3210 *Organometallics* **1998,** *17,* 3210−3221

Syntheses, Molecular Structures, and Reactivities of (π-Allyl)rhodium(I) Complexes Containing Bulky Bis(phosphino)methanes $R'_2PCH_2PiPr_2$ as Ligands

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The π-allyl complexes $[Rh(\eta^3\text{-}2\text{-}RC_3H_4)(\kappa^2\text{-}R'_2PCH_2PiPr_2)]$ (R = H, Me; R′ = *i*Pr, Cy, Ph) (**2**−**7**) were prepared from $[RhCl(\eta^4\text{-}C_8H_{12})]_2$, $2\text{-}RC_3H_4MgX$, and $R'_2PCH_2PiPr_2$ via $[Rh(\eta^3\text{-}2\text{-}RC_3H_4)(\eta^4\text{-}C_8H_{12})]$ as the intermediate. Reaction of **2**−**4** (R = H) with Broensted acids HX (X = Cl, CF_3CO_2, CF_3SO_3) led to cleavage of the allyl−metal bond and to the formation of the monohydridorhodium(III) compounds $[RhHX_2(\kappa^2\text{-}R'_2PCH_2PiPr_2)]$ (**8**−**12**). Variable-temperature NMR measurements of **8**−**12** confirm that these compounds are fluctional in solution. The reaction of **2**−**4** with CO gave in the initial step the 1:1 adducts $[Rh(\eta^3\text{-}C_3H_5)(CO)(\kappa^2\text{-}R'_2PCH_2PiPr_2)]$ (**16**−**18**), of which that with R′ = *i*Pr was characterized by X-ray structure analysis. Compounds **16** (R′ = *i*Pr) and **18** (R′ = Ph) reacted with excess carbon monoxide via migratory insertion of CO into the allyl−metal bond to yield the five-coordinate acylrhodium(I) complexes $[Rh\{C(O)CH_2CH{=}CH_2\}(CO)_2(\kappa^2\text{-}R'_2PCH_2PiPr_2)]$ (**19**, **20**). This insertion reaction is reversible. The analogous acyl compound $[Rh\{C(O)CH_2Ph\}(CO)_2(\kappa^2\text{-}iPr_2PCH_2PiPr_2)]$ (**22**) was obtained from $[Rh(\eta^3\text{-}CH_2Ph)(\kappa^2\text{-}iPr_2PCH_2PiPr_2)]$ and CO. Acid cleavage of the acyl−metal bond of **19** (R′ = *i*Pr) afforded the aldehyde $CH_2{=}CHCH_2CHO$ (**26**) and a mixture of **8** and $[RhHCl_2(CO)(\kappa^2\text{-}iPr_2PCH_2PiPr_2)]$ (**25**).

Introduction

In the context of our investigations on low-valent rhodium complexes containing $Rh(PiPr_3)_2$ as a molecular unit, we recently reported a high-yield synthesis of the π-allyl compounds $[Rh(\eta^3\text{-}2\text{-}RC_3H_4)(PiPr_3)_2]$ (R = H, Me, Ph) using $[RhCl(PiPr_3)_2]_2$ as the starting material.[1] This preparative route is somewhat different from that developed by Sivak and Muetterties,[2] who generated from $[RhCl(\eta^4\text{-}C_8H_{12})]_2$ (**1**) and C_3H_5MgBr the cyclooctadiene derivative $[Rh(\eta^3\text{-}C_3H_5)(\eta^4\text{-}C_8H_{12})]$ as an intermediate which on treatment with tertiary phosphines PR_3 gave $[Rh(\eta^3\text{-}C_3H_5)(PR_3)_2]$.[2,3] Similarly, the corresponding chelate complexes $[Rh(\eta^3\text{-}C_3H_5)\text{-}\{R'_2P(CH_2)_nPR'_2\}]$ (n = 2, 3) have been obtained.[4]

This paper describes the syntheses of the π-allyl compounds $[Rh(\eta^3\text{-}2\text{-}RC_3H_4)(\kappa^2\text{-}R'_2PCH_2PiPr_2)]$ and in particular their reactivities toward CO and Broensted acids. As chelating bis(phosphino)methanes, those with R′ = *i*Pr, C_6H_{11} (Cy), and Ph have been used, which were prepared by a new synthetic route from $Ph_3SnCH_2PiPr_2$ as the precursor.[5] With this methodology, also phosphino(stibino)methanes and arsino(phosphino)methanes have been obtained.[6] Some preliminary results regarding the synthesis of the unsymmetrical bis(phosphino)methanes $R'_2PCH_2PiPr_2$ and their rhodium complexes were already communicated.[7]

Results and Discussion

Preparations of the π-Allyl Complexes. The method first reported by Sivak and Muetterties could be successfully applied for the preparation of compounds **2**−**7** with $R'_2PCH_2PiPr_2$ (R′ = *i*Pr, Cy, Ph) as chelating ligands (Scheme 1). Treatment of a suspension of **1** in ether with an equimolar amount of C_3H_5MgBr in ether or $2\text{-}MeC_3H_4MgCl$ in THF at −20 °C results in the formation of a yellow solution which contains the cyclooctadiene derivative $[Rh(\eta^3\text{-}2\text{-}RC_3H_4)(\eta^4\text{-}C_8H_{12})]$ (R = H, Me) as the main component. The addition of 2 equiv of the bis(phosphino)methane $R'_2PCH_2PiPr_2$ in hexane to the reaction mixture generates a deep yellow solution from which the chelate complexes **2**−**7** are

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[7] Werner, H.; Stalke, D.; Wolf, J.; Manger, M.; Schmidt, U.; Gevert, O.; Laubender, M.; Teichert, M. In *Selective Reactions of Metal-Activated-Molecules, Vol. 3*; Werner, H.; Schreier, P., Eds.; Vieweg Verlag: Braunschweig, Germany, 1998.

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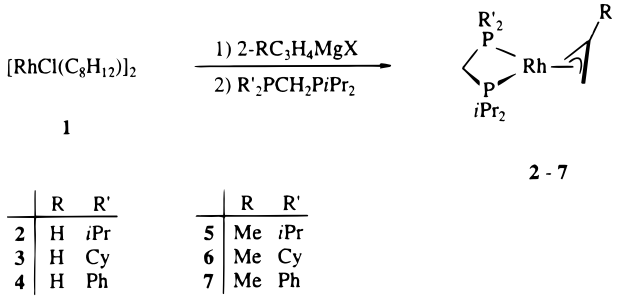
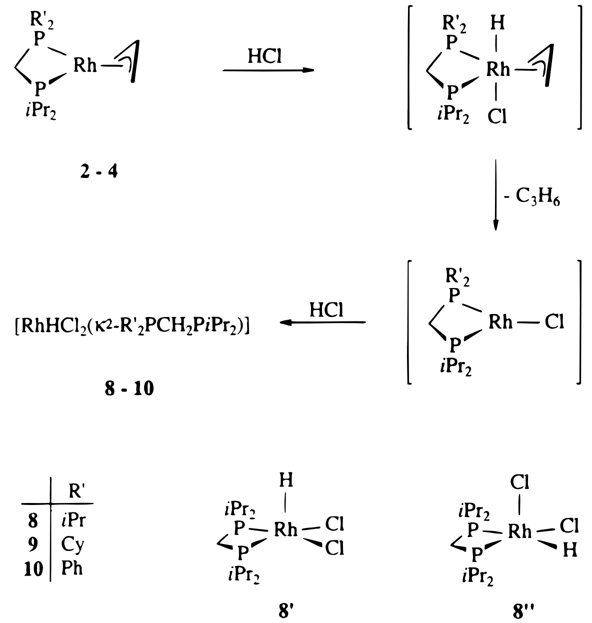
Scheme 1



	R	R'
2	H	*i*Pr
3	H	Cy
4	H	Ph

	R	R'
5	Me	*i*Pr
6	Me	Cy
7	Me	Ph

Scheme 2



	R'
8	*i*Pr
9	Cy
10	Ph

isolated in 60–80% yield. The yellow to orange-yellow solids are quite air-sensitive, are thermally only moderately stable, but can be stored at −20 °C for days. In chlorinated solvents, they slowly decompose. With regard to the mechanism of formation of **2**–**7** from the intermediate $[Rh(\eta^3\text{-}C_3H_5)(\eta^4\text{-}C_8H_{12})]$, we assume that in the initial step a nucleophilic attack of the phosphine on the metal occurs which is followed by the displacement of the diolefin. This mechanistic scheme is supported by recent investigations of Power et al., who isolated the 18-electron compounds $[M(\eta^3\text{-}2\text{-}MeC_3H_4)(\eta^4\text{-}C_8H_{12})(PH\mathit{t}Bu_2)]$ (M = Rh, Ir) upon treatment of the (π-allyl)rhodium and -iridium precursors with $PH\mathit{t}Bu_2$.[3b]

The ^1H, ^{13}C, and ^{31}P NMR data of the new bis(phosphino)methane rhodium complexes support the structural proposal shown in Scheme 1. Besides the expected sets of signals for the C_3H_5 and $2\text{-}CH_3C_3H_4$ ligands,[1–3,8] the ^1H NMR spectra of **2**–**7** display four resonances for the protons of the diastereotopic methyl groups of the $P\mathit{i}Pr_2$ unit(s), which due to $^{31}P,^1H$ and $^1H,^1H$ coupling are split into doublets of doublets. The most characteristic feature of the ^1H NMR spectra, however, is that the signal for the methylene protons of the PCH_2P' fragment appears as a multiplet which after ^{31}P decoupling gives the line shape of an AB system. The geminal coupling between the CH_2 protons is ca. 15 Hz. The fact that only one of the signals for the methylene protons shows an $^{103}Rh,^1H$ coupling could be explained by the difference in the torsional angles at the PCH_2P' unit of the (unsymmetrical) four-membered chelate ring, similar to the situation of the Karplus type.[9]

The ^{31}P NMR data of **2**–**7** deserve one more comment. While the spectra of **2** and **5** with $\mathit{i}Pr_2PCH_2P\mathit{i}Pr_2$ as ligand display a sharp doublet, the spectra of **3**, **4** and **6**, **7** show two doublet of doublets due to the inequivalence of the two ^{31}P nuclei. The values for the coupling constants $^1J(^{103}Rh,^{31}P)$ are in the range 168–177 Hz, and in the case of **3**, **4**, **6**, and **7**, those of $^2J(^{31}P,^{31}P)$ are between 66 and 73 Hz. In particular, the size of the phosphorus–phosphorus coupling is considerably different from that of the nonchelate compound $[Rh(\eta^3\text{-}2\text{-}MeC_3H_4)(PMe_3)(P\mathit{i}Pr_3)]$ (25.5 Hz)[1] and of the unsymmetrical chelate complex $[Rh(\eta^3\text{-}1\text{-}MeC_3H_4)(\kappa^2\text{-}\mathit{i}Pr_2PCH_2CH_2P\mathit{i}Pr_2)]$ (17.1 Hz).[4c] A reasonable explanation for this result is that in the (π-allyl)rhodium compounds the P–Rh–P bond angles differ significantly, being largest in the $Rh(\mathit{i}Pr_2PCH_2CH_2P\mathit{i}Pr_2)$ and smallest in the $Rh(R'_2PCH_2P\mathit{i}Pr_2)$ derivatives. With this stereochemical argument, the size of the $^{103}Rh,^{31}P$ coupling constant can also be rationalized, which for the bis(phosphino)methane complexes **2**–**7** is smaller by about 20–25 Hz compared with those of $[Rh(\eta^3\text{-}1\text{-}MeC_3H_4)(\kappa^2\text{-}\mathit{i}Pr_2PCH_2CH_2P\mathit{i}Pr_2)]$ and $[Rh(\eta^3\text{-}2\text{-}MeC_3H_4)(PMe_3)(P\mathit{i}Pr_3)]$.

Reactions of the π-Allyl Complexes with Broensted Acids. Following recent work from our laboratory,[1,10] which showed that, in rhodium(I) complexes of the general composition $[Rh(\eta^3\text{-}2\text{-}RC_3H_4)(L)_2]$, the allyl–metal bond can be easily cleaved by protic reagents, the reactivity of **2**–**4** toward Broensted acids HX was investigated. If a solution of **2**, **3**, or **4** in ether is stirred under an atmosphere of HCl at −30 °C, a rapid change of color from orange-yellow to almost colorless occurs. After a short period of time, an off-white or pale yellow solid precipitates, the elemental analysis of which corresponds to $[RhHCl_2(\kappa^2\text{-}R'_2PCH_2P\mathit{i}Pr_2)]$ (**8**–**10**). To explain the formation of these compounds, we assume (see Scheme 2) that, in agreement with recent results,[1b] in the initial step of the reaction an oxidative addition of HCl to the metal center takes place, followed by elimination of propene to afford the short-lived intermediate $[RhCl(\kappa^2\text{-}R'_2PCH_2P\mathit{i}Pr_2)]$. This 14-electron species then reacts with a second molecule of the acid to give the final product.

The ^1H NMR spectra of the hydrido complexes **8**–**10**, which are formed from **2**–**4** in virtually quantitative yield, display a resonance in the high-field region at δ −15 to −16. At room temperature, this signal is somewhat broadened, but in the case of **8**, it sharpens upon warming to 318 K to give a doublet of triplets. For **9** and **10**, both at 295 and 325 K, a multiplet for the hydride ligand is observed.

The conclusion, which can be drawn from the variable-temperature ^1H NMR spectra, that the five-coordinate compounds **8**–**10** possess a fluctional struc-

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(8) (a) Clerici, M. G.; Di Gioacchino, S.; Maspero, F.; Perotti, E.; Zanobi, A. *J. Organomet. Chem.* **1977**, *84*, 379–388. (b) Stühler, H.-O.; Müller, J. *Chem. Ber.* **1979**, *112*, 1359–1364. (c) Stühler, H.-O. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35*, 340–342.

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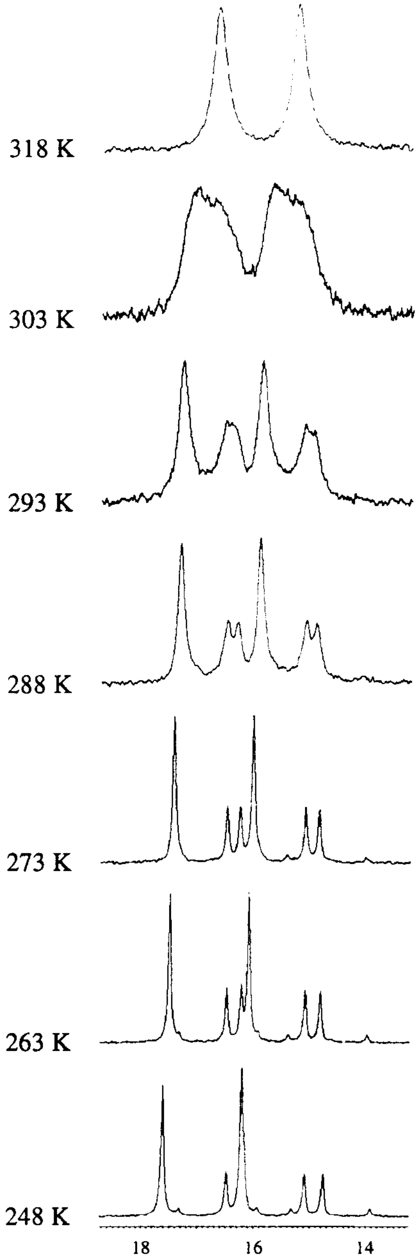

Figure 1. Variable-temperature ^{31}P NMR spectra of compound **8** (in $CDCl_3$).

ture in solution, is substantiated by the VT ^{31}P NMR data. For **8** as the most symmetrical molecule, the temperature dependence of the ^{31}P NMR spectra is shown in Figure 1. At 295 K, two broadened doublets appear at δ 16.5 and 15.7, revealing a $^{103}Rh,^{31}P$ coupling of ca. 113 Hz that is typical for rhodium(III) complexes with two cis-disposed phosphine ligands.[11] Upon an increase in temperature, the two signals coalesce and, at 318 K, finally give one relatively sharp doublet with $^{1}J(RhP) = 114.1$ Hz. Under these conditions, the two ^{31}P nuclei are chemically equivalent on the NMR time scale. When the temperature is lowered, already at 288 K a further splitting of the resonance appearing at higher field is observed. At 263 K, the pattern of this signal is consistent with the AB part of an ABX spectrum and confirms the stereochemical inequivalence of the two P*i*Pr$_2$ units. Continuous cooling of the solution of **8** in $CDCl_3$ to 248 K leads only to a slight high-field shift of the ABX-type resonance while the position of the doublet signal remains unchanged.

To rationalize the temperature dependence of the ^{31}P NMR spectrum of **8**, we assume that at low-temperature two diastereomers **8′** and **8″** exist in solution which both have a square-pyramidal configuration. At higher temperature, these isomers interconvert into each other. The argument that five-coordinate rhodium(III) complexes of the general type $[RhXY_2(L)_2]$ prefer instead of a trigonal-bipyramidal a square-pyramidal geometry is supported by the X-ray crystal structure analysis of $[Rh(COMe)I_2(\kappa^2\text{-}Ph_2PCH_2PPh_2)]$[11e] as well as by the structural and spectroscopic data of related compounds with two monodentate phosphine ligands in cis disposition.[11,12]

By use of an updated program for NMR spectral analysis,[13] the values of the chemical shifts and coupling constants of the AB part of the ABX spectrum of isomer **8″** have been calculated. The calculation provides two sets of data of which one [$\delta(P^A)$ 16.0, $\delta(P^B)$ 15.3; $^{2}J(P^AP^B) = 68.2$, $^{1}J(RhP^A) = 112.9$, $^{1}J(RhP^B) = 113.8$ Hz] fits quite well with the experiment.[14] Isomer **8″**, which has a rigid structure below 263 K on the NMR time scale, rearranges at higher temperature reversibly to **8′**, possibly by a variation of the Berry mechanism.[15] We assume that a similar intramolecular fluctuation also occurs for compounds **9** and **10**, although an exact analysis of the ^{31}P NMR spectra is not possible in these cases.

The reactions of **2** and **3** with trifluoracetic acid and trifluoromethanesulfonic acid also lead to the formation of rhodium(III) complexes of the general composition $[RhHX_2(\kappa^2\text{-}R'_2PCH_2P\textit{i}Pr_2)]$ (Scheme 3). By analogy to the behavior of $[Rh(\eta^3\text{-}C_3H_5)(P\textit{i}Pr_3)_2]$ toward CF_3CO_2H[1] and CF_3SO_3H,[16] we anticipated that the starting materials **2** and **3** would react with 1 equiv of these acids to afford four-coordinate rhodium(I) compounds $[Rh(\eta^2\text{-}X)(\kappa^2\text{-}R'_2PCH_2P\textit{i}Pr_2)]$ ($X = O_2CCF_3$, O_3SCF_3). Indeed, these species could be formed as intermediates, but in the presence of HX, they are probably very labile and rapidly react with HX to give the isolated products **11** and **12**. Even if a solution of **2** in ether/pentane is treated at −78 °C with an equimolar amount of CF_3SO_3H (or a solution of **3** is treated with an equimolar amount of CF_3CO_2H), compounds **11** and **12** are exclusively formed with a yield of 50%. For the preparation of pure samples of **11** and **12**, however, it is important

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(11) (a) Cheng, C.; Spivack, B. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1977**, *99*, 3003−3011. (b) Cheng, C.; Eisenberg, R. *Inorg. Chem.* **1979**, *18*, 1418−1424. (c) McGuiggan, M. F.; Doughty, D. H.; Pignolet, L. H. *J. Organomet. Chem.* **1980**, *185*, 241−249. (d) Shie, J.-Y.; Lin, Y.-C.; Wang, Y. *J. Organomet. Chem.* **1989**, *371*, 383−392. (e) Adams, H.; Bailey, N. A.; Mann, B. E.; Manuel, C. P. *Inorg. Chim. Acta* **1992**, *198−200*, 111−118.

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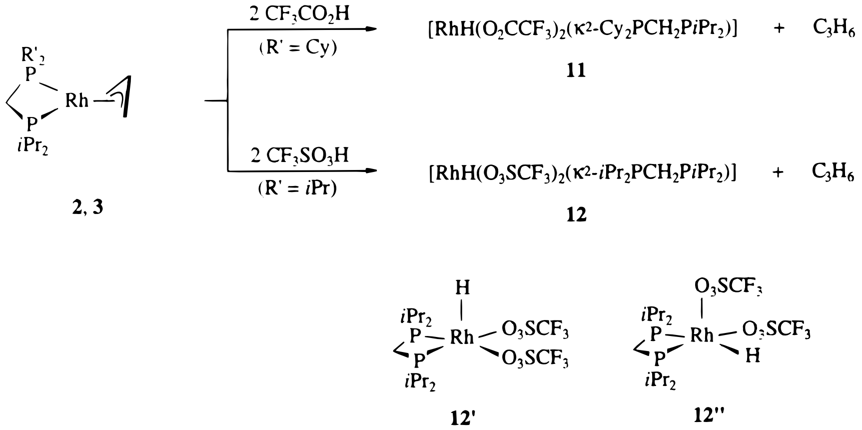
Scheme 3



to use not more than 2 equiv of the corresponding acid because an excess of acid is difficult to remove.

Like the chloro derivatives **8** and **9**, the hydridobis(trifluoracetato)- and hydridobis(triflato)rhodium(III) complexes **11** and **12** are air-stable solids which are readily soluble in polar organic solvents. In solution (even in $CHCl_3$), both **11** and **12** slowly decompose. In contrast to the IR spectrum of **11**, which indicates that one monodentate and one bidentate carboxylato ligand is coordinated,[17,18] the IR spectrum of **12** at room temperature provides no evidence for a chelating bonding mode of the O_3SCF_3 units.[19]

The NMR spectra of **11** and **12** indicate that both complexes are fluctional in solution. The ^{31}P NMR spectrum of **11** displays (in CD_2Cl_2) at room temperature two very broad signals for the P*i*Pr₂ and PCy₂ phosphorus nuclei at δ ca. 17.5 and 7.7. At 313 K, the AB pattern of the P^AP^BRh ABX spin system is observed which represents the high-temperature limiting spectrum of the fluctional process. Upon a decrease in temperature below 295 K, further broadening of the phosphorus resonances occurs and a complicated signal pattern at 193 K points to a transitional dynamic regime. It proved impossible to obtain the low-temperature limiting spectrum. That the high-temperature dynamics observed in the ^{31}P NMR spectra indeed reflect a ligand-scrambling process is supported by the appearance of two broad hydride resonances at δ −17.60 and −17.85 in the ^1H NMR spectrum at 295 K which coalesce upon raising the temperature. In the case of the bis(triflato) compound **12**, a single doublet resonance is observed in the ^{31}P NMR spectrum (in CD_2Cl_2) at 313 K, which indicates a rapid scrambling of the hydrido and triflato ligand positions. Upon cooling, at 243 K two ^{31}P resonance patterns are observed representing an AA′X and an ABX spin system which appear superimposed in Figure 2. We assign these resonances to the two possible configurational isomers **12′** and **12″** analogous to the dichloro derivatives **8′** and **8″** (see Scheme 2), respectively. Further cooling of the solution of **12** in CD_2Cl_2 leads to an additional splitting of the signals which due to its complexity cannot be exactly analyzed. We suppose that, under these conditions, the molecule possesses a rigid configuration with one monodentate and one bidentate O_3SCF_3 unit.

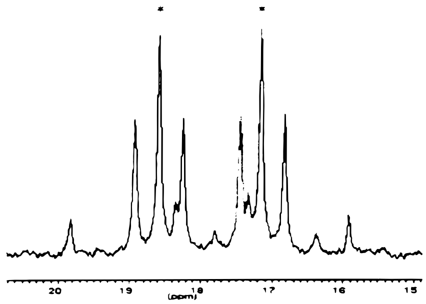
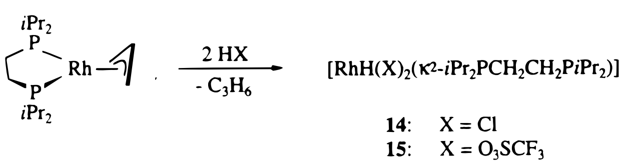


Figure 2. ^{31}P NMR spectrum of compound **12** (in CD_2Cl_2) at 243 K. The asterisks represent the isomer with chemically equivalent ^{31}P nuclei.

Scheme 4



To test whether the dynamic behavior observed for **8** and **12** also exists for related species not underlying the ring strain of the Rh(κ^2-$R'_2PCH_2PiPr_2$) system, the π-allyl complex **13** was treated with excess HCl as well as with 2 equiv of CF_3SO_3H. In both cases, elimination of propene occurred and the corresponding hydridorhodium(III) compounds **14** and **15** (Scheme 4) were formed in nearly quantitative yield. The pale yellow solids are air-stable and can be stored at room temperature for weeks. In contrast to the chloro derivative **14**, which according to the spectroscopic data has a rigid structure at room temperature, the triflato complex **15** under these conditions is fluctional in solution. The ^{31}P NMR spectrum of **15** displays at 295 K a broad multiplet which upon an increase in temperature sharpens and at 308 K becomes a doublet with a $^{103}Rh,^{31}P$ coupling of 141 Hz. A similar observation has been made for the hydride resonance in the ^1H NMR spectrum of **15**. Due to the number and splitting of the signals for the CH_3

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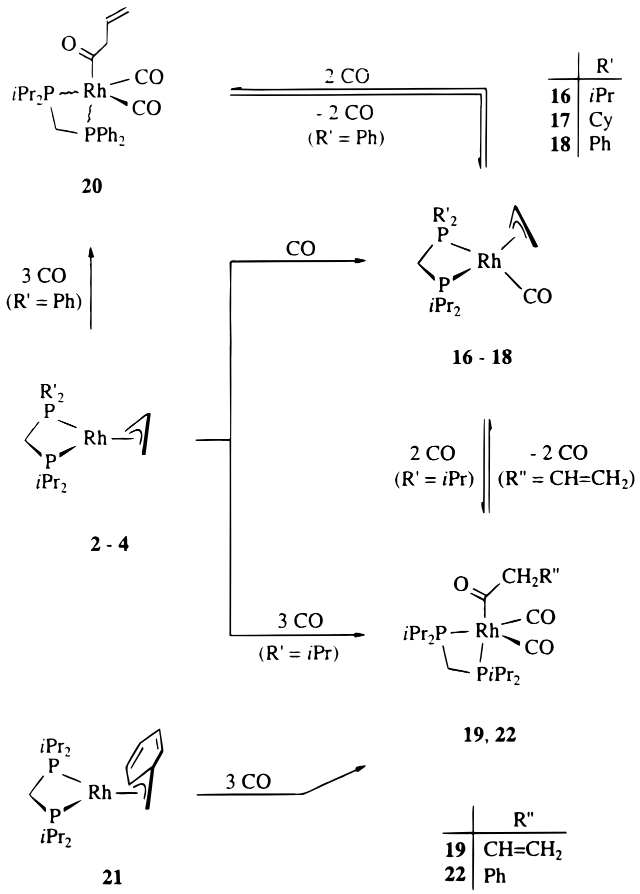
Scheme 5



protons of the isopropyl groups, we assume that the average structure of **15** is a square pyramid of symmetry C_S with η^1-bonded triflato ligands. Therefore, the fluctionality of the molecule probably consists of a concerted change of hapticity between η^1 and η^2 but not in a Berry-type rearrangement as discussed for compound **8**.

Reactions of the π-Allyl Complexes with CO. Like the bis(triisopropylphosphine) compound $[Rh(\eta^3\text{-}C_3H_5)(PiPr_3)_2]$,[1,20] the bis(phosphino)methane derivatives **2**−**4** also react quite rapidly with CO, in pentane even at −40 °C (Scheme 5). During the reaction, a characteristic change of color from orange-yellow to orange-red and finally to pale yellow is observed. In the case of **2** and **3** as the starting materials, after removal of the solvent, deep yellow or orange-yellow solids are isolated, the elemental analyses of which correspond to $[Rh(C_3H_5)(CO)(R'_2PCH_2PiPr_2)]$ (**16**, **17**). The product **18** obtained from **4** and CO is an oily substance which could only be characterized by spectroscopic techniques. Compounds **16** and **17** are only moderately air-sensitive but thermally rather unstable. In solvents such as $CHCl_3$, CH_2Cl_2, or CH_3OH, they slowly decompose. A typical feature of **16**−**18** is the strong ν(CO) stretch at 1940−2000 cm^{-1} in the IR spectra, which appears at positions similar to those of $[Rh(\eta^3\text{-}C_3H_5)(CO)(PiPr_3)_2]$ (1960 cm^{-1})[20] and $[Rh(\eta^3\text{-}C_3H_5)(CO)(PPh_3)_2]$ (1955 cm^{-1}).[21]

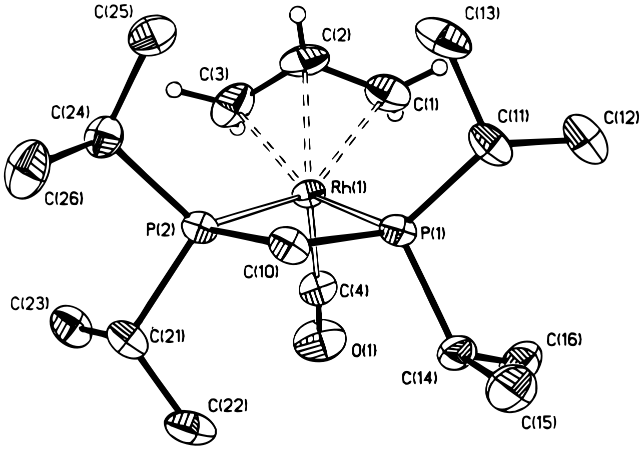


Figure 3. Molecular structure (ORTEP plot) of compound **16**.

The ^{31}P NMR spectrum of **16** shows at 295 K one broadened doublet which sharpens upon lowering the temperature. Compared to that of the precursor complex **2**, the ^{103}Rh,^{31}P coupling constant decreases from 169 to 129 Hz. The assumption that **16** (as well as **17** and **18**) possesses a nonrigid structure in solution is confirmed by VT ^{1}H NMR measurements. While at 295 K the ^{1}H NMR spectrum of **16** displays one unresolved broad signal at δ 2.56 (with the relative intensity of 4H) for the CH_2 protons of the allyl ligand, at 233 K two resonances at δ 2.90 and 2.09 appear, the latter overlapping with the signal of the PCH_2P protons. In agreement with previous studies,[2−4,22] the signal at lower field (δ 2.90) is assigned to the syn and that at higher field (δ 2.09) to the anti protons of the CH_2 groups. The nonrigidity of **16** (and also of **17** and **18**), which is likewise indicated by the line shape of the resonances in the ^{13}C NMR spectra, is probably due to a π−σ−π rearrangement of the C_3H_5 unit as is known for other compounds of the general type $[M(\eta^3\text{-}RC_3H_4)(L)(L')_2]$.[23]

The structural proposal for **16**, as shown in Scheme 5, has been substantiated by an X-ray crystal structure analysis. The ORTEP drawing (Figure 3) reveals that, provided that the C_3H_5 moiety is taken as a bidentate ligand, the rhodium is coordinated in a distorted square-pyramidal fashion. Thereby, the basal plane of the pyramid is occupied by the phosphorus atoms and the allylic CH_2 carbon atoms, in close analogy to the situation found for the related cationic complex $[Ir(\eta^3\text{-}C_3H_5)(NO)(PPh_3)_2]^+$.[24] The configuration of the C_3H_5 unit of **16** is such that the anti protons of the allyl moiety point into the direction of the apical CO group. Since the angle between the planes [C(1),C(2),C(3)] and [P(1),Rh,P(2)] is 64.3°, the distance Rh−C(2) is shorter than the corresponding distances Rh−C(1) and Rh−C(3)

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Table 1. Selected Bond Distances and Angles with Esd's for Compound 16

Bond Distances (Å)			
Rh−C(1)	2.213(2)	Rh−P(1)	2.303(1)
Rh−C(2)	2.125(2)	Rh−P(2)	2.286(1)
Rh−C(3)	2.187(2)	Rh−C(4)	1.927(2)
C(1)−C(2)	1.404(3)	C(4)−O(1)	1.140(2)
C(2)−C(3)	1.408(3)	P(1)−C(10)	1.853(2)
		P(2)−C(10)	1.846(2)
Bond Angles (deg)			
P(1)−Rh−P(2)	72.42(2)	Rh−C(4)−O(1)	177.2(2)
P(1)−C(10)−P(2)	94.27(8)	C(1)−C(2)−C(3)	116.8(2)
Rh−P(1)−C(10)	96.05(6)	Rh−C(1)−C(2)	67.77(11)
Rh−P(2)−C(10)	96.84(6)	Rh−C(2)−C(1)	74.53(11)
P(1)−Rh−C(4)	108.16(6)	Rh−C(2)−C(3)	73.33(12)
P(2)−Rh−C(4)	111.10(6)	Rh−C(3)−C(2)	68.59(11)

(Table 1). The bond length between the metal and the CO ligand is 1.927(2) Å and thus about 0.1 Å larger than those in square-planar rhodium(I) compounds *trans*-$[Rh(R)(CO)(P\mathit{i}Pr_3)_2]$.[25]

The (π-allyl)carbonylrhodium(I) complexes **16**−**18** are not the only products obtained from the starting materials and carbon monoxide. As mentioned above, from **2**−**4** and excess CO, a pale yellow solution is formed from which, after removal of the solvent in vacuo, deep yellow or orange-yellow compounds **16**−**18** are isolated. However, if the pale yellow solution formed from **2** is stored under a CO atmosphere at −78 °C, an almost white solid precipitates. According to the IR and NMR spectroscopic data, its composition corresponds to that of the acyl complex $[Rh\{C(O)CH_2CH{=}CH_2\}(CO)_2(\kappa^2\text{-}\mathit{i}Pr_2PCH_2P\mathit{i}Pr_2)]$ (**19**). From **4** and CO, as well as from the π-benzyl derivative **21**, first prepared by Fryzuk et al.,[26] and carbon monoxide related products, $[Rh\{C(O)CH_2CH{=}CH_2\}(CO)_2(\kappa^2\text{-}Ph_2PCH_2P\mathit{i}Pr_2)]$ (**20**) and $[Rh\{C(O)CH_2Ph\}(CO)_2(\kappa^2\text{-}\mathit{i}Pr_2PCH_2P\mathit{i}Pr_2)]$ (**22**) are obtained. Compound **20** is extremely labile and loses CO rapidly upon removing the CO atmosphere. The dicarbonyl complexes **19** and **20** can also be generated from **16** or **18** and carbon monoxide.

The structural proposals (based on the spectroscopic data) for **19**, **20**, and **22** are shown in Scheme 5. The IR spectrum of **19** confirms that, besides two metal-bonded CO ligands (exemplified by ν(CO) bands at 1974 and 1940 cm^{-1}), an acyl unit is present. The C=O stretching frequency appears at 1699 cm^{-1}, which is in the same region as that for the corresponding iridium complex $[Ir\{C(O)C_3H_5\}(CO)_2(PPh_3)_2]$.[21] The ^{31}P NMR spectrum of **19** (which, like those of **20** and **22**, has to be measured at low temperature in the presence of CO) displays in toluene-d_8 two doublets of doublets at δ 10.3 and 3.2, which differ considerably in the sizes of the ^{103}Rh,^{31}P coupling constants. For **22**, similar data have been obtained. In contrast, the ^{31}P NMR spectrum of **20** displays, due to the asymmetry of the bis(phosphino)methane ligand, two sets of signals, indicating that in solution two isomers exist. We assume that both have a trigonal-bipyramidal configuration, one with the PiPr$_2$ and the other with the PPh$_2$ unit in an apical position. In the ^1H NMR spectra of **19** and **20**, four signals for the protons of the $C(O)CH_2CH{=}CH_2$ ligand appear in the intensity ratio 1:1:1:2, the chemical shift and coupling constants of which are similar to those of related acylmetal compounds.[27] The most typical resonance is that of the single CH= proton, which, owing to the different H,H couplings with the adjacent four protons of the $CH_2CH{=}CH_2$ moiety, is split into a doublet of doublets of triplets.

Reliable ^{13}C NMR data of **19** providing valuable information about the structure of this complex have been obtained from the isotopomer **19a** generated from **2** and ^{13}CO. The ^{13}C NMR spectrum (measured under an atmosphere of ^{13}CO) of this product in the region of the CO nuclei is shown in Figure 4. For the carbon atoms of the two carbonyl ligands, only one resonance appears at δ 201.5, which confirms the equivalence of these ligands. The resonance is split into a doublet of doublets of doublets of doublets due to couplings with the ^{103}Rh, the two different ^{31}P, and the acylic $^{13}C(O)$ nuclei. A similar splitting results for the signal of the acyl carbon atom at δ 235.1, which is a doublet of doublets of doublets of triplets. The small value of 2.4 Hz for the coupling constant $^2J(^{13}C_E,^{13}C_{Ac})$ (for the assignment of the hydrogen, carbon, and phosphorus atoms of **19**, **19a**, and **20** see the Experimental Section) indicates that the carbonyl and the acyl ligands are probably orthogonal to each other.

The ^{31}P NMR spectrum of the ^{13}CO-labeled isotopomer **19a** is also in excellent agreement with the proposed structure for the insertion product. Instead of two doublets of doublets for the nonlabeled complex, it displays two doublets of doublets of doublets of triplets, the additional splitting being due to couplings between ^{31}P and the different ^{13}CO nuclei. A characteristic feature is the large coupling between the phosphorus in the apical position and the acyl carbon atom, which confirms that these two nuclei are trans disposed.

By using ^{13}CO and compound **16** as the starting materials, we can obtain some information about the course of the insertion process. The ^{13}C NMR spectrum of the product, which is formed upon passing a slow stream of ^{13}CO through a solution of **16** in toluene-d_8 at 233 K, displays for the carbon atoms of the CO ligands a doublet of doublets of doublets due to ^{103}Rh,^{13}C and ^{31}P,^{13}C couplings. Since no coupling between C_E and C_{Ac} (see Experimental Section) can be observed, we conclude that the π-allyl complex **16** is in equilibrium with the σ-bonded isomer **23**, which after attack of ^{13}CO affords the acylcarbonyl derivative **24** (Scheme 6). This species obviously reacts faster with a second molecule of ^{13}CO than it rearranges to the isomeric 18-electron compound $[Rh(\eta^1\text{-}C_3H_5)(CO)_2(\kappa^2\text{-}\mathit{i}Pr_2PCH_2P\mathit{i}Pr_2)]$. We note that the formation of the acyliridium complex $[Ir\{C(O)C_3H_4R\}(CO)_2(PPh_3)_2]$ from $[Ir(\eta^3\text{-}RC_3H_4)(CO)_2(PPh_3)_2]$ and carbon monoxide proceeds by a different mechanism, the initial step being the substitution of one phosphine ligand by CO.[21]

The carbon−metal bond of **19** is easily cleaved in the presence of HCl. If a slow stream of HCl is passed through a solution, which is generated from **2** and excess CO in ether/hexane at −40 °C, a pale yellow solid

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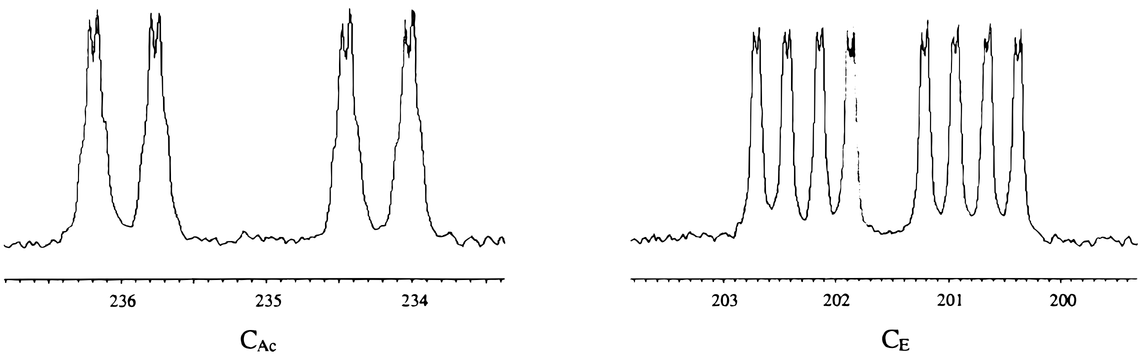
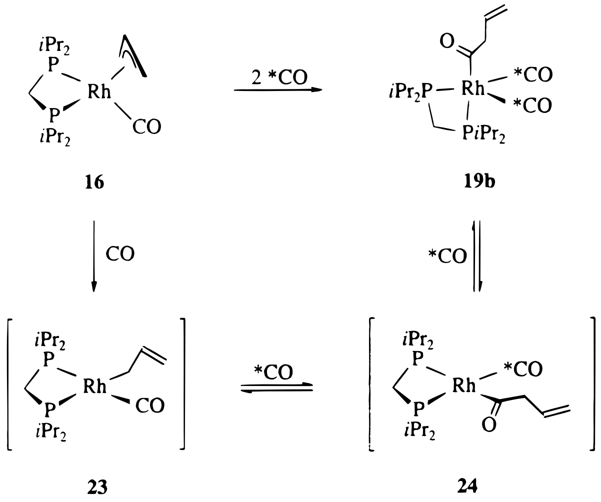


Figure 4. ^{13}C NMR spectrum of compound **19a** (in toluene-d_8) at 233 K in the region of the signals of the Rh−CO and the acyl CO carbon atoms.

Scheme 6



precipitates, which, from the IR and NMR spectroscopic data, is a mixture of **8** and **25** (see Scheme 7) in a ratio of approximately 1:5. In the solution, the unsaturated aldehyde CH_2═$CHCH_2CHO$ (**26**) can be detected by both GC/MS and ^{1}H NMR spectroscopy. The carbonyl complex **25** is rather labile and in chloroform at room temperature loses CO slowly to give **8**. Under the same conditions, in the presence of excess carbon monoxide, the reverse reaction from **8** to **25** does not occur. Since attempts to separate the two hydridorhodium(III) compounds by fractional crystallization or column chromatography failed, the carbonyl derivative was characterized by spectroscopic techniques. The ^{31}P NMR spectrum of **25** displays two doublets of doublets at δ 17.4 and −12.2, both of which show a ^{103}Rh,^{31}P coupling of about 90 Hz. This is in agreement with the oxidation state +III for rhodium. In the ^{13}C NMR spectrum of **25**, the carbonyl resonance appears at δ 183.2 as a doublet of doublets of doublets. The two phosphorus−carbon coupling constants of this signal are extremely different (144.1 and 4.4 Hz), indicating that one ^{31}P nucleus is trans and the other is cis disposed to the CO ligand.

Conclusions

The present work has shown that the (π-allyl)rhodium(I) complexes [Rh(η^3-C_3H_5)(κ^2-$R'_2PCH_2PiPr_2$)], which contain bulky symmetrical or unsymmetrical bis(phosphino)methanes as ligands, react with CO stepwise to give the acyl derivatives [Rh{C(O)CH_2CH═CH_2}(CO)$_2$(κ^2-$R'_2PCH_2PiPr_2$)] as the final products. These novel five-coordinate (albeit very labile) rhodium(I) compounds are formed via the 1:1 adducts [Rh(η^3-C_3H_5)(CO)(κ^2-$R'_2PCH_2PiPr_2$)], of which one (with R′ = *i*Pr) has been characterized by X-ray crystal structure analysis. At 233 K, the 18-electron acyl complexes are relatively inert but, at room temperature, lose CO reversibly to generate the monocarbonyl species. The stepwise conversion, e.g. of **2** via **16** to **19** (Scheme 5), is reminiscent of the mechanistic scheme proposed for the hydroformylation reaction, where the insertion/deinsertion of CO into an alkyl−metal bond plays a dominant role.[28,29]

The π-allyl complexes [Rh(η^3-C_3H_5)(κ^2-$R'_2PCH_2PiPr_2$)] are highly reactive not only toward CO but also toward Broensted acids HX. With the latter they react smoothly by complete cleavage of the allyl−metal bond. Despite several attempts, it has not been possible, however, to prove that the attack of HX leads initially to the formation of the expected (π-allyl)hydridorhodium(III) species [RhH(η^3-C_3H_5)X(κ^2-$R'_2PCH_2PiPr_2$)]. Since compounds of this type with Rh($PiPr_3$)$_2$ instead of Rh(κ^2-$R'_2PCH_2PiPr_2$) as the building block are known,[1,20] we assume that it is the ring strain of the chelate system which determines the lability of the products formed by oxidative addition of HX to the metal center.

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk tube techniques. The starting materials [RhCl(η^4-C_8H_{12})]$_2$ (**1**),[30] [Rh(η^3-CH_2Ph)(κ^2-$iPr_2PCH_2PiPr_2$)] (**21**),[26] and $R'_2PCH_2PiPr_2$ (R′ = *i*Pr, Cy, Ph)[5] were prepared as described in the literature. NMR spectra were recorded on Bruker AC 200 and AMX 400 instruments, and IR spectra, on a Perkin-Elmer 1420 infrared spectrophotometer. Melting points were measured by DTA. Assignment for protons of η^3-allyl ligands: H_M = proton at central carbon; H_A and $H_{A'}$ = protons of CH_2 groups anti to H_M; H_S and $H_{S'}$ = protons of CH_2 groups syn to H_M. $N = {}^3J(PH) + {}^5J(PH)$ or ${}^2J(PC) + {}^4J(PC)$.

Preparation of [Rh(η^3-C_3H_5)(κ^2-$iPr_2PCH_2PiPr_2$)] (2). A suspension of **1** (237 mg, 0.49 mmol) in 10 mL of ether was

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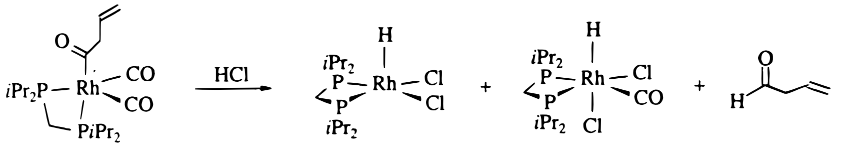
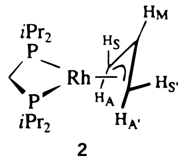
(30) Crabtree, R. H.; Giordano, G. *Inorg. Synth.* **1990**, *28*, 88−90.

Scheme 7



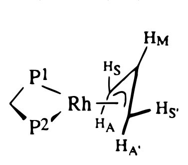
19 8 25 26

treated under vigorous stirring at −20 °C with a 1.22 M solution of C_3H_5MgBr (0.80 mL, 0.98 mmol) in ether. A change of color from orange-yellow to yellow occurred, and a white solid precipitated. The reaction mixture was stirred for 15 min, and then a solution of $i\mathrm{Pr_2PCH_2P}i\mathrm{Pr_2}$ (241 mg, 0.98 mmol) in 3 mL of hexane was added dropwise. After the solution was slowly warmed to room temperature, the solvent was removed in vacuo. The remaining residue was extracted three times with 10-mL portions of pentane, the combined extracts were filtered, and the filtrate was brought to dryness in vacuo. The oily residue was dissolved in 3 mL of acetone, and after the solution was stored for 18 h at −78 °C, orange-yellow crystals were isolated: yield 310 mg (81%); mp 73 °C dec. Anal. Calcd for $C_{16}H_{35}P_2Rh$: C, 48.99; H, 8.99. Found: C, 48.68; H, 8.89. ^{1}H NMR (C_6D_6, 400 MHz): δ 4.80 (dtt, $J(\mathrm{RhH_M}) = 1.6$, $J(\mathrm{H_AH_M}) = J(\mathrm{H_{A'}H_M}) = 13.2$, $J(\mathrm{H_SH_M}) = J(\mathrm{H_{S'}H_M}) = 7.4$ Hz, 1H, $\mathrm{H_M}$), 3.97 (d, $J(\mathrm{H_MH_S}) = J(\mathrm{H_MH_{S'}}) = 7.4$ Hz, 2H, $\mathrm{H_S}$ and $\mathrm{H_{S'}}$), 2.69 (m, in ^{1}H{^{31}P} dd, J(RhH) = 1.2, J(HH) = 15.6 Hz, 1H, $\mathrm{PCH_2P}$), 2.58 (m, in ^{1}H{^{31}P} d, J(HH) = 15.6 Hz, 1H, $\mathrm{PCH_2P}$), 2.20 (dvt, N = 6.8, $J(\mathrm{H_MH})$ = 13.5 Hz, 2H, $\mathrm{H_A}$ and $\mathrm{H_{A'}}$), 1.83, 1.72 (both m, in ^{1}H{^{31}P} both sept, J(HH) = 7.2 Hz, 2H each, $\mathrm{PC}H\mathrm{CH_3}$), 1.12 (dd, J(PH) = 17.2, J(HH) = 7.0 Hz, 6H, $\mathrm{PCHC}H_3$), 1.11 (dd, J(PH) = 18.8, J(HH) = 7.2 Hz, 6H, $\mathrm{PCHC}H_3$), 1.04 (dd, J(PH) = 14.4, J(HH) = 7.0 Hz, 6H, $\mathrm{PCHC}H_3$), 1.03 (dd, J(PH) = 14.8, J(HH) = 7.0 Hz, 6H, $\mathrm{PCHC}H_3$). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 108.3 (dt, J(RhC) = 4.9, J(PC) = 2.5 Hz, η^3-$\mathrm{CH_2}$−CH−$\mathrm{CH_2}$), 47.7 (dvt, J(RhC) = 6.5, N = 27.1 Hz, η^3−$C\mathrm{H_2}$−CH−$C\mathrm{H_2}$), 35.7 (dt, J(RhC) = 1.8, J(PC) = 13.2 Hz, $\mathrm{PCH_2P}$), 26.5 (dvt, J(RhC) = 3.0, N = 17.2 Hz, $\mathrm{P}C\mathrm{HCH_3}$), 26.3 (dvt, J(RhC) = 1.0, N = 13.5 Hz, $\mathrm{P}C\mathrm{HCH_3}$), 20.1, 19.9, 19.8, 19.4 (all br s, $\mathrm{PCH}C\mathrm{H_3}$). ^{31}P NMR ($C_6D_6$, 81.0 MHz): δ 17.7 (d, J(RhP) = 168.6 Hz).



2

Preparation of [Rh(η^3-C_3H_5)(κ^2-$\mathrm{Cy_2PCH_2P}i\mathrm{Pr_2}$)] (3). This compound was prepared as described for **2**, using **1** (477 mg, 0.97 mmol), a 1.10 M solution of C_3H_5MgBr (1.76 mL, 1.94 mmol) in ether, and $\mathrm{Cy_2PCH_2P}i\mathrm{Pr_2}$ (641 mg, 1.95 mmol) as starting materials. Orange-yellow crystals were isolated: yield 700 mg (76%); mp 78 °C dec. Anal. Calcd for $C_{22}H_{43}P_2Rh$: C, 55.93; H, 9.17. Found: C, 55.75; H, 9.56. ^{1}H NMR (C_6D_6, 400 MHz): δ 4.80 (br tt, $J(\mathrm{H_AH_M}) = J(\mathrm{H_{A'}H_M}) = 13.1$, $J(\mathrm{H_SH_M}) = J(\mathrm{H_{S'}H_M}) = 7.2$, 1H, $\mathrm{H_M}$), 3.97, 3.95 (both d, $J(\mathrm{H_MH})$ = 7.2 Hz, 2H, $\mathrm{H_S}$ and $\mathrm{H_{S'}}$), 2.82 (m, in ^{1}H{^{31}P} dd, J(RhH) = 1.4, J(HH) = 15.4 Hz, 1H, $\mathrm{PCH_2P}$), 2.70 (m, in ^{1}H{^{31}P} d, J(HH) = 15.4 Hz, 1H, $\mathrm{PCH_2P}$), 2.21, 2.19 (both m, in ^{1}H{^{31}P} both d, $J(\mathrm{H_MH})$ = 13.1 Hz, 2H, $\mathrm{H_A}$ and $\mathrm{H_{A'}}$), 2.02−1.23 (br m, 24H, $\mathrm{PC}H\mathrm{CH_3}$ and C_6H_{11}), 1.16 (dd, J(PH) = 14.8, J(HH) = 7.2 Hz, 6H, $\mathrm{PCHC}H_3$), 1.09 (dd, J(PH) = 14.8, J(HH) = 7.2 Hz, 3H, $\mathrm{PCHC}H_3$), 1.07 (dd, J(PH) = 14.0, J(HH) = 7.1 Hz, 3H, $\mathrm{PCHC}H_3$). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 108.3 (br m, η^3-$\mathrm{H_2C}$−CH−$\mathrm{CH_2}$), 47.9 (dd, J(RhC) = 6.3, J(PC) = 27.4 Hz, η^3-$\mathrm{H_2}C$−CH−$\mathrm{CH_2}$], 47.5 (dd, J(RhC) = 6.5, J(PC) = 27.0 Hz, η^3-$\mathrm{H_2C}$−CH−$C\mathrm{H_2}$), 37.1 (ddd, J(RhC) = 2.5, $J(\mathrm{P^1C})$ = 10.9, $J(\mathrm{P^2C})$ = 5.7 Hz, $\mathrm{P}C\mathrm{HCH_2}$), 36.7 (dd, J(RhC) = 2.9, J(PC) = 9.1 Hz, $\mathrm{P}C\mathrm{HCH_2}$), 35.1 (dt, J(RhC) = 1.9, $J(\mathrm{P^1C}) = J(\mathrm{P^2C})$ = 13.3 Hz, $\mathrm{P^1CH_2P^2}$), 30.5 (d, J(PC) = 3.3 Hz, $\mathrm{CH_2}$ of C_6H_{11}), 30.4 (d, J(PC) = 5.5 Hz, $\mathrm{CH_2}$ of C_6H_{11}), 30.2 (d, J(PC) = 3.0 Hz, $\mathrm{CH_2}$ of C_6H_{11}), 29.9 (d, J(PC) = 4.5 Hz, $\mathrm{CH_2}$ of C_6H_{11}), 27.7, 27.6, 27.5, 27.4, 26.9, 26.6 (all s, $\mathrm{CH_2}$ of C_6H_{11}), 26.5 (m, $\mathrm{P}C\mathrm{HCH_3}$), 26.3 (dd, J(RhC) = 4.2, J(PC) = 9.1 Hz, $\mathrm{P}C\mathrm{HCH_3}$), 20.1 (d, J(PC) = 4.7 Hz, $\mathrm{PCH}C\mathrm{H_3}$), 19.9 (br s, $\mathrm{PCH}C\mathrm{H_3}$), 19.9 (d, J(PC) = 2.2 Hz, $\mathrm{PCH}C\mathrm{H_3}$), 19.4 (d, J(PC) = 6.0 Hz, $\mathrm{PCH}C\mathrm{H_3}$). ^{31}P NMR ($C_6D_6$, 162.0 MHz): δ 17.8 (dd, $J(\mathrm{RhP^2})$ = 169.0, J(PP) = 66.5 Hz, $i\mathrm{Pr_2P}$), 7.3 (dd, $J(\mathrm{RhP^1})$ = 169.2, J(PP) = 66.5 Hz, $\mathrm{Cy_2P}$).



P^1 = PCy$_2$
P^2 = PiPr$_2$

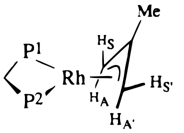
3

Preparation of [Rh(η^3-C_3H_5)(κ^2-$\mathrm{Ph_2PCH_2P}i\mathrm{Pr_2}$)] (4). This compound was prepared as described for **2**, using **1** (271 mg, 0.55 mmol), a 1.26 M solution of C_3H_5MgBr (0.88 mL, 1.11 mmol) in ether, and $\mathrm{Ph_2PCH_2P}i\mathrm{Pr_2}$ (351 mg, 1.11 mmol) as starting materials. An orange-yellow microcrystalline solid was obtained: yield 305 mg (60%); mp 78 °C dec. Anal. Calcd for $C_{22}H_{31}P_2Rh$: C, 57.40; H, 6.79. Found: C, 57.02; H, 7.28. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.84, 7.09 (both m, 10H, C_6H_5), 5.00 (br m, 1H, $\mathrm{H_M}$), 4.25 (br d, $J(\mathrm{H_MH_S})$ = 7.4 Hz, 1H, $\mathrm{H_S}$), 4.06 (br d, $J(\mathrm{H_MH_{S'}})$ = 7.2 Hz, 1H, $\mathrm{H_{S'}}$), 3.59 (m, 2H, $\mathrm{PCH_2P}$), 2.52 (br dd, $J(\mathrm{P^2H_A})$ = 6.4, $J(\mathrm{H_MH_A})$ = 13.4 Hz, 1H, $\mathrm{H_A}$), 2.31 (br dd, $J(\mathrm{P^1H_{A'}})$ = 7.2, $J(\mathrm{H_MH_{A'}})$ = 13.4 Hz, 1H, $\mathrm{H_{A'}}$), 1.72 (br m, 2H, $\mathrm{PC}H\mathrm{CH_3}$), 1.06 (dd, J(PH) = 14.1, J(HH) = 7.0 Hz, 3H, $\mathrm{PCHC}H_3$), 0.98 (dd, J(PH) = 14.2, J(HH) = 7.0 Hz, 3H, $\mathrm{PCHC}H_3$), 0.91 (dd, J(PH) = 14.2, J(HH) = 7.0 Hz, 3H, $\mathrm{PCHC}H_3$), 0.82 (dd, J(PH) = 14.3, J(HH) = 6.9 Hz, 3H, $\mathrm{PCHC}H_3$). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 139.4 (d, J(PC) = 6.2 Hz, *ipso*-C of C_6H_5), 138.9 (d, J(PC) = 5.6 Hz, *ipso*-C of C_6H_5), 132.9 (d, J(PC) = 15.5 Hz, *ortho*-C of C_6H_5), 132.6 (d, J(PC) = 16.0 Hz, *ortho*-C of C_6H_5), 129.2 (d, J(PC) = 2.1 Hz, *para*-C of C_6H_5), 129.0 (d, J(PC) = 1.6 Hz, *para*-C of C_6H_5), 128.4 (d, J(PC) = 9.3 Hz, *meta*-C of C_6H_5), 128.2 (d, J(PC) = 9.5 Hz, *meta*-C of C_6H_5), 109.7 (br m, η^3-$\mathrm{H_2C}$−CH−$\mathrm{C'H_2}$), 50.9 (dd, J(RhC) = 6.2, $J(\mathrm{P^2C})$ = 26.1, η^3-$\mathrm{H_2}C$−CH−$\mathrm{C'H_2}$), 48.0 (dd, J(RhC) = 6.6, $J(\mathrm{P^1C})$ = 28.3, η^3-$\mathrm{H_2C}$−CH−$C'\mathrm{H_2}$), 42.7 (ddd, J(RhC) = 2.3, $J(\mathrm{P^1C})$ = 20.1, $J(\mathrm{P^2C})$ = 12.5 Hz, $\mathrm{P^1CH_2P^2}$), 25.7 (m, $\mathrm{P}C\mathrm{HCH_3}$), 19.7, 19.2 (both d, J(PC) = 8.6 Hz, $\mathrm{PCH}C\mathrm{H_3}$), 18.8 (br d, J(PC) = 8.1 Hz, $\mathrm{PCH}C\mathrm{H_3}$). ^{31}P NMR ($C_6D_6$, 81.0 MHz): δ 19.0 (dd, $J(\mathrm{RhP^2})$ = 169.1, J(PP) = 72.5 Hz, $i\mathrm{Pr_2P}$), −8.4 (dd, $J(\mathrm{RhP^1})$ = 176.8, J(PP) = 72.5 Hz, $\mathrm{Ph_2P}$).

Preparation of [Rh(η^3-2-$\mathrm{MeC_3H_4}$)(κ^2-$i\mathrm{Pr_2PCH_2P}i\mathrm{Pr_2}$)] (5). This compound was prepared as described for **2**, using **1** (77 mg, 0.16 mmol), a 0.95 M solution of 2-$\mathrm{MeC_3H_4MgCl}$ (0.33 mL, 0.32 mmol) in THF, and $i\mathrm{Pr_2PCH_2P}i\mathrm{Pr_2}$ (0.32 mmol) as starting materials. An orange-yellow microcrystalline solid was obtained: yield 98 mg (75%); mp 38 °C dec. Anal. Calcd for $C_{17}H_{37}P_2Rh$: C, 50.20; H, 8.68. Found: C, 49.72; H, 8.71. ^{1}H NMR (C_6D_6, 400 MHz): δ 3.60 (br s, 2H, $\mathrm{H_S}$ and $\mathrm{H_{S'}}$), 2.67 (m, in ^{1}H{^{31}P} dd, J(RhH) = 1.6, J(HH) = 15.4 Hz, 1H, $\mathrm{PCH_2P}$), 2.48 (m, in ^{1}H{^{31}P} d, J(HH) = 15.4 Hz, 1H, $\mathrm{PCH_2P}$), 2.10 (vt, N = 8.0 Hz, 2H, $\mathrm{H_A}$ and $\mathrm{H_{A'}}$), 1.75 (br m, 4H, PC*H*CH$_3$), 1.72 (d, *J*(RhH) = 2.1 Hz, 3H, η^3-H$_2$C−C(C*H*$_3$)−CH$_2$), 1.14 (dd, *J*(PH) = 14.4, *J*(HH) = 7.0 Hz, 6H, PCHC*H*$_3$), 1.13 (dd, *J*(PH) = 14.4, *J*(HH) = 7.1 Hz, 6H, PCHC*H*$_3$), 1.06 (dd, *J*(PH) = 15.5, *J*(HH) = 7.0 Hz, 6H, PCHC*H*$_3$), 1.01 (dd, *J*(PH) = 14.5, *J*(HH) = 7.0 Hz, 6H, PCHC*H*$_3$). ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ 119.4 (dt, *J*(RhC) = 5.8, *J*(PC) = 2.1 Hz, η^3-CH$_2$−*C*(CH$_3$)−CH$_2$), 47.7 (dvt, *J*(RhC) = 6.5, *N* = 27.8 Hz, η^3−*C*H$_2$−C(CH$_3$)−*C*H$_2$), 36.0 (dt, *J*(RhC) = 1.9, *J*(PC) = 13.0 Hz, P*C*H$_2$P), 27.7 (d, *J*(RhC) = 1.4 Hz, η^3-H$_2$C−C(*C*H$_3$)−CH$_2$), 26.4 (dvt, *J*(RhC) = 0.9, *N* = 13.0 Hz, P*C*HCH$_3$), 25.9 (dvt, *J*(RhC) = 3.0, *N* = 17.3 Hz, P*C*HCH$_3$), 20.1−19.5 (br m, PCH*C*H$_3$). ^{31}P NMR (C$_6$D$_6$, 81.0 MHz): δ 19.6 (d, *J*(RhP) = 167.9 Hz).

Preparation of [Rh(η^3-2-MeC$_3$H$_4$)(κ^2-Cy$_2$PCH$_2$P*i*Pr$_2$)] (6). This compound was prepared as described for **2**, using **1** (125 mg, 0.25 mmol), a 0.90 M solution of 2-MeC$_3$H$_4$MgCl (0.58 mL, 0.51 mmol) in THF, and Cy$_2$PCH$_2$P*i*Pr$_2$ (0.51 mmol) as starting materials. Yellow crystals: yield 166 mg (67%); mp 56 °C dec. Anal. Calcd for C$_{23}$H$_{45}$P$_2$Rh: C, 56.79; H, 9.32. Found: C, 57.00; H, 9.45. ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ 3.62 (m, 2H, H$_S$ and H$_{S'}$), 2.72 (m, 2H, PCH$_2$P), 2.14 (br m, 2H, H$_A$ and H$_{A'}$), 1.76 (d, *J*(RhH) = 2.2 Hz, 3H, η^3-H$_2$C−C(C*H*$_3$)−C′H$_2$), 2.02−1.18 (br m, 24H, PC*H*CH$_3$ and C$_6$H$_{11}$), 1.18 (dd, *J*(PH) = 14.3, *J*(HH) = 7.0 Hz, 3H, PCHC*H*$_3$), 1.17 (dd, *J*(PH) = 14.7, *J*(HH) = 7.1 Hz, 3H, PCHC*H*$_3$), 1.08 (m, 6H, PCHC*H*$_3$). ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ 119.3 (br m, η^3-H$_2$C−*C*(CH$_3$)−CH$_2$), 47.9 (dd, *J*(RhC) = 6.5, *J*(PC) = 28.0, η^3-H$_2$*C*−C(CH$_3$)−CH$_2$), 47.4 (dd, *J*(RhC) = 6.5, *J*(PC) = 27.7 Hz, η^3-H$_2$C−C(CH$_3$)−*C*H$_2$), 37.0 (br dd, *J*(P^{1}C) = 18.4, *J*(P^{2}C) = 3.6 Hz, P*C*HCH$_2$), 36.3 (ddd, *J*(RhC) = 2.8, *J*(P^{1}C) = 11.1, *J*(P^{2}C) = 6.2 Hz, P*C*HCH$_2$), 35.4 (dt, *J*(RhC) = 2.0, *J*(P^{1}C) = *J*(P^{2}C) = 13.2 Hz, P*C*H$_2$P), 30.3 (br m, PCH*C*H$_2$), 27.7 (br s, η^3-H$_2$C−C(*C*H$_3$)−CH$_2$), 27.4 (m, CH$_2$ of C$_6$H$_{11}$), 26.7 (s, CH$_2$ of C$_6$H$_{11}$), 26.4 (br dd, *J*(P^{2}C) = 8.0, *J*(P^{1}C) = 4.0 Hz, P*C*HCH$_3$), 26.0 (ddd, *J*(RhC) = 3.0, *J*(P^{2}C) = 10.9, *J*(P^{1}C) = 6.5 Hz, P*C*HCH$_3$), 20.2−19.6 (br m, PCH*C*H$_3$). ^{31}P NMR (C$_6$D$_6$, 162.0 MHz): δ 20.1 (dd, *J*(RhP^2) = 167.1, *J*(PP) = 65.4 Hz, *i*Pr$_2$P), 10.0 (dd, *J*(RhP^1) = 166.4, *J*(PP) = 65.4 Hz, Cy$_2$P).

Preparation of [Rh(η^3-2-MeC$_3$H$_4$)(κ^2-Ph$_2$PCH$_2$P*i*Pr$_2$)] (7). This compound was prepared as described for **2**, using **1** (129 mg, 0.26 mmol), a 0.90 M solution of 2-MeC$_3$H$_4$MgCl (0.58 mL, 0.52 mmol) in THF, and Ph$_2$PCH$_2$P*i*Pr$_2$ (0.52 mmol) as starting materials. A yellow microcrystalline solid was obtained: yield 173 mg (70%); mp 51 °C dec. Anal. Calcd for C$_{23}$H$_{33}$P$_2$Rh: C, 58.24; H, 7.01. Found: C, 57.88; H, 6.59. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 7.90, 7.06 (both m, 10H, C$_6$H$_5$), 3.94 (d, *J*(RhH$_S$) = 2.4 Hz, 1H, H$_S$), 3.70 (d, *J*(RhH$_{S'}$) = 1.8 Hz, 1H, H$_{S'}$), 3.46 (m; in ^{1}H{^{31}P} dd, *J*(RhH) = 1.4, *J*(HH) = 15.1 Hz; in ^{1}H{^{31}P*i*Pr$_2$} ddd, *J*(RhH) = 1.4, *J*(P^{1}H) = 8.4, *J*(HH) = 15.1 Hz; in ^{1}H{^{31}PPh$_2$} ddd, *J*(RhH) = 1.4, *J*(P^{2}H) = 7.2, *J*(HH) = 15.1 Hz, 1H, PCH$_2$P), 3.29 (m; in ^{1}H{^{31}P} d, *J*(HH) = 15.1 Hz; in ^{1}H{^{31}P*i*Pr$_2$} dd, *J*(P^{1}H) = 8.5, *J*(HH) = 15.1 Hz; in ^{1}H{^{31}PPh$_2$} dd, *J*(P^{2}H) = 7.2, *J*(HH) = 15.1 Hz, 1H, PCH$_2$P), 2.44 (d, *J*(P^{2}H$_A$) = 6.0, 1H, H$_A$), 2.21 (d, *J*(P^{1}H$_{A'}$) = 6.4, 1H, H$_{A'}$), 1.82 (d, *J*(RhH) = 2.0 Hz, 3H, η^3-H$_2$C−C(C*H*$_3$)−C′H$_2$], 1.75, 1.62 (both m, 1H each, PC*H*CH$_3$), 1.07 (dd, *J*(PH) = 14.9, *J*(HH) = 7.3 Hz, 3H, PCHC*H*$_3$), 1.00 (dd, *J*(PH) = 14.9, *J*(HH) = 7.0 Hz, 3H, PCHC*H*$_3$), 0.99 (dd, *J*(PH) = 15.6, *J*(HH) = 7.2 Hz, 3H, PCHC*H*$_3$), 0.92 (dd, *J*(PH) = 12.5, *J*(HH) = 6.9 Hz, 3H, PCHC*H*$_3$). ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ 139.4 (m, *ipso*-C of C$_6$H$_5$), 132.9 (d, *J*(PC) = 16.2 Hz, *ortho*-C of C$_6$H$_5$), 132.7 (d, *J*(PC) = 16.9 Hz, *ortho*-C of C$_6$H$_5$), 129.1 (d, *J*(PC) = 1.6 Hz, *para*-C of C$_6$H$_5$), 129.0 (d, *J*(PC) = 1.9 Hz, *para*-C of C$_6$H$_5$), 128.4 (d, *J*(PC) = 9.5 Hz, *meta*-C of C$_6$H$_5$), 128.2 (d, *J*(PC) = 10.0 Hz, *meta*-C of C$_6$H$_5$), 121.2 (m, η^3-H$_2$C′−*C*(CH$_3$)−CH$_2$), 51.0 (dd, *J*(RhC) = 6.3, *J*(P^{2}C) = 27.3, η^3-H$_2$*C*−C(CH$_3$)−C′H$_2$), 47.8 (dd, *J*(RhC) = 6.5, *J*(P^{1}C) = 29.6, η^3-H$_2$C−C(CH$_3$)−*C*′H$_2$), 43.1 (ddd, *J*(RhC) = 2.3, *J*(P^{1}C) = 20.0, *J*(P^{2}C) = 12.4 Hz, P*C*H$_2$P), 27.6 (d, *J*(RhC) = 1.4 Hz, η^3-H$_2$C−C(*C*H$_3$)−C′H$_2$), 23.4 (m, P*C*HCH$_3$), 19.8, 19.3 (both d, *J*(PC) = 8.8 Hz, PCH*C*H$_3$), 18.8 (br s, PCH*C*H$_3$). ^{31}P NMR (C$_6$D$_6$, 81.0 MHz): δ 20.8 (dd, *J*(RhP^2) = 166.8, *J*(PP) = 71.6 Hz, *i*Pr$_2$P), −6.7 (dd, *J*(RhP^1) = 174.8, *J*(PP) = 71.6 Hz, Ph$_2$P).



P^1 = PPh$_2$
P^2 = P*i*Pr$_2$

7

Preparation of [RhHCl$_2$(κ^2-*i*Pr$_2$PCH$_2$P*i*Pr$_2$)] (8). A degassed solution of **2** (85 mg, 0.22 mmol) in 10 mL of ether was saturated at −30 °C with HCl, and the mixture was stirred for 5 min. A rapid change of color from orange-yellow to almost colorless occurred, and an off-white solid precipitated. After the mother liquor was removed, the remaining solid was washed five times with 5-mL portions of ether and twice with 5-mL portions of pentane and dried. An off-white solid was isolated: yield 90 mg (98%); mp 111 °C dec. Anal. Calcd for C$_{13}$H$_{31}$Cl$_2$P$_2$Rh: C, 36.90; H, 7.38. Found: C, 37.35; H, 6.97. IR (CH$_2$Cl$_2$): ν(RhH) 2100 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz, 295 K): δ 3.14 (br m, 2H, PCH$_2$P), 2.55, 2.23 (both m, 2H each, PC*H*CH$_3$), 1.46 (br dvt, *N* = 17.8, *J*(HH) = 7.3 Hz, 6H, PCHC*H*$_3$), 1.27 (br m, 18H, PCHC*H*$_3$), −15.80 (br dt, *J*(RhH) = 20.0, *J*(PH) = 20.2 Hz, 1H, RhH). ^{1}H NMR (CDCl$_3$, 200 MHz, 318 K): δ 3.29 (br m, 2H, PCH$_2$P), 2.58, 2.24 (both m, 2H each, PC*H*CH$_3$), 1.49 (dvt, *N* = 18.2, *J*(HH) = 7.3 Hz, 6H, PCHC*H*$_3$), 1.30 (br m, 18H, PCHC*H*$_3$), −15.80 (dt, *J*(RhH) = *J*(PH) = 20.0 Hz, 1H, RhH). ^{13}C NMR (CDCl$_3$, 50.3 MHz, 295 K): δ 30.0 (m, PCH$_2$P), 28.4 (vt, *N* = 16.4 Hz, P*C*HCH$_3$), 26.9 (vt, *N* = 18.0 Hz, P*C*HCH$_3$), 20.0, 19.2, 18.2, 17.5 (all s, PCH*C*H$_3$). ^{31}P NMR (CDCl$_3$, 81.0 MHz, 263 K): δ 16.8 (d, *J*(RhP) = 113.7 Hz), 16.0 (A-part of the ABX spin system, *J*(RhP^A) = 112.9, *J*(PP) = 68.2 Hz, P^A), 15.3 (B-part of the ABX spin system, *J*(RhP^B) = 113.8, *J*(PP) = 68.2 Hz, P^B). ^{31}P NMR (CDCl$_3$, 81.0 MHz, 295 K): δ 16.5 (br d, *J*(RhP) = 114.4 Hz), 15.7 (br d, *J*(RhP) = 112.0 Hz). ^{31}P NMR (CDCl$_3$, 81.0 MHz, 318 K): δ 16.0 (d, *J*(RhP) = 114.1 Hz).

Preparation of [RhHCl$_2$(κ^2-Cy$_2$PCH$_2$P*i*Pr$_2$)] (9). This compound was prepared as described for **8**, using **3** (120 mg, 0.25 mmol) as starting material. A pale yellow solid was obtained: yield 114 mg (91%); mp 89 °C dec. Anal. Calcd for C$_{19}$H$_{39}$Cl$_2$P$_2$Rh: C, 45.34; H, 7.81. Found: C, 45.74; H, 7.25. IR (KBr): ν(RhH) 2110 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz, 295 K): δ 3.12 (br m, 2H, PCH$_2$P), 2.53 (br m, 1H, PC*H*CH$_3$), 2.40−1.19 (br m, 32H, PC*H*C*H*$_3$ and C$_6$H$_{11}$), 1.46 (dd, *J*(PH) = 18.2, *J*(HH) = 6.9 Hz, 3H, PCHC*H*$_3$), −15.91 (br m, 1H, RhH). ^{13}C NMR (CDCl$_3$, 50.3 MHz, 295 K): δ 36.9 (d, *J*(PC) = 19.6 Hz, P*C*HCH$_2$), 34.6 (d, *J*(PC) = 23.9 Hz, P*C*HCH$_2$), 29.3 (m, PCH$_2$P), 27.5, 26.0, 25.6, 25.3, 25.2, 24.3, 24.0 (all s, CH$_2$ of C$_6$H$_{11}$), 26.9 (br m, P*C*HCH$_3$), 18.7, 17.8, 16.8, 16.0 (all s, PCH*C*H$_3$). ^{31}P NMR (CDCl$_3$, 81.0 MHz, 295 K): δ 18.2−14.8 (br m, *i*Pr$_2$P), 8.9−5.4 (br m, Cy$_2$P). ^{31}P NMR (CDCl$_3$, 81.0 MHz, 328 K): δ 16.3 (br dd, *J*(RhP^2) = 113.7 Hz, *J*(PP) = 66.1 Hz, *i*Pr$_2$P), 7.0 (br dd, *J*(RhP^1) = 114.8, *J*(PP) = 66.1 Hz, Cy$_2$P), 6.8 (br dd, *J*(RhP^1) = 113.7, *J*(PP) = 66.1 Hz, Cy$_2$P).

Preparation of [RhHCl$_2$(κ^2-Ph$_2$PCH$_2$P*i*Pr$_2$)] (10). This compound was prepared as described for **8**, using **4** (300 mg, 0.65 mmol) as starting material. A pale yellow solid was obtained: yield 242 mg (88%); mp 56 °C dec. Anal. Calcd for C$_{19}$H$_{27}$Cl$_2$P$_2$Rh: C, 46.46; H, 5.54. Found: C, 46.19; H, 5.27. IR (KBr): ν(RhH) 2110 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz, 295 K): δ 7.87 (m, 4H, *ortho*-H of C$_6$H$_5$), 7.38 (m, 6H, *meta*-H and *para*-H of C$_6$H$_5$), 4.29, 3.74 (both br m, 1H each, PCH$_2$P), 2.54, 2.24 (both m, 1H each, PC*H*CH$_3$), 1.11 (br m, 12H, PCHC*H*$_3$), −14.49 to −15.24 (m, 1H, RhH). ^{1}H NMR (CDCl$_3$, 200 MHz, 323 K): δ 7.89 (m, 4H, *ortho*-H of C$_6$H$_5$), 7.37 (m, 6H, *meta*-H and *para*-H of C$_6$H$_5$), 4.29, 3.75 (both br m, 1H each, PCH$_2$P), 2.58, 2.27 (both m, 1H each, PC*H*CH$_3$), 1.32 (dd, *J*(PH) = 17.8, *J*(HH) = 6.9 Hz, 3H, PCHC*H*$_3$), 1.23 (dd, *J*(PH) = 19.3, *J*(HH) = 6.9 Hz, 3H, PCHC*H*$_3$), 1.20 (m, 3H, PCHC*H*$_3$), 1.04 (dd, *J*(PH) = 18.5, *J*(HH) = 7.0 Hz, 3H, PCHC*H*$_3$), −14.90 (m, 1H, RhH). ^{13}C NMR (CDCl$_3$, 50.3 MHz, 295 K): δ 134.7 (br m, *ipso*-C of C$_6$H$_5$), 132.7 (br d, *J*(PC) = 11.4 Hz, *ortho*-C of C$_6$H$_5$), 131.6 (d, *J*(PC) = 13.5 Hz, *ortho*-C of C$_6$H$_5$), 128.8 (m, *meta*-C and *para*-C of C$_6$H$_5$), 37.0 (dd, *J*(P^{1}C) = 29.2, *J*(P^{2}C) = 24.0 Hz, PCH$_2$P), 28.5 (dd, *J*(P^{2}C) = 20.7, *J*(P^{1}C) = 4.3 Hz, P*C*HCH$_3$), 25.9 (d, *J*(PC) = 22.5 Hz, P*C*HCH$_3$), 19.5, 18.8, 18.2, 17.6 (all s, PCH*C*H$_3$). ^{31}P NMR (CDCl$_3$, 81.0 MHz, 295 K): δ 20.2 (dd, *J*(RhP^2) = 111.9, *J*(PP) = 77.0 Hz, *i*Pr$_2$P), 19.6−17.2 (m, *i*Pr$_2$P), −12.5 (dd, *J*(RhP^1) = 117.0, *J*(PP) = 77.0 Hz, Ph$_2$P), −10.3 to −16.5 (m, Ph$_2$P). ^{31}P NMR (CDCl$_3$, 81.0 MHz, 328 K): δ 21.0−18.8 (m, *i*Pr$_2$P), −11.2 to −14.7 (br m, Ph$_2$P).

Preparation of [RhH(O$_2$CCF$_3$)$_2$(κ^2-Cy$_2$PCH$_2$P*i*Pr$_2$)] (11). A solution of **3** (118 mg, 0.25 mmol) in 4 mL of pentane/ether (3:1) was treated at −78 °C with CF$_3$CO$_2$H (39 μL, 0.50 mmol). Quite rapidly, an orange-yellow oily solid precipitated. After the reaction mixture was stirred for 5 min, the solvent was removed in vacuo. The residue was washed at −20 °C three times with 4-mL portions of pentane/ether (3:1) and twice with 4-mL portions of pentane and dried. A pale yellow solid was obtained: yield 140 mg (85%); mp 41 °C dec. Anal. Calcd for C$_{23}$H$_{39}$F$_6$O$_4$P$_2$Rh: C, 41.96; H, 5.97. Found: C, 41.40; H, 5.19. IR (CH$_2$Cl$_2$): ν(RhH) 2115, ν(OCO$_{\mathrm{asym}}$) 1715, 1668, ν(OCO$_{\mathrm{sym}}$) 1455, 1443, ν(CF) 1195 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz, 295 K): δ 3.03, 2.85 (both m, 1H each, PCH$_2$P), 2.57 (br m, 1H, PC*H*CH$_2$), 2.28 (m, 2H, PC*H*CH$_3$), 1.91 (br m, 9H, PCHC*H*$_2$), 1.34 (br m, 24H, C$_6$H$_{11}$ and PCHC*H*$_3$), −17.60 (br m, RhH), −17.85 (br dt, *J*(RhH) = *J*(PH) = 21.0 Hz, RhH). ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz, 313 K): δ 2.98 (br m, 2H, PCH$_2$P), 2.70−1.30 (br m, 36H, C$_6$H$_{11}$ and PC*H*CH$_3$), −17.89 (br m, 1H, RhH). ^{13}C NMR (CD$_2$Cl$_2$, 100.6 MHz, 308 K): δ 163.8 (br m, O$_2$*C*CF$_3$), 116.2 (q, *J*(FC) = 287.3 Hz, O$_2$C*C*F$_3$), 36.9 (br d, *J*(PC) = 19.9 Hz, P*C*HCH$_2$), 36.0 (br d, *J*(PC) = 25.3 Hz, P*C*HCH$_2$), 29.3 (m, PCH$_2$P), 30.6, 28.0 (both s, PCH*C*H$_2$), 27.6−26.3 (m, P*C*HCH$_3$ and CH$_2$ of C$_6$H$_{11}$), 26.1, 25.9 (both s, CH$_2$ of C$_6$H$_{11}$), 19.8, 19.0, 17.8, 17.3 (all s, PCH*C*H$_3$). ^{19}F NMR (CD$_2$Cl$_2$, 376.6 Hz): δ −75.9 (s). ^{31}P NMR (CD$_2$Cl$_2$, 162.0 MHz, 295 K): δ 17.5 (br m, *i*Pr$_2$P), 7.7 (br m, Cy$_2$P). ^{31}P NMR (CD$_2$Cl$_2$, 81.0 MHz, 318 K): δ 18.6 (br dd, *J*(RhP^2) = 117.5 Hz, *J*(PP) = 71.0 Hz, *i*Pr$_2$P), 8.4 (br dd, *J*(RhP^1) = 113.4, *J*(PP) = 71.0 Hz, Cy$_2$P). ^{31}P NMR (CD$_2$Cl$_2$, 81.0 MHz, 195 K): δ 19.2−16.0 (br m, *i*Pr$_2$P), 9.9−7.2 (br m, Cy$_2$P).

Preparation of [RhH(O$_3$SCF$_3$)$_2$(κ^2-*i*Pr$_2$PCH$_2$P*i*Pr$_2$)] (12). A solution of **2** (78 mg, 0.20 mmol) in 4 mL of pentane/ether (3:1) was treated at −78 °C with a solution of CF$_3$SO$_3$H (36 μL, 0.40 mmol) in 3 mL of ether. A pale yellow solid precipitated. After the reaction mixture was stirred for 5 min, it was worked up as described for **11**. An off-white solid was obtained: yield 117 mg (90%); mp 50 °C dec. Anal. Calcd for C$_{15}$H$_{31}$F$_6$O$_6$P$_2$RhS$_2$: C, 27.70; H, 4.80; S, 9.86. Found: C, 27.32; H, 4.84; S, 9.48. IR (CH$_2$Cl$_2$): ν(OSO$_{\mathrm{asym}}$) 1300, ν(OSO$_{\mathrm{sym}}$) and ν(CF) 1225−1195, ν(S=O) 1025 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz, 295 K): δ 3.20−2.79 (m, 2H, PCH$_2$P), 2.38, 2.30 (both m, 2H each, PC*H*CH$_3$), 1.37 (br m, 24H, PCHC*H*$_3$), −18.56 (m, 1H, RhH). ^{19}F NMR (CDCl$_3$, 188.3 Hz): δ −78.3 (s). ^{31}P NMR (CD$_2$Cl$_2$, 81.0 MHz, 295 K): δ 15.7 (d, *J*(RhP) = 117.0 Hz). ^{31}P NMR (CD$_2$Cl$_2$, 81.0 MHz, 243 K): δ 17.9 (d, *J*(RhP) = 115.2 Hz), 18.5 (A-part of the ABX spin system, *J*(RhP$^{\mathrm{A}}$) = 121.0, *J*(PP) = 73.3 Hz, P$^{\mathrm{A}}$), 17.2 (B-part of the ABX spin system, *J*(RhP$^{\mathrm{B}}$) = 113.6, *J*(PP) = 73.3 Hz, P$^{\mathrm{B}}$).

Preparation of [RhHCl$_2$(κ^2-*i*Pr$_2$PCH$_2$CH$_2$P*i*Pr$_2$)] (14). This compound was prepared as described for **8**, using [Rh(η^3-C$_3$H$_5$)(κ^2-*i*Pr$_2$PCH$_2$CH$_2$P*i*Pr$_2$)] (**13**) (230 mg, 0.57 mmol) as starting material. A pale yellow solid was obtained: yield 235 mg (95%); mp 96 °C dec. Anal. Calcd for C$_{14}$H$_{33}$Cl$_2$P$_2$Rh: C, 38.46; H, 7.61. Found: C, 38.28; H, 7.07. IR (CH$_2$Cl$_2$): ν(RhH) 2140 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 2.18 (m, 4H, PC*H*$_2$C*H*$_2$P), 1.70 (m, 4H, PC*H*CH$_3$), 1.27, 1.08 (both m, 24H, PCHC*H*$_3$), −18.40 (br dt, *J*(RhH) = 18.9, *J*(PH) = 19.3 Hz, 1H, RhH). ^{13}C NMR (CDCl$_3$, 50.3 MHz): δ 27.8 (d, *J*(PC) = 25.0 Hz, P*C*HCH$_3$), 26.0 (d, *J*(PC) = 33.5 Hz, P*C*HCH$_3$), 21.4, 20.7 (both br m, P*C*H$_2$*C*H$_2$P), 19.7, 17.9, 17.8 (all s, PCH*C*H$_3$). ^{31}P NMR (CDCl$_3$, 81.0 MHz): δ 105.0 (d, *J*(RhP) = 134.4 Hz).

Preparation of [RhH(O$_3$SCF$_3$)$_2$(κ^2-*i*Pr$_2$PCH$_2$CH$_2$P*i*Pr$_2$)] (15). This compound was prepared as described for **12**, using **13** (208 mg, 0.51 mmol) as starting material. A pale yellow solid was obtained: yield 280 mg (82%); mp 80 °C dec. Anal. Calcd for C$_{16}$H$_{33}$F$_6$O$_6$P$_2$RhS$_2$: C, 28.92; H, 5.00; S, 9.65. Found: C, 28.85; H, 4.95; S, 9.27. IR (CH$_2$Cl$_2$): ν(OSO$_{\mathrm{asym}}$) 1297, ν(OSO$_{\mathrm{asym}}$) and ν(CF) 1265−1228, ν(OSO$_{\mathrm{sym}}$) 1213, 1168, ν(S=O) 1025 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz, 295 K): δ 2.49 (br m, 4H, PC*H*$_2$C*H*$_2$P), 1.89 (m, 4H, PC*H*CH$_3$), 1.27 (m, 24H, PCHC*H*$_3$), −21.02 (m, 1H, RhH). ^{1}H NMR (CDCl$_3$, 200 MHz, 308 K): δ 2.53 (br m, 4H, PC*H*$_2$C*H*$_2$P), 1.87 (br m, 4H, PC*H*CH$_3$), 1.38 (dd, *J*(PH) = 16.7, *J*(HH) = 6.9 Hz, 6H, PCHC*H*$_3$), 1.34 (dd, *J*(PH) = 15.6, *J*(HH) = 7.3 Hz, 6H, PCHC*H*$_3$), 1.31 (dd, *J*(PH) = 13.8, *J*(HH) = 6.9 Hz, 6 H, PCHC*H*$_3$), 1.23 (dd, *J*(PH) = 15.3, *J*(HH) = 6.9 Hz, 6H, PCHC*H*$_3$), −21.01 (br dt, *J*(RhH) = 21.8, *J*(PH) = 21.4 Hz, 1H, RhH). ^{13}C NMR (CD$_2$Cl$_2$, 50.3 MHz, 308 K): δ 120.2 (q, *J*(FC) = 323.9 Hz, CF$_3$), 27.3 (d, *J*(PC) = 25.0 Hz, P*C*HCH$_3$), 25.7 (d, *J*(PC) = 31.7 Hz, P*C*HCH$_3$), 21.5, 20.7 (both br m, P*C*H$_2$*C*H$_2$P), 20.1, 18.0, 17.8, 17.4 (all s, PCH*C*H$_3$). ^{19}F NMR (CDCl$_3$, 188.3 MHz, 308 K): δ −78.6 (s). ^{31}P NMR (CD$_2$Cl$_2$, 81.0 MHz, 295 K): δ 106.8 (br m). ^{31}P NMR (CDCl$_3$, 81.0 MHz, 308 K): δ 106.9 (d, *J*(RhP) = 141.0 Hz).

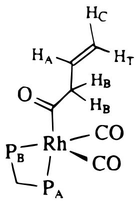
Preparation of [Rh(η^3-C$_3$H$_5$)(CO)(κ^2-*i*Pr$_2$PCH$_2$P*i*Pr$_2$)] (16). A degassed solution of **2** (111 mg, 0.28 mmol) in 15 mL of pentane was treated at −40 °C with CO and then under continuous stirring slowly (ca. 10 min) warmed to room temperature. A rapid change of color from orange-yellow to orange-red and finally to pale yellow occurred. After removal of the solvent in vacuo, the remaining yellow solid was washed at −40 °C twice with 2-mL portions of pentane and dried: yield 99 mg (83%); mp 32 °C dec. Anal. Calcd for C$_{17}$H$_{35}$OP$_2$Rh: C, 48.58; H, 8.39. Found: C, 48.77; H, 8.12. IR (C$_6$H$_6$): ν(C≡O) 1980 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 200 MHz, 295 K): δ 5.06 (m, 1H, H$_{\mathrm{M}}$), 2.56 (m, 4H, H$_{\mathrm{A}}$ and H$_{\mathrm{S}}$), 2.16 (br m, 2H, PCH$_2$P), 1.72 (m, 4H, PC*H*CH$_3$), 1.02, 0.95 (both dd, *J*(PH) = 14.6, *J*(HH) = 7.0 Hz, 12H each, PCHC*H*$_3$). ^{1}H NMR (C$_6$D$_5$CD$_3$, 200 MHz, 233 K): δ 5.12 (br m, 1H, H$_{\mathrm{M}}$), 2.90 (br d, *J*(H$_{\mathrm{M}}$H$_{\mathrm{S}}$) = 5.6 Hz, 2H, H$_{\mathrm{S}}$), 2.09 (br m, 4H, PCH$_2$P and H$_{\mathrm{A}}$), 1.59 (br m, 4H, PC*H*CH$_3$), 0.98 (m, 24H, PCHC*H*$_3$). ^{13}C NMR (C$_6$D$_5$CD$_3$, 50.3 MHz, 295 K): δ 201.4 (dt, *J*(RhC) = 76.8, *J*(PC) = 6.5 Hz, Rh−CO), 82.8 (br s, η^3-H$_2$C−*C*H−CH$_2$), 47.8 (br d, *J*(RhC) = 7.4 Hz, η^3-H$_2$*C*−CH−*C*H$_2$), 29.5 (br m, PCH$_2$P), 27.5 (br s, P*C*HCH$_3$), 19.1, 18.8 (both s, PCH*C*H$_3$). ^{31}P NMR (C$_6$D$_6$, 81.0 MHz, 295 K): δ 9.1 (br d, *J*(RhP) = 122.8 Hz). ^{31}P NMR (C$_6$D$_5$CD$_3$, 81.0 MHz, 233 K): δ 9.5 (d, *J*(RhP) = 129.0 Hz).

Preparation of [Rh(η^3-C$_3$H$_5$)(CO)(κ^2-Cy$_2$PCH$_2$P*i*Pr$_2$)] (17). This compound was prepared as described for **16**, using **3** (156 mg, 0.33 mmol) as starting material. An orange-yellow solid was obtained: yield 132 mg (80%); mp 41 °C dec. Anal. Calcd for C$_{23}$H$_{43}$OP$_2$Rh: C, 55.24; H, 8.66. Found: C, 55.73; H, 8.10. IR (C$_6$H$_6$): ν(C≡O) 1940 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 5.25 (m, 1H, H$_{\mathrm{M}}$), 2.79 (br m, 4H, H$_{\mathrm{A}}$ and H$_{\mathrm{S}}$), 2.35 (t, *J*(P^{1}H) = *J*(P^{2}H) = 6.0 Hz, 2H, PCH$_2$P), 1.73 (br m, 12H, PC*H*CH$_3$ and PC*H*CH$_2$), 1.23 (br m, 12H, C$_6$H$_{11}$), 1.07 (dd, *J*(PH) = 14.4, *J*(HH) = 7.2 Hz, 6H, PCHC*H*$_3$), 1.00 (dd, *J*(PH) = 14.4, *J*(HH) = 7.0 Hz, 6H, PCHC*H*$_3$). ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ 201.0 (br d, *J*(RhC) = 78.5 Hz, Rh−CO), 87.4 (br s, η^3-H$_2$C−*C*H−CH$_2$), 40.4 (br s, η^3-H$_2$*C*−CH−*C*H$_2$), 37.9 (br s, P*C*HCH$_2$), 29.6, 29.5, 29.4, 29.3 (all s, PCH*C*H$_2$), 27.7, 27.6 (both s, CH$_2$ of C$_6$H$_{11}$), 27.6 (m, P*C*HCH$_3$), 27.5, 27.4 (both s, CH$_2$ of C$_6$H$_{11}$), 27.2 (br m, PCH$_2$P), 26.7 (s, CH$_2$ of C$_6$H$_{11}$), 19.2, 19.2, 19.0, 18.9 (all s, PCH*C*H$_3$). ^{31}P NMR (C$_6$D$_6$, 81.0 MHz): δ 14.2 (dd, *J*(RhP^2) = 127.2, *J*(PP) = 19.1 Hz, *i*Pr$_2$P), 2.0 (dd, *J*(RhP^1) = 110.0, *J*(PP) = 19.1 Hz, Cy$_2$P).

Preparation of [Rh(η^3-C$_3$H$_5$)(CO)(κ^2-Ph$_2$PCH$_2$P*i*Pr$_2$)] (18). This compound was prepared as described for **16**, using

4 (85 mg, 0.18 mmol) as starting material. An orange-red oil was obtained which according to the NMR spectra contained some impurities. IR (C_6H_6): *ν*(C≡O) 2005 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz, 295 K): *δ* 7.54 (m, 4 H, *ortho*-H of C_6H_5), 7.03 (m, 6 H, *meta*-H and *para*-H of C_6H_5), 4.96 (br m, 1H, H_M), 2.77−2.40 (br m, 6H, PCH_2P and H_A and H_S), 1.82 (m, 2H, PC*H*CH$_3$), 0.92 (br dd, *J*(PH) = 14.6, *J*(HH) = 7.0 Hz, 12H, PCHC*H*$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): *δ* 31.7 (br m, *i*Pr$_2$P), −19.7 (br m, Ph$_2$P).

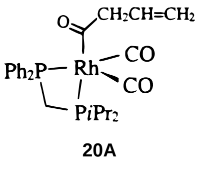
Preparation of [Rh{C(O)CH$_2$CH═CH$_2$}(CO)$_2$(*κ*^{2}-*i*Pr$_2$PCH$_2$P*i*Pr$_2$)] (19). (a) A degassed solution of **2** (100 mg, 0.25 mmol) in 6 mL of pentane was treated at −40 °C with CO, and the mixture was stirred for 10 min. A rapid change of color from orange-yellow to orange-red and finally to pale yellow occurred, and a white solid precipitated. While the CO atmosphere was maintained, the reaction mixture was cooled to −78 °C and the mother liquor was removed. The remaining white solid was washed at −78 °C with 1 mL of pentane and dried with a slow stream of CO: yield 46 mg (38%). (b) The method as described for (a) was used, with **16** (100 mg, 0.24 mmol) as starting material: yield 40 mg (35%).



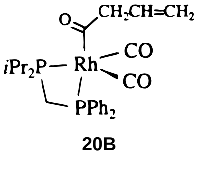
19

IR (pentane): *ν*(C≡O) 1974, 1940, *ν*(C═O) 1699 cm^{-1}. ^{1}H NMR ($C_6D_5CD_3$, 200 MHz, 233 K): *δ* 6.38 (ddt, *J*(H_TH_A) = 16.8, *J*(H_CH_A) = 10.5, *J*(H_BH_A) = 7.2 Hz, 1H, H_A), 5.09 (m, 2H, H_C and H_T), 3.96 (d, *J*(H_AH_B) = 7.2 Hz, 2H, H_B), 1.82 (m, 4H, PCH_2P and PC*H*CH$_3$), 1.55 (m, 2H, PC*H*CH$_3$), 1.16 (dd, *J*(PH) = 17.2, *J*(HH) = 7.0 Hz, 6H, PCHC*H*$_3$), 0.95 (dd, *J*(PH) = 16.2, *J*(HH) = 7.2 Hz, 6H, PCHC*H*$_3$), 0.87 (dd, *J*(PH) = 15.4, *J*(HH) = 7.0 Hz, 6H, PCHC*H*$_3$), 0.74 (dd, *J*(PH) = 14.2, *J*(HH) = 7.0 Hz, 6H, PCHC*H*$_3$). ^{31}P NMR ($C_6D_5CD_3$, 81.0 MHz, 233 K): *δ* 10.3 (dd, *J*(RhP) = 63.5, *J*(PP) = 54.2 Hz, P_A), 3.2 (dd, *J*(RhP) = 139.3, *J*(PP) = 54.2 Hz, P_B).

Preparation of [Rh{C(O)CH$_2$CH═CH$_2$}(CO)$_2$(*κ*^{2}-Ph$_2$PCH$_2$P*i*Pr$_2$)] (20). This compound was prepared similarly to method a for **19**, using **4** (95 mg, 0.21 mmol) as starting material. A pale yellow solid was obtained: yield 50 mg (45%). A mixture of two diastereoisomers in a **20A**:**20B** ratio of 60:40 was obtained. Isomer **20A**: IR (pentane) *ν*(C≡O) 1990, 1945 (*ν*(C═O) could not be exactly located); ^{1}H NMR ($C_6D_5CD_3$, 200 MHz, 233 K) 7.79 (m, *ortho*-H of C_6H_5), 7.01 (m, *meta*-H and *para*-H of C_6H_5), 6.27 (m, H_A), 4.95 (m, H_C and H_T), 3.87 (d, *J*(H_AH_B) = 7.0 Hz, 2H, H_B), 2.66 (m, PCH_2P), 1.34−1.10 (m, PC*H*CH$_3$ and PCHC*H*$_3$), 0.70 (m, PCHC*H*$_3$); ^{31}P NMR ($C_6D_5CD_3$, 81.0 MHz, 233 K) *δ* 15.5 (dd, *J*(RhP) = 63.2, *J*(PP) = 50.9 Hz, *i*Pr$_2$P), −25.7 (dd, *J*(RhP) = 143.1, *J*(PP) = 50.9 Hz, Ph$_2$P). Isomer **20B**: IR (pentane) *ν*(C≡O) 2010, 1960



20A

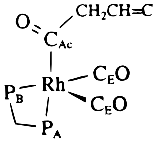


20B

(*ν*(C═O) could not be exactly located); ^{1}H NMR ($C_6D_5CD_3$, 200 MHz, 233 K) 7.91 (m, *ortho*-H of C_6H_5), 7.01 (m, *meta*-H and *para*-H of C_6H_5), 6.27 (m, H_A), 4.95 (m, H_C and H_T), 3.95 (d, *J*(H_AH_B) = 7.0 Hz, 2H, H_B), 2.66 (m, PCH_2P), 1.88 (m, PC*H*CH$_3$), 0.70 (m, PCHC*H*$_3$); ^{31}P NMR ($C_6D_5CD_3$, 81.0 MHz, 233 K) *δ* 8.0 (dd, *J*(RhP) = 142.4, *J*(PP) = 54.5 Hz, *i*Pr$_2$P), −13.0 (dd, *J*(RhP) = 64.7, *J*(PP) = 54.5 Hz, Ph$_2$P).

Preparation of [Rh{C(O)CH$_2$Ph}(CO)$_2$(*κ*^{2}-*i*Pr$_2$PCH$_2$P*i*Pr$_2$)] (22). This compound was prepared similarly to method a for **19**, using [Rh(*η*^{3}-CH$_2$Ph)(*κ*^{2}-*i*Pr$_2$PCH$_2$P*i*Pr$_2$)] (**21**) (58 mg, 0.13 mmol) as starting material. A white solid was obtained: yield 25 mg (37%). IR (pentane): *ν*(C≡O) 1984, 1940, *ν*(C═O) 1714 cm^{-1}. ^{1}H NMR ($C_6D_5CD_3$, 200 MHz, 233 K): *δ* 7.19 (m, 5H, C_6H_5), 4.40 (s, 2H, CH_2Ph), 1.81 (br m, 4H, PCH_2P and PC*H*CH$_3$), 1.57 (m, 2H, PC*H*CH$_3$), 0.98 (m, 24H, PCHC*H*$_3$). ^{31}P NMR ($C_6D_5CD_3$, 81.0 MHz, 233 K): *δ* 10.2 (dd, *J*(RhP) = 63.5, *J*(PP) = 55.1 Hz, P_A), 3.0 (dd, *J*(RhP) = 138.8, *J*(PP) = 55.1 Hz, P_B).

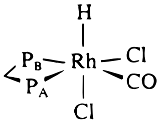
Preparation of [Rh{*C(O)CH$_2$CH═CH$_2$}(*CO)$_2$(*κ*^{2}-*i*Pr$_2$PCH$_2$P*i*Pr$_2$)] (19a). A degassed solution of **2** (54 mg, 0.14 mmol) in 1 mL of $C_6D_5CD_3$ was treated at −40 °C with ^{13}CO, and the mixture was stirred for 1 min. The resulting solution was studied by NMR spectroscopy. ^{1}H NMR ($C_6D_5CD_3$, 200 MHz, 233 K): *δ* 6.34 (m, 1H, H_A), 5.08 (m, 2H, H_C and H_T), 3.94 (m, 2H, H_B), 1.84 (m, 4H, PCH_2P and PC*H*CH$_3$), 1.55 (m, 2H, PC*H*CH$_3$), 1.15 (dd, *J*(PH) = 17.2, *J*(HH) = 7.0 Hz, 6H, PCHC*H*$_3$), 0.95 (dd, *J*(PH) = 16.2, *J*(HH) = 7.2 Hz, 6H, PCHC*H*$_3$), 0.88, 0.75 (both dd, *J*(PH) = 14.3, *J*(HH) = 6.9 Hz, 6H each, PCHC*H*$_3$). ^{13}C NMR ($C_6D_5CD_3$, 50.3 MHz, 233 K): *δ* 235.1 (br dddt, *J*(RhC_{Ac}) = 21.4, *J*(P_AC_{Ac}) = 87.6, *J*(P_BC_{Ac}) = 3.0, *J*(C_EC_{Ac}) = 2.4 Hz, C_{AC}), 201.5 (dddd, *J*(RhC_E) = 75.7, *J*(P_BC_E) = 28.6, *J*(P_AC_E) = 13.8, *J*($C_{Ac}C_E$) = 2.4 Hz, C_E); under the experimental conditions the signals of the other carbon atoms were not exactly located. ^{31}P NMR ($C_6D_5CD_3$, 81.0 MHz, 233 K): *δ* 10.3 (dddt, *J*(RhP) = 63.5, *J*(PP) = 54.2, *J*($C_{Ac}P_A$) = 87.6, *J*(C_EP_A) = 13.8 Hz, P_A), 3.2 (dddt, *J*(RhP) = 139.3, *J*(PP) = 54.2, *J*(C_EP_B) = 28.6, *J*($C_{Ac}P_B$) = 3.0 Hz, P_B).



19a

Preparation of [Rh{C(O)CH$_2$CH═CH$_2$}(*CO)$_2$(*κ*^{2}-*i*Pr$_2$PCH$_2$P*i*Pr$_2$)] (19b). A degassed solution of **16** (37 mg, 0.09 mmol) in 0.4 mL of $C_6D_5CD_3$ was treated at −40 °C with ^{13}CO, and the mixture was stirred for 1 min. The resulting solution was studied by NMR spectroscopy. ^{13}C NMR ($C_6D_5CD_3$, 50.3 MHz, 233 K): *δ* 201.6 (ddd, *J*(RhC) = 75.1, *J*(P_BC) = 28.4, *J*(P_AC) = 13.8 Hz, Rh−CO); under the experimental conditions the signals of the other carbon atoms were not exactly located. ^{31}P NMR ($C_6D_5CD_3$, 81.0 MHz, 233 K): *δ* 10.0 (ddt, *J*(RhP_A) = 62.8, *J*(PP) = 54.2, *J*(C_EP_A) = 13.8 Hz, P_A), 3.1 (ddt, *J*(RhP_B) = 138.8, *J*(PP) = 54.2, *J*(C_EP_B) = 28.6 Hz, P_B).

Reaction of 19 with HCl. A degassed solution of **2** (132 mg, 0.34 mmol) in 10 mL of ether was treated at −40 °C with CO, and the mixture was stirred for 10 min. As described above, under these conditions the acyl complex **19** was formed. While the CO atmosphere was maintained, a slow stream of HCl was passed through the reaction mixture, which led to the rapid formation of a pale yellow precipitate. After the mother liquor was removed, the remaining solid was washed at room temperature three times with 5-mL portions of ether and twice with 5-mL portions of pentane and dried with a slow stream of CO. A pale yellow solid was obtained, which according to the spectroscopic data consisted of a mixture of **8** and **25** in the ratio of approximately 1:5. Data for **25** are as follows. IR (CH_2Cl_2): *ν*(RhH) 2098, *ν*(C≡O) 1958. ^{1}H NMR ($CDCl_3$, 200 MHz): *δ* = 3.32 (br m, 1H, PCH_2P), 3.07−2.67



25

(m, 2H, PCH_2P and $PCHCH_3$), 2.48, 2.34, 2.18 (all m, 1H each, $PCHCH_3$), 1.29 (m, 24H, $PCHCH_3$), −13.27 (br dt, $J(RhH) = J(P_AH) = J(P_BH) = 16.0$ Hz, RhH). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 183.2 (ddd, $J(RhC) = 48.1$, $J(P_BC) = 144.1$, $J(P_AC) = 4.4$ Hz, Rh−CO), 29.0 (t, $J(P_AC) = J(P_BC) = 23.4$ Hz, PCH_2P), 28.2 (d, $J(PC) = 21.5$ Hz, $PCHCH_3$), 26.5 (d, $J(PC) = 19.0$ Hz, $PCHCH_3$), 26.0 (d, $J(PC) = 25.0$ Hz, $PCHCH_3$), 25.8 (d, $J(PC) = 21.3$ Hz, $PCHCH_3$), 20.3, 19.7, 19.3, 19.2 (all s, $PCHCH_3$), 18.3 (br s, $PCHCH_3$), 17.1 (d, $J(PC) = 6.2$ Hz, $PCHCH_3$), 16.1 (d, $J(PC) = 4.4$ Hz, $PCHCH_3$). ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ 17.4 (dd, $J(RhP) = 95.2$, $J(PP) = 62.5$ Hz, P_A), -12.2 (dd, $J(RhP) = 85.3$, $J(PP) = 62.5$ Hz, P_B).

Crystal Structure Determination of 16. Single crystals were obtained by cooling a saturated solution of **16** in pentane (from +25 to −25 °C). Data were collected at 133(2) K on a Huber-Stoe-Siemens diffractometer with a CCD area detector using an oil-coated shock-cooled crystal;[31] monochromated Mo Kα (λ = 0.710 73 Å) radiation was used. Crystal data: monoclinic, space group $P2_1/c$, $a = 8.617(2)$ Å, $b = 14.089(3)$ Å, $c = 17.177(3)$ Å, $\beta = 102.78(3)°$, $V = 2033.7(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.373$ g/cm^3, $F(000) = 880$, μ(Mo Kα) = 0.995 mm^{-1}, minimum/maximum transmission 0.636/0.865, crystal dimensions 0.50 × 0.38 × 0.15 mm^3, $4.86° \leq 2\theta \leq 55.14°$; 28 408 measured reflections of which 4697 were independent ($R_{int} = 0.0296$) and employed in the structure refinement (218 parameters, 6 restraints). $R1 = 0.0215$ [$I > 2\sigma(I)$], w$R2 = 0.0465$ (all data);[32] minimum/maximum residual electron density 0.379/−0.355 e Å^{-3}. The hydrogen atoms of the allyl ligand were refined with isotropic displacement parameters. C−H distances were restrained to a fixed value; H−H 1,3-distances were restrained to be equal. A semiempirical absorption correction was applied. The structure was solved by Patterson and Fourier methods with SHELXS-97[33] and refined by full-matrix least-squares procedures on F^2 (SHELXL-97).[34] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

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Supporting Information Available: Tables of crystal data and refinement parameters, bond lengths and angles, and positional and thermal parameters for **16** (5 pages). An X-ray crystallographic file, in CIF format for **16**, is available on the Internet only. Ordering and access information is given on any current masthead page.

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(32) $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; w$R2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, with $w = 1/\sigma^2[(F_o^2) + (0.0128P)^2 + 1.282P]$ where $P = (F_o^2 + 2F_c^2)/3$.

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(34) Sheldrick, G. M. SHELXL-97: program for crystal structure refinement. Universität Göttingen, 1996.