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Review

Vinylidenerhodium complexes as promising tools for C–C coupling reactions

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Dedicated to Professor Siegfried Ebel on the occasion of his 70th birthday

Contents

Abstract

Four-coordinate rhodium(I) complexes of the general composition *trans*-[Rh(R)(=C=CHR′)-(PiPr$_3$)$_2$] and *trans*-[Rh(R)(=C=CMe$_2$)(PiPr$_3$)$_2$], where R is an alkynyl, aryl, methyl or vinyl group, were prepared by substitution of the chlororhodium(I) precursors *trans*-[RhCl(=C=CHR′)(PiPr$_3$)$_2$] or *trans*-[RhCl(=C=CMe$_2$)(PiPr$_3$)$_2$] and a Grignard reagent. The alkynyl derivatives *trans*-[Rh(C≡CR)(=C=CHR)(PiPr$_3$)$_2$] are also accessible from [Rh(η^3-CH$_2$Ph)(PiPr$_3$)$_2$] and two equivalents of a terminal alkyne. The reaction of *trans*-[Rh(R)(=C=CHR′)(PiPr$_3$)$_2$] and *trans*-[Rh(Ph)(=C=CMe$_2$)(PiPr$_3$)$_2$] with CO led to a migration of the alkynyl, aryl, methyl or vinyl group to the α-carbon atom of the vinylidene ligand and gave the η^1-vinyl-, η^1-butadienyl- and η^1-enynylrhodiumcarbonyl complexes *trans*-[Rh{η^1-C(R)=CHR′}(CO)(PiPr$_3$)$_2$] in good to excellent yields. The (*Z*) isomers are preferentially formed. Even in the absence of CO, the methyl and vinyl compounds *trans*-[Rh(R)(=C=CHR′)(PiPr$_3$)$_2$] (R = CH$_3$, CH=CH$_2$) undergo an intramolecular C–C coupling reaction to give the η^3-allyl and η^3-butadienyl isomers [Rh(η^3-1-CH$_2$CHCHR′)(PiPr$_3$)$_2$] and [Rh(η^3-*trans*-CH$_2$CHC=CHR′)(PiPr$_3$)$_2$]. Acid-induced cleavage of the Rh–C σ-bond of *trans*-[Rh{η^1-C(R)=CHR′}(CO)(PiPr$_3$)$_2$] with acetic acid affords *trans*-[Rh(κ^1-O$_2$CCH$_3$)(CO)(PiPr$_3$)$_2$] and the corresponding olefin or diene, respectively. In contrast, the enynyl complexes *trans*-[Rh{η^1-C(C≡CR)=CHR′}(CO)(PiPr$_3$)$_2$] (R = R′ = Ph, *t*Bu) react with CF$_3$CO$_2$H to give almost exclusively the butatrienes RCH=C=C=CHR′. Treatment of [Rh(η^3-1-CH$_2$CHCHR′)(PiPr$_3$)$_2$] and [Rh(η^3-*trans*-CH$_2$CHC=CHR′)(PiPr$_3$)$_2$] with acid gives [Rh(κ^2-O$_2$CCH$_3$)(PiPr$_3$)$_2$] and the respective olefin or diene. With the chelate compound [Rh(κ^2-O$_2$CCH$_3$)(PiPr$_3$)$_2$] as the starting material, a stepwise trimerization of HC≡CCO$_2$Me can be performed which, however, does not lead to a trisubstituted arene but selectively to a hexadienyne derivative. The C$_4$-bridged vinylidenerhodium(I) complexes *trans*-[{Rh(=C=CHR)(PiPr$_3$)$_2$}$_2$(μ-C≡C−C≡C)] react with CO and 2,6-dimethylphenylisocyanide by a twofold migratory insertion to give the dinuclear compounds *trans*-[{Rh(CX)(PiPr$_3$)$_2$}$_2${μ-C(=CHR)C≡C−C≡C(=CHR)}], which contain a highly unsaturated eight-membered C$_8$ chain as the bridge.

Keywords: Vinylidene complexes; Alkynyl complexes; Allyl complexes; C–C coupling; Rhodium

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1. Introduction

Vinylidene, the simplest unsaturated carbene, plays an important role in organic chemistry [1]. Although the acetylene-to-vinylidene rearrangement is highly endothermic, it is now well known that in the coordination sphere of mainly electron-rich transition-metals this isomerisation process occurs quite readily (see reviews [2]). The driving force for the isomerisation can be seen in the excellent π-acceptor capabilities of: $C{=}CH_2$ and its congeners [3] which in some respects exceeds those of CO [4]. The result is that transition-metal complexes of the general composition $[M(=C=CHR)(L)_n]$ (R = H, alkyl, aryl, vinyl, etc.) are quite stable and in most cases even more stable than the related acetylene-metal isomers.

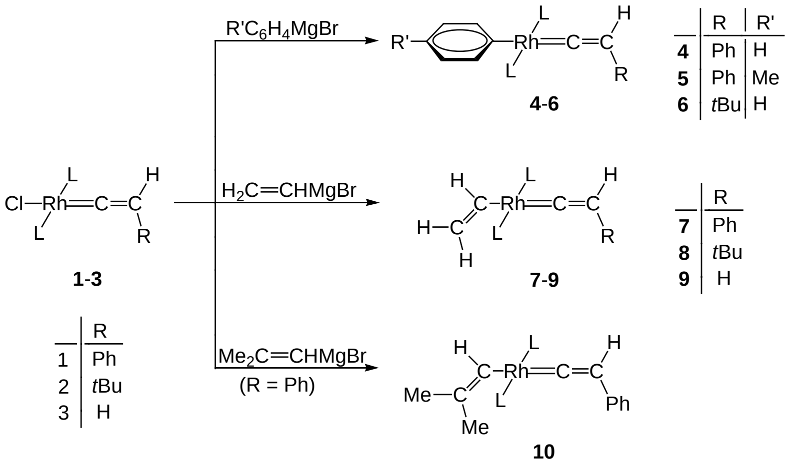
Our own work in the field of metal vinylidenes began with a mere accident. In the context of a broad investigation on the Lewis basicity of halfsandwich-type transition-metal complexes [5], we observed that in contrast to the square-planar compounds *trans*-$[RhCl(RC{\equiv}CR)(PiPr_3)_2]$ (where R is methyl or phenyl), which react with NaC_5H_5 to give the alkyne complexes $[(\eta^5\text{-}C_5H_5)Rh(RC{\equiv}CR)(PiPr_3)]$, the corresponding starting materials *trans*-$[RhCl(HC{\equiv}CR)(PiPr_3)_2]$ (where R is H, methyl or phenyl) afford upon treatment with NaC_5H_5 exclusively the vinylidene counterparts $[(\eta^5\text{-}C_5H_5)Rh(=C=CHR)(PiPr_3)]$ [6]. While studying the mechanism of this reaction in some detail, we found that in solution the four-coordinate rhodium(I) precursors *trans*-$[RhCl(HC{\equiv}CR)(PiPr_3)_2]$ are rather labile and rearrange at ambient temperatures to the vinylidene isomers *trans*-$[RhCl(=C=CHR)(PiPr_3)_2]$; the five-coordinate rhodium(III) compounds $[RhCl(H)(C{\equiv}CR)(PiPr_3)_2]$ are formed as intermediates [7]. Subsequent theoretical work revealed that the final step from the alkynyl(hydrido) complexes to the four-coordinate rhodium vinylidenes probably occurs by a bimolecular hydrogen shift which is favored by ca. 15 kcal/mol in free energy of activation compared with a unimolecular 1,3-H migration process [8].

The present account summarizes our studies about the reactivity of rhodium(I) vinylidenes (in some cases of the corresponding alkynyl(hydrido)rhodium(III) isomers) toward carbon nucleophiles. It is shown that in agreement with the work by Kostic and Fenske [3] the α-carbon atom of the Rh=C=CHR moiety appears to be somewhat electron-deficient and reveals a remarkable tendency to react intramolecularly with an organyl moiety to form of a new C–C bond. Since in most cases the so-formed σ- or π-bonded ligand can be easily released from the metal center, the rhodium vinylidenes can serve as mediators for the coupling of terminal alkynes with different organic substrates.

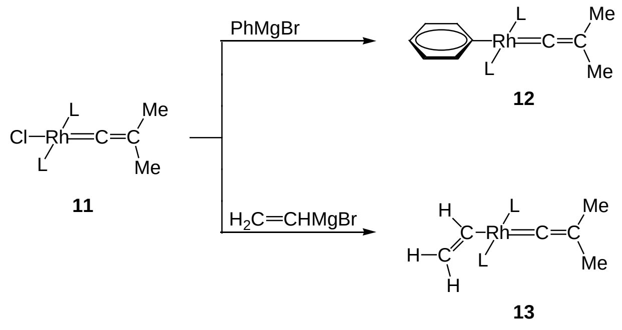
2. Preparation of the starting materials

The vinylidene complexes **1–3**, which are accessible from $[RhCl(PiP_3)_2]_2$ and terminal alkynes [7], react with aryl or vinyl Grignard reagents in ether/THF to give the aryl and vinyl rhodium(I) compounds **4–10** in good to excellent yields (Scheme 1) [9]. The related starting material **11**, which was prepared by an unexpected route from $[RhCl(PiP_3)_2]_2$, $Me_2C{=}CHBr$ and two equivalents of sodium [10], behaves similarly and upon treatment with PhMgBr or $CH_2{=}CHMgBr$ affords the corresponding phenyl and vinyl rhodium(I) complexes **12** and **13** (Scheme 2). Compounds **4–10** and **12**, **13** were isolated as violet or deep green microcrystalline solids, which are air-sensitive but under argon can be stored for weeks without decomposition.

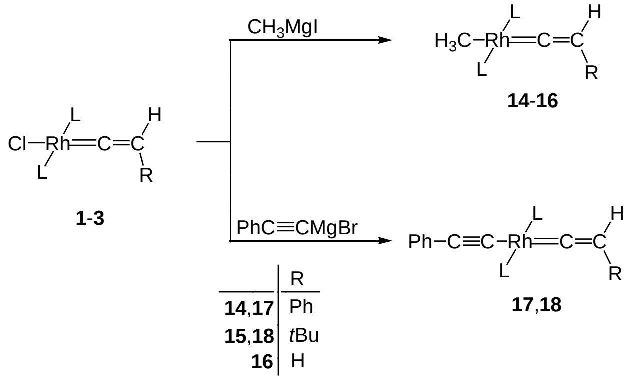
To obtain the methyl rhodium(I) derivatives **14–16**, the procedure used for the preparation of the aryl and vinyl counterparts had to be modified. After several unsuccessful attempts, we found that the method of choice is to treat a solid sample of the Grignard compound CH_3MgI with a solution of **1–3** in toluene at −30 °C [9]. Under these conditions, the required products could be isolated in 80–90% yield (Scheme 3). In contrast to **4–10** and **12**, **13**, the methyl



Scheme 1. L = $PiPr_3$.



Scheme 2. L = $PiPr_3$.



Scheme 3. L = $PiPr_3$.

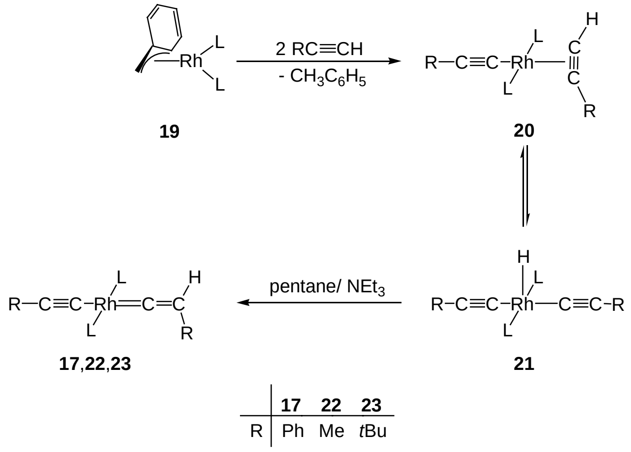
complexes **14–16** are only stable as solids and slowly decompose in solution.

The alkynyl rhodium(I) compounds **17** and **18** are also accessible by the Grignard route [9]. An alternative procedure to prepare **17** consists of the reaction of the η^3-benzyl complex **19** with phenylacetylene in the molar ratio of 1:2 [11]. In the same way, the related compounds **22** and **23** have been obtained. At lower temperature, intermediates **20** (for R = Me and Ph) and **21** (for R = *t*Bu) could be isolated which if dissolved in benzene, rearrange at 30–40 °C quantitatively to yield **17**, **22** and **23**, respectively (Scheme 4). With regard to the synthesis of **18**, we note that the exclusive formation of this complex from **2** and PhC≡CMgBr indicates that the vinylidene C=CH*t*Bu unit is not involved in the substitution process because otherwise the *trans*-[Rh(C≡C*t*Bu)(=C=CHPh)$(PiPr_3)_2$] isomer, supposed to be thermodynamically favored, would be generated.

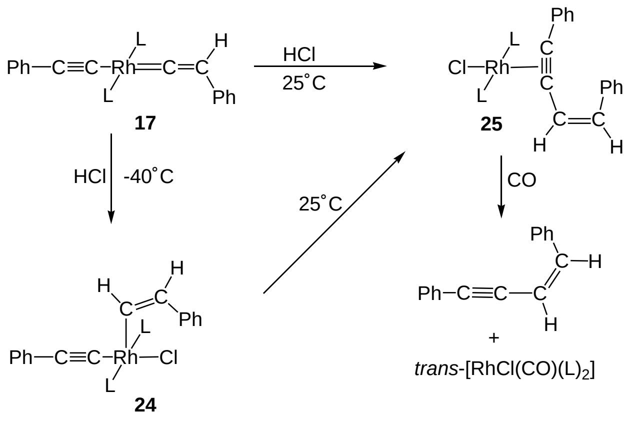
3. Lewis acid and base induced C–C coupling reactions

In contrast to what we had expected, the reaction of **17** with a solution of HCl in benzene at room temperature did not lead to the elimination of phenylacetylene but gave, quite surprisingly, the enyne complex **25** in about 50% yield [11]. If **17** was treated in ether at −40 °C with gaseous HCl, instead of **25** the alkynyl(vinyl)rhodium(III) compound **24** was formed exclusively (Scheme 5). We assume that in the initial step an oxidative addition of HCl to the metal center of **17** takes place generating the intermediate [RhCl(H)(C≡CPh)(=C=CHPh)$(PiPr_3)_2$], which reacts by migration of the hydride ligand to the α-carbon atom of the vinylidene moiety to give **24**. The exclusive formation of the (*Z*)-isomer of the metal-vinyl unit is probably due to the kinetically preferred transfer of the hydride from the side opposite to the phenyl group. The rearrangement of **24**–**25** occurs quantitatively in benzene at room temperature and is equally selective; only the compound containing the enyne in the (*Z*) configuration is formed. Treatment of **25** with CO led to a ligand exchange and gave the (*Z*)-configurated enyne PhCH=CHC≡CPh and the four-coordinate rhodium(I) carbonyl complex *trans*-[RhCl(CO)$(PiPr_3)_2$] [11].

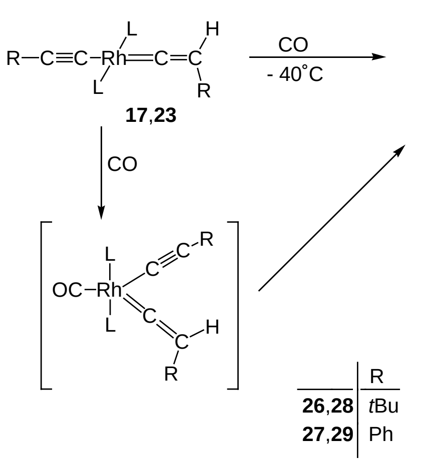
The coupling of the two C_2 fragments of **17** (and analogously of **23**) proceeds in a different way if the starting materials are treated with CO instead of HX. We found that both complexes **17** and **23** react with CO in pentane at −40 °C to give exclusively the (*Z*)-isomers of the enynyl rhodium(I) compounds **26** and **27** in about 80% yield (Scheme 6) [11]. Taking into consideration that the precursors **17** and **23** have a 16-electron count, we assume that the initial step of the reaction consists of the addition of carbon monoxide to the



Scheme 4. L = $PiPr_3$.



Scheme 5. L = $PiPr_3$.



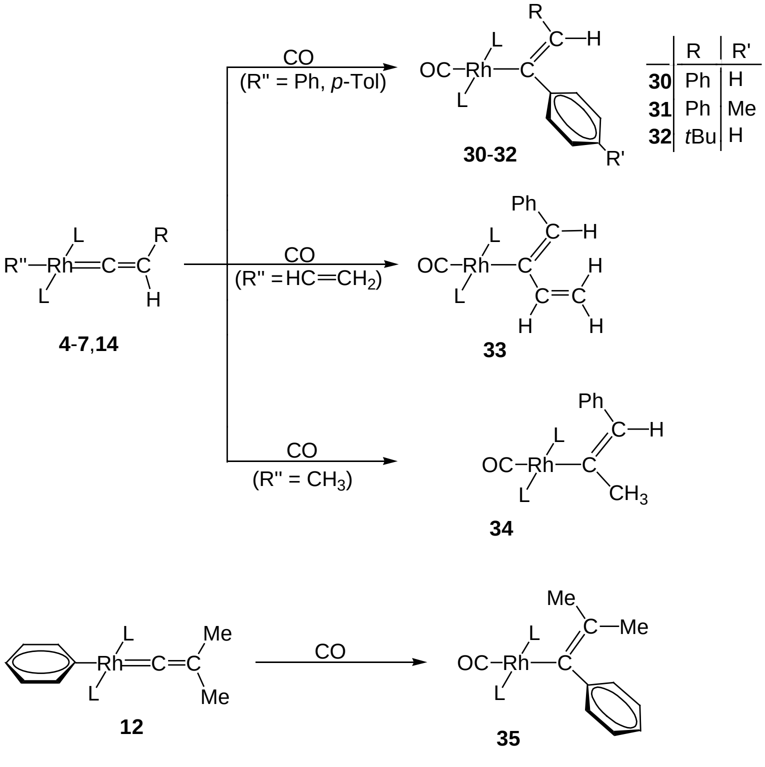
Scheme 6. L = $PiPr_3$.

metal center to generate a coordinatively saturated (probably short-lived) 18-electron intermediate, which after migration of the alkynyl ligand to the α-carbon atom of the vinylidene moiety affords the isolated product. The X-ray crystal structure analysis of an analogue of **26** and **27** with R = CO_2Me, being prepared from $[Rh(\kappa^2\text{-}O_2CMe)(PiPr_3)_2]$ and two equivalents of $HC{\equiv}CCO_2Me$ in the presence of Na_2CO_3 [12], illustrated that the enynyl unit lies perpendicular to the plane of the molecule and that there is no additional interaction between the C≡C triple bond or the cisoid ester group with the rhodium center. Photolysis of the solution of **26** or **27** in benzene led to an isomerization and gave the thermodynamically preferred compounds **28** and **29** [11].

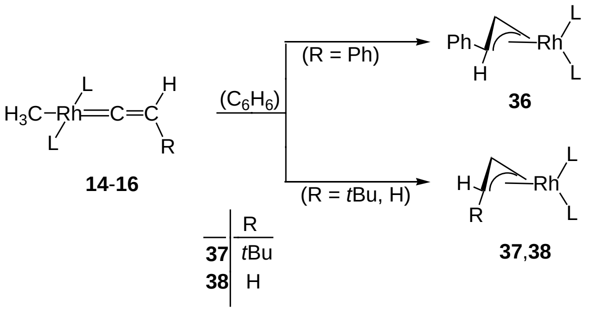
Not only compounds **17** and **22** but also the corresponding alkyl, aryl and vinyl counterparts **4–7**, **12** and **14** react quickly in toluene with carbon monoxide. Even at −30 °C, a smooth migration of the σ-bonded group R″ from rhodium to carbon occurred and after recrystallization from acetone the rhodium(I) complexes **30–35** were isolated in virtually quantitative yield (Scheme 7) [9]. Both the NMR-spectroscopic data of **30–35** and the X-ray crystal structure analysis of **33** confirmed that in analogy to the formation of **26** and **27** only the (*Z*)-isomers were generated. The reactions of **4** and **14** with t-butylisocyanide also proceeded selectively and afforded the compounds *trans*-$[Rh(CR{=}CHPh)(CNtBu)(PiPr_3)_2]$ (R = Ph, Me) in about 80% yield [9].

4. Thermally induced C–C coupling reactions

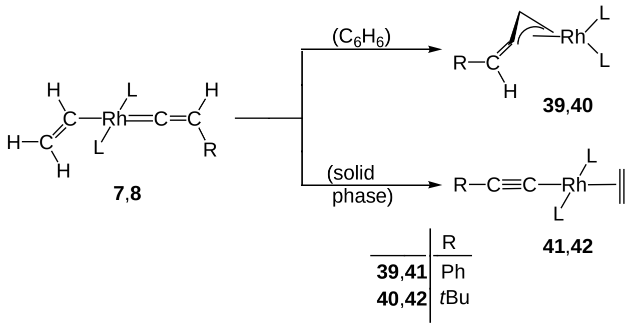
With the methylrhodium(I) compounds **14–16** as the starting materials, we found that a coupling of the two C-bonded ligands takes place even without the presence of a Lewis acid or base. If a solution of **14**, **15** or **16** in benzene was stirred at room temperature for 12 h, a change of color from deep blue or violet to yellow or orange occurred and microcrystalline products of general composition $[Rh(\eta^3\text{-}CH_2CHCHR)(PiPr_3)_2]$ (**36–38**) were isolated in 70–80%



Scheme 7. L = $PiPr_3$.



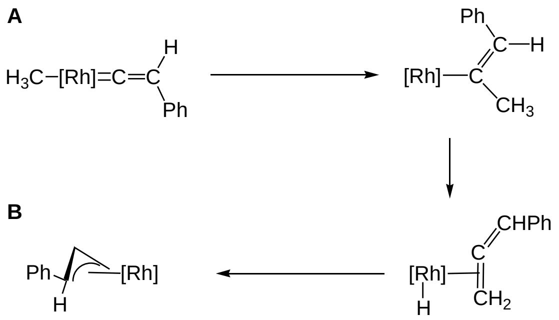
Scheme 8. L = $PiPr_3$.



Scheme 10. L = $PiPr_3$.

yield (Scheme 8) [9,13]. The parent derivative **38** was already known and prepared either from $[Rh(\eta^3\text{-}C_3H_5)(\eta^4\text{-}C_8H_{12})_2]$ (generated in situ) and $PiPr_3$ [14], or more directly from $[RhCl(PiP_3)_2]_2$ and C_3H_5MgBr [15]. The ^1H NMR spectra of the phenyl- and *t*-butyl-substituted complexes **36** and **37** reveal that in **36** the allylic unit is present in the syn- and in **37** in the anti-configuration. Moreover, we found that compound **37**, even after it had been stirred in benzene solution for 24 h, does not rearrange to the syn-isomer, which is supposed to be thermodynamically more stable.

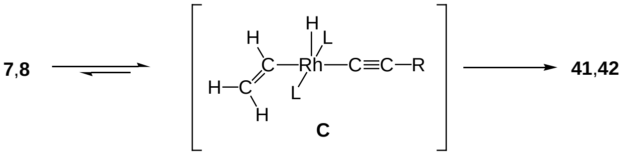
The proposed mechanism for the isomerization of the methyl(vinylidene) to the η^3-allyl complexes is shown in Scheme 9. In agreement with earlier studies [16], we assume that in the initial step a 14-electron species of composition **A** is generated which could be considered as an analogue of $[Rh(\eta^1\text{-}CH_2Ph)(PiPr_3)_2]$ [15]. This intermediate then undergoes a β-H shift to give the four-coordinate allene(hydrido)rhodium(I) derivative **B**. The final product is then formed by hydride transfer from the metal to the central carbon atom of the allene unit. Support for the assumption that a vinyl ligand as in **A** can rearrange to a 1-substituted allyl group comes from the work by Schwartz et al. [17] who observed that the iridium(I) compound *trans*-$[Ir\{(Z)\text{-}C(CH_3)=CHCH_3\}(CO)(PPh_3)_2]$ reacts on warming in benzene to give the allyl isomer $[Ir(\eta^3\text{-syn-}CH_2CHCHCH_3)(CO)(PPh_3)_2]$. Moreover, in the reaction of $[(\eta^5\text{-}C_5H_5)Mo(CH_3C\equiv CCH_3)(L)(L')]BF_4$ ($L = L' = P(OMe)_3$; $L = CO$, $L' = PEt_3$) with hydride donors a coordinatively unsaturated η^1-vinyl intermediate is equally formed and rearranges to the corresponding (η^3-1-methylallyl)molybdenum complex [18].



Scheme 9. [Rh] = $Rh(PiPr_3)_2$.

Not only the methyl(vinylidene) but also the vinyl(vinylidene)rhodium(I) compounds **7** and **8** rearrange in benzene at 40–50 °C without the support of a Lewis acid or base. The reactions proceed more slowly than those of **14–16** and afford the η^3-2,3,4-butadienyl metal derivatives **39** and **40** in 55–65% yield (Scheme 10) [9,13]. As the ^1H, ^{13}C and ^{31}P NMR spectra of **39** and **40** indicate, the allylic fragment of the butadienyl ligand is probably coordinated in an unsymmetrical fashion to rhodium. Based on a cross-over experiment, we conclude that the η^3-butadienyl units are generated by an intramolecular and not an intermolecular route. It was found that if a solution of both **8** and **14** in C_6D_6 was stirred at 50 °C, only the corresponding isomers **36** and **40** were obtained [9].

Quite surprisingly, the vinyl(vinylidene) complexes **7** and **8** are not only labile in solution but also in the solid state. If they are stored under argon for 10–14 days at room temperature, they transform almost quantitatively into the alkynyl(ethene)rhodium(I) compounds **41** and **42** (see Scheme 10). These compounds had previously been prepared from **19** and HC≡CR (R = Ph, *t*Bu) under an atmosphere of ethene [19]. With regard to the mechanism of the rearrangement of **7** and **8**–**41** and **42**, we assume that the initial step consists of a 1,3-H shift from the vinylidene β-carbon atom to the metal center (see Scheme 11). The five-coordinate intermediate **C** can then either regenerate the starting material **7**, **8** or react by intramolecular reductive coupling to give the ethene complexes **41** and **42**, respectively. It should be noted that a rearrangement of the alkynyl(hydrido)rhodium(III) complexes $[RhCl(H)(C\equiv CSiR_3)(PiPr_3)_2]$ (R = Me, Ph) to the vinylidene isomers *trans*-$[RhCl(=C=CHSiR_3)(PiPr_3)_2]$ has



Scheme 11. L = $PiPr_3$.

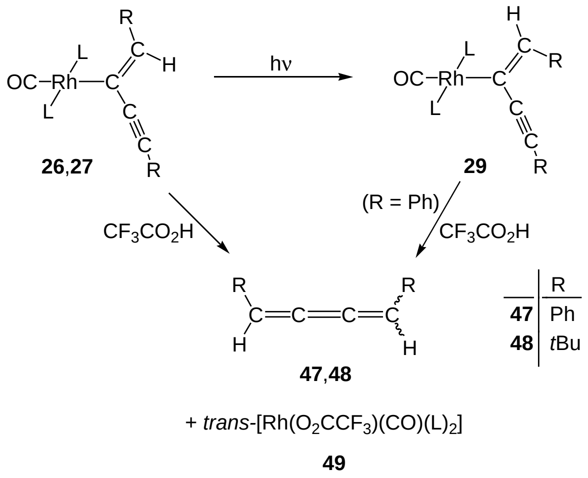
been observed to occur also in the solid state. This is a 1,3-shift in the reverse direction from the metal to the β-carbon atom of the alkynyl unit [20].

5. Generation of the uncoordinated C–C coupling products

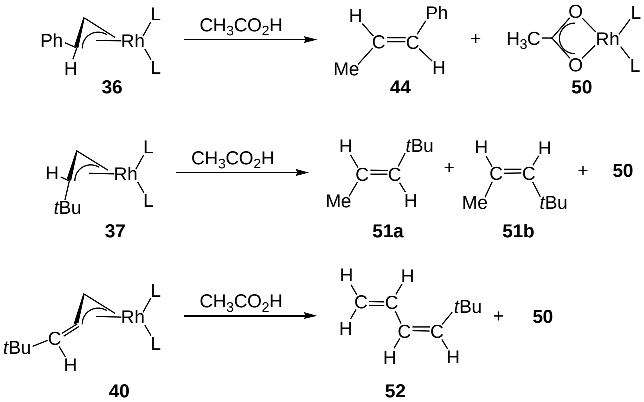
The vinyl- and dienylrhodium(I) complexes **30**, **33** and **34** react with acetic acid in benzene at room temperature to afford the acetato compound **45** plus the (*E*)-olefins **43**, **44** and **46** (see Scheme 12). Under the chosen reaction conditions, there is no rearrangement of (*E*) to (*Z*) isomers [9].

In contrast to what we expected, the cleavage of the enynyl-rhodium bond in **26**, **27** and **29** by CF_3CO_2H in acetone or benzene gives, besides the trifluoracetato complex **49** and small amounts of the corresponding enyne, the butatrienes **47** and **48** in 90–95% yield (Scheme 13) [11]. Whereas compound **27** is rather inert toward acetic acid, the reaction of **26** with CH_3CO_2H leads to a 40:60 mixture of (*E*)-*t*BuC≡CCH=CH*t*Bu and **48**, and that of **29** gives (*Z*)-PhC≡CCH=CHPh. Both the product distribution and the isomer ratio of the (*E*)/(*Z*)-butatrienes indicate that, with a stronger proton donor such as CF_3CO_2H, the attack of the acid does probably not occur at the Lewis basic metal center but directly at the triple bond of the enynyl ligand. It is conceivable that a cationic butatriene rhodium complex is formed as an intermediate from which the cumulene is displaced by the carboxylate anion.

The η^3-allyl and η^3-butadienyl complexes also react with acetic acid (Scheme 14). If the phenyl-substituted derivative **36** is used as the starting material, the same olefin **44** is generated which is formed from **34** and CH_3CO_2H. In contrast, the reaction of the *t*-butylallyl compound **37** with acetic acid gives a mixture of the (*E*) and (*Z*) isomers **51a** and **51b** with the former as the major species. To explain this observation, we assume that in the initial step an intermediate $[RhH(\eta^3\text{-}1\text{-}t\text{-}BuC_3H_4)(\kappa^1\text{-}O_2CCH_3)(PiPr_3)_2]$ is formed by oxidative addition, which could rearrange to an isomeric η^1-allyl(hydrido)rhodium(III) derivative. This species, depending on the site of attack of the metal-bound proton on the allylic ligand, could generate either the (*E*) or the (*Z*) olefin.

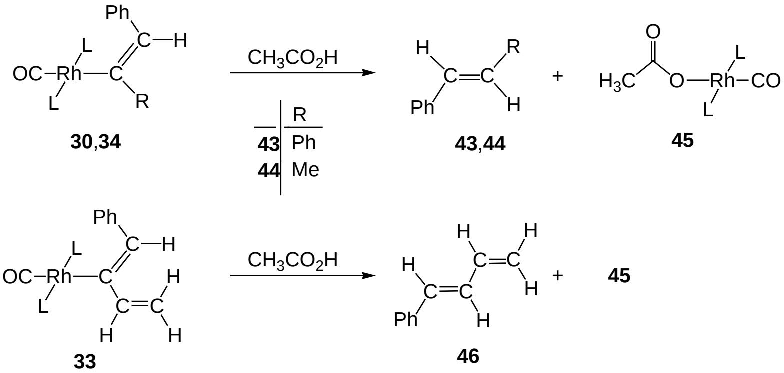


Scheme 13. L = $PiPr_3$.

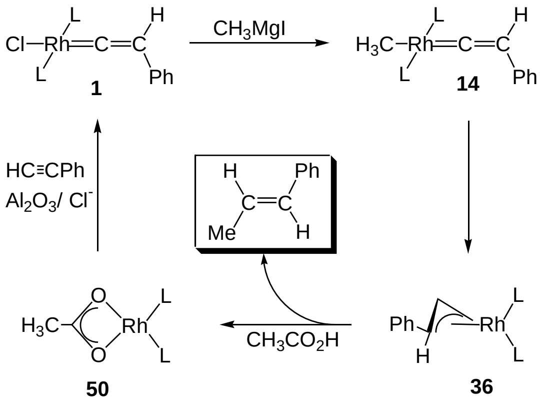


Scheme 14. L = $PiPr_3$.

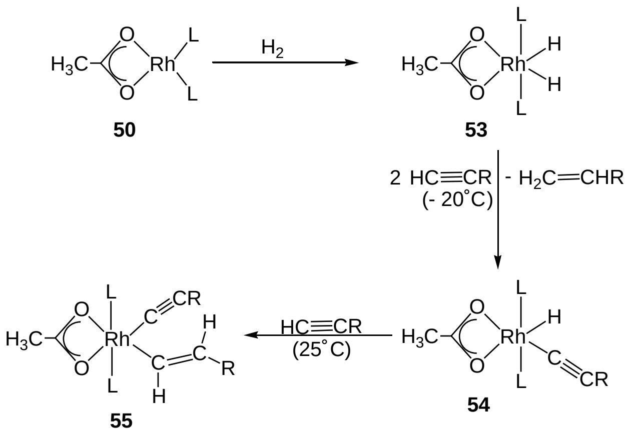
The corresponding reaction of **40** with acetic acid proceeds under the same conditions as that of **37** and affords regioselectively the butadiene derivative **52**. The exclusive formation of the (*Z*) isomer supports the assumption that in compound **40** (and probably also in **39**) the substituents at the non-coordinated C=C double bond are *cis*-disposed.



Scheme 12. L = $PiPr_3$.



Scheme 15. L = $PiPr_3$.



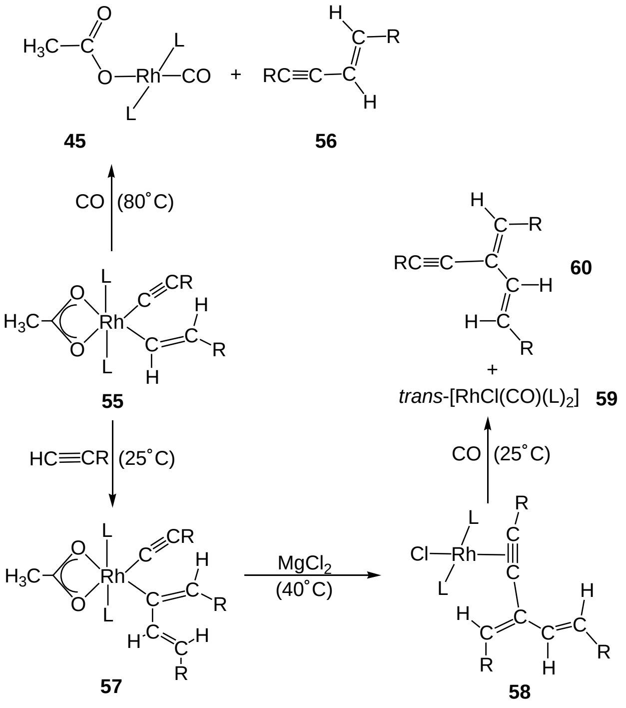
Scheme 16. L = $PiPr_3$, R = CO_2Me.

The rhodium-containing product of the reactions of **36**, **37** and **40** with CH_3CO_2H is the chelate complex **50** [15], which can be reconverted to the starting material **1**. This takes place in two steps, first by treatment of **50** with phenylacetylene, and second by column chromatography of the in situ generated rhodium(III) compound $[RhH(C{\equiv}CPh)(\kappa^2\text{-}O_2CCH_3)(PiPr_3)_2]$ [12] on Al_2O_3 in the presence of chloride ions. As a consequence, a cyclic process can be established (Scheme 15), in which an olefin RCH=CHR′ is regio- and eventually stereoselectively formed from a terminal alkyne HC≡CR, a Grignard reagent R′MgX and acetic acid by general assistance from rhodium(I). In this context we note that we have recently shown that not only olefins and butadienes but also vinylallenes can be prepared by a similar route, using instead of **1** the related allenylidene complex *trans*-$[RhCl(=C=C=CPh_2)(PiPr_3)_2]$ as the starting material [21].

6. The step-wise trimerization of an alkyne to a hexadienyne derivative

The chelate complex **50** reacts with methyl propiolate in pentane at −40 °C to afford the alkyne compound *trans*-$[Rh(\kappa^1\text{-}O_2CCH_3)(HC{\equiv}CCO_2Me)(PiPr_3)_2]$, which is quite labile and slowly decomposes in solution at room temperature [12]. In order to obtain the isomeric alkynyl(hydrido) complex **54**, the starting material **50** had first to be converted into the dihydridorhodium(III) derivative **53**, which reacts with two equivalents of $HC{\equiv}CCO_2Me$ in pentane at −20 °C to give **54** (Scheme 16) [22]. Subsequent treatment of **54** with an equimolar amount of methyl propiolate in pentane at room temperature affords the alkynyl(vinyl) complex **55** in quantitative yield. According to the NMR spectroscopic data there is no doubt that the two substituents at the C=C double bond are *trans*-disposed.

Compound **55** is thermally stable and under normal conditions inert in the presence of carbon monoxide. However, if a solution of **55** in benzene is warmed under a CO atmosphere to 80 °C, a reaction takes place which yields the carbonyl complex **45** and the (*E*)-butenyne **56** (Scheme 17) [22]. Quite remarkably, compound **55** reacts with methyl propiolate in benzene even at room temperature. In contrast to the reaction with CO, instead of a C–C coupling a formal insertion of the substrate into the metal–vinyl bond takes place. As the X-ray crystal structure analysis confirmed, the isolated complex **57** can be considered as a derivative of **55** with a 2-butadienyl instead of a vinyl group as a ligand. Both C=C bonds of the butadienyl unit have the more favored (*E*) configuration. With regard the mechanism of formation of **57**, we assume that initially the acetate-rhodium chelate bond is partially opened and one molecule of $HC{\equiv}CCO_2Me$ is added to the metal center. This step is probably followed



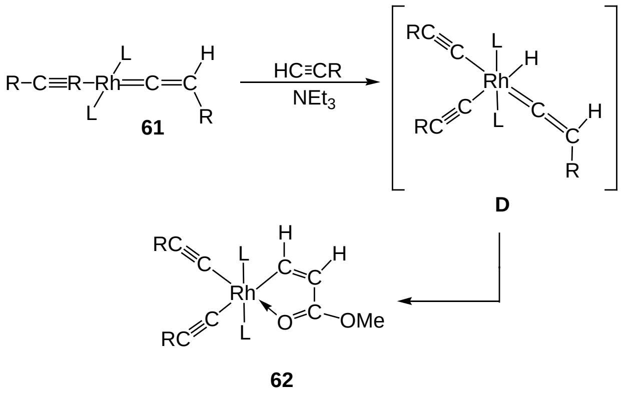
Scheme 17. L = $PiPr_3$, R = CO_2Me.

by a rearrangement of the coordinated 1-alkyne to the isomeric vinylidene, and finally a coupling of the vinyl and the vinylidene ligands occurs analogous to the reaction of **7** with CO.

Similar to **55**, compound **57** is thermally stable and even on heating to 60 °C no reaction takes place. However, the coupling of the butadienyl and the alkynyl ligands at rhodium can be achieved if a solution of **57** in diethyl ether is treated at 40 °C with an excess of $MgCl_2{\cdot}6H_2O$ and Na_2CO_3. Under these conditions, the four-coordinate rhodium(I) complex **58** was isolated in 79% yield [22]. As was shown crystallographically, there is a somewhat distorted square-planar coordination around the metal center with one of the alkyne carbon atoms lying above the plane formed by the ligated rhodium, chlorine, phosphorus and carbon atoms. The butadienyl substituent at the C≡C bond still has the (*E*,*E*) configuration which illustrates that in the course of the C–C coupling no (*E*)/(*Z*) isomerization takes place. In contrast to **57**, however, the C_4 unit of the hexadienyne ligand in **58** is *s-trans*.

In the same way as the butenyne complex **25**, compound **58** also reacts with CO at room temperature by ligand displacement to give the carbonylrhodium(I) derivative **59** and the formerly unknown substituted hexadienyne **60** (see Scheme 17). The latter has been characterized by GC/MS and ^1H NMR spectroscopy [22]. It should be mentioned that in contrast to the reaction of $[Ni(CO)_2(PPh_3)_2]$ with methyl propiolate [23], in the stepwise rhodium-assisted trimerization of $HC{\equiv}CCO_2Me$ no cyclic $C_6H_3(CO_2Me)_3$ isomer could be detected. As far as we know, only in the oligomerization of ferrocenylethyne HC≡CFc [Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$], catalyzed by $[Ni(CO)_2(PPh_3)_2]$, besides the corresponding butenyne and benzene derivatives a branched trimer structurally related to **60** is formed although merely in 45% yield [24].

The vinylidene complex **61**, prepared from **54** and an equimolar amount of $HC{\equiv}CCO_2Me$ in the presence of base, also reacts with methyl propiolate in neat NEt_3 as the solvent to give the chelate compound **62** (Scheme 18) [19b]. We assume that in the initial step a six-coordinate bis(alkynyl)(hydrido)rhodium(III) intermediate **D** is generated by oxidative addition, which after migration of the hydride to the α-carbon atom of the vinylidene ligand transforms to the product. The coordination of the C=O oxygen atom to the metal, which is clearly illustrated by the IR spectrum of **62**, can be compared to that of the iridium(III) complex $[IrCl(H)\{\kappa^2(C,O)\text{-}CH{=}CHC(OMe){=}O\}(PiPr_3)_2]$, which was prepared from $[IrCl(C_8H_{14})_2]_2/PiPr_3$ and methyl acrylate by C–H activation [25].

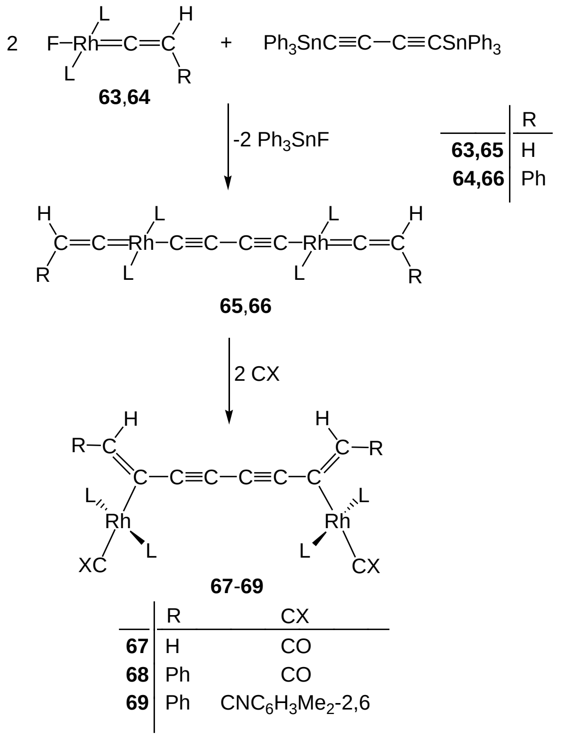


Scheme 18. L = $PiPr_3$, R = CO_2Me.

7. C–C coupling reactions of dinuclear vinylidenerhodium(I) complexes

After we found that rhodium vinylidenes of the general type *trans*-$[Rh(C{\equiv}CR)({=}C{=}CHR)(PiPr_3)_2]$ can be converted to η^1-enynyl complexes and subsequently to butatrienes (see Scheme 13), we became interested to find out what the reactivity of related binuclear compounds such as **65** and **66** is. The route to prepare these compounds followed our observation that rhodium(I) complexes with acetate or hydroxide ligands cleanly react with stannylalkynes $Ph_3SnC{\equiv}CR$ to give rhodium(I) alkynyls and Ph_3SnX (X = OAc, OH) [26,27].

The reaction of the fluoro(vinylidene)rhodium(I) derivatives **63** and **64**, which were prepared from $[Rh\{\eta^2\text{-}O_2S(O)CF_3\}(PiPr_3)_2]$ and the corresponding 1-alkyne in the presence of KF, with $Ph_3SnC{\equiv}C{-}C{\equiv}CSnPh_3$ in hexane affords besides Ph_3SnF the binuclear compounds **65** and **66** as green, moderately air-sensitive solids in excellent yields



Scheme 19. L = $PiPr_3$.

(Scheme 19) [28]. The carbonyl and isocyanide complexes $[(\mu\text{-}C_4)\{Rh(CX)(PiPr_3)_2\}_2]$ (CX=CO, $CNC_6H_3Me_2$-2,6) were obtained analogously. Treatment of **65** and **66** with CO at low temperatures or with $CNC_6H_3Me_2$-2,6 at 25 °C in pentane or hexane led to a twofold migratory insertion of the vinylidene units into the Rh–C σ-bonds and gave the dirhodium compounds **67**–**69** in 74–82% yield. As was shown by the X-ray crystal structure analysis of **68**, both metal centers are coordinated in a square-planar fashion. Although the central C_6 fragment of the molecule is nearly linear, the C_8 chain is not planar, the dihedral angle between the two halfes of the bridging unit being 27.0(2)°. Other noteworthy features are the planarity of both C=CHPh moieties and the cis disposition of the respective phenyl group and the metal-ligand unit at the C=C bonds. According to ^{1}H NOE experiments we assume that not only in **68** but also in **67** and **69** both C=C bonds possess the (*Z*)-configuration [28]. Despite the similarity in the physical properties of the mononuclear η^1-enynyl complexes **27** and **29** and the binuclear counterparts **67** and **68**, all attempts to cleave the Rh–C σ-bonds of **67** and **68** by protonation to generate the highly unsaturated hydrocarbons RCH=CH–C≡C–C≡C–CH=CHR failed.

8. Concluding remarks

The work summarized in this review illustrates that in the coordination sphere of rhodium(I) a stereoselective coupling of an alkyl, alkynyl, aryl, or vinyl group with a vinylidene ligand can occur. This process may be considered as a counterpart to the intramolecular coupling of a hydrocarbyl unit with a carbene moiety, of which several examples are known (see inter alia [29]). The remarkable feature is that the vinylidene coupling as shown in Schemes 6, 7 and 19 can not only be initiated by CO or isocyanides but in the case of the vinyl- and methylrhodium(I)-derivatives **7**, **8** and **14**–**16** can even proceed without the presence of a supporting Lewis base. As a result, a new synthetic route to η^3-allyl- and η^3-butadienylrhodium(I) complexes became known. The organic ligands generated by C–C coupling can easily be transformed to corresponding unsaturated hydrocarbons such as olefins, dienes, trienes or enynes by acid-induced cleavage of the σ-carbon- or π-carbon-metal bond. We finally note that CO-assisted C–C coupling reactions similar to those shown in Schemes 6 and 7 can also occur with iridium(I) vinylidenes and that with iridium(I) as the metal center even an intramolecular C–N coupling has been achieved [30].

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