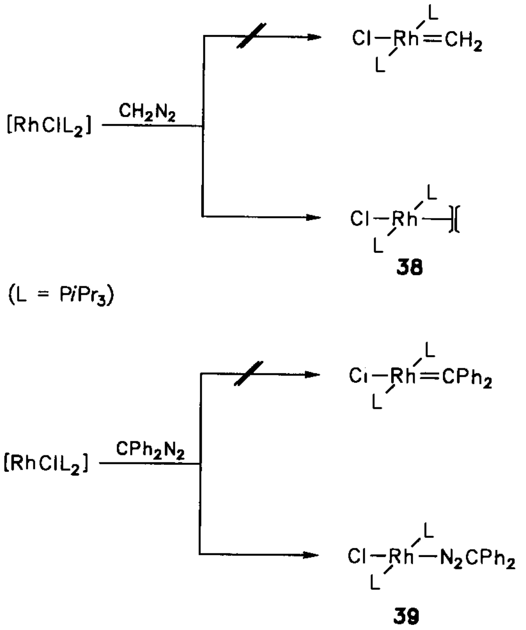
	R′	R
30, 34	Ph	Me
31, 35	Ph	Ph
32, 36	Ph	CH=CH₂
33, 37	tBu	Ph

Scheme 19.

The cleavage of the vinyl- or dienyl–metal bond in **34**–**37** by acetic acid in benzene proceeds slowly at room temperature and produces, besides the acetatorhodium complex *trans*-$[Rh(O_2CCH_3)(CO)(P^iPr_3)_2]$, the E olefins RCH=CHR′ and $PhCH{=}CHCH{=}CH_2$ exclusively. With **37** as a substrate, preliminary experiments indicate that with stronger acids the Rh–C cleavage reaction takes a different course and probably leads to the 1,3-disubstituted allene $PhCH{=}C{=}CHCH_3$ [27].

4. Alkenes as substrates: a novel rhodium-catalysed C–C coupling reaction

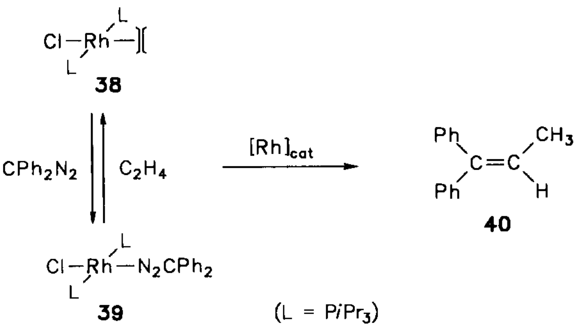
When we attempted to extend the vinylidene rhodium chemistry to the corresponding carbenerhodium complexes of the general type *trans*-$[RhCl({=}CR_2)(P^iPr_3)_2]$, we recently found that with $[RhCl(P^iPr_3)_2]_n$ as starting material, neither CH_2N_2 nor CPh_2N_2 form the expected product (see Scheme 20) but instead give the compounds *trans*-$[RhCl(C_2H_4)(P^iPr_3)_2]$ (**38**) and *trans*-$[RhCl(N_2CPh_2)(P^iPr_3)_2]$ (**39**), respectively [28]. Furthermore, we observed that between CPh_2N_2 and ethylene in the pres-



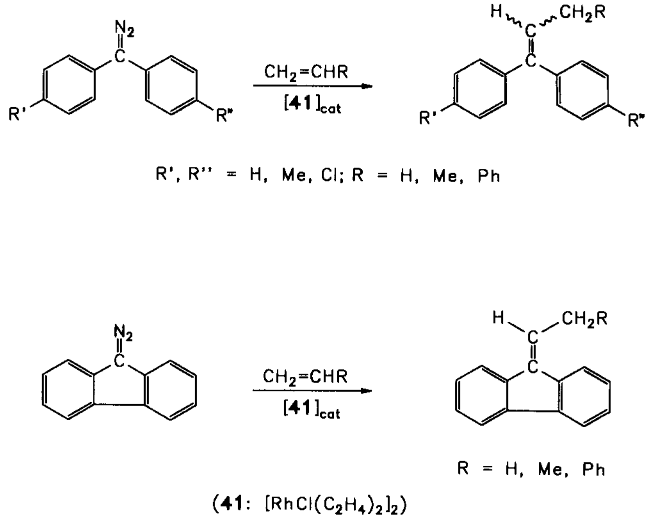
Scheme 20.

ence of a rhodium(I) complex such as **38** or **39**, a catalytic process generating 1,1-diphenylpropene **40** takes place (Scheme 21). This novel C–C coupling reaction is particularly noteworthy insofar as it is well known that rhodium(II) compounds such as $[Rh_2(O_2CCH_3)_4]$ belong to the most efficient catalysts for the formation of 1,1-diphenylcyclopropane from C_2H_4 and CPh_2N_2 [29].

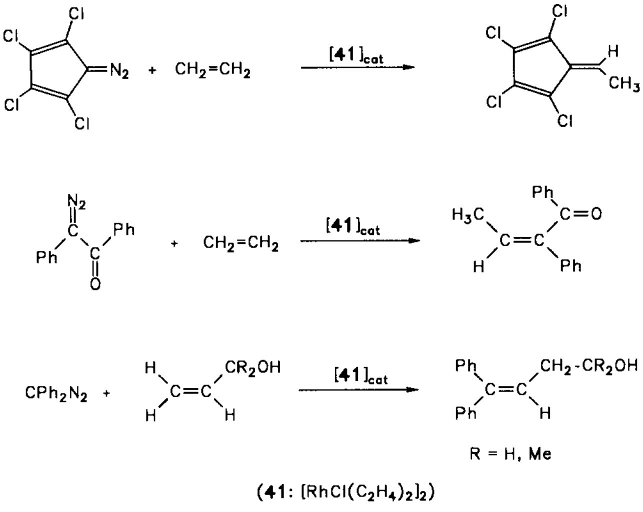
Among more than 20 rhodium(I) and iridium(I) complexes tested as catalysts for the above mentioned C–C bond forming reaction, the dimeric bis(ethene) compound $[RhCl(C_2H_4)_2]_2$ (**41**) proved to be the most efficient. With 20 mg of **41** in 15 ml of toluene at 40–50°C, turnover numbers of 200–500 for the systems shown in Scheme 22 are observed [28]. For other substrates, which may contain a functional group in either the starting olefin or the diazo derivative (for examples see Scheme 23), the turnover numbers vary from 5 to 30 [30]. In each case, the coupling product is built up regioselectively by the formal linking of the carbene fragment of the diazoalkane with the olefin isomer: CHR′ (R′ = CH_3, CH_2CR_2OH). For some reactions, *e.g.* for the formation of **43** from benzoyl(phenyl)diazomethane and ethene, a high degree of stereoselectivity is found. The turnover numbers do not depend on the solvent and remain almost the same regardless of whether toluene, ether or acetone is used [30b].



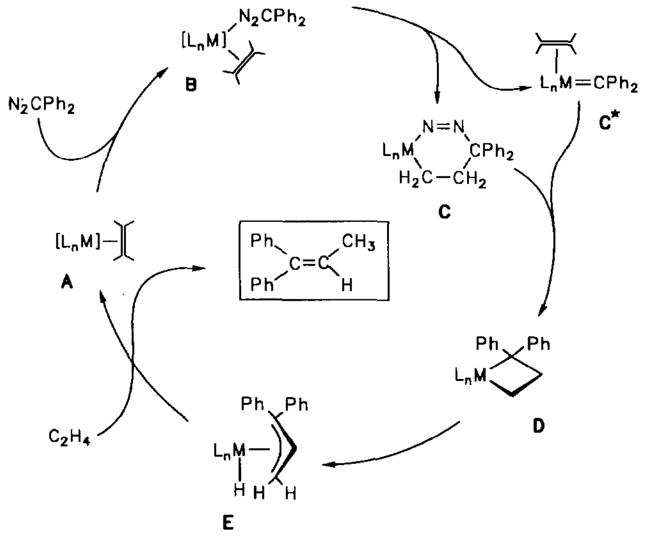
Scheme 21.



Scheme 22.



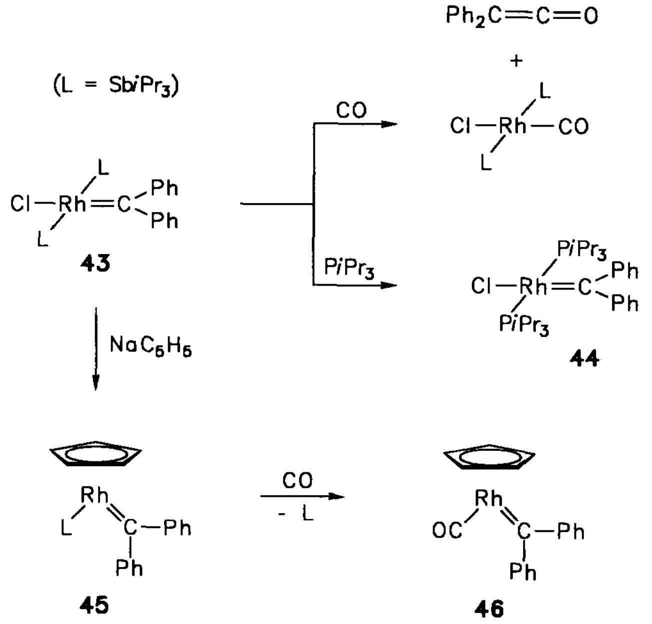
Scheme 23.



Scheme 24.

Concerning the mechanism of the new olefin synthesis, it is important to note that **40** is obtained from **38** and CPh_2N_2 as well as from **39** and C_2H_4. We therefore assume that in the initial stage of the reaction, both substrates are coordinated to the metal and form either a MN_2C_3 six-membered heterocycle **C** or a carbene(olefin)metal complex **C*** (Scheme 24). From both species, a metallacyclobutane derivative **D** may be generated, from which a η^3-allyl(hydrido) intermediate is obtained by a β-H shift. Finally, migration of the hydride ligand to the less substituted terminal carbon atom of the allyl group can lead to the product olefin, thus reforming the catalytically active species **A** [28].

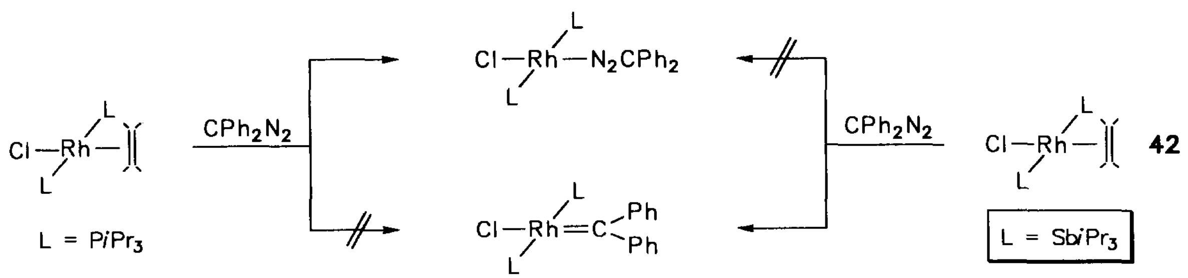
5. Novel rhodium carbenes: the missing link in the series of double bond systems



Scheme 26.

The synthesis of four-coordinate carbenerhodium complexes which possibly generates an intermediate such as **C*** shown in Scheme 24 has recently been achieved when a starting material similar to **38** but with two Sb^iPr_3 instead of two P^iPr_3 ligands in the *trans* position is used. Treatment of **42** (see Scheme 25) with CPh_2N_2 in pentane at room temperature leads to a rapid displacement of ethene by the diphenylcarbene ligand and affords compound **43** in 96% yield [31]. As the X-ray structure analysis of **43** reveals, the Rh–C bond length is surprisingly short (1.863(4)Å) and thus indicative of a strong Rh–C back bonding. With di-*p*-tolyldiazomethane, phenyl(*o*-tolyl)diazomethane and even with phenyl(trifluormethyl)diazomethane, carbene complexes structurally related to **43** are obtained, while with benzoyldiazomethane and azibenzil, a diazoalkanerhodium derivative (similar to **39**) is formed instead [31].

Scheme 26 illustrates that the rhodium carbene **43** has great potential as starting material for the synthesis of other organorhodium derivatives. The reaction with CO in pentane at room temperature leads almost quantitatively to the carbonyl complex *trans*-[RhCl(CO)(Sb^iPr_3)$_2$] [32] and diphenylketene. In contrast,

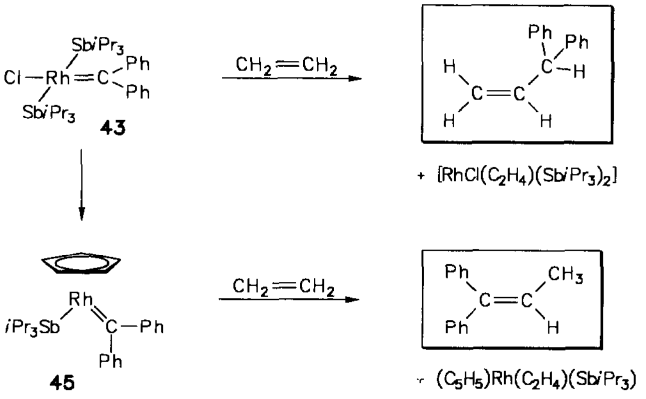


Scheme 25.

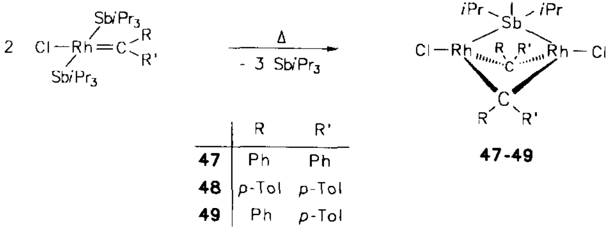
on treatment of **43** with P^{i}Pr$_3$, an exchange of the stibane by the phosphane takes place and compound **44**, which could not be prepared from either [RhCl(P^{i}Pr$_3$)$_2$]$_n$ or **38** and CPh$_2$N$_2$, is formed. With NaC$_5$H$_5$, nucleophilic substitution of the chloro by the cyclopentadienyl ligand occurs to give the half-sandwich type complex **45** in 80% yield [31]. In this compound, the Rh–Sb^{i}Pr$_3$ bond is rather labile and thus upon passing CO through a pentane solution of **45**, the mixed carbonyl(carbene)rhodium(I) complex **46** is obtained. The X-ray structural analysis of **46** shows that the Rh–CO bond is somewhat shorter (by 0.06 Å) than the Rh–CPh$_2$ bond [33], which is in agreement with the enhanced π-acceptor properties of CO if compared with CPh$_2$.

The studies carried out in order to find out whether the diphenylcarbene complexes **43** and **45** react with ethene and thus could be considered as models for the intermediate C* shown in Scheme 24, have led to a puzzling result [33]. Neither of the two rhodium compounds give 1,1-diphenylcyclopropane but form different olefins (see Scheme 27). Whereas the half-sandwich **45** affords 1,1-diphenyl-1-propene (**40**), which is the product also obtained in the catalytic reaction, the square-planar complex **43** reacts with ethene by insertion of the carbene into one of the C–H bonds to yield CH$_2$=CHCHPh$_2$, *i.e.* an isomer of **40**. Although the reason for the different behaviour is not yet clear, the finding nevertheless indicates that carbenerhodium(I) derivatives might be intermediates in the unprecedented Rh-catalysed C–C coupling reaction between C$_2$H$_4$ and CPh$_2$N$_2$.

In contrast to the bis(phosphane) compound **44** which is quite inert even in boiling benzene, the analogous bis(stibane) derivative **43** reacts on warming to 60°C by partial loss of the Sb^{i}Pr$_3$ ligands and formation of the dinuclear complex **47** in 80% yield [34]. The corresponding compounds **48** and **49** are similarly obtained (see Scheme 28). The X-ray structural analysis of **47** confirms the hitherto unknown capability of trialkylstibanes to behave as bridging ligands, *i.e.* to form two Rh–Sb bonds. The Rh–Rh distance is relatively short (2.535 Å) and indicates a direct metal–metal interaction. Noteworthy are the significantly larger (approx. 0.1 Å) Rh–Sb bond lengths in **47** if compared with **43**, which is in agreement with the bridging function of the Sb^{i}Pr$_3$ ligand. Surprisingly, the triisopropylstibane unit in **47** is easily substituted by SbMe$_3$ or SbEt$_3$ without opening the carbene bridges. This final result illustrates that not only SbR- and SbR$_2$-fragments but also SbR$_3$ molecules are able to link two metal centres and therefore along with CO, NO or isocyanides belong to the distinguished type of ligands L which form both terminal and bridging M–L bonds.



Scheme 27.



	R	R'
47	Ph	Ph
48	p-Tol	p-Tol
49	Ph	p-Tol

Scheme 28.

Acknowledgement

First and foremost I would like to thank my coworkers, in particular Dr. Justin Wolf, whose names appear in the literature citations. Without their activity and enthusiasm it would not have been possible to reach our goals. I also acknowledge the collaboration with Professor U. Schubert and (the late) Professor M.L. Ziegler who carried out several X-ray analyses. Finally, I extend my sincere thanks to the Deutsche Forschungsgemeinschaft (SFB 347), the Fonds der Chemischen Industrie and the Volkswagen-Stiftung for their continuous support of our work.

References

1 H. Werner, *Angew. Chem., 95* (1983) 932; *Angew. Chem., Int. Ed. Engl., 22* (1983)927.
2 D.F. Shriver, *Acc. Chem. Res., 3* (1970) 231.
3 H. Werner, R. Feser and W. Buchner, *Chem. Ber., 112* (1979) 834.
4 R. Feser and H. Werner, *J. Organomet. Chem., 233* (1982) 193.
5 (a) H. Werner, *Coord. Chem. Rev., 43* (1982) 165; (b) O. Kolb and H. Werner, *J. Organomet. Chem., 268* (1984) 49.
6 H. Werner and R. Feser, *J. Organomet. Chem., 232* (1982) 351.
7 J. Wolf, *Diplomarbeit*, Universität Würzburg, 1982.
8 C. Busetto, A. D'Alfonso, F. Maspero, G. Perego and A. Zazetta, *J. Chem. Soc., Dalton Trans.*, (1977) 1828.

9 (a) H. Werner, J. Wolf, U. Schubert and K. Ackermann, *J. Organomet. Chem.*, *243* (1983) C63; (b) H. Werner, J. Wolf, U. Schubert and K. Ackermann, *J. Organomet. Chem.*, *317* (1986) 327.

10 J. Wolf and H. Werner, *Organometallics*, *6* (1987) 1164.

11 H. Werner, J. Wolf, F.J. Garcia Alonso, M.L. Ziegler and O. Serhadli, *J. Organomet. Chem.*, *336* (1987) 397.

12 (a) F.J. Garcia Alonso, A. Höhn, J. Wolf, H. Otto and H. Werner, *Angew. Chem.*, *97* (1985) 401; *Angew. Chem., Int. Ed. Engl.*, *24* (1985) 406; (b) H. Werner, F.J. Garcia-Alonso, H. Otto and J. Wolf, *Z. Naturforsch., Teil B*, *43* (1988) 722; (c) H. Werner and U. Brekau, *Z. Naturforsch., Teil B*, *44* (1989) 1438.

13 (a) A. Höhn, H. Otto, M. Dziallas and H. Werner, *J. Chem. Soc., Chem. Commun.*, (1987) 852; (b) A. Höhn and H. Werner, *J. Organomet. Chem.*, *382* (1990) 255.

14 T. Rappert, O. Nürnberg and H. Werner, *Organometallics*, *12* (1993) 1359.

15 T. Rappert, O. Nürnberg, N. Mahr, J. Wolf and H. Werner, *Organometallics*, *11* (1992) 4156.

16 H. Werner, T. Rappert, M. Baum and A. Stark, *J. Organomet. Chem.*, *459* (1993) 319.

17 T. Rappert, *Dissertation*, Universität Würzburg, 1992.

18 H. Werner, T. Rappert, R. Wiedemann, J. Wolf and N. Mahr, *Organometallics*, in press.

19 J.P. Selegue, *Organometallics*, *1* (1982) 217.

20 (a) N. Pirio, D. Touchard, L. Toupet and P.H. Dixneuf, *J. Chem. Soc., Chem. Commun.*, (1991) 980; (b) A. Wolinska, D. Touchard, P.H. Dixneuf and A. Romero, *J. Organomet. Chem.*, *420* (1991) 217; (c) N. Pirio, D. Touchard and P.H. Dixneuf, *J. Organomet. Chem.*, *462* (1993) C18.

21 (a) M.I. Bruce, *Chem. Rev.*, *91* (1991) 197; (b) H. Werner, *Nachr. Chem. Tech. Lab.*, *40* (1992) 435.

22 H. Werner, M. Schäfer, O. Nürnberg and J. Wolf, *Chem. Ber.*, *127* (1994) 27.

23 (a) D.L. Thorn and J.A. Ibers, *Adv. Chem. Ser.*, *196* (1982) 117; (b) M. Schäfer, J. Wolf and H. Werner, *J. Chem. Soc., Chem. Commun.*, (1991) 1341.

24 (a) M. Schäfer, *Dissertation*, Universität Würzburg, 1994; (b) M. Schäfer, F. Kukla and H. Werner, *Organometallics*, submitted.

25 J. Silvestre and R. Hoffmann, *Helv. Chim. Acta*, *68* (1985) 1461.

26 M. Schäfer, N. Mahr, J. Wolf and H. Werner, *Angew. Chem.*, *105* (1993) 1377; *Angew. Chem., Int. Ed. Engl.*, *32* (1993) 1315.

27 R. Wiedemann, P. Steinert, M. Schäfer and H. Werner, *J. Am. Chem. Soc.*, *115* (1993) 9864.

28 (a) J. Wolf, L. Brandt, A. Fries and H. Werner, *Angew. Chem.*, *102* (1990) 584; *Angew. Chem., Int. Ed. Engl.*, *29* (1990) 510; (b) L. Brandt, A. Fries, N. Mahr, H. Werner and J. Wolf, in H. Werner, A. Griesbeck, W. Adam, G. Bringmann and W. Kiefer (eds.), *Selected Reactions of Metal-Activated Molecules*, Vieweg, Braunschweig, 1992, p. 171.

29 A. Padwa, D.J. Austin, A.T. Price, M.A. Semones, M.P. Doyle, M.N. Protopopova, W.R. Wincester and A. Tran, *J. Am. Chem. Soc.*, *115* (1993) 8669 and refs. therein.

30 (a) L. Brandt, *Dissertation*, Universität Würzburg, 1991; (b) A. Fries, *Dissertation*, Universität Würzburg, 1993; (c) N. Mahr, *Dissertation*, Universität Würzburg, 1994.

31 P. Schwab, N. Mahr, J. Wolf and H. Werner, *Angew. Chem.*, *105* (1993) 1498; *Angew. Chem., Int. Ed. Engl.*, *32* (1993) 1480.

32 H. Werner, P. Schwab, N. Mahr and J. Wolf, *Chem. Ber.*, *125* (1992) 2641.

33 P. Schwab, *Dissertation*, Universität Würzburg, 1994.

34 P. Schwab, N. Mahr, J. Wolf and H. Werner, *Angew. Chem.*, *106* (1994) 82; *Angew.Chem., Int. Ed. Engl.*, *33* (1994) 97.