Vinylidene Transition-Metal Complexes, XX[1]

Synthesis, Reactions, and Molecular Structure of Bis(arsane) and Bis(stibane) Rhodium(I) Complexes *trans*-[RhCl(L)(E*i*Pr$_3$)$_2$] (E = As, Sb) Including the Rhodium-Mediated Rearrangement of Alkynes to the Isomeric Allenes

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Reaction of the dimeric bis(olefin)rhodium(I) compounds [RhCl(olefin)$_2$]$_2$ [olefin = C$_8$H$_{14}$ (**2**), C$_2$H$_4$ (**5**)] with As*i*Pr$_3$ and Sb*i*Pr$_3$ gives mono- and dinuclear olefin(arsane) and olefin(stibane) complexes [RhCl(olefin)(E*i*Pr$_3$)]$_2$ [olefin = C$_8$H$_{14}$ (**3**, **4**), C$_2$H$_4$ (**6**, **7**)] and *trans*-[RhCl(C$_2$H$_4$)(E*i*Pr$_3$)$_2$] (**8**, **9**). Treatment of **8** and **9** with CO, H$_2$, and CPh$_2$N$_2$ leads to the displacement of the ethylene ligand with formation of the corresponding carbonyl (**10**, **11**), dihydrido (**12**, **13**), and diazoalkane (**14**) rhodium derivatives. In solution, compound **14** loses CPh$_2$ to give *trans*-[RhCl(N$_2$)(As*i*Pr$_3$)$_2$] (**15**). The alkyne complexes *trans*-[RhCl(HC≡CR)(As*i*Pr$_3$)$_2$] (**16**–**18**), which are prepared either from **8** or [RhH$_2$Cl(As*i*Pr$_3$)$_2$] (**12**) and HC≡CR (R = H, Ph, CO$_2$Me), rearrange in solution to produce the vinylidenerhodium isomers *trans*-[RhCl(=C=CHR)(As*i*Pr$_3$)$_2$] (**19**–**21**). Reaction of **8** with HC≡CMe and HC≡C*t*Bu leads directly to the vinylidene complexes **22**, **23**. Compound **8** reacts with excess propyne, but-2-yne, or 2,2-dimethylpent-2-yne to give the rhodium allenes *trans*-[RhCl(η^2-CH$_2$=C=CHR)(As*i*Pr$_3$)$_2$] (**25**–**27**) in nearly quantitative yields. With DC≡CMe as a substrate, it is shown that two propyne molecules are involved in the rearrangement to generate the coordinated allene. The crystal and molecular structure of *trans*-[RhCl(η^2-CH$_2$=C=CH$_2$)(As*i*Pr$_3$)$_2$] (**27**) has been determined.

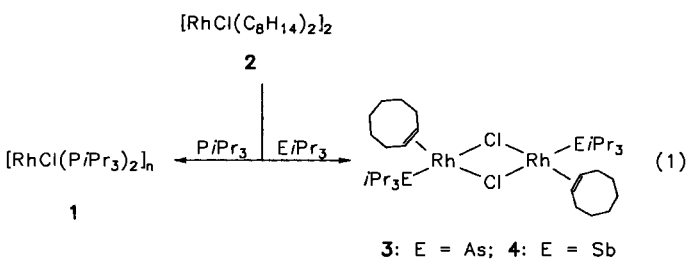
We have recently shown that the bis(triisopropylphosphane)rhodium(I) complex [RhCl(P*i*Pr$_3$)$_2$] (**1**) is an excellent starting material for the synthesis of alkyne, vinylidene, and allenylidene rhodium derivatives of the general composition *trans*-[RhCl(L)(P*i*Pr$_3$)$_2$] (L = RC≡CR′, :C=CRR′, :C=C=CRR′)[2]. Compound **1** is a dimer in the crystalline state[3], but a monomer in solution[4], and it is certainly the coordinative unsaturation of the rhodium center (with the coordination number three) which determines the high reactivity of the molecule.

The work reported in this paper was initiated by two questions: 1) Is it possible by using As*i*Pr$_3$ and Sb*i*Pr$_3$ instead of P*i*Pr$_3$ as ligands to prepare compounds of the type [RhCl(E*i*Pr$_3$)$_2$]$_n$ (E = As, Sb), and 2) are these species (or derivatives thereof) appropriate precursors for the synthesis of new alkyne and vinylidene rhodium(I) complexes? There is a general belief that trialkylarsanes and -stibanes are weaker σ donors than the corresponding trialkylphosphanes[5], and that also the π acceptor properties are significantly reduced along the series PR$_3$ > AsR$_3$ > SbR$_3$[6]. Both arguments could be considered as not favoring the stability of bis(triisopropylarsane) and bis(triisopropylstibane) compounds of the composition *trans*-[RhCl(L)(E*i*Pr$_3$)$_2$], in particular for L = RC≡CR′ and :C=CRR′. For As*i*Pr$_3$ as the ligand, this turned out not to be true. We describe here the preparation of a series of new rhodium(I) complexes containing [RhCl(As*i*Pr$_3$)$_2$] and [RhCl(Sb*i*Pr$_3$)$_2$] as building blocks and discuss an unexpected rearrangement of propyne MeC≡CH to the isomeric allene CH$_2$=C=CH$_2$ in which two molecules of the alkyne are involved.

Results

Preparation of Olefin, Carbonyl, and Hydrido Complexes

The bis(cyclooctene)rhodium(I) complex [RhCl(C$_8$H$_{14}$)$_2$]$_2$ (**2**) reacts with excess P*i*Pr$_3$ to give the violet, highly reactive compound **1**[7]. In contrast, the analogous reaction of **2** with As*i*Pr$_3$ and Sb*i*Pr$_3$ does not lead to the formation of the olefin-free products [RhCl(E*i*Pr$_3$)$_2$]$_n$ but gives the dimers [RhCl(C$_8$H$_{14}$)(E*i*Pr$_3$)]$_2$ [E = As (**3**), Sb (**4**)] in quantitative yields. Even if a large excess of E*i*Pr$_3$ (ca. 1:20) is used and



(1)

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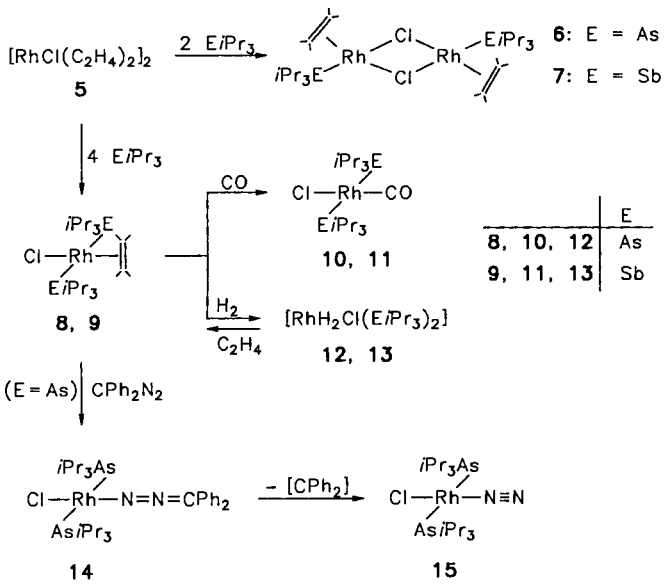
the temperature increased from 25 to 50 °C, only compounds **3** and **4** are obtained. The orange crystalline solids are moderately air-sensitive and soluble in all common organic solvents. For both products correct elemental analyses have been obtained.

The reactions of the bis(ethylene)rhodium(I) complex $[RhCl(C_2H_4)_2]_2$ (**5**) with As*i*Pr$_3$ and Sb*i*Pr$_3$ lead to two different types of products (Scheme 1). If a molar ratio of **5**: E*i*Pr$_3$ = 1:2 is used, the dimers $[RhCl(C_2H_4)(EiPr_3)]_2$ [E = As (**6**), Sb (**7**)], analogous in structure to **3** and **4**, are formed. For the isolation of analytically pure samples, it is necessary to add a diluted solution of the arsane or stibane to a concentrated solution of **5** in THF. Otherwise, a mixture of $[RhCl(C_2H_4)(EiPr_3)]_2$ (**6**, **7**) and *trans*-$[RhCl(C_2H_4)(EiPr_3)_2]$ [E = As (**8**), Sb (**9**)] is obtained. The dimeric compounds **6** and **7** form orange, slightly air-sensitive crystals which are soluble in benzene and polar organic solvents. The ^{1}H-NMR spectra show at room temperature besides the signals for the isopropyl units a broad singlet for the C_2H_4 protons which is unexpected insofar as owing to the assumed non-planarity of the molecular skeleton, two signals should appear. The most reasonable explanation is that the ethylene ligands rotate around the Rh–C_2H_4 bond, analogously as has been observed for the triisopropylphosphane derivative $[RhCl(C_2H_4)(PiPr_3)]_2$[8].

Scheme 1



The mononuclear complexes **8** and **9** are formed in ca. 85% yield if the starting material **5** is treated with four equivalents of triisopropylarsane or -stibane, respectively. The yellow (**8**) or orange-yellow (**9**) solids can shortly be handled in air and stored under argon for weeks at temperatures below −15 °C. In solution, both compounds start to decompose after a few hours. The proposed structure (see Scheme 1), in particular the *trans* position of the arsane and stibane ligands, is mainly supported by the ^{1}H-NMR spectra which show only one signal for the methyl protons of the isopropyl groups. It should be noted that an analog of complex **8**, namely *trans*-$[RhCl(C_2H_4)(AsPh_3)_2]$, has previously been prepared by Wilkinson et al.[9] either from $[RhCl(C_2H_4)_2]_2$ and $AsPh_3$ in the molar ratio of 1:4 or from $[RhCl(AsPh_3)_3]$ and excess ethylene.

The reactions of the ethylene compounds **8** and **9** with CO, H_2, and diphenyldiazomethane are summarized in Scheme 1. They proceed under mild conditions and lead to the formation of the carbonyl, dihydrido, and diazoalkane complexes **10**–**14** in almost quantitative yields. The carbonyls **10** and **11** are yellow air-stable solids which are similar in structure to *trans*-$[RhCl(CO)(PiPr_3)_2]$[8]. The CO stretching frequencies of **10**, **11** and the bis(triisopropylphosphane) derivative are virtually identical.

In contrast to the carbonyls **10** and **11**, the dihydrides **12** and **13** form air-sensitive solids which have either a trigonal-bipyramidal (tbp) or a square-pyramidal (sqp) structure. There are good arguments that both $[RhH_2Cl(PiPr_3)_2]$[7,10] and $[RhH_2Cl(PCy_3)_2]$[11] possess a tbp configuration whereas X-ray data confirm a sqp structure for $[RhH_2Cl(PtBu_3)_2]$[12]. As in the ^{1}H-NMR spectra of **12** and **13** only one signal (doublet due to Rh-H coupling) in the high-field region (**12**: δ = −23.6; **13**: −22.9) is observed, it can be concluded that the two hydrido ligands are equivalent. If C_2H_4 is passed through a solution of **12** or **13** in pentane hydrogenation occurs to yield ethane, and **8** and **9** are reformed on the subsequent coordination of the free ethylene to the metal centers.

The preparation of the (diphenyldiazomethane)rhodium(I) compound **14** is achieved by treatment of a pentane solution of **8** with a twofold excess of CPh_2N_2. Besides **14**, 1,1-diphenyl-1-propene $Ph_2C{=}CHMe$ is formed. We have recently shown that the dimeric bis(ethylene)rhodium(I) complex **5** is an excellent catalyst for the formation of $Ph_2C{=}CHMe$ from ethylene and diphenyldiazomethane[13]. Compound **14**, which has been isolated as a dark green, very air-sensitive solid, on direct irradiation with UV light in benzene gives the $Rh(N_2)$ compound **15**. As there are also some byproducts formed which could not be completety separated from **15**, no accurate elemental analysis of the dinitrogen complex has been obtained. The IR and ^{1}H-NMR data of **15** correspond to those of the bis(triisopropylphosphane) derivative *trans*-$[RhCl(N_2)(PiPr_3)_2]$[8,14] and thus leave no doubt that the structure shown in Scheme 1 is correct. We note that even on prolonged stirring of solutions of **8** under nitrogen no substitution of the ethylene ligand by N_2 occurs. Attempts to prepare *trans*-$[RhCl(N_2CPh_2)(SbiPr_3)_2]$, the stibane analog of **14**, from compound **9** and CPh_2N_2 have failed.

Reactions of *trans*-$[RhCl(C_2H_4)(AsiPr_3)_2]$ (8) and $[RhH_2Cl(AsiPr_3)_2]$ (12) with Acetylene and 1-Alkynes

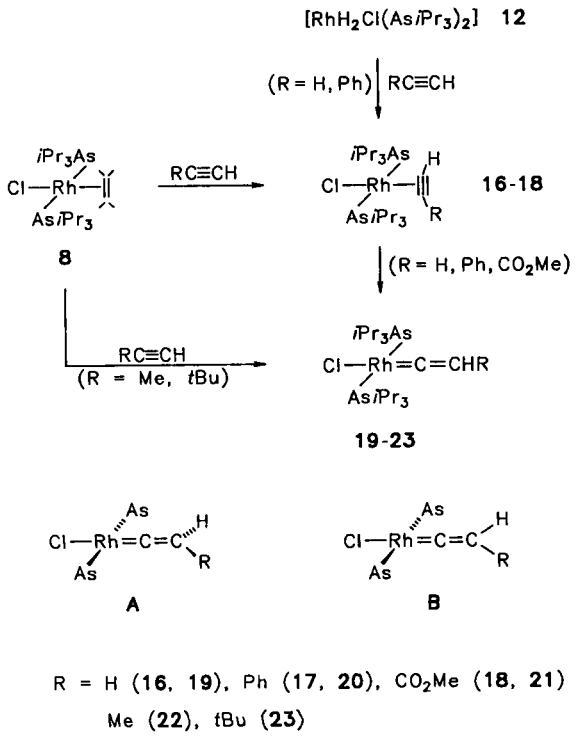
Vinylidene rhodium(I) complexes of the type *trans*-$[RhCl(=C=CHR)(PiPr_3)_2]$ have usually been prepared from compound **1**. It reacts with acetylene and 1-alkynes to give first the alkyne metal derivatives *trans*-$[RhCl(HC{\equiv}CR)(PiPr_3)_2]$ which, depending on the reaction conditions, more or less rapidly rearrange [via the alkynyl(hydrido)rhodium-

(III) intermediates] to the vinylidene rhodium(I) isomers[15–17]. By varying the 1-alkyne and the phosphane ligands, it has recently been found that also the ethylene compounds *trans*-[RhCl(C_2H_4)(PR_3)$_2$] (PR_3 = P*i*Pr$_3$, PMe*t*Bu$_2$) can be used as starting materials for the synthesis of the corresponding vinylidene complexes *trans*-[RhCl(=C=CHR)(PR_3)$_2$][18,19].

Following this observation, we have attempted to prepare bis(arsane) and bis(stibane) vinylidene compounds of the general composition *trans*-[RhCl(=C=CHR)(E*i*Pr$_3$)$_2$] (E = As, Sb) from the ethylene derivatives **8**, **9** and 1-alkynes, including acetylene as the parent substrate. Although the immediate color change (from yellow to dark red), which occurs after treatment of the bis(stibane) compound **9** with HC≡CH and HC≡CPh, indicates that a reaction takes place, we have been unable to isolate a pure product.

In contrast, the bis(arsane) derivative **8** reacts at ambient temperatures with HC≡CH, HC≡CPh and also with HC≡CCO$_2$Me to give by ethylene displacement the alkyne rhodium(I) complexes *trans*-[RhCl(HC≡CR)(As*i*Pr$_3$)$_2$] (**16**–**18**) in moderate (R = H) to good yields (R = Ph, CO$_2$Me). As in the reaction of **8** with acetylene (in pentane at 25°C) besides **16** also small amounts of the vinylidene isomer *trans*-[RhCl(=C=CH$_2$)(As*i*Pr$_3$)$_2$] (**19**) are formed, we have prepared the alkyne complex also by a different route. We have recently reported that treatment of the dihydridoiridium compound [IrH$_2$Cl(P*i*Pr$_3$)$_2$] with acetylene produces the iridium vinylidene *trans*-[IrCl(=C=CH$_2$)(P*i*Pr$_3$)$_2$][20]. The reaction of the bis(arsane) rhodium complex **12** with HC≡CH and also with HC≡CPh proceeds similarly and leads almost quantitatively to the formation of **16** and **17** (see Scheme 2). Ethylene and styrene have been detected as byproducts by ^{1}H-NMR measurements. Compounds **16**–**18** are yellow to orange, air-sensitive crystalline solids which are readily soluble in all common organic solvents. Correct elemental analyses have been obtained. The most characteristic feature in the ^{1}H-NMR spectra is the doublet at δ ca. 3–4 which corresponds to the ≡CH proton(s) of the coordinated alkyne. As in the spectra of **17** and **18** (at room temperature) two signals for the methyl protons of the isopropyl arsane groups are observed, we assume that the rotation around the metal–alkyne bond is significantly hindered, likewise as in *trans*-[RhCl(HC≡CR)(P*i*Pr$_3$)$_2$][21].

Scheme 2



Whereas compounds **16**–**18** are stable as solids, they slowly rearrange in solution to the isomeric vinylidene rhodium complexes **19**–**21** in 75–85% yield. The reaction is accompanied by a characteristic color change from yellow (or orange-yellow) to violet. The related methyl- and *tert*-butylvinylidene derivatives **22** and **23** are directly obtained from **8** and HC≡CMe or HC≡C*t*Bu, respectively. Although attempts to isolate an intermediary species in these reactions have failed, we nevertheless believe that the corresponding 1-alkyne rhodium compounds *trans*-[RhCl(HC≡CR)(As*i*Pr$_3$)$_2$] (R = Me, *t*Bu) are primarily formed. If the reaction mixture obtained from **8** and HC≡C*t*Bu in pentane is worked up before the solution becomes dark violet, a brownish oily residue remains whose IR spectrum shows a band at 1830 cm^{-1} typical of a coordinated alkyne. In the IR spectra of the final products **19**–**23** an absorption at 1610–1680 cm^{-1} is observed which corresponds to the C=C stretching frequency of the vinylidene ligand. Regarding the NMR-spectroscopic data, the low-field signal in the ^{13}C-NMR spectra at δ = 280–295 is most noteworthy and indicative of the metal-bound carbon atom of the Rh=C=CHR moiety. This signal appears in the same region as the ^{13}C-NMR signal of a coordinated carbene C atom[22].

The question which of the two possible conformers of the complexes *trans*-[RhCl(=C=CHR)(As*i*Pr$_3$)$_2$] is preferred – one (**A**) with the α- or *ipso*-C atom of the substituent R in the *same* plane as the Rh, Cl, and As atoms, or one (**B**) with these atoms in a plane *perpendicular* to the first one – cannot be conclusively answered on the basis of the spectroscopic data. As there is only one set of signals for the arsane CH$_3$ atoms in the ^{1}H- and ^{13}C-NMR spectra, we assume that at least at room temperature the respective vinylidene complexes **19**–**23** possess a non-rigid structure in solution and thus behave in a similar manner as the bis(phosphane) compounds *trans*-[RhCl(=C=CHR)(P*i*Pr$_3$)$_2$][15,16]. In this case, for R = CH$_3$ it has been shown by X-ray structural analysis that the allene-type configuration **B** is preferred and frozen out in the crystalline state[15].

Attempts to displace one (or both) of the arsane ligands in **20** by carbon monoxide in order to obtain a carbonyl(vinylidene)rhodium(I) compound have led to the formation of the bis(arsane) carbonyl derivative **10**. In addition, phenylacetylene is generated and identified by ^{1}H-NMR spectroscopy. With regard to recent results on the behavior of similar bis(triisopropylphosphane) rhodium vinylidenes[2,23] it is conceivable that the primary step in the rection of

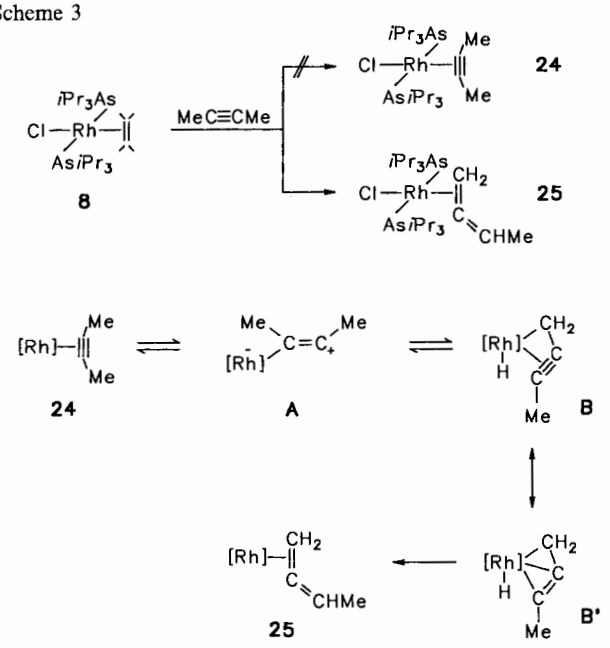
20 with CO consists in the rearrangement of the Rh=C=CHPh to a RhH(C≡CPh) unit which, by reductive elimination, gives the carbonyl complex and the alkyne.

Synthesis of Allene Rhodium(I) Complexes *trans*-[RhCl(η²-CH₂=C=CHR)(As*i*Pr₃)₂] (25–27) from Alkynes

An unexpected observation has been made in the preparation of the but-2-yne complex *trans*-[RhCl(MeC≡CMe)(As*i*Pr₃)₂] (**24**) from **8** and MeC≡CMe. On treatment of the ethylene compound with an equimolar amount of the alkyne even at −78 °C in pentane, the isomeric methylallene rhodium(I) complex **25**, together with some unreacted starting material, is obtained. If the solution of **8** is treated with an excess of but-2-yne, the allene derivative **25** is isolated in 91% yield. It forms orange, moderately air-sensitive crystals which like the ethylene complex are easily soluble in most organic solvents.

The spectroscopic data of **25** support the proposal (see Scheme 3) that it is the unsubstituted C=C bond of the methylallene which is coordinated to the metal. The ^{13}C-NMR data in particular are similar to those of the corresponding substituted allene bis(triisopropylphosphane)-rhodium complex *trans*-[RhCl(η²-CH₂=C=CH(CO₂Et))-(P*i*Pr₃)₂], the structure of which has been determined by X-ray crystallography[24]. Concerning the mechanism of the reaction of **8** with MeC≡CMe, we assume that in the primary step the expected (but very labile) alkyne compound **24** is formed which rearranges via **A** and **B** (or **B'**) to the final product **25**. The structure of the supposed transient **A** is reminiscent to that of the transition state postulated by Silvestre and Hoffmann[25] for the concerted rearrangement of 1-alkynes to vinylidenes for which, however, also a two-step mechanism is conceivable[2,26]. Evidence for the preferential formation of the final intermediary species **B** is provided by the structurally characterized osmium complex [Os(η³-PhC₃CHPh)(PMe₃)₄]⁺ formed from *cis*-[Os(C≡CPh)₂(PMe₃)₄], AgPF₆, and a proton source[27].

Scheme 3



There is some precedent for the metal-initiated rearrangement of an alkyne into the isomeric allene. Richards et al. have reported on the formation of the complex [ReCl(η²-CH₂=C=CHPh)(diphos)₂] from *trans*-[ReCl(N₂)(diphos)₂] (diphos = Ph₂PCH₂CH₂PPh₂) and PhC≡CMe[28], and we have observed the isomerization of *trans*-[IrCl(MeC≡CMe)(P*i*Pr₃)₂] to the methylallene compound *trans*-[IrCl(η²-CH₂=C=CHMe)(P*i*Pr₃)₂][29]. With rhodium as the metal center, the but-2-yne complex [C₅H₅Rh(MeC≡CMe)(P*i*Pr₃)] rearranges to the isomeric allene derivative [C₅H₅Rh(η²-CH₂=C=CHMe)(P*i*Pr₃)] if a solution of the alkyne complex is chromatographed on deactivated Al_2O_3[30]. In this case, the isomerization is initiated by the acid/base couple H_2O/OH^- which has been confirmed by deuteration experiments.

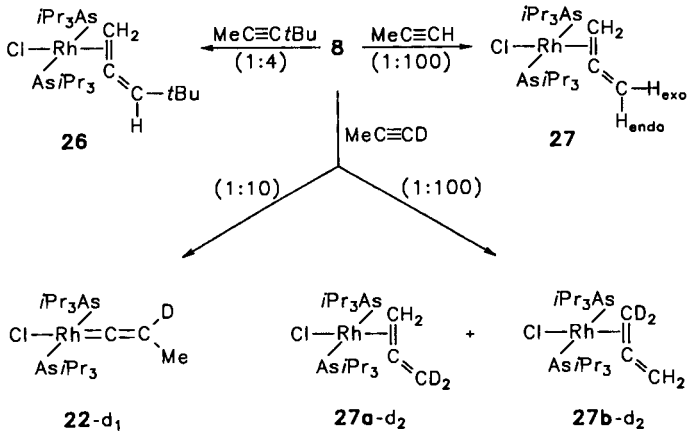
The new method for the preparation of four-coordinate allene rhodium(I) compounds from alkynes can also be applied to the *tert*-butylallene and even the parent allene derivative. The synthesis of **26** and **27** follows almost exactly the procedure given for **25** with the emphasis that good yields of **27** are only obtained if a larger excess of HC≡CMe (molar ratio ca. 1:100) is used. The ^{1}H-NMR spectrum of **27** (in C_6D_6) shows three signals for the allene protons, one at relatively high field (δ = 2.47) for the equivalent protons of the metal-bound CH_2 group and two at lower field (δ = 5.32 and 5.51) for the non-equivalent hydrogens (H_{exo} and H_{endo}) of the uncoordinated CH_2 allene unit. This assignment is in line with data for analogous systems[31]. This finding together with the appearance of two doublets for the diastereotopic CH_3 protons of the arsane ligands points to a hindered rotation around the allene-to-metal bond and also to a rigid structure of the whole molecule. Evidence for the non-fluctional behavior of the C_3H_4 ligand in complex **27** is also provided by the ^{13}C-NMR spectrum where a large difference in the chemical shift between the signals of the two CH_2 carbons (δ = 96.4 and 4.9) is observed. With regard to the rigid allene–metal bond it should further be mentioned that the displacement of the C_3H_4 moiety in **27** by CO occurs quite slowly; with HC≡CMe instead of CO, no ligand substitution takes place.

Insight into the mechanism of the formation of **27** comes from a detailed investigation by using the monodeuterated alkyne $CH_3C{\equiv}CD$ as the substrate. The obvious assumption that the reaction follows a similar course as that of **8** with but-2-yne (see Scheme 3) is probably wrong as only if a large excess of propyne is used, the allene complex is formed. Otherwise, the methylvinylidene rhodium compound **22** is the sole reaction product. However, whereas in agreement with this result the reaction of **8** with up to a tenfold excess of [1-D] propyne gives *trans*-[RhCl(=C=CD-CH₃)(As*i*Pr₃)₂] (**22**-d_1), treatment of **8** with $CH_3C{\equiv}CD$ in the molar ratio of approximately 1:100 affords the *dideuterated* allene derivative *trans*-[RhCl(η²-CH₂=C=CD₂)-(As*i*Pr₃)₂] (**27**-d_2). As most of the spectroscopic data of **27**-d_2

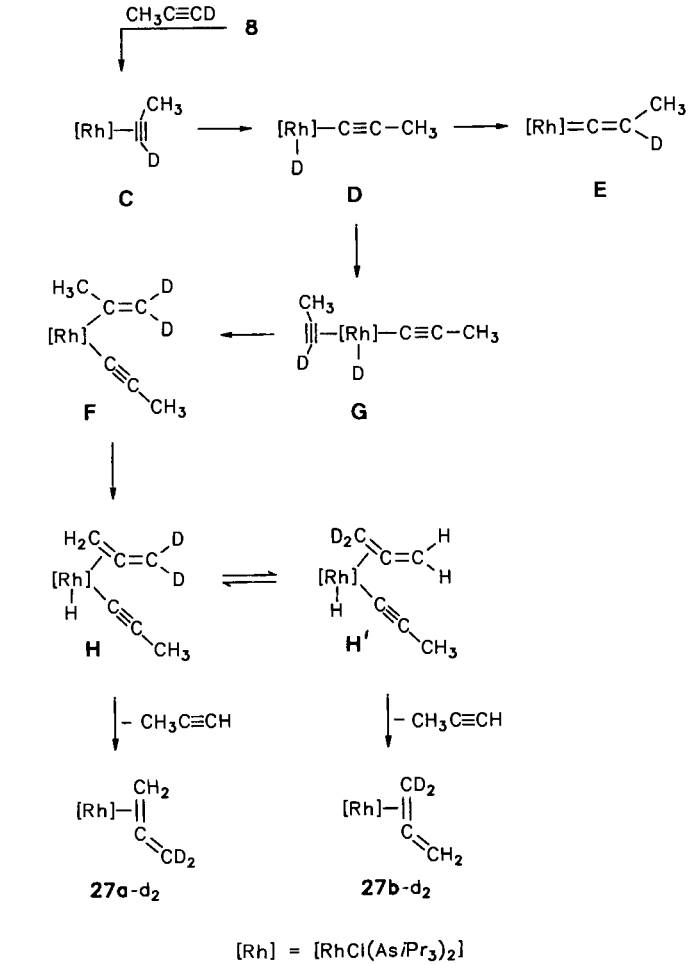
are very similar to those of the non-deuterated compound **27** (with the difference of a lower intensity of the proton signals of the coordinated and the free CH_2 allene group) we are convinced that both isomers **27a**-d_2 and **27b**-d_2 (see Scheme 4) are present in solution.

The proposed mechanism for the formation of **27a/b**-d_2 is outlined in Scheme 5. Following the idea that the vinylidene complexes *trans*-[RhCl(=C=CHR)(As*i*Pr$_3$)$_2$] are generated from **8** and HC≡CR via the 1-alkyne rhodium isomer *trans*-[RhCl(HC≡CR)(As*i*Pr$_3$)$_2$], we assume that by using $CH_3C{\equiv}CD$ as the substrate, the corresponding intermediate *trans*-[RhCl(DC≡CCH$_3$)(As*i*Pr$_3$)$_2$] (**C**) is formed in the first step. In the absence of a larger excess of [1-D] propyne, compound **C** rearranges to produce **D** and finally **E** and thus behaves like the bis(phosphane) derivatives *trans*-[RhCl(HC≡CR)(P*i*Pr$_3$)$_2$], which react under mild conditions to give *trans*-[RhCl(=C=CHR)(P*i*Pr$_3$)$_2$][2]. With a high concentration of $CH_3C{\equiv}CD$ present, the intermediary species **D** (that is coordinatively unsaturated) can add one molecule of $CH_3C{\equiv}CD$ to form **G** [containing six-coordinate rhodium(III)], which by insertion of the alkyne into the Rh–D bond affords species **F**. There is precedence for this step as we have recently observed that on treatment of *trans*-[Rh(C≡CR)(=C=CHR)(P*i*Pr$_3$)$_2$][32] with HCl labile five-coordinate alkynyl(vinyl)rhodium(III) compounds are obtained[2,18]. With regard to the arguments mentioned obove (see Scheme 3), the further rearrangement of **F** to **H** is straightforward. The reductive elimination of propyne finally leads to the formation of the dideuterated product.

Scheme 4



Scheme 5



Molecular Structure of Complex 27

A single-crystal X-ray diffraction study of the allene complex **27** confirms the structure proposed in Scheme 4. The

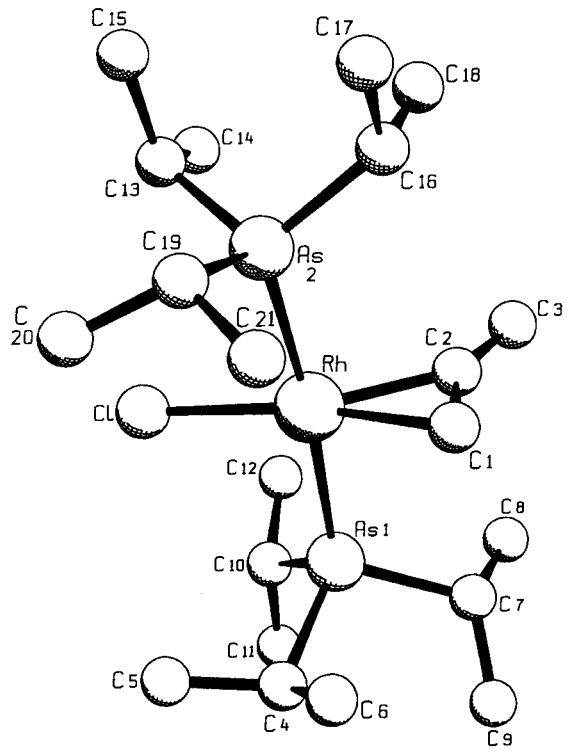


Figure 1. Molecular structure of **27**; selected bond distances [Å] and bond angles [°]: Rh–As1 2.432(2), Rh–As2 2.425(2), Rh–Cl 2.365(4), Rh–C1 2.14(1), Rh–C2 1.98(1), C1–C2 1.39(2), C2–C3 1.31(2); As1–Rh–As2 172.98(5), As1–Rh–Cl 87.7(1), As1–Rh–C1 91.9(4), As1–Rh–C2 93.0(4), As2–Rh–Cl 87.8(2), As2–Rh–C1 91.0(4), As2–Rh–C2 93.2(4), Cl–Rh–C1 164.3(3), Cl–Rh–C2 156.4(4), C1–Rh–C2 39.3(5), Rh–C1–C2 64.3(7), Rh–C2–C1 76.4(7), Rh–C2–C3 137(1), C1–C2–C3 146(1)

SCHAKAL drawing (Figure 1) reveals that the geometry about the rhodium(I) center is distorted square-planar. The two arsanes are *trans* to each other, and the chlorine is *trans* to the allene moiety. The degree of elongation of the coordinated C=C bond [1.39(2) vs. 1.31(2) Å; see Figure 1] is similar to that found in other allene transition-metal complexes[31,33]. Structurally closely related to **27** are the corresponding bis(phosphane)rhodium(I) compounds *trans*-[RhCl(η^2-CH_2=C=CH(CO_2Et))(P*i*Pr_3)$_2$] (**28**) and *trans*-[RhI(η^2-CH_2=C=CH_2)(PPh_3)$_2$] (**29**) for which C=C distances of 1.390(7) and 1.338(7) Å (for **28**)[24] or 1.35(6) and 1.34(7) Å (for **29**)[34] have been determined. Concerning the structural parameters of **29**, it must be considered that the deviations are unusually large because of the high *R* value of the X-ray analysis. The elongation of the C=C bond of the C_3H_4 molecule in **27** upon coordination is accompanied by a bending of the allene ligand [C1−C2−C3 146(1)°] which is comparable to that found in **28** [141.8(5)°] and [Pt(η^2-CH_2=C=CH_2)(PPh_3)$_2$] [142(3)°][35] and more pronounced than in **29** [158(4)°]. The Rh−C bond lengths in **27** differ by 0.16 Å which is in the range to be expected for four-coordinate (allene)rhodium(I) derivatives[33,34].

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Experimental

All operations were carried out under argon with the Schlenk-tube technique. The starting materials **2**[36], **5**[37], and MeC≡CLi[38] were prepared by published procedures; As*i*Pr_3 and Sb*i*Pr_3 were prepared analogously as described for the *n*-propyl derivatives[39,40]. – Melting points: measured by DTA. – IR: Perkin Elmer 1420. – ^{1}H NMR: Varian EM 360 L, Jeol FX 90 Q, Bruker AC 200, Bruker AMX 400. – ^{13}C NMR: Jeol FX 90 Q, Bruker AC 200, Bruker AMX 400. – MS: Finnigan 90 MAT (70 eV).

1. *Preparation of [RhCl(C_8H_{14})(AsiPr$_3$)]$_2$* (**3**) *and [RhCl(C_8H_{14})(SbiPr$_3$)]$_2$* (**4**): A suspension of 50 mg (0.07 mmol) of **2** in 10 ml of hexane was treated with 27 µl (0.14 mmol) of As*i*Pr_3 or 29 µl (0.14 mmol) of Sb*i*Pr_3 and stirred for 2 h at 40°C. An orange-brown solution was formed from which on cooling first to 0°C and then to −78°C an orange solid precipitated. It was filtered off, repeatedly washed with pentane (0°C), and dried in vacuo; yield 62 mg (98%) of **3** and 66 mg (94%) of **4**.

3: m.p. 60°C (dec.). – ^{1}H NMR (C_6H_6, 60 MHz): δ = 3.42−3.08, 2.52−2.02, 1.45−1.02 (each m, C_8H_{14}), 1.92 [sept, *J*(HH) = 7.1 Hz, AsC*H*CH_3], 1.23 [d, *J*(HH) = 7.1 Hz, AsCHC*H*$_3$].

$C_{34}H_{70}As_2Cl_2Rh_2$ (905.5) Calcd. C 45.10 H 7.79
Found C 44.90 H 8.03

4: m.p. 52°C (dec.). – ^{1}H NMR (C_6H_6, 60 MHz): δ = 4.18−3.27, 2.35−2.28, 1.78−1.27 (each m, C_8H_{14}), 1.82 [sept, *J*(HH) = 6.9 Hz, SbC*H*CH_3], 1.28 [d, *J*(HH) = 6.9 Hz, SbCHC*H*$_3$].

$C_{34}H_{70}Cl_2Rh_2Sb_2$ (999.15) Calcd. C 40.87 H 7.06
Found C 40.72 H 7.33

2. *Preparation of [RhCl(C_2H_4)(AsiPr$_3$)]$_2$* (**6**) *and [RhCl(C_2H_4)(SbiPr$_3$)]$_2$* (**7**): To a solution of 38 mg (0.10 mmol) of **5** in 2 ml of THF was added dropwise a solution of 39 µl (0.20 mmol) of As*i*Pr_3 or 41 µl (0.20 mmol) of Sb*i*Pr_3 in 5 ml of THF. The solution was stirred for 1 h at room temp., and then the solvent was removed in vacuo. The solid residue was repeatedly washed with pentane (0°C) and recrystallized from 5 ml of THF/pentane (1:1). After the solution had been stored at −78°C, orange crystals had formed which were filtered off, washed with pentane (0°C), and dried in vacuo; yield 71 mg (98%) of **6** and 75 mg (90%) of **7**.

6: m.p. 120°C. – ^{1}H NMR (C_6H_6, 60 MHz): δ = 3.21 (s, br, C_2H_4), 1.81 [sept, *J*(HH) = 7.0 Hz, AsC*H*CH_3], 1.17 [d, *J*(HH) = 7.0 Hz, AsCHC*H*$_3$].

$C_{22}H_{50}As_2Cl_2Rh_2$ (741.2) Calcd. C 35.65 H 6.80
Found C 35.51 H 6.69

7: m.p. 64°C (dec.). – ^{1}H NMR (C_6H_6, 60 MHz): δ = 3.45 (s, br, C_2H_4), 1.88 [sept, *J*(HH) = 6.8 Hz, SbC*H*CH_3], 1.18 [d, *J*(HH) = 6.8 Hz, SbCHC*H*$_3$].

$C_{22}H_{50}Cl_2Rh_2Sb_2$ (834.9) Calcd. C 31.65 H 6.04
Found C 31.46 H 6.29

3. *Preparation of trans-[RhCl(C_2H_4)(AsiPr$_3$)$_2$]* (**8**) *and trans-[RhCl(C_2H_4)(SbiPr$_3$)$_2$]* (**9**): A solution of 150 mg (0.39 mmol) of **5** in 20 ml of ether was treated with 306 µl (1.56 mmol) of As*i*Pr_3 or 323 µl (1.56 mmol) of Sb*i*Pr_3 and stirred for 1 h at room temp. The solvent was removed, the solid residue repeatedly washed with pentane (0°C) and then recrystallized from 20 ml of THF/pentane (1:10). After the solution had been stored at −78°C, yellow (**8**) or orange-yellow (**9**) crystals had formed which were filtered off, washed with pentane (0°C), and dried in vacuo; yield 386 mg (86%) of **8** and 428 mg (82%) of **9**.

8: m.p. 93°C (dec.). – ^{1}H NMR (C_6D_6, 90 MHz): δ = 2.94 [d, *J*(RhH) = 2.2 Hz, C_2H_4], 2.29 [sept, *J*(HH) = 7.2 Hz, AsC*H*CH_3], 1.32 [d, *J*(HH) = 7.2 Hz, AsCHC*H*$_3$].

$C_{20}H_{46}As_2ClRh$ (574.8) Calcd. C 41.79 H 8.07
Found C 41.57 H 8.26
Mol. mass 574 (MS)

9: m.p. 50°C. – ^{1}H NMR (C_6H_6, 60 MHz): δ = 3.45 (s, br, C_2H_4), 2.12 [sept, *J*(HH) = 7.0 Hz, SbC*H*CH_3], 1.36 [d, *J*(HH) = 7.0 Hz, SbCHC*H*$_3$].

$C_{20}H_{46}ClRhSb_2$ (668.45) Calcd. C 35.94 H 6.94
Found C 35.65 H 7.06

4. *Preparation of trans-[RhCl(CO)(AsiPr$_3$)$_2$]* (**10**) *and trans-[RhCl(CO)(SbiPr$_3$)$_2$]* (**11**): A slow stream of CO was passed for ca. 10 s through a solution of 47 mg (0.08 mmol) of **8** or 54 mg (0.08 mmol) of **9** in 10 ml of pentane at room temp. After stirring for 15 min, the solution was concentrated to ca. 2 ml and then stored at −78°C. A light yellow crystalline precipitate formed which was washed with small quantities of pentane (0°C), and dried in vacuo; yield 43 mg (91%) of **10** and 50 mg (93%) of **11**.

10: m.p. 171°C. – IR (KBr): $\tilde{\nu}$ = 1937 cm^{-1} (C=O). – ^{1}H NMR (C_6H_6, 60 MHz): δ = 2.45 [sept, *J*(HH) = 7.0 Hz, AsC*H*CH_3], 1.35 [d, *J*(HH) = 7.0 Hz, AsCHC*H*$_3$].

$C_{19}H_{42}As_2ClORh$ (574.75) Calcd. C 39.71 H 7.37
Found C 39.47 H 7.52

11: m.p. 122°C. – IR (KBr): $\tilde{\nu}$ = 1938 cm^{-1} (C=O). – ^{1}H NMR (C_6H_6, 60 MHz): δ = 2.25 [sept, *J*(HH) = 6.8 Hz, SbC*H*CH_3], 1.37 [d, *J*(HH) = 6.8 Hz, SbCHC*H*$_3$].

$C_{19}H_{42}ClORhSb_2$ (668.4) Calcd. C 34.14 H 6.33
Found C 34.37 H 6.58

5. *Preparation of [RhH$_2$Cl(AsiPr$_3$)$_2$]* (**12**) *and [RhH$_2$Cl(SbiPr$_3$)$_2$]* (**13**): A solution of 60 mg (0.10 mmol) of **8** or 55 mg (0.08 mmol) of **9** in 10 ml of benzene was stirred under 1 atm of H_2

for 30 min at room temp. The solvent was removed and the solid residue recrystallized from 3 ml of pentane (25 to −78°C). The yellow (**12**) or brown (**13**) crystalline precipitate was filtered off, washed with small quantities of pentane (0°C), and dried in vacuo; yield 47 mg (86%) of **12** and 41 mg (79%) of **13**.

12: m.p. 41°C (dec.). – IR (C_6H_6): $\tilde{\nu}$ = 2118 cm^{-1} (RhH). – ^1H NMR (C_6D_6, 90 MHz): δ = 2.21 [sept, *J*(HH) = 6.8 Hz, AsC*H*CH_3], 1.24 [d, *J*(HH) = 6.8 Hz, AsCHC*H*$_3$], −23.56 [d, *J*(RhH) = 22.0 Hz, RhH_2].

$C_{18}H_{44}As_2ClRh$ (548.75) Calcd. C 39.40 H 8.08
Found C 39.19 H 8.07

13: m.p. 64°C (dec.). – IR (C_6H_6): $\tilde{\nu}$ = 2100 cm^{-1} (RhH). – ^1H NMR (C_6D_6, 90 MHz): δ = 2.18 [sept, *J*(HH) = 7.1 Hz, SbC*H*CH_3], 1.41 [d, *J*(HH) = 7.1 Hz, SbCHC*H*$_3$], −22.89 [d, *J*(RhH) = 21.3 Hz, RhH_2].

$C_{18}H_{44}ClRhSb_2$ (642.2) Calcd. C 33.65 H 6.90
Found C 33.67 H 6.99

6. *Preparation of trans-[RhCl(N$_2$CPh$_2$)(AsiPr$_3$)$_2$]* (**14**): A solution of 57 mg (0.10 mmol) of **8** in 10 ml of pentane was treated at −78°C with a solution of 38 mg (0.20 mmol) of diphenyldiazomethane in 3 ml of pentane. After the solution had been warmed to room temp., it was stirred for 2 h, then concentrated in vacuo to ca. 6 ml and filtered. The filtrate was stored for 2 d at −78°C. Dark green crystals formed which were filtered off, washed with pentane (0°C), and dried in vacuo; yield 66 mg (89%), m.p. 82°C (dec.). – IR (hexane): $\tilde{\nu}$ = 1941 cm^{-1} (CN_2). – ^1H NMR (C_6D_6, 400 MHz): δ = 8.11−6.85 (m, C_6H_5), 2.28 [sept, *J*(HH) = 7.2 Hz, AsC*H*CH_3], 1.31 [d, *J*(HH) = 7.2 Hz, AsCHC*H*$_3$]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 160.96 (s, *ipso*-C of C_6H_5), 129.71, 128.84, 125.21, 124.27 (each s, C_6H_5), 77.87 (s, Ph_2CN_2), 24.76 (s, AsCHCH$_3$), 21.01 (s, AsCHC*H*$_3$).

$C_{31}H_{52}As_2ClN_2Rh$ (741.0) Calcd. C 50.25 H 7.07 N 3.78
Found C 50.52 H 7.40 N 3.31

7. *Preparation of trans-[RhCl(N$_2$)(AsiPr$_3$)$_2$]* (**15**): A solution of 30 mg (0.04 mmol) of **14** in 3 ml of benzene was irradiated for 30 min with a UV lamp (Osram HBO 500 W). A color change from green to dark brown occurred. After the solvent had been removed, the brown residue was characterized by IR and ^1H-NMR spectroscopy. – IR (C_6H_6): $\tilde{\nu}$ = 2100 cm^{-1} (N_2). – ^1H NMR (C_6H_6, 60 MHz): δ = 2.26 [sept, *J*(HH) = 7.1 Hz, AsC*H*CH_3], 1.16 [d, *J*(HH) = 7.1 Hz, AsCHC*H*$_3$].

8. *Preparation of trans-[RhCl(HC≡CH)(AsiPr$_3$)$_2$]* (**16**)

a) Through a solution of 64 mg (0.11 mmol) of **8** in 10 ml of pentane a slow stream of acetylene was passed for 20 s at room temp. A spontaneous color change from yellow to brown occurred. The solution was stirred for 15 min, then filtered, and the filtrate was concentrated to ca. 2 ml in vacuo. After the residual filtrate had been stored at −78°C for 3 h, yellow crystals precipitated which were filtered off, washed several times with a small amount of pentane (0°C), and dried in vacuo; yield 25 mg (39%).

b) Acetylene was passed for 10 s through a solution of 55 mg (0.10 mmol) of **12** in 10 ml of pentane at −78°C. After the solution had been warmed to room temp., it was stirred for 5 min and then concentrated to ca. 3 ml in vacuo. The concentrate was kept at −78°C for 3 h which led to the formation of a yellow precipitate; yield 48 mg (84%), m.p. 48°C. – IR (KBr): $\tilde{\nu}$ = 1707 cm^{-1} (C≡C). – ^1H NMR (C_6D_6, 60 MHz): δ = 3.12 [d, *J*(RhH) = 2.4 Hz, HC≡CH], 2.25 [sept, *J*(HH) = 6.8 Hz, AsC*H*CH_3], 1.38 [d, *J*(HH) = 6.8 Hz, AsCHC*H*$_3$].

$C_{20}H_{44}As_2ClRh$ (572.8) Calcd. C 41.94 H 7.74
Found C 42.19 H 8.06

9. *Preparation of trans-[RhCl(HC≡CPh)(AsiPr$_3$)$_2$]* (**17**)

a) A solution of 70 mg (0.12 mmol) of **8** in 15 ml of pentane was treated with stirring with 13 μl (0.12 mmol) of phenylacetylene at room temp. A quick color change from yellow to brown occurred. After the solution had been stirred for 10 min, the solvent was removed, the residue washed with a small amount of pentane (0°C) and then recrystallized from 3 ml of pentane (25 to −78°C). Yellow crystals formed which were washed with pentane (−20°C), and dried in vacuo; yield 72 mg (92%).

b) Analogously as described for **16**, by using 66 mg (0.12 mmol) of **12** as starting material; yield 69 mg (90%), m.p. 73°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1817 cm^{-1} (C≡C). – ^1H NMR (C_6D_6, 90 MHz): δ = 8.24−7.02 (m, C_6H_5), 3.80 [d, *J*(RhH) = 2.6 Hz, *H*C≡CPh], 2.20 [sept, *J*(HH) = 7.1 Hz, AsC*H*CH_3], 1.30 and 1.25 [both d, *J*(HH) = 7.1 Hz, AsCHC*H*$_3$].

$C_{26}H_{48}As_2ClRh$ (648.9) Calcd. C 48.13 H 7.46
Found C 47.87 H 7.28

10. *Preparation of trans-[RhCl(HC≡CCO$_2$Me)(AsiPr$_3$)$_2$]* (**18**): A solution of 103 mg (0.18 mmol) of **8** in 15 ml of pentane was treated at −78°C with 16 μl (0.18 mmol) of HC≡CCO_2Me and with stirring slowly (in ca. 20 min) warmed to room temp. The solvent was removed in vacuo, the orange-brown residue washed several times with a small amount of pentane (0°C) and recrystallized from 3 ml of pentane (25 to −78°C). After the pentane solution had been stored for 24 h at −78°C, orange-yellow crystals precipitated which were filtered off, washed with pentane (−20°C), and dried in vacuo; yield 93 mg (82%), m.p. 85°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1796 (C≡C), 1677 cm^{-1} (C=O). – ^1H NMR (C_6D_6, 200 MHz): δ = 4.82 [d, *J*(RhH) = 2.3 Hz, *H*C≡CCO_2Me], 3.56 (s, CO_2CH_3), 2.24 [sept, *J*(HH) = 7.2 Hz, AsC*H*CH_3], 1.31 and 1.29 [both d, *J*(HH) = 7.2 Hz, AsCHC*H*$_3$].

$C_{22}H_{46}As_2ClO_2Rh$ (630.8) Calcd. C 41.89 H 7.35
Found C 42.05 H 7.50

11. *Preparation of trans-[RhCl(=C=CH$_2$)(AsiPr$_3$)$_2$]* (**19**)

a) A solution of 45 mg (0.08 mmol) of **16** in 2 ml of benzene was stirred for 30 min at 50°C. The solution was cooled to room temp., the solvent was removed and the residue extracted with 2 ml of pentane. After the extract had been kept at −78°C for 3 d, dark violet crystals precipitated which were filtered off, washed with small quantities of pentane (0°C), and dried in vacuo; yield 34 mg (75%).

b) A solution of 50 mg (0.09 mmol) of **16** in 2 ml of benzene was irradiated with a UV lamp (Osram HBO 500 W) for 20 min at room temp. The further workup was carried out as described for a); yield 40 mg (80%), m.p. 57°C. – IR (C_6H_6): $\tilde{\nu}$ = 1620 cm^{-1} (C=C). – ^1H NMR (C_6D_6, 400 MHz): δ = 2.70 [sept, *J*(HH) = 7.2 Hz, AsC*H*CH_3], 1.40 [d, *J*(HH) = 7.2 Hz, AsCHC*H*$_3$], −0.01 [d, *J*(RhH) = 0.9 Hz, =CH_2]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 294.70 [d, *J*(RhC) = 54.3 Hz, Rh=C], 92.47 [d, *J*(RhC) = 16.1 Hz, =CH_2], 24.67 (s, AsCHCH$_3$), 20.87 (s, AsCHC*H*$_3$).

$C_{20}H_{44}As_2ClRh$ (572.8) Calcd. C 41.94 H 7.74
Found C 42.17 H 7.67

12. *Preparation of trans-[RhCl(=C=CHPh)(AsiPr$_3$)$_2$]* (**20**)

a) A solution of 50 mg (0.08 mmol) of **17** in 2 ml of benzene was stirred for 3 h at 50°C. After the solution had been cooled to room temp., the solvent was removed, the residue washed with a small amount of pentane (0°C) and then recrystallized from 2 ml of pentane (25 to −78°C). After 2 d, dark violet crystals precipitated which were washed twice with pentane (0°C), and dried in vacuo; yield 41 mg (81%).

b) A solution of 50 mg (0.08 mmol) of **17** in 2 ml of benzene was irradiated with a UV lamp (Osram HBO 500 W) for 45 min at

room temp. The further workup was carried out as described for a); yield 43 mg (84%), m.p. 74°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1636 cm^{-1} (C=C). – ^1H NMR (C_6D_6, 90 MHz): δ = 7.20–7.10 (m, C_6H_5), 2.57 [sept, *J*(HH) = 7.1 Hz, AsC*H*CH_3], 1.67 [d, *J*(RhH) = 1.5 Hz, =C*H*C_6H_5], 1.34 [d, *J*(HH) = 7.1 Hz, AsCHCH_3]. – ^{13}C NMR (C_6D_6, 22.5 MHz): δ = 290.49 [d, *J*(RhC) = 53.7 Hz, Rh=C], 128.61, 128.52, 125.36, 125.06 (each s, C_6H_5), 116.00 [d, *J*(RhC) = 13.6 Hz, =*C*HC_6H_5], 25.40 (s, AsCHCH$_3$), 21.00 (s, AsCHCH$_3$).

$C_{26}H_{48}As_2ClRh$ (648.9) Calcd. C 48.13 H 7.46
Found C 48.33 H 7.28

13. *Reaction of* **20** *with CO:* A slow stream of CO was passed for 20 s through a solution of 50 mg (0.08 mmol) of **20** in 10 ml of pentane at room temp. After the solution had been stirred for 1 h, a color change from violet to yellow-brown had occurred.The solvent was removed in vacuo, the residue washed with small quantities of pentane (0°C), and dried in vacuo; yield 44 mg (95%). The IR and ^1H-NMR spectra of the product were identical with those of the carbonyl complex **10**.

14. *Preparation of trans-[RhCl(=C=CHCO$_2$Me)(AsiPr$_3$)$_2$]* (**21**): A solution of 43 mg (0.07 mmol) of **18** in 0.5 ml of benzene was irradiated in a NMR tube with a UV lamp (Osram HBO 500 W) for 5 h at room temp. The solution was chromatographed on Al_2O_3 (neutral, activity grade V, length of column 10 cm) with hexane. A violet fraction was eluted which was evaporated to dryness in vacuo. The residue was recrystallized from 2 ml of pentane (25 to –78°C) to give violet crystals, which were washed with a small amount of pentane (0°C), and dried in vacuo; yield 37 mg (85%), m.p. 88°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1700 (C=O), 1612 cm^{-1} (C=C). – ^1H NMR (C_6D_6, 200 MHz): δ = 3.48 (s, CO_2CH_3), 2.61 [sept, *J*(HH) = 7.2 Hz, AsC*H*CH_3], 1.56 [d, *J*(RhH) = 1.1 Hz, =C*H*CO_2CH_3], 1.33 [d, *J*(HH) = 7.2 Hz, AsCHCH_3]. – ^{13}C NMR (C_6D_6, 50.3 MHz); δ = 280.25 [d, *J*(RhC) = 57.2 Hz, Rh=C], 158.43 (s, *C*O_2CH_3), 108.75 [d, *J*(RhC) = 14.7 Hz, =*C*HCO_2CH_3], 50.45 (s, CO_2CH_3), 25.40 (s, AsCHCH$_3$), 20.79 (s, AsCHCH$_3$).

$C_{22}H_{46}As_2ClO_2Rh$ (630.8) Calcd. C 41.89 H 7.35
Found C 42.08 H 7.59

15. *Preparation of trans-[RhCl(=C=CHMe)(AsiPr$_3$)$_2$]* (**22**): Propyne (ca. 40 mg, ca. 0.96 mmol) was condensed into a cooled Schlenk tube (–78°C) and then with stirring treated dropwise with a cooled (–40°C) solution of 58 mg (0.10 mmol) of **8** in 15 ml of pentane. The reaction mixture was warmed to 20°C and stirred for 15 min at room temp. The solvent was removed, the oily residue washed several times with a small amount of pentane (0°C) and then recrystallized from 2 ml of pentane (25 to –78°C) to give brown-violet crystals; yield 47 mg (81%), m.p. 96°C. – IR (C_6H_6): $\tilde{\nu}$ = 1680 cm^{-1} (C=C). – ^1H NMR (C_6D_6, 400 MHz): δ = 2.60 [sept, *J*(HH) = 7.3 Hz, AsC*H*CH_3], 2.33 [dq, *J*(HH) = 7.5, *J*(RhH) = 0.6 Hz, =C*H*CH_3], 1.79 [d, *J*(HH) = 7.5 Hz, =CHCH_3], 1.37 [d, *J*(HH) = 7.3 Hz, AsCHCH_3]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 286.36 [d, *J*(RhC) = 51.9 Hz, Rh=C], 102.48 [d, *J*(RhC) = 14.9 Hz, =*C*HCH_3], 24.62 (s, AsCHCH$_3$), 20.90 (s, AsCHCH$_3$), 1.35 (s, =CHCH_3).

$C_{21}H_{46}As_2ClRh$ (586.8) Calcd. C 42.98 H 8.06
Found C 43.10 H 7.92

16. *Preparation of trans-[RhCl(=C=CDMe)(AsiPr$_3$)$_2$]* (**22**-d_1): Solid MeC≡CLi (45 mg, 0.98 mmol) was treated dropwise at room temp. with 50 µl (1.23 mmol) of CD_3OD. The generated [1-D]-propyne was condensed into a cooled Schlenk tube (–78°C) to which a solution (–40°C) of 58 mg (0.10 mmol) of **8** in 15 ml of pentane was added. The workup of the reaction mixture was carried out as described for **22**. Violet crystals were obtained; yield 33 mg (80%), m.p. 96°C. – IR (C_6H_6): $\tilde{\nu}$ = 1675 cm^{-1} (C=C). – ^1H NMR (C_6D_6, 400 MHz): δ = 2.62 [sept, *J*(HH) = 7.2 Hz, AsC*H*CH_3], 1.78 (s, =CD*CH*$_3$), 1.37 [d, *J*(HH) = 7.2 Hz, AsCH*CH*$_3$].

$C_{21}H_{45}As_2ClDRh$ (587.8) Calcd. C 42.91 H 7.90
Found C 43.19 H 8.13

17. *Preparation of trans-[RhCl(=C=CHtBu)(AsiPr$_3$)$_2$]* (**23**): A solution of 120 mg (0.21 mmol) of **8** in 20 ml of pentane was treated with 30 µl (0.23 mmol) of 3,3-dimethylbut-1-yne and stirred for 3 h at room temp. A color change from yellow to brown-violet occurred. The solution was concentrated to ca. 2 ml and then stored at –78°C. After 24 h, dark violet crystals precipitated which were filtered off, washed twice with pentane (0°C), and dried in vacuo; yield 110 mg (84%), m.p. 108°C (dec.). – IR (C_6H_6): $\tilde{\nu}$ = 1640 cm^{-1} (C=C). – ^1H NMR (C_6D_6, 400 MHz): δ = 2.70 [sept, *J*(HH) = 7.3 Hz, AsC*H*CH_3], 1.39 [d, *J*(HH) = 7.3 Hz, AsCHCH_3], 1.03 (s, *t*Bu), 0.00 [d, *J*(RhH) = 1.2 Hz, =C*H*tBu]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 286.64 [d, *J*(RhC) = 53.7 Hz, Rh=C], 120.93 [d, *J*(RhC) = 14.1 Hz, =C*H*tBu], 31.40 [s, *C*$(CH_3)_3$], 26.33 [s, C(*C*$H_3)_3$], 24.69 (s, AsCHCH$_3$), 21.16 (s, AsCHCH$_3$).

$C_{24}H_{52}As_2ClRh$ (628.9) Calcd. C 45.84 H 8.33
Found C 46.09 H 8.41

18. *Preparation of trans-[RhCl(η^2-CH$_2$=C=CHMe)(AsiPr$_3$)$_2$]* (**25**): A solution of 64 mg (0.11 mmol) of **8** in 15 ml of pentane was treated with stirring at –78°C with 20 µl (0.26 mmol) of but-2-yne. The reaction mixture was warmed to room temp., stirred for 30 min, and then concentrated to ca. 2 ml in vacuo. After the residual mixture had been stored at –78°C orange-yellow crystals precipitated which were filtered off, washed several times with a small amount of pentane (0°C), and dried in vacuo; yield 60 mg (91%), m.p. 73°C. – IR (KBr): $\tilde{\nu}$ = 1731 cm^{-1} (C=C=C). – ^1H NMR (C_6D_6, 400 MHz): δ = 5.55 (m, =C*H*CH_3), 2.43 (m, CH_2), 2.30 [sept, *J*(HH) = 7.2 Hz, AsC*H*CH_3], 1.95 [d, *J*(HH) = 6.4 Hz, =CHCH_3], 1.35 and 1.34 [both d, *J*(HH) = 7.2 Hz, AsCHCH_3]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 159.37 [d, *J*(RhC) = 21.1 Hz, =C=], 105.15 [d, *J*(RhC) = 2.8 Hz, =*C*HCH_3], 25.10 (s, AsCHCH$_3$), 21.37 (s, =CH*CH*$_3$), 21.16 and 21.13 (both s, AsCH*CH*$_3$), 6.89 [d, *J*(RhC) = 11.1 Hz, CH_2].

$C_{22}H_{48}As_2ClRh$ (600.8) Calcd. C 43.98 H 8.05
Found C 43.86 H 8.39

19. *Preparation of trans-[RhCl(η^2-CH$_2$=C=CHtBu)(AsiPr$_3$)$_2$]* (**26**): A solution of 130 mg (0.23 mmol) of **8** in 20 ml of pentane was treated with stirring at –78°C with 96 mg (1.00 mmol) of 2,2-dimethylpent-2-yne. The reaction mixture was warmed to room temp., stirred for 20 min, and then the solvent was removed. The oily residue was dissolved in 2 ml of benzene, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, length of column 10 cm). With hexane a yellow fraction was eluted which was evaporated to dryness in vacuo. The remaining yellow oil was recrystallized from 2 ml of pentane (25 to –78°C) to give yellow crystals which were filtered off, washed several times with a small amount of pentane (0°C), and dried in vacuo; yield 137 mg (92%), m.p. 64°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1733 cm^{-1} (C=C=C). – ^1H NMR (C_6D_6, 200 MHz): δ = 5.59 [dt, *J*(RhH) = 0.4, ^{4}*J*(HH) = 2.8 Hz, C*H*tBu], 2.50 (m, CH_2), 2.34 [sept, *J*(HH) = 7.3 Hz, AsC*H*CH_3], 1.36 and 1.33 [both d, *J*(HH) = 7.3 Hz, AsCHCH_3], 1.12 [s, C$(CH_3)_3$]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 154.89 [d, *J*(RhC) = 20.4 Hz, =C=], 120.28 [d, *J*(RhC) = 1.6 Hz, *C*H*t*Bu], 33.66 [s, *C*$(CH_3)_3$], 30.69 [s, C(*C*$H_3)_3$], 24.64 (s, AsCHCH$_3$), 21.33 and 21.19 (both s, AsCH*CH*$_3$), 7.88 [d, *J*(RhC) = 11.8 Hz, CH_2].

$C_{25}H_{54}As_2ClRh$ (642.9) Calcd. C 46.71 H 8.47
Found C 46.74 H 8.89

20. *Preparation of trans-[RhCl(η^2-CH_2=C=CH_2)($AsiPr_3$)$_2$]* (**27**): Propyne (ca. 400 mg, ca. 9.6 mmol) was condensed into a cooled Schlenk tube (−78 °C) and with stirring treated dropwise with a cooled (−40 °C) solution of 60 mg (0.10 mmol) of **8** in 15 ml of pentane. The reaction mixture was warmed to room temp., stirred for 15 min, and then concentrated to ca. 2 ml in vacuo. After the residual mixture had been cooled to −78 °C, light yellow crystals precipitated which were filtered off, washed with small quantities of pentane (0 °C), and dried in vacuo; yield 51 mg (83%), m.p. 90 °C. − IR (KBr): $\tilde{\nu}$ = 1729 cm^{-1} (C=C=C). − ^{1}H NMR (C_6D_6, 400 MHz): δ = 5.51 [ddt, *J*(RhH) = 0.3, ^2J(HH) = 1.4, ^4J(HH) = 2.8 Hz, H_{exo} of C=CH_2], 5.32 [ddt, *J*(RhH) = 0.5, ^2J(HH) = 1.4, ^4J(HH) = 2.8 Hz, H_{endo} of C=CH_2], 2.47 [ddd, *J*(RhH) = $^4J(HH_{exo})$ = $^4J(HH_{endo})$ = 2.8 Hz, η^2-CH_2=C], 2.34 [sept, *J*(HH) = 7.2 Hz, AsC*H*CH_3], 1.36 and 1.35 [both d, *J*(HH) = 7.2 Hz, AsCH*C*H_3]. − ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 170.69 [d, *J*(RhC) = 20.5 Hz, =C=], 96.43 [d, *J*(RhC) = 2.9 Hz, CH_2 uncoord.], 25.19 (s, AsC*H*CH_3), 21.29 and 21.19 (both s, AsCH*C*H_3), 4.91 [d, *J*(RhC) = 11.7 Hz, CH_2 coord.].

$C_{21}H_{46}As_2ClRh$ (586.8) Calcd. C 42.98 H 7.90
Found C 42.90 H 8.17

21. *Preparation of trans-[RhCl(η^2-CH_2=C=CD_2)($AsiPr_3$)$_2$]* (**27a**-d_2)/*trans-[RhCl(η^2-CD_2=C=CH_2)($AsiPr_3$)$_2$]* (**27b**-d_2): Solid MeC≡CLi (450 mg, 9.8 mmol) was treated dropwise at room temp. with 1 ml (24.6 mmol) of CD_3OD. The generated [1-D]propyne was condensed into a cooled Schlenk tube (−78 °C) to which a solution (−40 °C) of 52 mg (0.09 mmol) of **8** in 15 ml of pentane was added. The workup of the reaction mixture was carried out as described for **27**. Yellow crystals were obtained; yield 43 mg (82%), m.p. 89 °C. − IR (KBr): $\tilde{\nu}$ = 1720 cm^{-1} (C=C=C). − ^{1}H NMR (C_6D_6, 400 MHz): δ = 5.49 [d, br, *J*(RhH) = 0.3 Hz, H_{exo} of CH_2 of **27b**-d_2], 5.29 [d, br, *J*(RhH) = 0.5 Hz, H_{endo} of CH_2 of **27b**-d_2], 2.47 [d, br, *J*(RhH) = 2.8 Hz, CH_2 of **27a**-d_2], 2.34 [sept, *J*(HH) = 7.2 Hz, AsC*H*CH_3], 1.35 and 1.34 [both d, *J*(HH) = 7.2 Hz, AsCH*C*H_3]. − ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 170.75 [d, *J*(RhC) = 20.5 Hz, =C=], 96.49 [d, *J*(RhC) = 2.8 Hz, CH_2 uncoord.], 25.11 (s, AsC*H*CH_3), 21.23 and 21.15 (both s, AsCH*C*H_3), 4.98 [d, *J*(RhC) = 11.8 Hz, CH_2 coord.].

$C_{21}H_{44}As_2ClD_2Rh$ (588.8) Calcd. C 42.84 H 7.90
Found C 43.10 H 7.92

22. *X-ray Structure Analysis of* **27**: Single crystals were grown from methanol/2-propanol (1:1). A crystal (0.2 × 0.2 × 0.15 mm) was mounted on an Enraf Nonius CAD4 diffractometer. Mo-K_α radiation (λ = 0.70930 Å, graphite monochromator) was used for all measurements. Centering and refinement of 23 reflections (11° < Θ < 15°) gave the unit cell parameters: *a* = 8.894(5), *b* = 12.411(5), *c* = 12.862(7) Å, α = 68.67(5), β = 84.76(4), γ = 84.73(4)°, *V* = 1314 Å^3, *Z* = 2, *d*(calcd.) = 1.483 gcm^{-3}, μ = 32.4 cm^{-1}, space group *P*1 (2). Intensities were measured in an ω/2Θ-scan mode; 2Θ(max) = 42°; *T* = 293 K. Reflections measured: 3026, unique reflections: 2795, reflections with $F_o > 3\sigma(F_o)$: 2203. Intensity data were corrected for Lorentz and polarization effects; an empirical absorption correction was applied (Ψ-scan method, min. transmission 85.27%). The structure was solved by direct methods (SHELXS-86). The position of the hydrogen atoms were calculated according to ideal geometry; for the final refinement the riding model was used. Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares. The reflection to parameter ratio was 9.75. R = 0.045, R_w = 0.057 (226 parameters, Enraf Nonius SDP). Residual electron density +0.87/−0.99 eÅ^{-3}. The atomic parameters of **27** are listed in Table 1. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-56343, the names of the authors, and the journal citation.

Table 1. Atomic parameters of **27**. *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: B_{eq} = (4/3) [$a^2B(1,1)$ + $b^2B(2,2)$ + $c^2B(3,3)$ + $ab(\cos\gamma)B(1,2)$ + $ac(\cos\beta)B(1,3)$ + $bc(\cos\alpha)B(2,3)$]

Atom	x/a	y/b	z/c	B_{eq}[Å^2]
Rh	0.2398(1)	0.29376(8)	0.74414(8)	3.16(2)
As1	0.1891(1)	0.1123(1)	0.7258(1)	3.25(3)
As2	0.2979(2)	0.4605(1)	0.7856(1)	3.23(3)
Cl	0.0826(5)	0.2384(3)	0.9112(3)	5.54(9)
C1	0.428(2)	0.319(1)	0.6236(9)	4.1(3)
C2	0.290(1)	0.370(1)	0.582(1)	3.8(3)
C3	0.219(2)	0.432(1)	0.493(1)	6.1(4)
C4	0.317(2)	-0.021(1)	0.824(1)	4.8(4)
C5	0.266(2)	-0.044(1)	0.947(1)	7.1(5)
C6	0.479(2)	0.005(1)	0.797(1)	6.5(5)
C7	0.236(2)	0.102(1)	0.575(1)	4.9(4)
C8	0.111(2)	0.162(1)	0.497(1)	7.2(5)
C9	0.279(2)	-0.017(1)	0.572(1)	7.6(5)
C10	-0.010(2)	0.065(1)	0.774(1)	6.3(4)
C11	-0.055(2)	-0.049(1)	0.769(1)	6.7(4)
C12	-0.139(2)	0.162(1)	0.727(1)	7.4(5)
C13	0.130(2)	0.526(1)	0.859(1)	4.6(3)
C14	-0.017(2)	0.548(1)	0.798(1)	6.1(4)
C15	0.167(2)	0.628(1)	0.888(1)	6.1(4)
C16	0.386(1)	0.591(1)	0.662(1)	3.9(3)
C17	0.488(2)	0.666(1)	0.693(1)	5.3(4)
C18	0.262(2)	0.668(1)	0.589(1)	5.5(4)
C19	0.460(2)	0.416(1)	0.895(1)	4.5(3)
C20	0.397(2)	0.331(1)	1.008(1)	5.9(4)
C21	0.595(2)	0.364(1)	0.850(1)	5.1(4)

[1] Part XIX.: H. Werner, A. Stark, M. Schulz, J. Wolf, *Organometallics* **1992**, *11*, 1126−1130.
[2] Review: H. Werner, *Nachr. Chem. Tech. Lab.* **1992**, *40*, 435−444.
[3] J. Haas, Dissertation, Universität Kaiserslautern, **1990**.
[4] D. Schneider, H. Werner, *Angew. Chem.* **1991**, *103*, 710−712; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 700−702.
[5] W. Levason, C. A. McAuliffe, *Acc. Chem. Res.* **1978**, *11*, 363−368.
[6] W. Levason, C. A. McAuliffe, *Phosphine, Arsine and Stibine Complexes of the Transition Elements*, Elsevier, Amsterdam, **1977**.
[7] H. Werner, J. Wolf, A. Höhn, *J. Organomet. Chem.* **1985**, *287*, 395−407.
[8] C. Busetto, A. D'Alfonso, F. Maspero, G. Perego, A. Zazzetta, *J. Chem. Soc., Dalton Trans.* **1977**, 1828−1834.
[9] J. T. Mague, G. Wilkinson, *J. Chem. Soc. A* **1966**, 1736−1740.
[10] D. L. Thorn, J. A. Ibers, *Adv. Chem. Ser.* **1982**, *196*, 117−133.
[11] H. L. M. van Gaal, J. M. J. Verlaak, T. Posno, *Inorg. Chim. Acta* **1977**, *23*, 43−51.
[12] T. Yoshida, S. Otsuka, M. Matsumoto, K. Nakatsu, *Inorg. Chim. Acta* **1978**, *29*, L257−L259.
[13] J. Wolf, L. Brandt, A. Fries, H. Werner, *Angew. Chem.* **1990**, *102*, 584−586; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 510−512.
[14] D. L. Thorn, T. H. Tulip, J. A. Ibers, *J. Chem. Soc., Dalton Trans.* **1979**, 2022−2025.
[15] [15a] F. J. Garcia Alonso, A. Höhn, J. Wolf, H. Otto, H. Werner, *Angew. Chem.* **1985**, *97*, 401−402; *Angew. Chem. Int. Ed. Engl.*

1985, *24*, 406–408. – [15b] H. Werner, F. J. Garcia Alonso, H. Otto, J. Wolf, *Z. Naturforsch., Teil B.* **1988**, *43*, 722–726.
[16] H. Werner, U. Brekau, *Z. Naturforsch., Teil B*, **1989**, *44*, 1438–1446.
[17] H. Werner, T. Rappert, J. Wolf, *Isr. J. Chem.* **1990**, *30*, 377–384.
[18] M. Schäfer, Dissertation, Universität Würzburg, to be submitted.
[19] F. Kukla, Diplomarbeit, Universität Würzburg, **1992**.
[20] [20a] A. Höhn, H. Otto, M. Dziallas, H. Werner, *J. Chem. Soc., Chem. Commun.* **1987**, 852–854. – [20b] H. Werner, A. Höhn, M. Schulz, *J. Chem. Soc., Dalton Trans.* **1991**, 777–781.
[21] H. Werner, J. Wolf, F. J. Garcia Alonso, M. L. Ziegler, O. Serhadli, *J. Organomet. Chem.* **1987**, *336*, 397–411.
[22] [22a] G. M. Bodner, S. B. Kahl, K. Bork, B. N. Storhoff, J. E. Wuller, L. J. Todd, *Inorg. Chem.* **1973**, *12*, 1071–1074. – [22b] K. H. Dötz, H. Fischer, P. Hofmann, F. R. Kreissl, U. Schubert, K. Weiss, *Transition Metal Carbene Complexes*, Verlag Chemie, Weinheim, **1983**, Chap. 2.
[23] T. Rappert, Dissertation, Universität Würzburg, **1992**.
[24] [24a] D. Schneider, Dissertation, Universität Würzburg, **1992**. – [24b] D. Schneider, O. Nürnberg, H. Werner, *J. Chem. Soc., Chem. Commun.*, submitted for publication.
[25] J. Silvestre, R. Hoffmann, *Helv. Chim. Acta* **1985**, *68*, 1461–1506.
[26] H. Werner, *Angew. Chem.* **1990**, *102*, 1109–1121; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1077–1089.
[27] J. Gotzig, H. Otto, H. Werner, *J. Organomet. Chem.* **1985**, *287*, 247–254.
[28] D. L. Hughes, A. J. L. Pombeiro, C. J. Pickett, R. L. Richards, *J. Chem. Soc., Chem. Commun.* **1984**, 992–993.
[29] [29a] H. Werner, A. Höhn, *J. Organomet. Chem.* **1984**, *272*, 105–113. – [29b] A. Höhn, Dissertation, Universität Würzburg, **1986**.
[30] J. Wolf, H. Werner, *Organometallics* **1987**, *6*, 1164–1169.
[31] S. Otsuka, A. Nakamura, *Adv. Organomet. Chem.* **1976**, *14*, 245–283.
[32] M. Schäfer, J. Wolf, H. Werner, *J. Chem. Soc., Chem. Commun.* **1991**, 1341–1342.
[33] B. L. Shaw, A. J. Stringer, *Inorg. Chim. Acta Rev.* **1973**, *7*, 1–10.
[34] T. Kashiwagi, N. Yasuoka, N. Kasai, M. Kukudo, *Chem. Commun.* **1969**, 317–318.
[35] M. Kadonaga, N. Yasuoka, N. Kasai, *Chem. Commun.* **1971**, 1597.
[36] A. van der Ent, A. L. Onderdelinden, *Inorg. Synth.* **1973**, *14*, 92–95.
[37] R. Cramer, *Inorg. Synth.* **1974**, *15*, 14–18.
[38] U. Schöllkopf, *Methoden Org. Chem. (Houben-Weyl) 4th Ed.* **1970**, vol. XIII/1, p. 118.
[39] C. R. Mitchell, R. A. Zingaro, *Synth. React. Inorg. Met.-Org. Chem.* **1981**, *11*, 1–6.
[40] S. Samaan, *Methoden Org. Chem. (Houben-Weyl) 4th Ed.*, **1978**, vol. XIII/8, p. 445.

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2: 12279-09-3 / **3**: 143171-58-8 / **4**: 143171-59-9 / **5**: 12081-16-2 / **6**: 143171-60-2 / **7**: 143171-61-3 / **8**: 143171-62-4 / **9**: 143171-63-5 / **10**: 143171-64-6 / **11**: 143171-65-7 / **12**: 143171-66-8 / **13**: 143171-67-9 / **14**: 143171-68-0 / **15**: 143171-69-1 / **16**: 143171-70-4 / **17**: 143171-82-8 / **18**: 143171-83-9 / **19**: 143171-71-5 / **20**: 143171-72-6 / **21**: 143171-73-7 / **22**: 143171-74-8 / **22**-d_1: 143171-76-0 / **23**: 143171-75-9 / **25**: 143171-77-1 / **26**: 143171-78-2 / **27**: 143171-79-3 / **27a**-d_2: 143171-81-7 / **27b**-d_2: 143171-80-6 / As*i*Pr_3: 57538-64-4 / Sb*i*Pr_3: 73300-45-5 / Ph_2CN_2: 883-40-9 / HC≡CH: 74-86-2 / PhC≡CH: 536-74-3 / $MeO_2CC{\equiv}CH$: 922-67-8 / MeC≡CH: 74-99-7 / MeC≡CD: 7299-37-8 / MeC≡CLi: 4529-04-8 / *t*BuC≡CH: 917-92-0 / MeC≡CMe: 503-17-3 / MeC≡C*t*Bu: 999-78-0