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Vinylidene transition-metal complexes XXXVI. Olefin, alkyne, vinylidene, carboxylate and hydrido complexes containing $[Rh(P^tBu_2Me)_2]$ as a molecular unit ☆

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Abstract

The reaction of $[RhCl(C_2H_4)_2]_2$ (**1**) with P^tBu_2Me yields the square-planar complex *trans*-$[RhCl(C_2H_4)(P^tBu_2Me)_2]$ (**2**) which upon treatment with H_2 gives the dihydride $[RhH_2Cl(P^tBu_2Me)_2]$ (**3**) and ethane. The alkynerhodium(I) compounds *trans*-$[RhCl(HC{\equiv}CR)(P^tBu_2Me)_2]$ (**4–6**) which have been prepared from **3** and HC≡CR (R = H, Me, Ph), thermally rearrange to the isomeric vinylidene derivatives *trans*-$[RhCl(=C=CHR)(P^tBu_2Me)_2]$ (**7–9**). The synthesis of the π-allyl complexes $[Rh(\eta^3\text{-}2\text{-}RC_3H_4)(P^tBu_2Me)_2]$ (**11, 12**) has been achieved by the stepwise reaction of **1** or $[RhCl(C_8H_{14})_2]_2$ (**10**) with $2\text{-}RC_3H_4MgX$ and the phosphine. From **11** or **12** and acetic or trifluoracetic acid the monomeric carboxylate compounds $[Rh(\eta^2\text{-}O_2CR)(P^tBu_2Me)_2]$ (**13, 14**) have been obtained. Further reaction of **13** and **14** with CO gives the carbonyl derivatives *trans*-$[Rh(\eta^1\text{-}O_2CR)(CO)(P^tBu_2Me)_2]$ (**16, 17**) while on treatment of **14** with ethylene at −20 °C the corresponding 1:1 adduct *trans*-$[Rh(\eta^1\text{-}O_2CCF_3)(C_2H_4)(P^tBu_2Me)_2]$ (**18**) is formed. Both **13** and **14** react with H_2 to yield the dihydrido complexes $[RhH_2(\eta^2\text{-}O_2CR)(P^tBu_2Me)_2]$ (**19, 20**) and with O_2 to afford the dioxygen adducts $[Rh(\eta^2\text{-}O_2)(\eta^2\text{-}O_2CR)(P^tBu_2Me)_2]$ (**21, 22**). The O_2 ligand in **21** and **22** is rather weakly coordinated and can be easily displaced by H_2 to give **19** and **20**, respectively.

Keywords: Rhodium complexes; Olefin complexes; Alkyne complexes; Vinylidene complexes; Carboxylate complexes; Hydrido complexes

1. Introduction

We have been interested for a number of years in the chemistry of vinylidene transition-metal complexes and, if the metal is rhodium, the vinylidene is best stabilized by using triisopropylphosphine as the supporting ligand [2]. With $[RhCl(P^iPr_3)_2]_n$ [3] as the starting material, we succeeded not only in the preparation of the complete series of isomeric alkyne-, alkynyl(hydrido)- and vinylidenerhodium compounds **A**, **B** and **C** [4] but we were also able to generate the corresponding vinylvinylidene- and allenylidenemetal derivatives **D** and **E** (see Fig. 1) by a straightforward route [5]. Since we failed to use compounds of the type **C**, **D** or **E** as metal carbene analogues, for instance in olefin metathesis or carbene transfer reactions, we attempted to replace the rather bulky triisopropylphosphine in these complexes by smaller or less symmetrical phosphine ligands. These attempts were unsuccessful with PMe_3 and PPh_3 but successful with P^tBu_2Me, a ligand which we have already used in ruthenium, osmium and iridium chemistry [6].

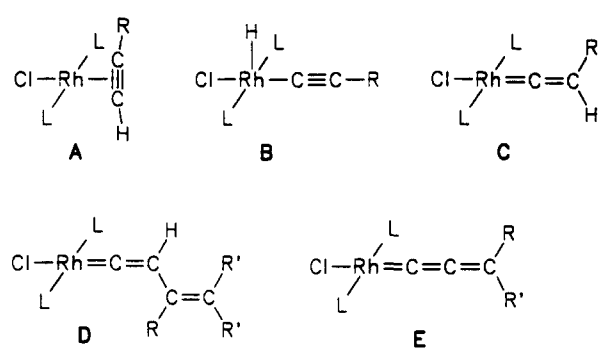

Fig. 1. Rhodium complexes obtained from $[RhCl(P^iPr_3)_2]_n$ as the starting material ($L = P^iPr_3$).

☆ Dedicated to the late Professor Ugo Croatto in recognition of his scientific work and his outstanding service to inorganic chemistry. For Part XXXV see Ref. [1].

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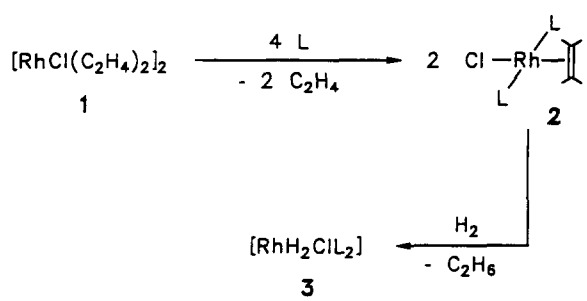
The present article describes the synthesis of a series of ethene-, alkyne-, vinylidene-, allyl-, carboxylate- and hydridorhodium compounds which all contain $[Rh(P^tBu_2Me)_2]$ as a molecular unit [7].

2. Results and discussion

2.1. Hydrido, alkyne and vinylidene complexes

Whereas the dimeric bis(cyclooctene) complex $[RhCl(C_8H_{14})_2]_2$ reacts with excess triisopropylphosphine to give $[RhCl(P^iPr_3)_2]_n$ [3], the corresponding reaction with P^tBu_2Me yields a mixture of products. If, however, the bis(ethene)rhodium(I) derivative $[RhCl(C_2H_4)_2]_2$ (**1**) is treated with 4 equiv. of P^tBu_2Me, the mononuclear olefinbis(phosphine) complex **2** is formed almost quantitatively (Scheme 1). The yellow microcrystalline solid is only slightly air-sensitive and soluble in most common organic solvents. The ^1H and ^{31}P NMR spectroscopic data leave no doubt that the phosphine ligands are *trans* disposed.

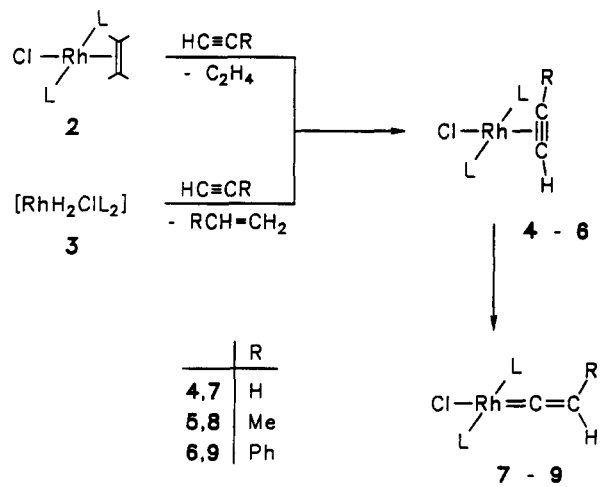
Since recent studies have shown that in some cases (depending on the substituent R) rhodium vinylidenes of composition *trans*-$[RhCl(=C=CHR)(P^iPr_3)_2]$ are preferentially obtained from $[RhH_2Cl(P^iPr_3)_2]$ instead of $[RhCl(P^iPr_3)_2]_n$ as the starting material [8], the dihydridorhodium(III) compound **3** has also been prepared. Upon stirring a solution of **2** in benzene for 24 h under an H_2 atmosphere it is formed in 96% isolated yield. The ^1H NMR spectrum of the yellow solid, which in contrast to **2** is quite air-sensitive, displays a high-field signal at δ −22.4 which due to Rh–H and P–H coupling appears as a doublet-of-triplets. Since the spectroscopic data reveal that the two phosphines are equivalent, the five-coordinate rhodium(III) species could have either a trigonal-bipyramidal or a square-pyramidal geometry, in the latter case with the chloride in the apical position. There is good evidence that both $[RhH_2Cl(PCy_3)_2]$ [9] and $[IrH_2Cl(P^tBu_2Me)_2]$ [6g] possess a trigonal-bipyramidal configuration and thus the same could also be true for **3**.



Scheme 1.

The synthesis of the alkyne complexes **4–6** (Scheme 2) has been achieved from the dihydrido compound **3** and the corresponding terminal alkyne. If instead of **3** the ethene derivative **2** is treated with HC≡CH, HC≡CMe or HC≡CPh (benzene, 25–40 °C), a mixture of products is formed. Although it contains **4**, **5** or **6** as the main component, it could not be completely separated by column chromatography or fractional crystallization. Especially for acetylene and propyne, polymers are also formed in addition to the rhodium-containing species which make the work-up procedure even more difficult. With **3** as the starting material, the yield of the alkyne complexes **4–6**, isolated as red-brown air-sensitive solids, is 70–85%. The corresponding olefin CH_2=CHR (R = H, Me, Ph) has been detected as a by-product by NMR measurements. As far as the spectroscopic data of **4–6** are concerned, the most characteristic features are the intense C≡C stretching frequency in the IR spectra in the 1700–1800 cm^{-1} region and, for **5** and **6**, the appearance of two virtual triplets for the protons of the t-butyl groups which due to the absence of a mirror plane passing through the phosphorus atoms are diastereotopic.

While compounds **4–6** are stable as solids, they rearrange in solution to the isomeric vinylidenerhodium(I) complexes **7–9**. The rate of this rearrangement, which is accompanied by a characteristic change of color from red-brown to deep violet, is significantly slower than in the case of the corresponding bis(triisopropylphosphine) derivatives [4b]. Since various attempts to isolate an intermediate such as **B** (see Fig. 1) in these reactions have failed [7], we believe that in contrast to similar transformations of square-planar 1-alkyne to vinylidene complexes [2] the isomerization does not proceed stepwise but follows a 'slippage' process [10]. Support for this assumption

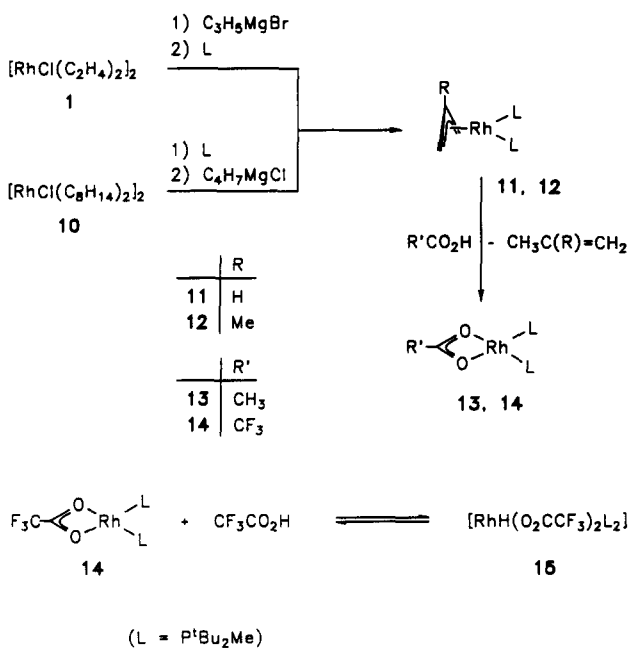


Scheme 2.

arises from the observation that the rearrangement of **4–6** to **7–9** occurs even in neat pyridine and under these conditions does not lead to octahedral pyridine adducts $[RhH(C{\equiv}CR)Cl(py)(P^tBu_2Me)_2]$ (for comparison see Ref. [4]). Regarding the NMR spectroscopic data of the vinylidene complexes **7–9**, which are only moderately air-sensitive, the low field signal in the ^{13}C NMR spectra at δ 293–305 is most noteworthy and indicative of the metal-bound carbon atom of the Rh=C=CHR moiety. We note that this signal appears in the same region as for compounds **C** and **D** (Fig. 1) and as that of a coordinated carbene C atom [11].

2.2. Allyl and carboxylate complexes

In order to broaden the scope of reactive compounds containing the $[Rh(P^tBu_2Me)_2]$ unit, the π-allyl complexes **11** and **12** (Scheme 3) have been prepared. Since a starting material of general composition $[RhClL_2]_n$ with $L=P^tBu_2Me$ is not available, on treatment of **1** with C_3H_5MgBr we first generated the very labile intermediate $[Rh(\eta^3\text{-}C_3H_5)(C_2H_4)_2]$ and reacted this in situ with excess phosphine. Compound **11** was thus obtained in 76% yield. To prepare the 2-methallyl complex **12**, the reverse sequence of reaction steps was applied, i.e. the bis(olefin)rhodium(I) derivative **10** was treated in ether solution at −20 °C first with P^tBu_2Me and then with the Grignard reagent C_4H_7MgCl. In this case the yield was 64%. It should be noted that the synthetic procedure for **12** is analogous to that which was already used for the preparation of the iridium complexes $[Ir(\eta^3\text{-}2\text{-}RC_3H_4)(P^iPr_3)_2]$ (R=H, Me) [12] and which had recently also been applied for $[Rh(\eta^3\text{-}2\text{-}MeC_3H_4)(P^iPr_3)(PMe_3)]$ [13]. Although the π-allyl compounds **11** and **12** are very air-sensitive solids, which slowly decompose even under argon at low temperatures, they both have been characterized by elemental analyses and spectroscopic means. The ^1H NMR spectra of **11** and **12** reveal only one resonance for the *syn* and one for the *anti* protons of the CH_2 units and therefore indicate that symmetrical π-allyl ligands are present.

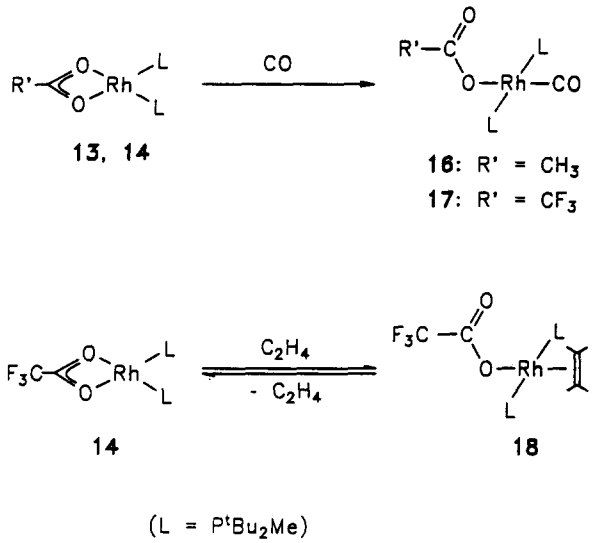


Scheme 3.

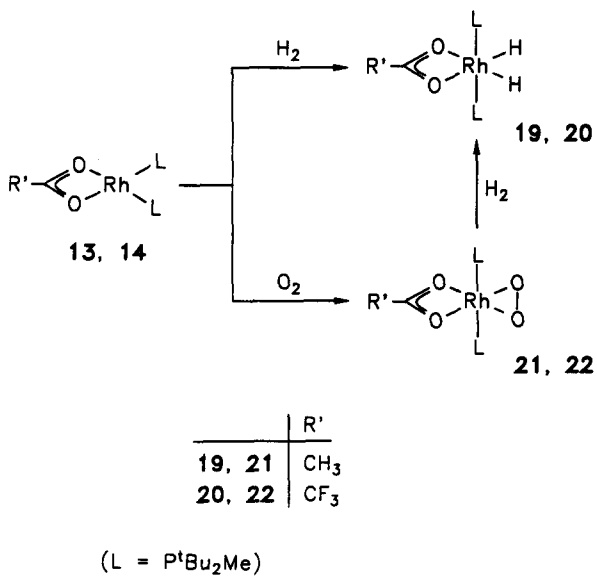
Treatment of the π-allyl complexes **11** and **12** with CH_3CO_2H and CF_3CO_2H affords the carboxylate derivatives **13** and **14** in moderate to good yields. Both compounds are dark red crystalline solids which are rather air-sensitive but can be stored under argon at −20 °C for weeks. Although X-ray structural investigations of several rhodium(I) carboxylates have shown that at least in the solid state they are dimers [14], the IR spectroscopic data of **13** and **14** with ν(OCO) at 1525 and 1440 cm^{-1} (for **13**) and 1610 and 1460 cm^{-1} (for **14**) suggest that these compounds like $[Rh(\eta^2\text{-}O_2CCH_3)(P^iPr_3)_2]$ (ν(OCO) 1535 and 1440 cm^{-1}) [13] are monomeric species. It has been pointed out [15] that the positions of the symmetric and asymmetric OCO stretching frequencies as well as their energy difference are distinctly different for monodentate, bidentate and bridging (chelating) carboxylate ligands, and the reference data for compounds of general composition $[M(\eta^2\text{-}O_2CR)L_n]$ support our structural proposal. With regard to the mechanism of the reaction of **11** and **12** with RCO_2H, we assume that initially an oxidative addition of the carboxylic acid to the metal center takes place (for comparison see Ref. [13]) which is followed by a reductive elimination of propene or isobutene, respectively. That compounds structurally related to **11** and **12** are able to react with RCO_2H by addition to give hydrido(carboxylate)metal species is illustrated by the formation of $[RhH(O_2CCF_3)_2(P^tBu_2Me)_2]$ (**15**) (Scheme 3). The yellow crystalline substance which is stable as a solid readily dissociates in solution to reform the starting materials **14** and CF_3CO_2H.

The pronounced ability of chelating carboxylate metal complexes to open the metal–chelate bond is equally found for **13** and **14**. If a slow stream of CO is passed through a solution of **13** or **14** in pentane, a rapid change of color from deep red to yellow occurs and the carbonylrhodium(I) compounds **16** and **17** are formed almost quantitatively (Scheme 4). Since the signal pattern in the ^1H NMR spectra for both the PCH_3 and $PCCH_3$ protons of the phosphine ligands corresponds to a virtual triplet [16], there is no doubt that **16** and **17** have a square-planar *trans*-configuration.

Whereas compound **13** is rather inert toward ethylene at room temperature, the trifluoracetate complex **14** reacts with C_2H_4 in pentane at −20 °C slowly to give the 1:1 adduct **18** in about 60% yield. In analogy to **15**, the ethylene complex **18** is quite labile and even



Scheme 4.



Scheme 5.

if it is stored under argon at 0 °C it loses the olefinic ligand to regenerate the starting material. Despite the lability of **18**, the ^1H and ^{31}P NMR spectra could be measured and are in good agreement with the structural proposal shown in Scheme 4.

The carboxylate compounds **13** and **14** not only react with CO and C_2H_4 but also with H_2 and O_2 to yield the corresponding dihydrido and η^2-dioxygen complexes **19, 20** and **21, 22**, respectively (Scheme 5). All these compounds are crystalline, quite air-stable solids which are easily soluble in most organic solvents. Due to the striking similarities in both the IR and NMR spectroscopic data of **19, 20** and **21, 22**, it is clear that the dihydrido as well as the η^2-dioxygen rhodium derivatives possess an octahedral geometry. In each case the *trans*-position of the phosphine ligands is evident from the appearance of only one signal in the ^{31}P NMR spectra and from the virtual coupling observed for the resonances of the PCH_3 and $PCCH_3$ protons in the ^1H NMR spectra. The latter display only one resonance at high fields (for **19** at δ −22.96 and for **20** at δ −23.60) which confirms that the two hydride ligands are also equivalent.

Although in contrast to $[Rh(\eta^2\text{-}O_2)(\eta^2\text{-}O_2CR)(P^iPr_3)_2]$ [17] the dioxygen complexes **21** and **22** are stable in solution (benzene or CH_2Cl_2) for days, they nevertheless smoothly react with H_2 to give the dihydrido compounds **19** and **20** almost quantitatively. The reverse reaction from **19** and **20** with oxygen to yield **21** and **22** does not occur, at least not at room temperature and 1 atm of O_2. We failed to detect H_2O or H_2O_2 as by-products in the reaction of **21** and **22** with H_2 and therefore we have to assume that it is a simple ligand displacement process.

3. Conclusions

The work described here has confirmed that starting from the bis(olefin)metal compounds **1** and **10** a series of rhodium(I) and rhodium(III) complexes with $[Rh(P^tBu_2Me)_2]$ as a molecular building block is accessible. Particularly promising for further studies are both the dihydridometal derivatives **3, 19** and **20** as well as the π-allyl complexes **11** and **12** which according to recent findings with bis(triisopropylphosphine)-rhodium counterparts $[RhH_2X(P^iPr_3)_2]$ and $[Rh(\eta^3\text{-}2\text{-}RC_3H_4)(P^iPr_3)_2]$ can possibly be used as starting materials for C–C coupling [18] and catalytic hydrogenation reactions [19]. Whether compounds such as **13** and **14** are also candidates for the C–H activation of olefinic and aromatic hydrocarbons is one topic of our current research interests.

4. Experimental

All reactions were carried out under an atmosphere of argon by Schlenk tube techniques. The starting materials $[RhCl(C_2H_4)_2]_2$ (**1**) [20], $[RhCl(C_8H_{14})_2]_2$ (**10**) [21], and the phosphine P^tBu_2Me [22] were prepared as described in the literature. NMR spectra were recorded at room temperature on JEOL FX 90 Q, Varian EM 360 L and Bruker AMX 400 instruments, and IR spectra on a Perkin-Elmer 1420 spectrophotometer. Melting points were determined with a Büchi SMP 20 apparatus. Abbreviations used: s = singlet, d = doublet, t = triplet, q = quartet, vt = virtual triplet, m = multiplet, br = broad, $N = {}^3J(PH) + {}^5J(PH)$, $N' = {}^2J(PH) + {}^4J(PH)$.

4.1. Trans-[RhCl(C_2H_4)(P^tBu_2Me)$_2$] (2)

A solution of **1** (136 mg, 0.35 mmol) in 40 ml of ether was treated at −20 °C with P^tBu_2Me (0.28 ml, 1.40 mmol). After warming to room temperature the solvent was removed, the residue was extracted with 20 ml of pentane, and the extract was brought to dryness in vacuo. A yellow solid was obtained which was washed twice with 3 ml of pentane (0 °C), and dried in vacuo; yield 293 mg (86%); m.p. 124 °C (dec.). IR (KBr): ν(C=C) 1465 cm^{-1}. ^{1}H NMR (C_6D_6, 90 MHz): δ 2.19 (dt, J(RhH) = 2.1, J(PH) = 4.2 Hz, 4H, C_2H_4), 1.40 (vt, N = 12.5 Hz, 36 H, PCCH$_3$), 0.44 (m, 6H, PCH$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 27.03 (d, J(RhP) = 123.1 Hz). *Anal.* Calc. for $C_{20}H_{46}ClP_2Rh$: C, 49.34; H, 9.52. Found: C, 49.23; H, 9.78%.

4.2. [$RhH_2Cl(P^tBu_2Me)_2$] (3)

A solution of **2** (80 mg, 0.16 mmol) in 10 ml of benzene was stirred under an atmosphere of hydrogen for 24 h at room temperature. The solvent was removed, and the residue was extracted with 20 ml of pentane. The extract was concentrated in vacuo until a precipitate occurred and was then stored at −78 °C. Yellow crystals were formed which were filtered off, repeatedly washed with pentane (0 °C), and dried in vacuo; yield 71 mg (96%); m.p. 86 °C (dec.). IR (KBr): ν(RhH) 2100 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 1.43 (m, 6H, PCH$_3$), 1.17 (vt, N = 13.0 Hz, 36H, PCCH$_3$), −22.40 (dt, J(RhH) = 25.6, J(PH) = 15.2 Hz, 2H, RhH$_2$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 55.82 (d, J(RhP) = 115.0 Hz). *Anal.* Calc. for $C_{18}H_{44}ClP_2Rh$: C, 46.91; H, 9.62. Found: C, 47.62; H, 10.25%.

4.3. Trans-[RhCl(HC≡CH)($P^tBu_2Me)_2$] (4)

A stream of acetylene was passed through a solution of **3** (80 mg, 0.17 mmol) in 5 ml of pentane for ~15 s. After the solution was stirred for 24 h at room temperature, the solvent was removed and the residue was extracted with 20 ml of pentane. The extract was concentrated in vacuo to ~3 ml and then stored at −78 °C. Red–brown air-sensitive crystals were formed, which were filtered off, repeatedly washed with pentane (0 °C), and dried thoroughly; yield 59 mg (70%); m.p. 103 °C (dec.). IR (KBr): ν(≡CH) 3140, ν(C≡C) 1705 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 3.15 (d, J(RhH) = 2.6 Hz, 2H, C_2H_2), 1.39 (vt, N = 12.4 Hz, 36 H, PCCH$_3$), 0.38 (m, 6H, PCH$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 28.07 (d, J(RhP) = 119.0 Hz). *Anal.* Calc. for $C_{20}H_{44}ClP_2Rh$: C, 49.54; H, 9.15. Found: C, 49.50; H, 9.33%.

4.4. Trans-[RhCl(HC≡CMe)($P^tBu_2Me)_2$] (5)

This compound was prepared as described for **4**, using **3** (85 mg, 0.18 mmol) and propyne as starting materials. Red–brown air-sensitive crystals were obtained; yield 77 mg (86%); m.p. 98 °C (dec.). IR (KBr): ν(≡CH) 3110, ν(C≡C) 1825 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 2.53 (dq, J(HH) = 2.5, J(RhH) = 2.4 Hz, 1H, ≡CH), 1.83 (dd, J(HH) = 2.5, J(RhH) = 0.8 Hz, 3H, ≡CMe), 1.45 (vt, N = 12.7 Hz, 18H, PCCH$_3$), 1.40 (vt, N = 12.0 Hz, 18H, PCCH$_3$), 0.45 (vt, N' = 4.1 Hz, 6H, PCH$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 30.07 (d, J(RhP) = 121.7 Hz). *Anal.* Calc. for $C_{21}H_{46}ClP_2Rh$: C, 50.56; H, 9.29. Found: C, 50.42; H, 9.73%.

4.5. Trans-[RhCl(HC≡CPh)($P^tBu_2Me)_2$] (6)

A solution of **3** (80 mg, 0.17 mmol) in 5 ml of pentane was treated with phenylacetylene (38.4 μl, 0.34 mmol) and stirred for 24 h at room temperature. The solvent was removed in vacuo and the residue was extracted with 20 ml of pentane. The extract was concentrated to ~3 ml and then stored at −78 °C. A brown air-sensitive solid was formed, which was filtered off, washed twice with ~3 ml of pentane (0 °C), and dried in vacuo; yield 78 mg (82%); m.p. 93 °C (dec.). IR (KBr): ν(≡CH) 3100, ν(C≡C) 1805 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 6.58–8.02 (m, 5H, C_6H_5), 3.78 (d, J(RhH) = 2.6 Hz, 1H, ≡CH), 1.44 (vt, N = 12.8 Hz, 18H, PCCH$_3$), 1.37 (vt, N = 12.0 Hz, 18H, PCCH$_3$), 0.36 (vt, N' = 4.1 Hz, 6H, PCH$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 30.61 (d, J(RhP) = 118.1 Hz). *Anal.* Calc. for $C_{26}H_{48}ClP_2Rh$: C, 55.67; H, 8.62. Found: C, 56.41; H, 9.06%.

4.6. Trans-[RhCl(=C=CH_2)($P^tBu_2Me)_2$] (7)

A solution of **4** (87 mg, 0.18 mmol) in 5 ml of benzene was stirred for 24 h at room temperature. A change of color from brown to violet occurred. The solvent was removed, and the residue was extracted with 20 ml of pentane. The extract was concentrated to ~3 ml in vacuo and then stored at −78 °C. Violet moderately air-sensitive crystals were formed, which were filtered off, washed twice with ~ 3 ml of pentane (0 °C), and dried in vacuo; yield 58 mg (65%); m.p. 101 °C (dec.). IR (KBr): ν(C=C) 1625 cm^{-1}. ^{1}H NMR (C_6D_6, 90 MHz): δ 1.37 (vt, N = 12.9 Hz, PCCH$_3$), −0.06 (s, 2H, =CH_2), signal of PCH$_3$ probably covered by signal of PCCH$_3$. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 304.70 (s, br, Rh=*C*=C), 90.51 (s, br, Rh=C=*C*), 34.11 (s, br, PCCH$_3$), 29.00 (s, br, PCCH$_3$), 4.46 (s, br, PCH$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 32.26 (d, J(RhP) = 115.8 Hz). *Anal.* Calc. for $C_{20}H_{44}ClP_2Rh$: C, 49.54; H, 9.15. Found: C, 49.52; H, 9.41%.

4.7. *Trans-[RhCl(=C=CHMe)(P^{t}Bu$_2$Me)$_2$] (8)*

This compound was prepared as described for **7**, using **5** (100 mg, 0.20 mmol) as starting material. After the solution had been stirred for 48 h at room temperature, the solvent was removed in vacuo, and the red residue was extracted with 20 ml of pentane. The extract was concentrated to ~ 3 ml and stored at −78 °C. Moderately air-sensitive crystals were formed, which were filtered off, repeatedly washed with 3 ml of pentane (0 °C), and dried thoroughly; yield 58 mg (58%); m.p. 93 °C (dec.). ^{1}H NMR (C_6D_6, 400 MHz): δ 1.77 (dt, J(PH) = 2.6, J(HH) = 7.4 Hz, 3H, =CHCH_3), 1.37 (vt, N = 12.1 Hz, 36H, PCCH_3), 0.61 (m, 6H, PCH_3), 0.38 (tq, J(PH) = 3.7, J(HH) = 7.4 Hz, 1H, =CHCH$_3$). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 293.50 (s, br, Rh=C=C), 99.51 (s, br, Rh=C=C), 33.72 (s, br, PCCH$_3$), 28.96 (s, br, PCCH$_3$), 4.35 (s, br, PCH$_3$), −2.94 (s, =CHCH$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 34.16 (d, J(RhP) = 156.8 Hz). *Anal.* Calc. for $C_{21}H_{46}ClP_2Rh$: C, 50.56; H, 9.29. Found: C, 50.81; H, 9.49%.

4.8. *Trans-[RhCl(=C=CHPh)(P^{t}Bu$_2$Me)$_2$] (9)*

This compound was prepared as described for **7**, using **6** (90 mg, 0.16 mmol) as starting material. The reaction mixture was stirred for 5 days at room temperature. Violet crystals were obtained; yield 56 mg (62%); m.p. 104 °C (dec.). ^{1}H NMR (C_6D_6, 400 MHz): δ 7.15 (m, 5H, C_6H_5), 1.38 (vt, N = 13.1 Hz, PCCH$_3$), 1.28 (m, 6H, PCH$_3$), signal of =CHPh probably covered by signal of PCCH$_3$. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 295.01 (s, br, Rh=C=C), 111.81 (s, br, Rh=C=C), 127.44, 123.82, 123.62 (all s, C_6H_5), 34.04 (s, br PCCH$_3$), 28.97 (s, br, PCCH$_3$), 4.36 (s, br, PCH$_3$), signal of *ipso*-C_6H_5 probably covered by signal of C_6D_6. ^{31}P NMR (C_6D_6, 36.2 MHz): δ 33.07 (d, J(RhP) = 139.2 Hz). *Anal.* Calc. for $C_{26}H_{48}ClP_2Rh$: C, 55.67; H, 8.62. Found: C, 56.10; H, 8.30%.

4.9. *[Rh(η^3-C_3H_5)(P^{t}Bu$_2$Me)$_2$] (11)*

A solution of **1** (272 mg, 0.70 mmol) in 40 ml of ether was added dropwise to an ether solution of (C_3H_5)MgBr (1.53 ml, 0.72 mmol) at −20 °C. The yellow reaction mixture was then treated with P^{t}Bu$_2$Me (0.28 ml, 1.40 mmol) and stirred for 10 min at room temperature. The solvent was removed, the residue was extracted with 40 ml of pentane, and the extract was brought to dryness in vacuo. Yellow, very air-sensitive crystals were formed which were filtered off, washed twice with 3 ml of acetone (0 °C), and dried in vacuo; yield 247 mg (76%); m.p. 86 °C (dec.). ^{1}H NMR (C_6D_6, 400 MHz): δ 4.63 (dtt, J(RhH) = 2.1, J(HH) = 6.7, J(HH) = 11.7 Hz, 1H, CH of allyl), 3.74 (d, J(HH) = 6.7 Hz, 2H, H *syn* of CH$_2$), 1.92 (dd, J(PH) = 6.1, J(HH) = 11.7 Hz, 2H, H *anti* of CH$_2$), 1.22 (d, J(PH) = 12.0 Hz, 18H, PCCH$_3$), 1.14 (d, J(PH) = 4.3 Hz, 6H, PCH$_3$), 1.11 (d, J(PH) = 11.6 Hz, 18H, PCCH$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 53.25 (d, J(RhP) = 196.4 Hz). *Anal.* Calc. for $C_{21}H_{47}P_2Rh$: C, 54.31; H, 10.20. Found: C, 54.82; H, 10.32%.

4.10. *[Rh(η^3-2-MeC_3H_4)(P^{t}Bu$_2$Me)$_2$] (12)*

A suspension of **10** (250 mg, 0.35 mmol) in 40 ml of ether was first treated at −20 °C with P^{t}Bu$_2$Me (0.14 ml, 0.70 mmol) and then dropwise with an ether solution of 2-MeC_3H_4MgBr (1.60 ml, 0.72 mmol). After the pale yellow reaction mixture was stirred for 5 min, a second quantity of P^{t}Bu$_2$Me (0.14 ml, 0.70 mmol) was added. The solvent was removed, the residue was extracted with 40 ml of pentane, and the extract was brought to dryness in vacuo. Yellow, very air-sensitive crystals were formed which were repeatedly washed with 3 ml of acetone (0 °C), and dried thoroughly; yield 214 mg (64%); m.p. 98 °C (dec.). ^{1}H NMR (C_6D_6, 400 MHz): δ 3.50 (s, 2H, H *syn* of CH$_2$), 2.01 (d, J(PH) = 6.2 Hz, 2H, H *anti* of CH$_2$), 1.81 (d, J(RhH) = 2.4 Hz, 3H, *Me*C_3H_4), 1.22 (d, J(PH) = 11.9 Hz, 18H, PCCH$_3$), 1.15 (d, J(PH) = 11.6 Hz, 18H, PCCH$_3$), 0.80 (d, J(PH) = 4.3 Hz, 6H, PCH$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 53.86 (d, J(RhP) = 194.3 Hz). *Anal.* Calc. for $C_{22}H_{49}P_2Rh$: C, 55.23; H, 10.32. Found: C, 55.54; H, 10.48%.

4.11. *[Rh(η^2-O_2CCH$_3$)(P^{t}Bu$_2$Me)$_2$] (13)*

A solution of **11** (90 mg, 0.20 mmol) in 5 ml of benzene was treated with acetic acid (11.4 μl, 0.20 mmol) and stirred for 1 h at room temperature. A change of color from yellow to dark red occurred. The solvent was removed in vacuo and the residue dissolved in 3 ml of acetone. After the solution was cooled to −78 °C, dark red air-sensitive crystals were formed which were filtered off, washed twice with 2 ml of pentane (0 °C), and dried thoroughly; yield 58 mg (60%); m.p. 114 °C (dec.). IR (pentane): ν(OCO) 1525, 1440 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 1.77 (s, 3H, O_2CCH$_3$), 1.42 (d, J(PH) = 12.1 Hz, 36H, PCCH$_3$), 0.75 (dd, J(PH) = 7.8, J(RhH) = 1.5 Hz, 6H, PCH$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 62.44 (d, J(RhP) = 206.6 Hz). *Anal.* Calc. for $C_{20}H_{45}O_2P_2Rh$: C, 49.79; H, 9.40. Found: C, 49.86; H, 9.60%.

4.12. *[Rh(η^2-O_2CCF$_3$)(P^{t}Bu$_2$Me)$_2$] (14)*

This compound was prepared as described for **13**, using **11** and an ether solution of CF_3CO_2H (0.40 ml, 0.20 mmol) as starting materials. Dark red air-sensitive crystals were obtained; yield 57 mg (53%); m.p. 106 °C (dec.). IR (pentane): ν(OCO) 1610, 1460 cm^{-1}. ^{1}H

NMR (C_6D_6, 400 MHz): δ 1.27 (d, J(PH) = 12.5 Hz, 36H, $PCCH_3$), 1.24 (dd, J(PH) = 7.0, J(RhH) = 1.5 Hz, 6H, PCH_3). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 63.65 (d, J(RhP) = 215.4 Hz). *Anal.* Calc. for $C_{20}H_{42}F_3O_2P_2Rh$: C, 44.78; H, 7.89. Found: C, 44.26; H, 8.18%.

4.13. *[RhH(O$_2$CCF$_3$)$_2$(P^{t}Bu$_2$Me)$_2$] (15)*

A solution of **14** (80 mg, 0.15 mmol) in 10 ml of ether was treated dropwise with an ether solution of CF_3CO_2H (0.80 ml, 0.40 mmol) at −20 °C. A change of color from red to yellow occurred. After the reaction mixture was warmed to room temperature, it was concentrated to ~5 ml in vacuo and then stored at −78 °C. Yellow air-sensitive crystals were formed which were filtered off, washed twice with 2 ml of pentane (0 °C), and dried in vacuo; yield 40 mg (62%); m.p. 65 °C (dec.). IR (KBr): ν(OCO) 1670 cm^{-1}. ^1H NMR (C_6D_6, 400 MHz): δ 1.22 (vt, N = 14.4 Hz, $PCCH_3$), −23.58 (dt, J(PH) = 14.8, J(RhH) = 27.6 Hz, 1H, RhH), signal of PCH_3 probably covered by signal of $PCCH_3$. ^{31}P NMR (C_6D_6, 36.2 MHz): δ 58.92 (d, J(RhP) = 115.8 Hz). *Anal.* Calc. for $C_{22}H_{43}F_6O_4P_2Rh$: C, 40.63; H, 6.66. Found: C, 39.92; H, 6.66%.

4.14. *Trans-[Rh(η^1-O$_2$CCH$_3$)(CO)(P^{t}Bu$_2$Me)$_2$] (16)*

A slow stream of carbon monoxide was passed through a solution of **13** (77 mg, 0.16 mmol) in 10 ml of pentane for 2 min at room temperature. A change of color from dark red to yellow occurred. The reaction mixture was concentrated to ~5 ml in vacuo and then stored at −78 °C. Yellow air-stable crystals were formed which were filtered off, repeatedly washed with 2 ml of pentane (0 °C), and dried thoroughly; yield 74 mg (90%); m.p. 185 °C (dec.). IR (KBr): ν(CO) 1935, ν(OCO) 1615, 1370 cm^{-1}. ^1H NMR (C_6D_6, 400 MHz): δ 2.12 (s, 3H, O_2CCH_3), 1.35 (vt, N = 13.3 Hz, 36H, $PCCH_3$), 1.32 (vt, N' = 6.5 Hz, 6H, PCH_3). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 50.70 (d, J(RhP) = 129.0 Hz). *Anal.* Calc. for $C_{21}H_{45}O_3P_2Rh$: C, 49.41; H, 8.89. Found: C, 49.69; H, 9.11%.

4.15. *Trans-[Rh(η^1-O$_2$CCF$_3$)(CO)(P^{t}Bu$_2$Me)$_2$] (17)*

This compound was prepared as described for **16**, using **14** (86 mg, 0.16 mmol) as starting material. Yellow air-stable crystals were obtained; yield 79 mg (88%); m.p. 188 °C (dec.). IR (KBr): ν(CO) 1950, ν(OCO) 1695, 1475 cm^{-1}. ^1H NMR (C_6D_6, 400 MHz): δ 1.27 (vt, N = 13.5 Hz, 36H, $PCCH_3$), 1.21 (vt, N' = 5.7 Hz, 6H, PCH_3). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 48.86 (d, J(RhP) = 124.6 Hz). *Anal.* Calc. for $C_{21}H_{42}F_3O_3P_2Rh$: C, 44.69; H, 7.50. Found: C, 44.80; H, 7.46%.

4.16. *Trans-[Rh(η^1-O$_2$CCF$_3$)(C$_2$H$_4$)(P^{t}Bu$_2$Me)$_2$] (18)*

A stream of ethylene was passed through a solution of **14** (86 mg, 0.16 mmol) in 10 ml of pentane for 10 min at −20 °C. A change of color from red to yellow occurred. The reaction mixture was then cooled to −78 °C. Yellow air-stable crystals were formed which were filtered off, washed twice with 2 ml of pentane (0 °C), and dried in vacuo; yield 56 mg (62%); m.p. 81 °C (dec.). IR (KBr): ν(=CH) 3055, ν(OCO) 1690, ν(C=C) 1460 cm^{-1}. ^1H NMR (C_6D_6, 400 MHz): δ 2.15 (s, br, 4H, C_2H_4), 1.33 (vt, N = 13.0 Hz, 36H, $PCCH_3$), 0.38 (m, 6H, PCH_3). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 30.42 (d, J(RhP) = 123.1 Hz). *Anal.* Calc. for $C_{22}H_{46}F_3O_2P_2Rh$: C, 46.81; H, 8.21. Found: C, 45.91; H. 8.45%.

4.17. *[RhH$_2$(η^2-O$_2$CCH$_3$)(P^{t}Bu$_2$Me)$_2$] (19)*

A solution of **13** (80 mg, 0.17 mmol) in 10 ml of pentane was stirred under an atmosphere of hydrogen for 24 h at room temperature. A change of color from red to yellow occurred. The solvent was removed in vacuo, and the residue was extracted with 20 ml of pentane. The extract was concentrated until a precipitate occurred, and was then stored at −78 °C for 12 h. Yellow crystals were formed, which were filtered off, repeatedly washed with pentane (0 °C), and dried in vacuo; yield 77 mg (93%); m.p. 131 °C (dec.). IR (KBr): ν(RhH) 2150, ν(OCO) 1540 cm^{-1}. ^1H NMR (C_6D_6, 400 MHz): δ 2.19 (s, 3H, O_2CCH_3), 1.47 (vt, N' = 5.4 Hz, 6H, PCH_3), 1.35 (vt, N = 12.7 Hz, 36H, $PCCH_3$), −22.96 (dt, J(RhH) = 24.0, J(PH) = 15.2 Hz, 2H, RhH_2). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 61.28 (d, J(RhP) = 117.2 Hz). *Anal.* Calc. for $C_{20}H_{47}O_2P_2Rh$: C, 49.59; H, 9.78. Found: C, 49.62; H, 9.91%.

4.18. *[RhH$_2$(η^2-O$_2$CCF$_3$)(P^{t}Bu$_2$Me)$_2$] (20)*

This compound was prepared as described for **19**, using **14** (91 mg, 0.17 mmol) as starting material. Yellow moderately air-sensitive crystals were obtained; yield 81 mg (89%); m.p. 122 °C (dec.). IR (KBr): ν(RhH) 2160, ν(OCO) 1625 cm^{-1}. ^1H NMR (C_6D_6, 400 MHz): δ 1.21 (vt, N = 13.0 Hz, $PCCH_3$), −23.60 (dt, J(RhH) = 27.2, J(PH) = 15.2 Hz, 2H, RhH_2), signal of PCH_3 probably covered by signal of $PCCH_3$. ^{31}P NMR (C_6D_6, 36.2 MHz): δ 58.92 (d, J(RhP) = 115.8 Hz). *Anal.* Calc. for $C_{20}H_{44}F_3O_2P_2Rh$: C, 44.78; H, 8.27. Found: C, 44.76; H, 8.46%.

4.19. *[RhO$_2$(η^2-O$_2$CCH$_3$)(P^{t}Bu$_2$Me)$_2$] (21)*

A solution of **13** (80 mg, 0.17 mmol) in 10 ml of pentane was stirred under an atmosphere of oxygen for 1 h at room temperature. A change of color from red to pale green occurred. The solvent was removed,

and the residue was extracted with 20 ml of pentane. The extract was concentrated in vacuo until a precipitate occurred, and was then stored at −78 °C for 12 h. Yellow air-stable crystals were formed, which were filtered off, repeatedly washed with pentane (0 °C), and dried thoroughly; yield 79 mg (90%); m.p. 118 °C (dec.). IR (pentane): ν(OCO) 1545, ν(O–O) 905 cm^{-1}. ^1H NMR (C_6D_6, 60 MHz): δ 1.75 (s, 3H, O_2CCH_3), 1.42 (vt, N = 16.5 Hz, 36H, $PCCH_3$), 1.02 (vt, N' = 6.0 Hz, 6H, PCH_3). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 32.48 (d, J(RhP) = 105.5 Hz). *Anal.* Calc. for $C_{20}H_{45}O_4P_2Rh$: C, 46.70; H, 8.82. Found: C, 46.47; H, 8.84%.

4.20. $[RhO_2(\eta^2\text{-}O_2CCF_3)(P^tBu_2Me)_2]$ (22)

This compound was prepared as described for **21**, using **14** (91 mg, 0.17 mmol) as starting material. Yellow air-stable crystals were obtained; yield 82 mg (85%); m.p. 95 °C (dec.). IR (KBr): ν(OCO) 1610, ν(O–O) 905 cm^{-1}. ^1H NMR (C_6D_6, 60 MHz): δ 1.37 (vt, N = 13.0 Hz, 36H, $PCCH_3$), 0.89 (vt, N' = 6.0 Hz, 6H, PCH_3). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 30.06 (d, J(RhP) = 99.7 Hz). *Anal.* Calc. for $C_{20}H_{42}F_3O_4P_2Rh$: C, 42.26; H, 7.45. Found: C, 42.38; H, 7.77%.

4.21. Reactions of compounds 21 and 22 with H_2

A solution of **21** (100 mg, 0.20 mmol) or **22** (100 mg, 0.18 mmol) in 10 ml of pentane was stirred under an atmosphere of hydrogen for 1 h at room temperature. After the same work-up procedure was applied as described for **19** and **20**, yellow crystalline solids were obtained which by spectroscopic means were identified as **19** and **20**, respectively.

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References

[1] H. Werner, A. Stark, P. Steinert, C. Grünwald and J. Wolf, *Chem. Ber., 128* (1995) 49.

[2] H. Werner, *Nachr. Chem. Tech. Lab., 40* (1992) 435; *J. Organomet. Chem., 475* (1994) 45.

[3] (a) Preparation in situ: C. Busetto, A. D'Alfonso, F. Maspero, G. Perego and A. Zazzetta, *J. Chem. Soc., Dalton Trans.*, (1977) 1828; (b) Isolation: H. Werner, J. Wolf and A. Höhn, *J. Organomet. Chem., 287* (1985) 395; (c) Molecular structure: P. Binger, J. Haas, G. Glaser, R. Goddard and C. Krüger, *Chem. Ber., 127* (1994) 1927.

[4] (a) H. Werner, J. Wolf, F.J. Garcia Alonso, M.L. Ziegler and O. Serhadli, *J. Organomet. Chem., 336* (1987) 397; (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; (d) H. Werner, T. Rappert and J. Wolf, *Isr. J. Chem., 30* (1990) 377; (e) T. Rappert, O. Nürnberg and H. Werner, *Organometallics, 12* (1993) 1359.

[5] (a) T. Rappert, O. Nürnberg, N. Mahr, J. Wolf and H. Werner, *Organometallics, 11* (1992) 4156; (b) H. Werner and T. Rappert, *Chem. Ber., 126* (1993) 669; (c) H. Werner, T. Rappert, R. Wiedemann, J. Wolf and N. Mahr, *Organometallics, 13* (1994) 2721.

[6] (a) H. Werner, M.A. Esteruelas, U. Meyer and B. Wrackmeyer, *Chem. Ber., 120* (1987) 11; (b) A. Andriollo, M.A. Esteruelas, U. Meyer, L.A. Oro, R.A. Sanchez-Delgado, E. Sola, C. Valero and H. Werner, *J. Am. Chem.Soc., 111* (1989) 7431; (c) H. Werner, U. Meyer, K. Peters and H.G. von Schnering, *Chem. Ber., 122* (1989) 2097; (d) U. Meyer and H. Werner, *Chem. Ber., 123* (1990) 697; (e) M. Aracama, M.A. Esteruelas, F.J. Lahoz, J.A. Lopez, U. Meyer, L.A. Oro and H. Werner, *Inorg. Chem., 30* (1991) 288; (f) W. Knaup and H. Werner, *J. Organomet. Chem., 411* (1991) 471; (g) H. Werner, T. Dirnberger and A. Höhn, *Chem. Ber., 124* (1991) 1957; (h) H. Werner, R. Weinand, W. Knaup, K. Peters and H.G. von Schnering, *Organometallics, 10* (1991) 3967; (i) M.A. Esteruelas, F.J. Lahoz, J.A. Lopez, L.A. Oro, C. Schlünken, C. Valero and H. Werner, *Organometallics, 11* (1992) 2034; (j) H. Werner, T. Daniel, O. Nürnberg, W. Knaup and U. Meyer, *J. Organomet. Chem., 445* (1993) 229; (k) C. Schlünken and H. Werner, *J. Organomet. Chem., 454* (1993) 243; (l) T. Daniel, W. Knaup, M. Dziallas and H. Werner, *Chem. Ber., 126* (1993) 1981; (m) H. Werner, T. Daniel, W. Knaup and O. Nürnberg, *J. Organomet. Chem., 462* (1993) 309; (n) T. Daniel and H. Werner, *J. Chem. Soc., Dalton Trans.*, (1994) 221.

[7] F. Kukla, *Diploma Thesis*, Universität Würzburg, Germany, 1992.

[8] M. Schäfer, *Dissertation*, Universität Würzburg, Germany, 1994.

[9] H.L.M. van Gaal, J.M.J. Verlaak and T. Posno, *Inorg. Chim. Acta, 23* (1977) 43.

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

[11] G.M. Bodner, S.B. Kahl, K. Bork, B.N. Storhoff, J.E. Wuller and L.J. Todd, *Inorg. Chem., 12* (1973) 1071.

[12] M. Schulz and H. Werner, *J. Organomet. Chem., 470* (1994) 243.

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

[14] (a) $[Rh(\mu\text{-}O_2CR)(CO)_2]_2$ (R = CH_3, CF_3): D.N. Lawson and G. Wilkinson, *J. Chem. Soc.*, (1965) 1900; (b) $[Rh(\mu\text{-}O_2CCH_3)(C_7H_8)]_2$: A.H. Reis, Jr., C. Willi, S. Siegel and B. Tani, *Inorg. Chem., 18* (1979) 1859; (c) $[Rh(\mu\text{-}O_2CCH_3)(C_2H_4)_2]_2$: B. Windmüller, *Dissertation*, Universität Würzburg, Germany, 1995.

[15] (a) S.D. Robinson and M.F. Uttley, *J. Chem. Soc., Dalton Trans.*, (1973) 1912; (b) G.B. Deacon and R.J. Phillips, *Coord. Chem. Rev., 33* (1980) 227.

[16] R.K. Harris, *Can. J. Chem., 42* (1964) 2275.

[17] M. Schäfer, J. Wolf and H. Werner, *J. Organomet. Chem., 476* (1994) 85.

[18] (a) M. Schäfer, N. Mahr, J. Wolf and H. Werner, *Angew. Chem., 105* (1993) 1377; Angew. Chem., Int. Ed. Engl., 32 (1993) 1315; (b) H. Werner, M. Schäfer, J. Wolf, K. Peters and H.G. von Schnering, *Angew. Chem., 107* (1995) 213; *Angew. Chem., Int. Ed. Engl., 34* (1995) 191.

[19] (a) U. Möhring, M. Schäfer, F. Kukla, M. Schlaf and H. Werner, *J. Mol. Catal.*, accepted for publication; (b) M. Schlaf, *Diploma Thesis*, Universität Würzburg, Germany, 1992; (c) U. Möhring, *Dissertation*, Universität Würzburg, Germany, 1995.

20] R. Cramer, *Inorg. Synth.*, *15* (1974) 14.

[21] A. van der Ent and A.L. Onderdelinden, *Inorg. Synth.*, *14* (1973) 92.

[22] (a) P.C. Crofts and D.M. Parker, *J. Chem. Soc., C* (1970) 332; (b) M. Field, O. Stelzer and R. Schmutzler, *Inorg. Synth.*, *14* (1973) 4.