Mono- and Dinuclear Rhodium(I) and Rhodium(III) Complexes with the Bulky Phosphine 2,6-$Me_2C_6H_3CH_2CH_2PtBu_2$, Including the First Structurally Characterized Cis-Configurated Dicarbonyl Compound, *cis*-[$RhCl(CO)_2(PR_3)$]

Giuseppe Canepa, Carsten D. Brandt, and Helmut Werner*

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Received December 4, 2003

The bulky functionalized phosphine 2,6-$Me_2C_6H_3CH_2CH_2PtBu_2$ (**3**) was prepared in a stepwise fashion from the Grignard reagent 2,6-$Me_2C_6H_3CH_2CH_2MgCl$, $tBuPCl_2$, and *t*BuLi. Phosphine **3** reacts with the olefin compounds $[RhCl(C_2H_4)_2]_2$ and $[RhCl(C_8H_{14})_2]_2$ to give the substitution products $[RhCl(olefin)(\mathbf{3})]_2$ (**8**, **9**), of which **9** (olefin = C_2H_4) has been characterized crystallographically. While **9** is rather inert toward **3**, it reacts with **3** under a hydrogen atmosphere to give the dihydrido complex $[RhH_2Cl(\mathbf{3})_2]$ (**11**) via the dimer $[RhH_2Cl(\mathbf{3})]_2$ (**10**) as an intermediate. In the presence of ethene, **11** is reconverted to **9**. The reaction of **8** (olefin = C_8H_{14}) with the phosphonium salt **3**·HCl affords a mixture of $[RhHCl_2(\mathbf{3})]_2$ (**12**) and **3**, which upon warming at 60 °C produces $[RhHCl_2(\mathbf{3})_2]$ (**13**). The attempted separation of **12** by column chromatography on Al_2O_3 led unexpectedly to the formation of the novel half-sandwich-type compound [(η^6-2,6-$Me_2C_6H_3CH_2CH_2PtBu_2$-κP)RhCl] (**14**). Treatment of either **8** or **14** with CO gives *cis*-$[RhCl(CO)_2(\mathbf{3})]$ (**15**), which represents the first structurally characterized dicarbonyl complex with the CO ligands in a cis disposition. In the absence of carbon monoxide, **15** is rather labile and readily converted to $[RhCl(CO)(\mathbf{3})]_2$ (**16**). The reaction of **9** with HCl affords the dinuclear ethylrhodium(III) compound **18**, being built up by two 14-electron $[RhCl_2(C_2H_5)(\mathbf{3})]$ units. These units are linked by two bridging chlorides which are unsymmetrically situated between the two metal centers. Compound **18** reacts with CO to give **15** and with **3** to give **13**, presumably in both cases via $[RhHCl_2(C_2H_4)(\mathbf{3})]$ as an intermediate. The half-sandwich-type complexes [(η^6-2,6-$Me_2C_6H_3CH_2CH_2PtBu_2$-κP)Rh(olefin)]PF_6 (**20**, **21**), obtained from $[Rh(acetone)_2(C_8H_{14})_2]PF_6$ as the precursor, react in acetone in the presence of H_2 to give $[RhH_2(acetone)_3(\mathbf{3})]PF_6$ (**22**), which upon addition of diethyl ether generates the dihydride [(η^6-2,6-$Me_2C_6H_3CH_2CH_2PtBu_2$-κP)-RhH_2]PF_6 (**23**). Compound **23** is a suitable starting material for the preparation of compounds having the general composition [(η^6-2,6-$Me_2C_6H_3CH_2CH_2PtBu_2$-κP)Rh(L)]PF_6, where L is acetone, $CH_2{=}CHR$ (R = *t*Bu, Ph), PhC≡CH, and CO, respectively.

Introduction

Recently, we reported the preparation and derivatization of the new phosphines $iPr_2P(CH_2)_2C_6H_5$ and $tBu_2P(CH_2)_2C_6H_5$, which are not only sterically demanding but, in contrast to P*i*Pr$_3$ and P*t*Bu$_3$, can behave either as 2-electron or (2 + 6)-electron ligands.[1] Moreover, these phosphines, in the presence of (olefin)-rhodium(I) or (olefin)iridium(I) compounds, undergo C−H activation of the six-membered ring to give arylhydridometal(III) complexes, the aryl group being part of a C,P-bonded chelating system.[2,3] Since in the reactions of $[RhCl(C_8H_{14})_2]_2$ or $[IrCl(C_8H_{14})_2]_2$ with $R_2P(CH_2)_2C_6H_5$, for example, the insertion of the metal occurs exclusively into the phenyl C−H bond situated in a position ortho to the $CH_2CH_2PR_2$ substituent, we were interested to find out what the behavior of a phosphine such as $tBu_2PCH_2CH_2C_6H_3$-2,6-Me_2 is, which has the two ring carbon atoms next to the β-phosphinoethyl moiety blocked by methyl groups. In this context it is appropriate to mention the pioneering work by Milstein et al. illustrating that the pincer-type ligand C_6H-1,3-$(CH_2PtBu_2)_2$-2,4,6-Me_3 reacts even at room temperature with $[MCl(C_8H_{14})_2]_2$ (M = Rh, Ir) by C−C bond cleavage to give the methylrhodium(III) and -iridium(III) derivatives $[MCl(CH_3)(C_6H$-2,4-$(CH_2PtBu_2)_2$-3,5-Me_2-$\kappa^3P,C,P)]$, respectively.[4]

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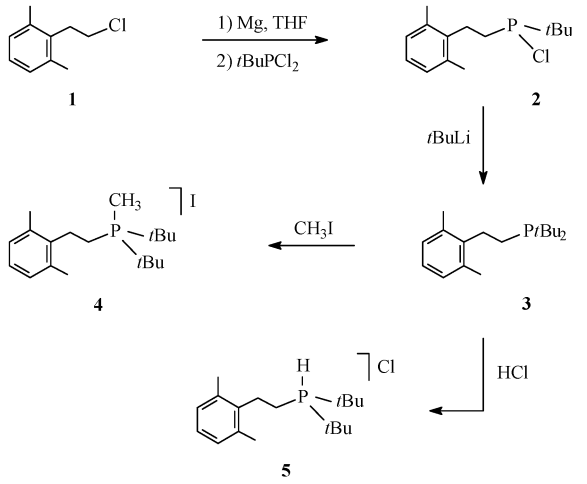
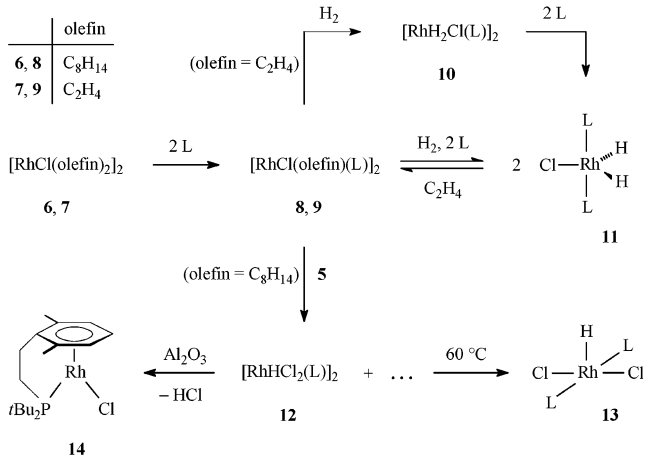
10.1021/om034348p CCC: $27.50
Publication on Web 02/04/2004

Scheme 1



Scheme 2[a]



[a] L = 2,6-$Me_2C_6H_3CH_2CH_2PtBu_2$.

The present paper describes the synthesis and ligand behavior of the title phosphine, the isolation of the first structurally characterized cis-configurated dicarbonylrhodium(I) complex, *cis*-[$RhCl(CO)_2(PR_3)$], the generation and crystallographic identification of an unusual dinuclear alkylrhodium(III) compound, and the preparation of a series of half-sandwich-type complexes in which the functionalized phosphine coordinates to rhodium(I) or rhodium(III) in a chelating fashion. Some preliminary results of this work have already been communicated.[5]

Results and Discussion

Preparation and Derivatization of the Title Phosphine 3. One of the well-known procedures for the preparation of alkyldiphenylphosphines $Ph_2P(CH_2)_nC_6H_5$ (n = 2, 3) consists of the reaction of $LiPPh_2$ or $KPPh_2$ with the respective benzene derivative $C_6H_5(CH_2)_nX$ (X = Cl, Br), which in most cases affords the required phosphine in good to excellent yields.[6] This procedure, however, could not be applied to di-*tert*-butylphosphine analogues such as **3**, since dialkyl phosphides MPR_2 upon treatment with alkyl halides R′X undergo a halide−metal exchange which gives via reaction of MPR_2 with the intermediately formed R_2PX the corresponding diphosphines.[7] Attempts to prepare **3** by hydrophosphination of CH_2=CHC_6H_3-2,6-Me_2 with $HPtBu_2$ in the presence of AIBN (azaisobutyronitrile) as a radical starter afforded a mixture of products which contained the title phosphine in about 10−15% yield but could not be separated by common techniques.

The successful route to obtain phosphine **3** is outlined in Scheme 1. The first step consists of the formation of the Grignard reagent $ClMgCH_2CH_2C_6H_3$-2,6-Me_2, which is generated by addition of a solution of **1** in THF to a suspension of finely divided Mg in the same solvent. This Grignard reagent reacted at 0 °C with $tBuPCl_2$ in THF to give in addition to $MgCl_2$ the chlorophosphine **2**, which after fractional distillation at 0.002 bar was isolated as a colorless air- and moisture-sensitive solid melting at around room temperature. Subsequent treatment of **2** with a solution of *t*BuLi in pentane afforded, after hydrolysis and workup by extraction and fractional distillation, the required phosphine **3** as an oily liquid in about 80% yield. Since no correct elemental analysis of **3** could be obtained, due to the extreme sensitivity toward air, **3** was characterized by MS and NMR spectra as well as by derivatization to the corresponding phosphonium salts **4** and **5**. The ^{31}P NMR spectra of **4** and **5** display in each case a singlet resonance at around δ 49.0, which is shifted downfield by ca. 17 ppm compared with the neutral phosphine **3**.

Reactions of Phosphine 3 with $[RhCl(olefin)_2]_2$. In contrast to related trialkylphosphines such as tBu_2PCH_3,[8] the title compound **3** does not react with $[RhCl(olefin)_2]_2$ (olefin = C_2H_4, C_8H_{14}) to give the mononuclear olefinrhodium(I) complex *trans*-[$RhCl(olefin)(\mathbf{3})_2$]. With **6** and **7** as the starting materials and a 2-fold excess of **3**, the dinuclear compounds **8** and **9** are formed instead (Scheme 2). Both **8** and **9** are yellow, moderately air-sensitive solids, which differ quite significantly in their solubility in organic solvents. While **8** is readily soluble in benzene and dichloromethane (but less so in diethyl ether), the solubility of **9**, even in CD_2Cl_2, is rather scarce. Despite this limitation, the ^{31}P NMR spectrum of **9** could be measured, which, owing to the appearance of one doublet at δ 67.0, indicated that probably only one species is present. In contrast, the ^{31}P NMR spectrum of **8** displayed two resonances (equally doublets) at δ 64.8 and 65.5, of which that at slightly higher field dominates and is thus tentatively assigned to the supposedly thermodynamically preferred trans isomer. The $^{31}P-^{103}Rh$ coupling constants of both signals are nearly the same (188.2 and 185.7 Hz) and are in good agreement with the value for $[RhCl(C_8H_{14})(PiPr_3)]_2$ of $^1J(Rh,P)$ = 183.2 Hz.[9]

To find out whether the single species observed in the ^{31}P NMR spectrum of **9** is the cis or the trans isomer of the dinuclear complex, an X-ray crystal structure analysis was carried out. As shown in Figure 1, the two

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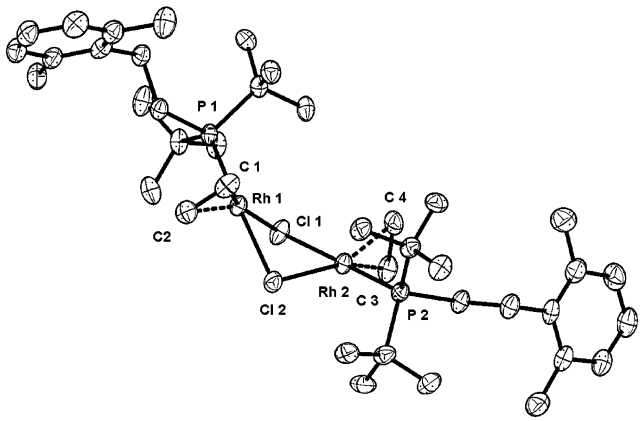

Figure 1. Molecular diagram of compound **9**. Selected bond distances (Å) and angles (deg): Rh(1)−C(1) = 2.107(6), Rh(1)−C(2) = 2.106(5), Rh(1)−P(1) = 2.2653(16), Rh(1)−Cl(1) = 2.4077(16), Rh(1)−Cl(2) = 2.4293(15), Rh(2)−C(3) = 2.105(5), Rh(2)−C(4) = 2.104(5), Rh(2)−P(2) = 2.2701(16), Rh(2)−Cl(1) = 2.4310(16), Rh(2)−Cl(2) = 2.4078(16); Cl(1)−Rh(1)−Cl(2) = 80.01(6), Cl(1)−Rh(2)−Cl(2) = 79.98(6), Cl(1)−Rh(1)−P(1) = 96.99(6), Cl(2)−Rh(1)−P(1) = 176.70(4), Cl(1)−Rh(2)−P(2) = 176.75(5), Cl(2)−Rh(2)−P(2) = 97.10(6).

ethene and the two phosphine ligands are disposed trans to each other, as has also been found in $[RhCl(CO)(PMePh_2)]_2$.[10] The C_2H_4 units are symmetrically linked to the metal centers and lie nearly perpendicular to the coordination planes around Rh(1) and Rh(2). The central Rh_2Cl_2 four-membered ring is bent, the dihedral angle between the two planes $[RhCl_2(C_2H_4)(\mathbf{3})]$ being 143.3°. A similar bending of about the same size has been observed for $[RhCl(CO)(PMe_2Ph)]_2$ and for compounds of the general formula $[RhCl(L)_2]_2$ with L = C_2H_4,[11] cyclohexene,[12] CO,[13] PF_3[14] as well. It should be mentioned that although only the trans isomer of **9** has been found in the crystal, we cannot exclude the possibility that in solution small amounts of the cis isomer are present. Their identification might be prevented by the unfavorable signal-to-noise ratio as a result of the low solubility of the product.

In contrast to what we expected, compounds **8** and **9** do not react with an excess of **3** at room temperature to afford either *trans*-$[RhCl(olefin)(\mathbf{3})_2]$ or $[RhCl(\mathbf{3})_2]_2$. When the starting materials are heated in benzene at ca. 75 °C, a complicated mixture of products is formed, among which the half-sandwich-type complex **14** could be detected. All attempts to separate these mixtures by column chromatography failed.

The attempted conversion of **9**, under a hydrogen atmosphere in order to eliminate and hydrogenate the olefin, with 2 equiv of **3** to $[RhCl(\mathbf{3})_2]_n$ (n = 1, 2) affords the dihydrido complex **11** in practically quantitative yield. Typical features of **11**, which is a yellow, moderately air-sensitive solid, are the high-field ^{1}H NMR signal at δ −23.03 (split into a doublet of triplets due to ^{1}H−^{103}Rh and ^{1}H−^{31}P coupling) and the Rh−H stretching mode at 2122 cm^{-1} in the IR spectrum. The ^{31}P NMR spectrum of **11** displays a doublet resonance, indicating that the two phosphine ligands are stereochemically equivalent.

Regarding the mechanism of formation of **11**, we conclude from the inert behavior of **9** toward phosphine **3** that in the initial step an oxidative addition of H_2 followed by the elimination of ethane takes place. This is supported by the observation that upon stirring a solution of **9**, in the absence of **3**, under a H_2 atmosphere a hydridorhodium(III) compound can be detected which presumably is the dimer **10** (see Scheme 2). Since this species is only stable in the presence of excess hydrogen, it has been characterized by spectroscopic techniques. The ^{1}H NMR spectrum of **10** shows a hydride signal at δ −21.50, which like the single ^{31}P NMR resonance at δ 96.4 is somewhat broadened at 295 K. After the temperature is increased to 313 K, the ^{1}H NMR spectrum displays a sharp doublet at δ −21.48, the chemical shift being in agreement with the assumption that the hydrido ligands occupy terminal but not bridging positions. This proposal is supported by the IR spectrum, which shows two ν(RhH) vibrations at 2149 and 2125 cm^{-1}: i.e., in a region where the stretching modes of terminal Rh−H bonds appear.[15] To explain the broadening of the NMR resonances at 295 K, it is conceivable that an equilibrium between a $[(PR_3)H_2Rh(\mu\text{-}Cl)_2RhH_2(PR_3)]$ dimer and a corresponding isomer with one or two bridging hydrides exists which at higher temperatures is shifted to the aforementioned molecule. Addition of **3** to the CH_2Cl_2 solution of **10** yields exclusively the monomeric dihydrido complex **11**.

Compound **11** is completely inert toward cyclooctene and 3,3-dimethyl-1-butene and does not afford $[RhCl(\mathbf{3})_2]_n$ (n = 1, 2) by abstraction of H_2. It reacts, however, in pentane at room temperature with excess ethene to give the dimeric product **9**. Uncoordinated phosphine **3** can also be detected. The reaction is rather slow at 295 K and 1 bar, and thus even after 3 days small amounts (ca. 10%) of the starting material are still present. Replacing the ethene by a hydrogen atmosphere reconverts the mixture of **9** and **3** to **11**.

An Unprecedented Half-Sandwich-Type (Arene)rhodium(I) Complex. While **9** and its cyclooctene counterpart **8** are fairly inert toward **3**, the latter reacts with the phosphonium salt **5** in diethyl ether at room temperature. If the molar ratio of **8** to **5** is 1:2, a mixture of products is isolated which consists of equal amounts of **5** and a new compound, which we assume is the dichlorohydridorhodium(III) complex **12** (see Scheme 2). The ^{1}H NMR spectrum of **12** displays a doublet of doublets resonance at δ −22.48 (for comparison see **10**: δ −21.48) and the IR spectrum a Rh−H stretching vibration at 2146 cm^{-1} (see **10**: 2149 and 2125 cm^{-1}). On the basis of the relative intensities of the ^{1}H NMR signals, we believe that **12** is an analogue of **10**, with only one hydride and one chloride being

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terminally bonded to each rhodium and two chlorides being in bridging positions. Warming the solution of **5** and **12** in benzene for 2 h at 60 °C leads to the formation of the monomer **13**, which after removal of the solvent is isolated as an orange air-stable solid in 71% yield. Typical spectroscopic features of **13** are the high-field signal (doublet of triplets) at δ −31.03 in the ^{1}H NMR and the doublet resonance at δ 50.0 in the ^{31}P NMR spectrum, both of which are in support of the proposed structure.

After we failed to prepare an analogue of either [RhCl(PCy$_3$)$_2$][16] or [RhCl(P*i*Pr$_3$)$_2$]$_2$[17] with the general composition [RhCl(**3**)$_2$]$_n$ from **8** or **9** and phosphine **3**, we attempted to prepare the required product by treating the dichloro hydrido complex **13** with NEt$_3$ in benzene. Although the reaction is quite fast, as indicated by a quick change of color from orange to light brown and the precipitation of a white solid ([HNEt$_3$]Cl), the target compound [RhCl(**3**)$_2$]$_n$ is not formed. Quite surprisingly, the unusual half-sandwich-type complex **14** is generated instead. Since **14**, similarly to [HNEt$_3$]Cl, is only sparingly soluble in benzene, it could not be completely separated from the ammonium salt and was thus, in the initial part of our studies, only characterized by spectroscopic means.

A clean method to obtain **14** as an analytically pure compound was found by an unexpected route. While we attempted to separate the mixture of **5** and **12** using column chromatography on Al$_2$O$_3$, we observed that from the yellow material a green fraction could be eluted with CH$_2$Cl$_2$. Removal of the solvent afforded a green, very air-sensitive solid which is readily soluble in polar organic solvents but nearly insoluble in hydrocarbons. Conductivity measurements confirmed that **14** is a nonelectrolyte. The coordination of the arene ring to the metal center is clearly indicated by the ^{1}H and ^{13}C NMR spectra, in which the signals for the C−H protons and the ring carbon atoms are shifted considerably to higher fields compared with those for the free arene. Characteristic in particular is the resonance for the CH carbon atom in a position para to the CH$_2$CH$_2$P*t*Bu$_2$ substituent, which appears at δ 94.1 as a doublet of doublets due to ^{13}C−^{103}Rh and ^{13}C−^{31}P coupling. The corresponding signal (singlet) for the free phosphine **3** is observed at δ 126.1. Since to the best of our knowledge neutral complexes of the general formula [(η^6-arene)Rh(PR$_3$)X] (X = halide) are unknown,[18] the existence of **14** illustrates quite clearly the supportive influence of the functionalized phosphine **3** for the formation of half-sandwich-type arenerhodium(I) derivatives.

The First Structurally Characterized Dicarbonylrhodium(I) Complex, *cis*-[RhCl(CO)$_2$(PR$_3$)]. As we assumed, in analogy to the behavior of phosphines such as Ph$_2$P(CH$_2$)$_n$C$_6$H$_5$ (n = 2, 3)[6,19] and R$_2$P(CH$_2$)$_2$C$_6$H$_5$ (R = *i*Pr, *t*Bu),[1,3] that in compound **14** the chelating phosphine **3** is coordinated as a hemilabile ligand, we were prompted to find out what the reactivity of **14** toward carbon monoxide is. Being aware of the fact that rhodium(I) complexes of the type *cis*-[RhCl(CO)$_2$(PR$_3$)] have been reported by various authors to be key intermediates in the reactions of [RhCl(CO)$_2$]$_2$ with PR$_3$ and of [RhCl(CO)(PR$_3$)]$_2$ with CO,[20] we were quite optimistic that upon treatment of **14** with carbon monoxide a dicarbonyl derivative of the required composition could be generated.

The reactions of both **14** and dimer **8**, the latter containing a labile cyclooctene ligand, with CO in pentane or dichloromethane are indeed very fast and lead in a few seconds to the formation of a yellow compound, the ^{31}P NMR spectrum of which displays a single resonance at δ 57.8 (in CD$_2$Cl$_2$). However, after evaporation of the solvent in vacuo a yellow air-stable product is isolated which is not the initially formed species but a mixture of the cis and trans isomers of the dimer **16**. The ^{31}P NMR spectrum of this mixture shows two resonances (both doublets) at δ 79.4 (^1J(Rh,P) = 172.9 Hz) and 78.6 (^1J(Rh,P) = 174.6 Hz), which are assigned to *cis*-[RhCl(CO)(**3**)]$_2$ and *trans*-[RhCl(CO)(**3**)]$_2$, respectively. Since the cis isomer is more readily soluble in pentane, it can be washed out and the trans isomer **16** is thus obtained in analytically pure form. The proposed structure for **16** is supported by the observation of a doublet of doublets at δ 186.8 for the CO carbon atoms in the ^{13}C NMR spectrum, the chemical shift and the ^1J(Rh,C) and ^2J(P,C) coupling constants being similar to those of *trans*-[RhCl(CO)(PPh$_3$)]$_2$.[21]

Taking into account that the intermediate, initially generated from **14** or **8** and carbon monoxide, is rather labile and rapidly eliminates CO, we applied a different methodology to isolate the dicarbonyl **15**. We started with **16** as the precursor, treated this in pentane with carbon monoxide, and removed the solvent not in vacuo but with a stream of CO. Using this procedure, we were able to obtain a light yellow air-stable solid, correctly analyzed as **15** in 95% yield (Scheme 3). The IR spectrum of **15** displays (in contrast to that of **16**, which shows a single ν(CO) mode at 1962 cm^{-1}) two stretching vibrations at 2086 and 1999 cm^{-1} (in KBr), indicating that the two CO ligands are in different environments. In the ^{13}C NMR spectrum of **15** also two CO resonances appear at δ 184.8 and 181.1, the first of which has a ^2J(P,C) coupling constant of 16.2 and the latter a ^2J(P,C) coupling constant of 112.5 Hz. The first signal is thus assigned to the CO ligand cis and the second signal to the CO ligand trans to the phosphine. Under argon (1 bar) compound **15** is stable both as a solid and in

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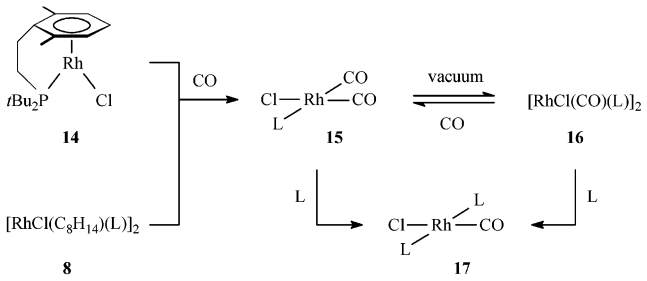
Scheme 3[a]



[a] L = 2,6-$Me_2C_6H_3CH_2CH_2PtBu_2$.

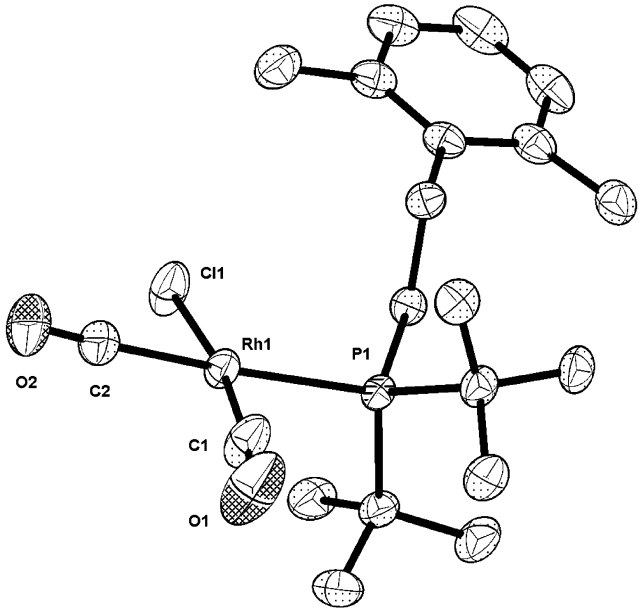


Figure 2. Molecular diagram of compound **15**. Selected bond distances (Å) and angles (deg): Rh(1)−C(1) = 1.826(2), Rh(1)−C(2) = 1.9112(19), Rh(1)−P(1) = 2.4004(4), Rh(1)−Cl(1) = 2.3414(5), C(1)−O(1) = 1.135(3), C(2)−O(2) = 1.116(2); Rh(1)−C(1)−O(1) = 172.8(2), Rh(1)−C(2)−O(2) = 177.1(2), Cl(1)−Rh(1)−P(1) = 92.354(16), Cl(1)−Rh(1)−C(1) = 171.60(8), Cl(1)−Rh(1)−C(2) = 86.43(6), C(1)−Rh(1)−C(2) = 88.19(9), C(1)−Rh(1)−P(1) = 93.31(6), C(2)−Rh(1)−P(1) = 177.08(6).

solution, which is in sharp contrast to observations reported for other rhodium(I) compounds *cis*-[RhCl(CO)$_2$(PR$_3$)].[20,22] In agreement with the assumption that **15** is an intermediate in the formation of **16** from **8** and **14**, it is easily converted to **16** in vacuo either in solution or in the solid state.

The result of the X-ray crystal structure analysis of **15** is outlined in Figure 2. As expected, the coordination geometry around rhodium is square planar with bond angles P−Rh−Cl and P−Rh−C(1), which are slightly larger than 90°, and bond angles C(2)−Rh−Cl and C(1)−Rh−C(2), which are slightly smaller than 90°. The effect of the sterically demanding phosphine is obvious. The Rh−C(2)−O(2) axis is nearly linear (177.1(2)°), while the Rh−C(1)−O(1) axis is somewhat bent (172.8(2)°), which could equally be due to the steric hindrance between the cis-disposed CO ligand and the substituents at phosphorus. The most noteworthy feature, however, is the difference in the Rh−C bond lengths (1.826(2) vs 1.9112(19) Å), which clearly reflects the trans influence of the phosphine. The bulky alkyl substituent CH_2-$CH_2C_6H_3$-2,6-Me_2 is pointing away from the basal coordination plane, which means that no interaction between the arene ring and the metal center exists. Moreover, an intermolecular π-stacking between the six-membered rings can also be excluded.

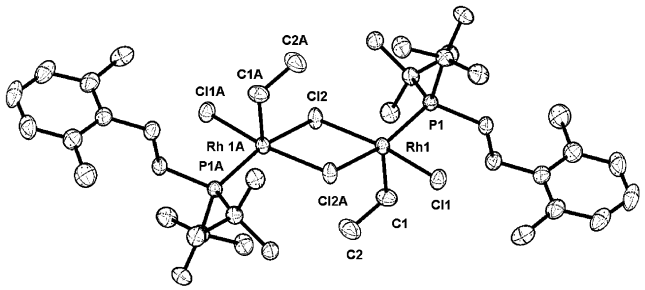


Figure 3. Molecular diagram of compound **18**. Selected bond distances (Å) and angles (deg): Rh(1)−C(1) = 2.059(3), C(1)−C(2) = 1.480(4), Rh(1)−P(1) = 2.2711(7), Rh(1)−Cl(1) = 2.3059(7), Rh(1)−Cl(2) = 2.3561(6), Rh(1)−Cl(2A) = 2.5257(6); Cl(1)−Rh(1)−Cl(2) = 167.52(2), Cl(1)−Rh(1)−Cl(2A) = 87.19(2), Cl(1)−Rh(1)−P(1) = 92.63(2), Cl(1)−Rh(1)−C(1) = 87.77(9), Cl(2)−Rh(1)−P(1) = 99.29(2), Cl(2)−Rh(1)−C(1) = 94.97(9), Cl(2)−Rh(1)−Cl(2A) = 80.34(2), P(1)−Rh(1)−C(1) = 94.25(8), P(1)−Rh(1)−Cl(2A) = 161.02(2), C(1)−Rh(1)−Cl(2A) = 104.70(8), Rh(1)−C(1)−C(2) = 111.7(2), Rh(1)−Cl(2)−Rh(1A) = 99.66(2).

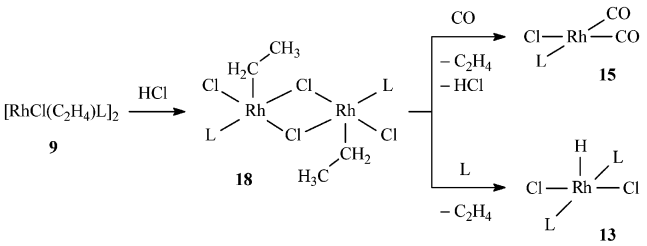
The dicarbonyl derivative **15** as well as the dimer **16** react with phosphine **3** to give the monocarbonyl complex **17** in nearly quantitative yields (see Scheme 3). The yellow air-stable solid is thermally remarkably stable and decomposes at 188 °C. The ^{31}P NMR spectrum displays one doublet resonance at δ 55.9, which confirms that the two phosphine ligands are trans disposed.

A Dinuclear Alkylrhodium(III) Complex Built up by Two 14-Electron Units. The reaction of dimer **9** with HCl, undertaken to generate the five-coordinate dichlorohydridorhodium(III) complex [RhHCl$_2$(C_2H_4)(**3**)] that would be structurally related to **13**, led to a surprising result. Passing a slow stream of dry HCl gas through a suspension of **9** in CH_2Cl_2 for 10 s at room temperature affords, after evaporation of the solvent, an orange solid, the elemental analysis of which is in agreement with the expected composition [RhHCl$_2$(C_2H_4)(**3**)]. However, the ^{1}H NMR spectrum of the product shows no signals for hydridic and for olefinic hydrogens but resonances at δ 4.60 and 1.14**,** which are assigned to the CH_2 and CH_3 units of an ethyl group. The ^{13}C NMR spectrum equally displays two signals at δ 23.7 and 24.6 for the CH_2 and CH_3 carbon atoms.

The existence of a Rh−C_2H_5 moiety in the isolated product has been confirmed by an X-ray crystal structure analysis. The molecular diagram of **18** (Figure 3) reveals that a dinuclear ethylrhodium(III) complex is formed in which two 14-electron [RhCl$_2$(C_2H_5)(**3**)] fragments are linked by two bridging chloro ligands. The midpoint of the planar Rh_2Cl_2 ring constitutes a center of inversion. Since the terminal chlorides Cl(1) and Cl(3) lie exactly and the phosphorus atoms P(1) and P(2) nearly in the plane of the Rh_2Cl_2 ring, the coordination geometry around Rh(1) and Rh(2) can be best described as square pyramidal with the C_2H_5 ligand in the apical

(22) Arena, C. G.; Faraone, F.; Lanfranchi, M.; Rotondo, E.; Tiripicchio, A. *Inorg. Chem.* **1992**, *31*, 4797−4802.

Scheme 4[a]



[a] L = 2,6-$Me_2C_6H_3CH_2CH_2PtBu_2$.

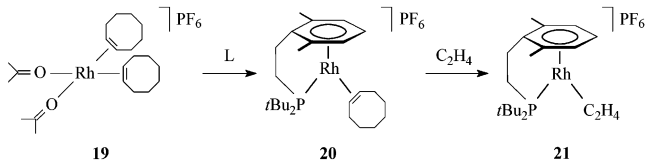
position. The ethyl groups of the two fragments are located in a trans configuration: i.e., on opposite sides of the Rh_2Cl_2 plane. The bond length Rh(1)−C(1) of 2.059(3) Å is comparable to those in other alkylrhodium(III) compounds[23] but significantly shorter (ca. 0.11 Å) than in the Milstein complex [RhCl(CH_3)(C_6H-2,4-(CH_2PtBu_2)$_2$-3,5-Me_2-κ^3P,C,P)].[4a]

The reactivity of the dinuclear ethylrhodium(III) derivate **18** is quite unusual. Treatment of **18** with phosphine **3**, undertaken to prepare the mononuclear five-coordinate complex [$RhCl_2(C_2H_5)$(**3**)$_2$] via chloride-bridge cleavage, gives the dichloro hydrido compound **13** (Scheme 4). To explain the formation of this molecule, we assume that in solution an equilibrium between a (possibly monomeric) Rh(C_2H_5) and RhH(C_2H_4) isomer exists[24] and that **13** is formed from the latter by olefin/phosphine exchange.

The same (ethene)hydridorhodium(III) intermediate is possibly also involved in the reaction of **18** with CO. Stirring a solution of **18** in CH_2Cl_2 under a CO atmosphere (1 bar) for 1 h at room temperature affords a light yellow solution which contains, according to the IR and ^{31}P NMR spectra, the dicarbonyl complex **15**. Careful investigation of the gas phase indicated that ethene and HCl were eliminated. We assume that the postulated intermediate [$RhHCl_2(C_2H_4)$(**3**)] reacts with CO to give initially [$RhHCl_2$(CO)(**3**)], which in the presence of CO eliminates HCl and with a second molecule of carbon monoxide yields **15**.

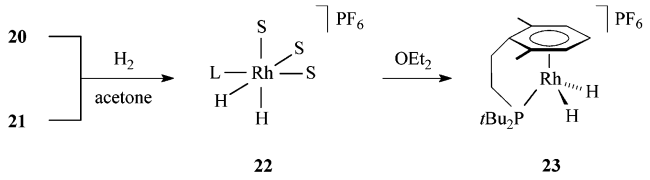
Half-Sandwich-Type Complexes with Phosphine 3 as Chelating Ligand. Following our research on the coordination capabilities of $R_2P(CH_2)_2C_6H_5$ (R = *i*Pr, *t*Bu),[1,3] we were also interested in investigating the behavior of the highly reactive bis(cyclooctene)rhodium(I) cation **19** toward **3**. It reacts with an equimolar amount of **3** by displacement of one cyclooctene and both acetone ligands to give the half-sandwich-type complex **20**, being isolated as an orange, slightly air-sensitive solid in 94% yield (Scheme 5). The ^{1}H and ^{13}C NMR

Scheme 5[a]



[a] L = 2,6-$Me_2C_6H_3CH_2CH_2PtBu_2$.

Scheme 6[a]



[a] L = 2,6-$Me_2C_6H_3CH_2CH_2PtBu_2$; S = acetone.

spectra of **20** show, similarly to those of **14**, the signals for the proton and the carbon nuclei of the CH unit trans to the ipso C atom of the ring at relatively high chemical shifts, indicating a pronounced shielding of this CH unit by the metal center.

The cyclooctene ligand of **20** is not firmly bound, and upon stirring a solution of **20** in CH_2Cl_2 under an ethene atmosphere can be substituted by C_2H_4. However, the reaction is rather slow, probably due to the fact that the rhodium center in the starting material has an 18-electron count. The ^{1}H NMR spectrum of the generated Rh(C_2H_4) complex **21**, being an orange solid, displays at room temperature only a broadened singlet for the C_2H_4 protons at δ 3.25, which indicates that under these conditions the rotation of the olefin around the Rh−C_2H_4 axis is quite fast. A similar dynamic behavior has also been observed for the analogue of **21** with ^{i}Pr$_2$P-(CH_2)$_2C_6H_5$ instead of **3** as a ligand and studied in detail by VT-NMR spectroscopy.[1]

The conversion of the (olefin)rhodium(I) derivatives **20** and **21** to the cationic dihydridorhodium(III) compound **23** proceeds stepwise. Stirring a solution of one of the starting materials in acetone for 12 h under a hydrogen atmosphere leads to a smooth change of color from orange-red to brown-yellow and, after partial evaporation of the solvent and addition of diethyl ether, yields a light brown, moderately air-stable solid with the analytical composition corresponding to **23** (Scheme 6). If, however, the reaction is monitored by ^{1}H or ^{31}P NMR spectroscopy, the formation of the intermediate **22**, also containing two hydride ligands, can be observed. Typical features of **22** are the high-field signal (doublet of doublets) in the ^{1}H NMR spectrum at δ −23.40 and the doublet resonance in the ^{31}P NMR spectrum at δ 92.1. The half-sandwich-type compound **23** is soluble in nitromethane and dichloromethane but is reconverted to the solvated species **22** in the presence of excess acetone. Both **22** and **23** behave in CH_3NO_2 as 1:1 electrolytes. The dihydrido complex **23**, which can be stored under argon at −20 °C for a few days, shows a characteristic ^{1}H NMR signal for the Rh−H protons at δ −12.51 and thus ca. 11 ppm downfield compared with **22**.

The tris(solvato)rhodium(III) compound **22**, if generated from **23** and acetone, is stable under hydrogen for hours but rearranges, after the H_2 atmosphere is re-

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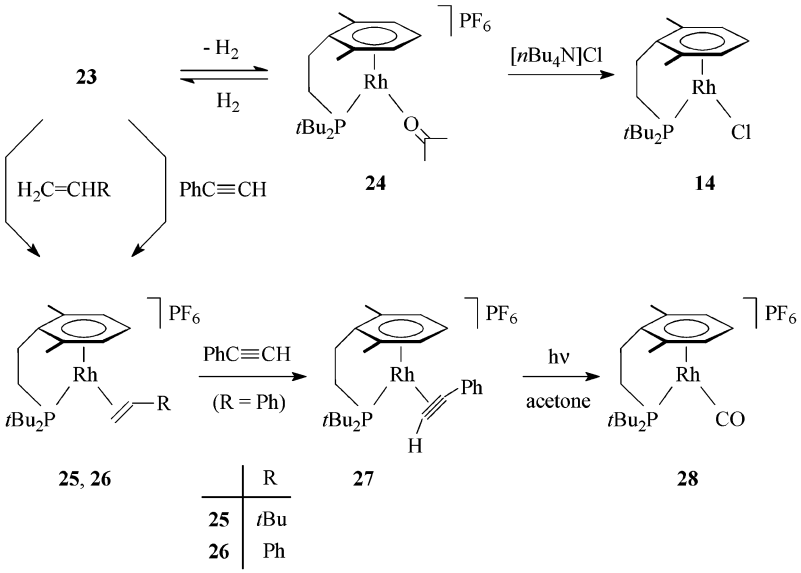
Scheme 7



placed by argon, very slowly to the chelate complex **24** (Scheme 7). The conversion is completed after storing a solution of **23** in acetone for ca. 4 weeks at room temperature. Since in the absence of acetone compound **24** decomposes quite rapidly, it could only be characterized by spectroscopic techniques. The ^{1}H and ^{13}C NMR spectra of **24** display in acetone-d_6 only the signals for phosphine **3**, indicating that obviously a fast exchange between coordinated and free acetone occurs. The assumption that the phosphine is linked via the phosphorus atom and the arene ring to the metal center is strongly supported by the NMR parameters for the CH unit trans to the $CH_2CH_2PtBu_2$ substituent at the ring, which are very similar to those of **25**−**28** (see below). Addition of [N*n*Bu$_4$]Cl to an acetone solution of **24** leads to an exchange of $OCMe_2$ for chloride and gives the neutral half-sandwich-type complex **14**. If this compound is dissolved in CD_2Cl_2 and the solution treated with acetone, the cation of **24** is regenerated.

By attempting to facilitate the elimination of H_2 from **22**, the starting material **23** was treated with 3,3-dimethyl-1-butene, which is known to be a good acceptor for dihydrogen. However, instead of **24** the half-sandwich-type compound **25** was isolated as a yellow solid in 78% yield. In contrast to **24**, the olefin derivative is surprisingly stable, decomposing at 110 °C, and can be handled for a short period of time in air. Although it is less stable in solution, the NMR spectra clearly confirm that an analogue of the ethene compound **21** is present.

The dihydrido complex **23** reacts not only with 3,3-dimethyl-1-butene but also with phenylacetylene. If an excess of HC≡CPh is used, the alkynerhodium(I) compound **27** is formed exclusively. With an equimolar amount of phenylacetylene, the styrene complex **26** is initially generated, which subsequently reacts with the alkyne to give **27**. A clean synthesis of **26** is possible by treatment of **23** with styrene, which affords the product as an orange air-stable solid in 95% isolated yield (see Scheme 7). Regarding the spectroscopic data of **26**, a typical feature is that in the ^{1}H NMR spectrum two signals for the protons in 3- and 5-positions at the ring appear, one of them at unusually high field at δ 5.03. We assume that for steric reasons only this proton is effected by the π-electrons of the phenyl ring attached to the C=C double bond of the styrene. Similarly to **26**, the alkyne complex **27** is an orange air-stable solid which slowly decomposes in solvents such as acetone and dichloromethane. Since the IR spectrum of **27** displays the ν(≡CH) and ν(C≡C) stretching modes at, respectively, 3163 and 1827 cm^{-1}, there is no doubt that during the synthesis no isomerization of the alkyne to the corresponding vinylidene has taken place.

By attempting to initiate photochemically a rearrangement of **27** to the isomer [(η^6-2,6-$Me_2C_6H_3CH_2$-CH_2PtBu_2-κP)Rh(=C=CHPh)]PF_6, we received a surprising result. UV irradiation of a solution of **27** in acetone for 72 h at room temperature led to a gradual change of color from orange to yellow and gave, after removal of the solvent, the carbonyl complex **28** in 91% yield. If, instead of acetone, CH_2Cl_2 is used as the solvent, only decomposition of the starting material occurs. We assume that, during the extended photochemical process, a C−C bond cleavage of the acetone ligand takes place, similar to that in a Norrish type I reaction.[25] Typical spectroscopic data of **28** (being a light yellow, air-stable solid) are the ν(CO) absorption at 2001 cm^{-1} in the IR and the doublet of doublets resonance for the carbonyl carbon atom at δ 185.9 in the ^{13}C NMR spectrum. An independent experiment, carried out in an NMR tube, confirmed that **28** is also generated upon UV irradiation of a solution of **26** in the presence of CO.

Concluding Remarks

The work presented in this paper illustrates that at least in some respects the title phosphine **3** behaves differently compared with the less bulky analogues $iPr_2P(CH_2)_2C_6H_5$ and $tBu_2P(CH_2)_2C_6H_5$, respectively. This statement is particularly supported by two results. The first is the formation and molecular structure of the dinuclear alkylrhodium(III) compound **18**, which is built up by two 14-electron [$RhCl_2(C_2H_5)(PR_3)$] units. Although there are a number of rhodium complexes

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$[RhCl(L)_2]_2$ or $[RhCl(L)(L')]_2$ known,[26] which similarly to **18** are also composed of two 14-electron fragments, in all of these compounds the metal is in the oxidation state +I and not +III. Independently from our work, Budzelaar, Gal, et al. reported the preparation and structural characterization of an analogue of **18**, with a bulky chelating β-diiminato ligand (instead of one chloro ligand and phosphine **3**), two phenyl instead of two ethyl groups, and two bridging bromides.[27] In contrast to **18**, this complex was obtained from the 14-electron rhodium(I) monomer [Rh(β-diiminate-κ^2)(C_8H_{14})] by oxidative addition with bromobenzene. From a structural point of view, both **18** and the Budzelaar−Gal compound are remarkable indeed. The nearest relative of these dinuclear complexes, we are aware of, is the mononuclear hydridosilylrhodium(III) compound $[RhHCl\{Si(CH_2Ph)_3\}(P\textit{i}Pr_3)]_2$, prepared by oxidative addition of $HSi(CH_2Ph)_3$ to $[RhCl(P\textit{i}Pr_3)_2]_2$.[28] With regard to **18**, the unusual feature is that in solution obviously an equilibrium between a $Rh(C_2H_5)$ and a $RhH(C_2H_4)$ isomer exists, of which the latter is responsible for the pronounced reactivity of **18** toward CO and the title phosphine **3**.

The second significant aspect constitutes the isolation of the mononuclear four-coordinate dicarbonyl compound **15**, representing, to the best of our knowledge, the first structurally characterized rhodium(I) complex of the general composition *cis*-$[RhCl(CO)_2(PR_3)]$. Although it has been reported by several groups that compounds of this type can be generated,[20,22] evidence for the exact configuration with cis-disposed CO ligands was lacking. In agreement with previous observations, the dicarbonyl complex is quite labile and readily eliminates one CO unit to give **16** (see Scheme 3). However, the abstraction of the remaining CO ligand is kinetically hindered, and thus compound **16** is not an appropriate starting material for complex **14**. Whether this novel half-sandwich-type compound, for which under appropriate conditions a change in coordination of the title phosphine **3** from a chelating to a terminal P-bonded mode seems possible, can be used as a catalyst or a catalyst precursor should be proved by further investigations.

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **1**,[29] tBuPCl$_2$,[30] **6**,[31] **7**,[32] and **19**[33] were prepared as described in the literature. NMR spectra were recorded (if not otherwise stated) at room temperature on Bruker AC 200, Bruker DRX 300, and Bruker AMX 400 instruments, IR spectra were recorded on a IFS 25 FT-IR infrared spectrometer, and mass spectra were recorded on a Finnigan MAT 90 (70 eV) or on a Hewlett-Packard G 1800 GCD instrument. Coupling constants are given in hertz. Abbreviations used: s, singlet; d, doublet; t, triplet; m, multiplet; v, virtual coupling; br, broadened signal; $N = {}^3J(PH) + {}^5J(PH)$ or ${}^1J(PC) + {}^3J(PC)$. Melting points were measured by differential thermal analysis (DTA). The molar conductivity Λ_M was determined in nitromethane.

Preparation of (2,6-Me$_2$C$_6$H$_3$CH$_2$CH$_2$)(tBu)PCl (2). A solution of 2-(2,6-dimethylphenyl)ethyl chloride (19.7 g, 0.12 mol) in THF (40 mL) was added dropwise to a suspension of Mg (2.8 g, 0.12 mol) in THF (10 mL) at room temperature. The reaction mixture was warmed under reflux for 30 min and after cooling to room temperature stirred for 1 h. The solution thus formed solution was added dropwise at 0 °C to a solution of tBuPCl$_2$ (18.6 g, 0.12 mol) in THF (60 mL), which led to the precipitation of a white solid. After the mixture was warmed to room temperature, the solvent was evaporated and the residue was extracted six times with diethyl ether (80 mL each). The combined extracts were brought at only slightly reduced preasure to dryness, and the remaining oil was distilled at 0.002 bar. A colorless liquid (bp 106−108 °C) was obtained, which became a solid if it was stored in the refrigerator. Yield: 13.5 g (45%). (For NMR data see ref 5.)

Preparation of 2,6-Me$_2$C$_6$H$_3$CH$_2$CH$_2$PtBu$_2$ (3). A solution of **2** (13.0 g, 50.7 mmol) in benzene (40 mL) was treated dropwise at 5 °C with a 1.6 M solution of tBuLi (44 mL, 70.4 mmol) in pentane. After the reaction mixture was warmed to room temperature, it was stirred for 8 h and then hydrolyzed with argon-saturated water (20 mL). Diethyl ether (40 mL) was added, and the two phases were separated. The organic phase was dried with Na_2SO_4 and then filtered. The solvent was evaporated in vacuo and the oily residue distilled at 0.002 bar. A colorless liquid (bp 105 °C) was obtained. Yield: 11.5 g (81%). MS (CI): m/z 279 ($M^+ + H$), 278 (M^+). (For NMR data see ref 5.)

Preparation of [(2,6-Me$_2$C$_6$H$_3$CH$_2$CH$_2$)P(CH$_3$)tBu$_2$]I (4). A solution of **3** (560 mg, 2.01 mmol) in hexane (20 mL) was treated with methyl iodide (144 μL, 2.30 mmol) and stirred for 3 h at room temperature. A white solid precipitated, which was separated from the mother liquor, washed twice with diethyl ether (10 mL each) and twice with pentane (10 mL each), and dried. Yield: 763 mg (90%). Mp: 258 °C. ^{1}H NMR (200 MHz, CD_3NO_2): δ 7.06 (s, 3 H, C_6H_3), 3.05 (m, 2 H, PCH_2CH_2), 2.35 (s, 6 H, $C_6H_3(CH_3)_2$), 2.31 (m, 2 H, PCH_2), 1.99 (d, J(PH) = 11.7 Hz, 3 H, PCH_3), 1.53 (d, J(PH) = 15.7 Hz, 18 H, $PCCH_3$). ^{13}C NMR (50.3 MHz, CD_3NO_2): δ 137.6 (s, ortho C of C_6H_3), 137.5 (d, J(PC) = 13.6 Hz, ipso C of C_6H_3), 130.0 (s, meta C of C_6H_3), 128.5 (s, para C of C_6H_3), 34.9 (d, J(PC) = 38.3 Hz, $PCCH_3$), 27.0 (s, $PCCH_3$), 25.0 (d, J(PC) = 5.2 Hz, PCH_2CH_2), 20.2 (s, $C_6H_3(CH_3)_2$), 16.9 (d, J(PC) = 37.7 Hz, PCH_2), −0.1 (d, J(PC) = 48.1 Hz, PCH_3). ^{31}P NMR (81.0 MHz, CD_3NO_2): δ 48.9 (s). Anal. Calcd for $C_{19}H_{34}IP$: C, 54.29; H, 8.15. Found: C, 53.98; H, 8.10.

Preparation of [(2,6-Me$_2$C$_6$H$_3$CH$_2$CH$_2$)P(H)tBu$_2$]Cl (5). A slow stream of gaseous HCl was passed for 60 s through a solution of **3** (432 mg, 1.55 mmol) in hexane (10 mL) at room temperature. A white solid precipitated, which was separated from the mother liquor, washed twice with pentane (5 mL each), and dried. Yield: 454 mg (93%). Mp: 118 °C. (For NMR data see ref 5.)

Preparation of [Rh(μ-Cl)(C_8H_{14})(2,6-Me$_2$C$_6$H$_3$CH$_2$CH$_2$-PtBu$_2$-κP)]$_2$ (8). A suspension of **6** (307 mg, 0.43 mmol) in benzene (3 mL) was treated with a solution of **3** (238 mg, 0.86 mmol) in benzene (7 mL) at room temperature. After the reaction mixture was stirred for 5 min, an orange solution was formed. The solvent was evaporated in vacuo, and the residue

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was dissolved in pentane (6 mL). A yellow solid precipitated, which was filtered, washed with pentane (3 mL), and dried. Yield: 365 mg (81%). Mp: 64 °C dec. ^{1}H NMR (200 MHz, C_6D_6): δ 6.93 (m, 6 H, C_6H_3), 3.54 (m, 4 H, =CH of C_8H_{14}), 2.85 (m, 4 H, PCH_2CH_2), 2.52 (m, 4 H, CH_2 of C_8H_{14}), 2.56 (s, 12 H, $C_6H_3(CH_3)_2$), 1.68−1.17 (m, 24 H, PCH_2 and CH_2 of C_8H_{14}), 1.53 (d, J(PH) = 12.4 Hz, 36 H, $PCCH_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 140.0 (d, J(PC) = 8.4 Hz, ipso C of C_6H_3), 135.8 (s, ortho C of C_6H_3), 129.1 (s, meta C of C_6H_3), 126.5 (s, para C of C_6H_3), 59.2 (d, J(RhC) = 17.5 Hz, =CH of C_8H_{14}), 37.4 (d, J(PC) = 17.5 Hz, $PCCH_3$), 31.3 (d, J(PC) = 3.9 Hz, $PCCH_3$), 21.2 (s, $C_6H_3(CH_3)_2$), 18.8 (d, J(PC) = 22.7 Hz, PCH_2); the signals of PCH_2CH_2 and the CH_2 carbon atoms of C_8H_{14} could not be exactly located. ^{31}P NMR (81.0 MHz, C_6D_6): δ 65.5 (d, J(RhP) = 185.7 Hz, cis dimer), 64.8 (d, J(RhP) = 188.2 Hz, trans dimer). Anal. Calcd for $C_{52}H_{90}P_2Cl_2Rh_2$: C, 59.26; H, 8.61. Found: C, 59.27; H, 8.46.

Preparation of [Rh(μ-Cl)(C_2H_4)(2,6-$Me_2C_6H_3CH_2CH_2$-P*t*Bu_2-κP)]$_2$ (9). This compound was prepared as described for **8** from **7** (94 mg, 0.24 mmol) and **3** (135 mg, 0.48 mmol) in benzene (8 mL). A yellow microcrystalline solid was obtained. Yield: 199 mg (93%). Mp: 77 °C dec. Anal. Calcd for $C_{40}H_{70}P_2Cl_2Rh_2$: C, 54.00; H, 7.93. Found: C, 53.97; H, 7.87. (For NMR data see ref 5.)

Generation of [RhH_2(μ-Cl)(2,6-$Me_2C_6H_3CH_2CH_2$P*t*Bu_2-κ-*P*)]$_2$ (10). A suspension of **9** (23 mg, 0.03 mmol) in CD_2Cl_2 (0.5 mL) was stirred under a hydrogen atmosphere at room temperature. After a few minutes, a yellow solution was formed, which was shown by the NMR spectra to contain exclusively compound **10**. Since all attempts to isolate this compound failed or gave **11**, it was characterized spectroscopically. IR (CH_2Cl_2): ν(RhH) 2149, 2125 cm^{-1}. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 6.97 (m, 6 H, C_6H_3), 3.05 (dt, J(PH) = 12.8, J(HH) = 3.9 Hz, 4 H, PCH_2CH_2), 2.38 (s, 12 H, $C_6H_3(CH_3)_2$), 1.86 (m, 4 H, PCH_2), 1.43 (d, J(PH) = 13.8 Hz, 36 H, $PCCH_3$), −21.50 (br s, 4 H, RhH). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 140.1 (d, J(PC) = 13.4 Hz, ipso C of C_6H_3), 136.6 (s, ortho C of C_6H_3), 128.4 (s, meta C of C_6H_3), 126.0 (s, para C of C_6H_3), 36.6 (d, J(PC) = 21.0 Hz, $PCCH_3$), 30.5 (d, J(PC) = 2.9 Hz, $PCCH_3$), 28.9 (s, PCH_2CH_2), 25.7 (d, J(PC) = 25.7 Hz, PCH_2), 20.8 (s, $C_6H_3(CH_3)_2$). ^{31}P NMR (81.0 MHz, CD_2Cl_2, 293 K): δ 96.4 (br s). ^{31}P NMR (81.0 MHz, CD_2Cl_2, 313 K): δ 97.8 (d, J(RhP) = 162.8 Hz).

Preparation of [RhH_2Cl(2,6-$Me_2C_6H_3CH_2CH_2$P*t*Bu_2-κP)$_2$] (11). (a) A suspension of **7** (46 mg, 0.12 mmol) in benzene (3 mL) was treated with a solution of **3** (132 mg, 0.47 mmol) in benzene (6 mL), and the mixture was stirred for 8 h under a hydrogen atmosphere (1 bar). The solvent was evaporated in vacuo and the residue suspended in pentane (6 mL). A yellow microcrystalline solid precipitated, which was filtered, washed twice with pentane (3 mL each), and dried. Yield: 150 mg (90%).

(b) **11** was obtained analogously as described for (a), from **9** (77 mg, 0.09 mmol) and **3** (48 mg, 0.17 mmol). Yield: 111 mg (94%). Mp: 104 °C dec. IR (KBr): ν(RhH) 2122 cm^{-1}. Anal. Calcd for $C_{36}H_{64}P_2ClRh$: C, 62.02; H, 9.25. Found: C, 61.96; H, 9.01. (For NMR data see ref 5.)

Reaction of Compound 11 with Ethene. A solution of **11** (77 mg, 0.11 mmol) in pentane (5 mL) was stirred under an ethene atmosphere (1 bar) for 3 days. A yellow solid precipitated, which was filtered and then dissolved in C_6D_6 (0.5 mL). The ^{1}H and ^{31}P spectra confirmed that both the ethene complex **9** and the phosphine **3** were formed. If the solution was stored under H_2 (1 bar), the starting material **11** was regenerated.

Generation of [RhHCl(μ-Cl)(2,6-$Me_2C_6H_3CH_2CH_2$P*t*Bu_2-κP)]$_2$ (12). A suspension of **5** (144 mg, 0.46 mmol) in diethyl ether (5 mL) was treated with a solution of **8** (241 mg, 0.23 mmol) in diethyl ether (15 mL), and the mixture was stirred for 1 h at room temperature. The solvent was evaporated in vacuo, and the yellow residue was washed three times with pentane (10 mL each) and dried. The NMR spectra showed that the solid consisted of equal quantities of **5** and **12**. Attempts to separate the two compounds failed. Spectroscopic data for **12** are as follows. IR (CH_2Cl_2): ν(RhH) 2146 cm^{-1}. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 6.93 (m, 6 H, C_6H_3), 3.05 (m, 4 H, PCH_2CH_2), 2.43 (s, 12 H, $C_6H_3(CH_3)_2$), 2.16 (m, 4 H, PCH_2), 1.47 (d, J(PH) = 13.8 Hz, 36 H, $PCCH_3$), −22.48 (dd, J(RhH) = 21.7, J(PH) = 11.8 Hz, 2 H, RhH). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 139.9 (d, J(PC) = 12.3 Hz, ipso C of C_6H_3), 137.2 (s, ortho C of C_6H_3), 128.6 (s, meta C of C_6H_3), 125.8 (s, para C of C_6H_3), 37.6 (d, J(PC) = 20.1 Hz, $PCCH_3$), 30.9 (br s, $PCCH_3$), 26.4 (s, PCH_2CH_2), 21.8 (s, $C_6H_3(CH_3)_2$), 14.3 (d, J(PC) = 21.4 Hz, PCH_2). ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ 77.5 (br d, J(RhP) = 142.4 Hz).

Preparation of [$RhHCl_2$(2,6-$Me_2C_6H_3CH_2CH_2$P*t*Bu_2-κP)$_2$] (13). A solution of **8** (112 mg, 0.11 mmol) in benzene (6 mL) was treated with **5** (67 mg, 0.21 mmol), and the mixture was then stirred for 2 h at 60 °C. An orange solution was formed, from which, after cooling to 20 °C, the solvent was evaporated in vacuo. The remaining orange solid was washed twice with diethyl ether (5 mL each) and twice with pentane (5 mL each) and dried. Yield: 115 mg (71%). Mp: 103 °C dec. Anal. Calcd for $C_{36}H_{63}P_2Cl_2Rh$: C, 59.10; H, 8.68. Found: C, 59.53; H, 8.50. (For NMR data see ref 5.)

Preparation of [(η^6-2,6-$Me_2C_6H_3CH_2CH_2$P*t*Bu_2-κP)RhCl] (14). A suspension of **5** (225 mg, 0.71 mmol) in diethyl ether (7 mL) was treated with a solution of **8** (377 mg, 0.36 mmol) in diethyl ether (25 mL), and the mixture was stirred for 1 h at room temperature. The solvent was evaporated in vacuo, and the residue was washed three times with pentane (10 mL each) and dried. It was then dissolved in dichloromethane (2 mL), and the solution was chromatographed on Al_2O_3 (acidic, activity grade III, length of column 4 cm). With dichloromethane a green-yellow fraction was eluted, from which the solvent was removed in vacuo. The oily residue was washed three times with pentane (6 mL each). After it was stored at −30 °C for 6 h, a green microcrystalline solid was obtained. Yield: 169 mg (57%). Mp: 58 °C dec. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 6.59 (m, 2 H, meta H of C_6H_3), 5.13 (m, 1 H, para H of C_6H_3), 2.17 (s, 6 H, $C_6H_3(CH_3)_2$), 2.15−1.94 (m, 4 H, PCH_2 and PCH_2CH_2), 1.36 (d, J(PH) = 13.5 Hz, 18 H, $PCCH_3$). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 113.0 (d, J(PC) = 4.6 Hz, ortho C of C_6H_3), 109.3 (s, meta C of C_6H_3), 94.1 (dd, J(PC) = 12.0, J(RhC) = 1.9 Hz, para C of C_6H_3), 85.6 (dd, J(PC) = 9.3, J(RhC) = 2.8 Hz, ipso C of C_6H_3), 37.2 (dd, J(PC) = 17.6, J(RhC) = 1.9 Hz, $PCCH_3$), 32.7 (d, J(PC) = 21.3 Hz, PCH_2), 29.6 (d, J(PC) = 3.7 Hz, $PCCH_3$), 27.6 (d, J(PC) = 4.6 Hz, PCH_2CH_2), 19.3 (s, $C_6H_3(CH_3)_2$). ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ 108.7 (d, J(RhP) = 203.5 Hz). Anal. Calcd for $C_{18}H_{31}ClPRh$: C, 51.87; H, 7.50. Found: C, 51.84; H, 7.64.

Preparation of *cis*-[$RhCl(CO)_2$(2,6-$Me_2C_6H_3CH_2CH_2$-P*t*Bu_2-κP)] (15). A suspension of **16** (67 mg, 0.08 mmol) in pentane (7 mL) was stirred under a CO atmosphere (1 bar) for 1 h at room temperature. A light yellow solution was formed, from which the solvent was evaporated with a stream of CO. A light yellow solid was isolated. Yield: 68 mg (95%). Mp: 94 °C dec. IR (KBr): ν(CO) 2086, 1999 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.00 (s, 3 H, C_6H_3), 3.02 (m, 2 H, PCH_2CH_2), 2.44 (s, 6 H, $C_6H_3(CH_3)_2$), 2.31 (m, 2 H, PCH_2), 1.48 (d, J(PH) = 13.2 Hz, 18 H, $PCCH_3$). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 184.8 (dd, J(RhC) = 71.5, J(PC) = 16.2 Hz, CO trans to Cl), 181.1 (dd, J(PC) = 112.5, J(RhC) = 58.2 Hz, CO cis to Cl), 139.1 (d, J(PC) = 12.4 Hz, ipso C of C_6H_3), 136.9 (s, ortho C of C_6H_3), 128.8 (s, meta C of C_6H_3), 126.4 (s, para C of C_6H_3), 36.0 (d, J(PC) = 17.2 Hz, $PCCH_3$), 30.6 (d, J(PC) = 3.8 Hz, $PCCH_3$), 26.6 (s, PCH_2CH_2), 21.3 (s, $C_6H_3(CH_3)_2$), 19.5 (d, J(PC) = 15.3 Hz, PCH_2). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 57.8 (d, J(RhP) = 122.1 Hz). Anal. Calcd for $C_{20}H_{31}O_2PClRh$: C, 50.81; H, 6.61. Found: C, 50.83; H, 6.68.

Preparation of [Rh(μ-Cl)(CO)(2,6-$Me_2C_6H_3CH_2CH_2$-P*t*Bu_2-κ*P*)]$_2$ (16). (a) A suspension of **8** (114 mg, 0.11 mmol) in pentane (8 mL) was stirred under a CO atmosphere at room temperature. In less than 10 s a light yellow solution was formed, the ^{31}P NMR spectrum of which confirmed that compound **15** was generated. While the solution was concentrated in vacuo, a light yellow solid precipitated, which was shown by the NMR spectra to consist of a mixture of *cis*-**16** (δ_P 79.4, *J*(RhP) = 172.9 Hz; ca. 10%) and *trans*-**16** (δ_P 78.6, *J*(RhP) = 174.6 Hz; ca. 90%). After the precipitate was suspended in pentane (10 mL), part of the solid (mainly the cis dimer) was dissolved. The solvent was evaporated in vacuo; the remaining light yellow solid (consisting only of the trans dimer) was washed twice with pentane (5 mL each) and dried. Yield: 85 mg (87%).

(b) A solution of **14** (54 mg, 0.13 mmol) in dichloromethane (2 mL) was stirred under a CO atmosphere (1 bar). In less than 10 s a change of color from red-brown to light yellow occurred. The solution was worked up as described for (a). Yield: 47 mg (81%). Mp: 195 °C dec. IR (KBr): ν(CO) 1962 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.99 (m, 6 H, C_6H_3), 3.15 (m, 4 H, PCH_2CH_2), 2.43 (s, 12 H, $C_6H_3(CH_3)_2$), 2.15 (m, 4 H, PCH_2), 1.52 (d, *J*(PH) = 13.2 Hz, 36 H, $PCCH_3$). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 186.8 (dd, *J*(RhC) = 80.2, *J*(PC) = 17.2 Hz, CO), 139.2 (d, *J*(PC) = 13.4 Hz, ipso C of C_6H_3), 136.8 (s, ortho C of C_6H_3), 128.8 (s, meta C of C_6H_3), 126.3 (s, para C of C_6H_3), 37.1 (d, *J*(PC) = 20.0 Hz, $PCCH_3$), 30.6 (d, *J*(PC) = 2.9 Hz, $PCCH_3$), 26.9 (s, PCH_2CH_2), 23.7 (d, *J*(PC) = 18.1 Hz, PCH_2), 21.3 (s, $C_6H_3(CH_3)_2$). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 78.6 (d, *J*(RhP) = 174.6 Hz). Anal. Calcd for $C_{38}H_{62}O_2P_2Cl_2Rh_2$: C, 51.31; H, 7.02. Found: C, 51.61; H, 7.09.

Preparation of *trans*-[RhCl(CO)(2,6-$Me_2C_6H_3CH_2CH_2$-P*t*Bu_2-κ*P*)$_2$] (17). (a) A suspension of **16** (56 mg, 0.06 mmol) in pentane (5 mL) was treated with a solution of **3** (36 mg, 0.13 mmol) in pentane (4 mL). After ca. 10 s a light yellow solution was formed, which was concentrated to ca. 1 mL in vacuo and then chromatographed on Al_2O_3 (neutral, activity grade III, length of column 10 cm). First, with hexane a colorless fraction was eluted, containing **3** and the corresponding phosphine oxide. Second, with benzene a light yellow fraction was eluted and brought to dryness in vacuo. The remaining yellow solid was washed twice with pentane (5 mL each) and dried. Yield: 83 mg (91%).

(b) **17** was obtained analogously as described for (a) from **15** (92 mg, 0.19 mmol) and **3** (54 mg, 0.19 mmol). Yield: 122 mg (87%). Mp: 188 °C dec. IR (CH_2Cl_2): ν(CO) 1937 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 7.01 (m, 6 H, C_6H_3), 3.23 (m, 4 H, PCH_2CH_2), 2.55 (s, 12 H, $C_6H_3(CH_3)_2$), 2.45 (m, 4 H, PCH_2), 1.42 (vt, *N* = 12.9 Hz, 36 H, $PCCH_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 190.8 (dt, *J*(RhC) = 73.4, *J*(PC) = 15.3 Hz, CO), 140.1 (vt, *N* = 12.4 Hz, ipso C of C_6H_3), 136.9 (s, ortho C of C_6H_3), 129.1 (s, meta C of C_6H_3), 126.4 (s, para C of C_6H_3), 36.1 (vt, *N* = 15.3 Hz, $PCCH_3$), 30.9 (m, $PCCH_3$), 27.1 (s, PCH_2CH_2), 21.8 (s, $C_6H_3(CH_3)_2$), 20.4 (vt, *N* = 13.4 Hz, PCH_2). ^{31}P NMR (162.0 MHz, C_6D_6): δ 55.9 (d, *J*(RhP) = 120.4 Hz). Anal. Calcd for $C_{37}H_{62}OP_2ClRh$: C, 61.45; H, 8.64. Found: C, 61.06; H, 8.71.

Preparation of [Rh(μ-Cl)Cl(C_2H_5)(2,6-$Me_2C_6H_3CH_2CH_2$-P*t*Bu_2-κ*P*)]$_2$ (18). A slow stream of gaseous HCl was passed through a suspension of **9** (123 mg, 0.14 mmol) in dichloromethane (3 mL) for 10 s at room temperature. An orange solution was formed, from which the solvent was evaporated in vacuo. The remaining orange solid was washed three times with pentane (5 mL each) and dried. Yield: 112 mg (83%). Mp: 102 °C dec. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.01 (m, 6 H, C_6H_3), 4.60 (br, 4 H, CH_2CH_3), 3.05 (br, 4 H, PCH_2CH_2), 2.42 (s, 6 H, $C_6H_3(CH_3)_2$), 2.15 (br, 4 H, PCH_2), 1.60 (d, *J*(PH) = 13.2 Hz, 36 H, $PCCH_3$), 1.14 (t, *J*(HH) = 7.1 Hz, 6 H, CH_2CH_3). ^{1}H NMR (200 MHz, CD_2Cl_2, 313 K): δ 7.02 (m, 6 H, C_6H_3), 4.63 (ddq, *J*(HH) = 7.1, *J*(PH) = *J*(RhH) = 2.2 Hz, 4 H, CH_2CH_3), 3.11 (m, 4 H, PCH_2CH_2), 2.45 (s, 6 H, $C_6H_3(CH_3)_2$), 2.20 (m, 4 H, PCH_2), 1.63 (d, *J*(PH) = 13.2 Hz, 36 H, $PCCH_3$), 1.15 (t, *J*(HH) = 7.1 Hz, 6 H, CH_2CH_3). ^{13}C NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 138.9 (d, *J*(PC) = 12.0 Hz, ipso C of C_6H_3), 136.7 (s, ortho C of C_6H_3), 128.8 (s, meta C of C_6H_3), 126.5 (s, para C of C_6H_3), 39.4 (d, *J*(PC) = 20.7 Hz, $PCCH_3$), 31.0 (s, $PCCH_3$), 26.1 (d, *J*(PC) = 2.6 Hz, PCH_2CH_2), 24.6 (d, *J*(RhC) = 2.9 Hz, CH_2CH_3), 23.7 (br, CH_2CH_3), 21.4 (d, *J*(PC) = 14.9 Hz, PCH_2), 21.2 (s, $C_6H_3(CH_3)_2$). ^{31}P NMR (81.0 MHz, CD_2Cl_2, 293 K): δ 60.2 (d, *J*(RhP) = 152.6 Hz). Anal. Calcd for $C_{40}H_{72}P_2Cl_4Rh_2$: C, 49.91; H, 7.54; Rh, 21.38. Found: C, 49.88; H, 7.29; Rh, 21.62.

Preparation of [(η^6-2,6-$Me_2C_6H_3CH_2CH_2$P*t*Bu_2-κ*P*)Rh(C_8H_{14})]PF_6 (20). A solution of **19** (505 mg, 0.86 mmol) in acetone (3 mL) was treated dropwise with a solution of **3** (241 mg, 0.86 mmol) in acetone (5 mL), and the mixture was stirred for 5 min at room temperature. After the solution was concentrated to ca. 3 mL in vacuo, diethyl ether (10 mL) was added. An orange solid precipitated, which was filtered, washed three times with diethyl ether (5 mL each) and twice with pentane (5 mL each), and dried. Yield: 516 mg (94%). Mp: 58 °C dec. Λ_M = 101 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (400 MHz, acetone-d_6): δ 6.86 (m, 2 H, meta H of C_6H_3), 5.77 (m, 1 H, para H of C_6H_3), 4.03 (m, 2 H, =CH of C_8H_{14}), 2.81 (m, 4 H, PCH_2 and PCH_2CH_2), 2.60 (s, 6 H, $C_6H_3(CH_3)_2$), 2.34, 1.80 (both m, 2 H each, CH_2 of C_8H_{14}), 1.66−1.35 (m, 8 H, CH_2 of C_8H_{14}), 1.36 (d, *J*(PH) = 13.5 Hz, 18 H, $PCCH_3$). ^{13}C NMR (100.6 MHz, acetone-d_6): δ 120.5 (s, ortho C of C_6H_3), 117.9 (dd, *J*(PC) = 5.1, *J*(RhC) = 4.1 Hz, ipso C of C_6H_3), 112.2 (s, meta C of C_6H_3), 91.6 (dd, *J*(PC) = 10.2, *J*(RhC) = 3.1 Hz, para C of C_6H_3), 68.3 (d, *J*(RhC) = 13.2 Hz, =CH of C_8H_{14}), 39.2 (dd, *J*(PC) = 16.3, *J*(RhC) = 2.0 Hz, $PCCH_3$), 38.7 (d, *J*(PC) = 23.4 Hz, PCH_2), 33.5, 32.7, 26.6 (all s, CH_2 of C_8H_{14}), 30.5 (s, PCH_2PCH_2), 30.2 (d, *J*(PC) = 3.0 Hz, $PCCH_3$), 19.2 (s, $C_6H_3(CH_3)_2$). ^{31}P NMR (162.0 MHz, acetone-d_6): δ 92.7 (d, *J*(RhP) = 191.8 Hz, *t*Bu_2P), −144.1 (sept, *J*(FP) = 708.5 Hz, PF_6). Anal. Calcd for $C_{26}H_{45}F_6P_2Rh$: C, 49.06; H, 7.13. Found: C, 49.50; H, 6.91.

Preparation of [(η^6-2,6-$Me_2C_6H_3CH_2CH_2$P*t*Bu_2-κ*P*)Rh(C_2H_4)]PF_6 (21). A solution of **20** (202 mg, 0.32 mmol) in dichloromethane (3 mL) was stirred under an atmosphere of ethene at 75 °C for 1.5 h. After the heating bath was removed, the volatile materials were removed in vacuo. The yellow residue was washed with diethyl ether (10 mL) and dried. It was dissolved in CH_2Cl_2 (3 mL), and the preparative procedure (stirring under ethene at 75 °C for 1.5 h, removal of the volatiles) was repeated four times. Finally, the residue was dissolved in acetone (4 mL), the solution was filtered, and the filtrate was concentrated to ca. 2 mL in vacuo. After diethyl ether (10 mL) was added, an orange solid precipitated, which was separated from the mother liquor, washed twice with diethyl ether (5 mL each) and twice with pentane (5 mL each), and dried. Yield: 156 mg (88%). Mp: 175 °C dec. Λ_M 92 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.08 (m, 2 H, meta H of C_6H_3), 5.16 (m, 1 H, para H of C_6H_3), 3.25 (br s, 4 H, =CH_2), 2.90−2.84 (m,4 H, PCH_2 and PCH_2PCH_2), 2.63 (s, 6 H, $C_6H_3(CH_3)_2$), 1.30 (d, *J*(PH) = 13.8 Hz, 18 H, $PCCH_3$). ^{13}C NMR (100.6 MHz, acetone-d_6): δ 121.6 (d, *J*(RhC) = 2.9 Hz, ortho C of C_6H_3), 120.5 (dd, *J*(RhC) = 4.8, *J*(PC) = 3.8 Hz, ipso C of C_6H_3), 109.1 (s, meta C of C_6H_3), 89.4 (dd, *J*(PC) = 11.0, *J*(RhC) = 3.3 Hz, para C of C_6H_3), 42.4 (d, *J*(RhC) = 14.3 Hz, =CH_2), 39.1 (d, *J*(PC) = 23.8 Hz, PCH_2), 38.7 (dd, *J*(PC) = 17.2, *J*(RhC) = 1.9 Hz, $PCCH_3$), 30.3 (d, *J*(PC) = 2.9 Hz, $PCCH_3$), 27.0 (s, PCH_2CH_2), 19.1 (s, $C_6H_3(CH_3)_2$). ^{31}P NMR (162.0 MHz, acetone-d_6): δ 96.0 (d, *J*(RhP) = 185.3 Hz, *t*Bu_2P), −144.1 (sept, *J*(FP) = 708.4 Hz, PF_6). Anal. Calcd for $C_{20}H_{35}F_6P_2Rh$: C, 43.33; H, 6.36. Found: C, 42.86; H, 6.05.

Generation of [Rh(H)$_2${O=C(CD_3)$_2$}$_3$(2,6-$Me_2C_6H_3CH_2CH_2$P*t*Bu_2-κ*P*)]PF_6 (22). A solution of **21** (41 mg, 0.07 mmol) in acetone-d_6 (0.5 mL) was stirred under a hydrogen atmosphere (1 bar) for 12 h at room temperature. A gradual change of color from orange to brown-yellow occurred. The solution was then investigated by spectroscopic techniques. IR (acetone-

d_6): ν(RhH) 2127, 2067 (br) cm^{-1}. ^1H NMR (400 MHz, acetone-d_6): δ 6.99 (m, 3 H, C_6H_3), 3.02 (m, 2 H, PCH_2CH_2), 2.35 (s, 6 H, $C_6H_3(CH_3)_2$), 1.91 (m, 2 H, PCH_2), 1.35 (d, J(PH) = 12.6 Hz, 18 H, $PCCH_3$), −23.40 (dd, J(RhH) = J(PH) = 27.9 Hz, 2 H, RhH). ^{13}C NMR (100.6 MHz, acetone-d_6): δ 211.5 (br s, C=O), 140.0 (d, J(PC) = 13.4 Hz, ipso C of C_6H_3), 136.5 (s, ortho C of C_6H_3), 129.1 (s, meta C of C_6H_3), 126.8 (s, para C of C_6H_3), 36.5 (d, J(PC) = 23.8 Hz, $PCCH_3$), 30.1 (d, J(PC) = 2.9 Hz, $PCCH_3$), 28.6 (s, PCH_2PCH_2), 25.0 (d, J(PC) = 24.8 Hz, PCH_2), 20.5 (s, $C_6H_3(CH_3)_2$). ^{31}P NMR (162.0 MHz, acetone-d_6): δ 92.1 (br d, J(RhP) = 165.7 Hz, tBu$_2$P), −144.2 (sept, J(FP) = 708.4 Hz, PF_6).

Preparation of [(η^6-2,6-Me$_2$C$_6$H$_3$CH$_2$CH$_2$PtBu$_2$-κP)RhH$_2$]PF$_6$ (23). (a) A solution of **21** (263 mg, 0.47 mmol) in acetone (6 mL) was stirred under a hydrogen atmosphere (1 bar) for 12 h at room temperature. A gradual change of color from orange to brown-yellow occurred. The solution was concentrated to ca. 2 mL in vacuo and then layered with diethyl ether (12 mL). After the mixture was stored for 6 h, a pale brown solid precipitated, which was filtered, washed twice with diethyl ether (5 mL each) and twice with pentane (5 mL each), and dried. Yield: 224 mg (90%).

(b) A solution of **20** (101 mg, 0.16 mmol) in acetone (3 mL) was stirred under a hydrogen atmosphere (1 bar) for 14 days at room temperature. A smooth change of color from orange-red to brown-yellow occurred, and a metallic-like solid precipitated. The solution was filtered, concentrated in vacuo to ca. 1 mL, and then layered with diethyl ether (10 mL). After the mixture was stored for 6 h, a pale-brown solid precipitated, which was worked up as described for (a). Yield: 51 mg (61%). Mp: 67 °C dec. Λ_M = 99 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR (KBr): ν(RhH) 2127, 2067 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ 6.85 (m, 2 H, meta H of C_6H_3), 6.21 (m, 1 H, para H of C_6H_3), 3.13−2.96 (m, 4 H, PCH_2 and PCH_2CH_2), 2.52 (s, 6 H, $C_6H_3(CH_3)_2$), 1.25 (d, J(PH) = 15.3 Hz, 18 H, $PCCH_3$), −12.51 (dd, J(RhH) = 25.9, J(PH) = 19.9 Hz, 2 H, RhH). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 132.0 (dd, J(PC) = 5.7, J(RhC) = 1.9 Hz, ipso C of C_6H_3), 121.3 (s, ortho C of C_6H_3), 109.4 (s, meta C of C_6H_3), 93.4 (dd, J(PC) = 6.7, J(RhC) = 1.9 Hz, para C of C_6H_3), 40.2 (d, J(PC) = 21.0 Hz, PCH_2), 37.9 (dd, J(PC) = 23.9, J(RhC) = 1.9 Hz, $PCCH_3$), 28.9 (d, J(PC) = 3.8 Hz, $PCCH_3$), 27.3 (s, PCH_2PCH_2), 19.3 (s, $C_6H_3(CH_3)_2$). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 130.6 (d, J(RhP) = 152.6 Hz, tBu$_2$P), −144.4 (sept, J(FP) = 710.6 Hz, PF_6). Anal. Calcd for $C_{18}H_{33}F_6P_2Rh$: C, 40.92; H, 6.30. Found: C, 40.59; H, 6.13.

Generation of [(η^6-2,6-Me$_2$C$_6$H$_3$CH$_2$CH$_2$PtBu$_2$-κP)Rh(O=CMe$_2$)]PF$_6$ (24). A solution of **23** (43 mg, 0.08 mmol) in acetone (2 mL) was stored for 4 weeks at room temperature. A smooth change of color from light yellow to brown occurred. The ^{31}P NMR spectrum displayed a new resonance at δ 108.3 (d, J(RhP) = 198.4 Hz), while the signal of **23** had disappeared. Attempts to isolate the product failed or led to decomposition of the material. Spectroscopic data for **24** are as follows. ^1H NMR (200 MHz, acetone-d_6): δ 6.87 (m, 2 H, meta H of C_6H_3), 5.46 (m, 1 H, para H of C_6H_3), 2.42−2.28 (m, 4 H, PCH_2 and PCH_2CH_2), 2.38 (s, 6 H, $C_6H_3(CH_3)_2$), 1.36 (d, J(PH) = 12.8 Hz, 18 H, $PCCH_3$). ^{13}C NMR (50.3 MHz, acetone-d_6): δ 114.9 (d, J(PC) = 6.5 Hz, ortho C of C_6H_3), 109.2 (d, J(RhC) = 1.9 Hz, meta C of C_6H_3), 90.8 (dd, J(PC) = 10.6, J(RhC) = 3.3 Hz, para C of C_6H_3), 85.5 (dd, J(PC) = 8.3, J(RhC) = 4.6 Hz, ipso C of C_6H_3), 37.3 (d, J(PC) = 17.6 Hz, $PCCH_3$), 33.0 (d, J(PC) = 24.0 Hz, PCH_2), 29.2 (d, J(PC) = 4.6 Hz, $PCCH_3$), 27.6 (s, PCH_2CH_2), 19.3 (s, $C_6H_3(CH_3)_2$). ^{31}P NMR (81.0 MHz, acetone-d_6): δ 108.3 (d, J(RhP) = 198.4 Hz, tBu$_2$P), −142.7 (sept, J(FP) = 707.0 Hz, PF_6).

Reaction of Compound 23 with [nBu$_4$N]Cl. A solution of **23** (56 mg, 0.11 mmol) in acetone (2 mL) was stored for 4 weeks at room temperature. After the solution was cooled to −78 °C, it was treated with [nBu$_4$N]Cl (29 mg, 0.10 mmol) and then warmed to room temperature. The solvent was evaporated in vacuo, the residue was dissolved in dichloromethane (2 mL), and the solution was chromatographed on Al_2O_3 (acidic, activity grade III, length of column 4 cm). With CH_2Cl_2 a green-yellow fraction was eluted, which was brought to dryness in vacuo. The ^1H and ^{31}P NMR spectra showed that the residue consisted of a mixture (ca. 1:1) of **14** and [nBu$_4$N]PF_6, which could not be separated by either repeated chromatography or fractional crystallization.

Preparation of [(η^6-2,6-Me$_2$C$_6$H$_3$CH$_2$CH$_2$PtBu$_2$-κ-P)Rh(CH$_2$=CHtBu)]PF$_6$ (25). A solution of **23** (95 mg, 0.18 mmol) in acetone (2 mL) was treated with 3,3-dimethyl-1-butene (93 μL, 0.72 mmol) and stirred for 15 min at room temperature. After diethyl ether (15 mL) was added, a yellow solid precipitated, which was filtered, washed twice with diethyl ether (5 mL each) and with pentane (5 mL), and dried. Yield: 86 mg (78%). Mp: 110 °C dec. Λ_M = 93 $cm^2\ \Omega^{-1}\ mol^{-1}$. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.04, 6.44 (both m, 1 H each, meta H of C_6H_3), 5.27 (m, 1 H, para H of C_6H_3), 4.51 (dddd, J(HH) = 13.6, 8.9, J(PH) = 4.7, J(RhH) = 2.7 Hz, 1 H, =CHC(CH$_3$)$_3$), 3.18 (ddd, J(HH) = 13.6, 1.0, J(RhH) = 2.1 Hz, 1 H, one H of =CH$_2$ cis to tBu), 2.93 (dddd, J(HH) = 8.9, 1.0, J(PH) = 2.6, J(RhH) = 1.0 Hz, 1 H, one H of =CH$_2$ trans to tBu), 2.77−2.58 (m, 4 H, PCH_2 and PCH_2CH_2), 2.53, 2.52 (both s, 3 H each, $C_6H_3(CH_3)_2$), 1.41 (d, J(PH) = 13.6 Hz, 9 H, $PCCH_3$), 1.20 (d, J(PH) = 13.4 Hz, 9 H, $PCCH_3$), 1.02 (s, 9 H, =CHC(CH_3)$_3$). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 122.3, 119.5 (both d, J(RhC) = 2.9 Hz, ortho C of C_6H_3), 118.2 (dd, J(PC) = 4.9, J(RhC) = 3.8 Hz, ipso C of C_6H_3), 108.9 (s, meta C of C_6H_3), 108.0 (dd, J(PC) = 3.2, J(RhC) = 1.9 Hz, meta C of C_6H_3), 89.3 (dd, J(PC) = 10.6, J(RhC) = 2.9 Hz, para C of C_6H_3), 79.2 (d, J(RhC) = 12.4 Hz, =CHC-(CH$_3$)$_3$), 40.2 (dd, J(PC) = 13.8, J(RhC) = 2.2 Hz, $PCCH_3$), 40.0 (d, J(RhC) = 12.7 Hz, =CH$_2$), 38.0 (dd, J(PC) = 16.4, J(RhC) = 2.2 Hz, $PCCH_3$), 37.6 (d, J(PC) = 23.6 Hz, PCH_2), 35.2 (s, =CHC(CH$_3$)$_3$), 30.8 (s, $PCCH_3$), 30.7 (s, =CHC(CH$_3$)$_3$), 29.3 (d, J(PC) = 2.9 Hz, $PCCH_3$), 26.7 (s, PCH_2CH_2), 19.4, 18.9 (both s, $C_6H_3(CH_3)_2$). ^{31}P NMR (81.0 MHz, acetone-d_6): δ 93.7 (d, J(RhP) = 188.2 Hz, tBu$_2$P), −142.7 (sept, J(FP) = 707.0 Hz, PF_6). Anal. Calcd for $C_{24}H_{43}F_6P_2Rh$: C, 47.22; H, 7.10. Found: C, 47.00; H, 7.00.

Preparation of [(η^6-2,6-Me$_2$C$_6$H$_3$CH$_2$CH$_2$PtBu$_2$-κP)Rh(CH$_2$=CHPh)]PF$_6$ (26). A solution of **23** (67 mg, 0.13 mmol) in acetone (2 mL) was treated with styrene (73 μL, 0.63 mmol), and the mixture was stirred for 2 min at room temperature. A rapid change of color from light yellow to orange-red occurred. The solution was concentrated to ca. 0.5 mL in vacuo and then layered with diethyl ether (10 mL). An orange solid precipitated, which was filtered, washed twice with diethyl ether (5 mL each) and pentane (5 mL), and dried. Yield: 76 mg (95%). Mp: 156 °C dec. Λ_M 77 $cm^2\ \Omega^{-1}\ mol^{-1}$. ^1H NMR (400 MHz, acetone-d_6): δ 7.41 (m, 2 H, ortho H of =CHC_6H_5), 7.35 (m, 1 H, meta H of C_6H_3), 7.32 (m, 2 H, meta H of =CHC_6H_5), 7.21 (m, 1 H, para H of =CHC_6H_5), 5.39 (dddd, J(HH) = 12.8, 8.2, J(PH) = 3.3, J(RhH) = 2.7 Hz, 1 H, =CHC$_6$H$_5$), 5.03 (m, 1 H, meta H of C_6H_3), 4.91 (m, 1 H, para H of C_6H_3), 4.27 (ddd, J(HH) = 12.8, 1.8, J(RhH) = 2.1 Hz, 1 H, one H of =CH$_2$ cis to tBu), 3.00 (dddd, J(HH) = 8.2, 1.8, J(PH) = 3.7, J(RhH) = 2.1 Hz, 1 H, one H of =CH$_2$ trans to tBu), 2.96−2.68 (m, 4 H, PCH_2 and PCH_2CH_2), 2.52, 2.46 (both s, 3 H each, $C_6H_3(CH_3)_2$), 1.56, 1.32 (both d, J(PH) = 13.5 Hz, 9 H each, $PCCH_3$). ^{13}C NMR (100.6 MHz, acetone-d_6): δ 145.1 (s, ipso C of =CHC_6H_5), 129.5, 127.6, 126.8 (all s, ortho, meta, and para C of =CHC_6H_5), 121.6 (d, J(RhC) = 2.9 Hz, ortho C of C_6H_3), 120.1 (d, J(RhC) = 1.9 Hz, ortho C of C_6H_3), 119.1 (dd, J(PC) = 5.7, J(RhC) = 3.8 Hz, ipso C of C_6H_3), 114.3 (dd, J(PC) = 2.9, J(RhC) = 1.9 Hz, meta C of C_6H_3), 111.1 (s, meta C of C_6H_3), 93.3 (dd, J(PC) = 10.5, J(RhC) = 3.9 Hz, para C of C_6H_3), 63.1 (d, J(RhC) = 12.4 Hz, =CHC$_6$H$_5$), 40.0 (dd, J(PC) = 15.3, J(RhC) = 2.9 Hz, $PCCH_3$), 38.7 (d, J(PC) = 23.8 Hz, PCH_2), 38.2 (dd, J(PC) = 16.2, J(RhC) = 1.9 Hz, $PCCH_3$), 37.3 (d, J(RhC) = 13.4 Hz, =CH$_2$), 30.6 (d, J(PC) = 3.8 Hz, $PCCH_3$), 29.8 (d, J(PC) = 2.8 Hz, $PCCH_3$), 26.9 (s, PCH_2CH_2), 19.1, 18.8 (both s, $C_6H_3(CH_3)_2$). ^{31}P NMR (162.0 MHz, acetone-d_6): δ 94.2

Table 1. Crystallographic Data for 9, 15, and 18

	9	15	18
formula	$C_{40}H_{70}Cl_2P_2Rh_2$	$C_{20}H_{31}ClO_2PRh$	$C_{40}H_{72}Cl_4P_2Rh_2$
fw	889.62	472.78	962.54
cryst size, mm	0.30 × 0.20 × 0.20	0.35 × 0.16 × 0.16	0.18 × 0.15 × 0.10
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
cell dimens determn	5000 rflns, 2.60° < θ < 25.00°	6959 rflns, 2.400° < θ < 28.140°	5357 rflns, 2.428° < θ < 28.183°
a, Å	8.5713(17)	7.9221(4)	10.0093(6)
b, Å	8.5866(17)	8.6663(4)	15.4273(9)
c, Å	30.745(6)	16.9724(9)	14.0090(8)
α, deg	94.76(3)	90.0310(10)	90
β, deg	94.61(3)	90.6400(10)	92.7580(10)
γ, deg	112.88(3)	11.7650(10)	90
V, Å^3	2061.8(7)	1082.10(9)	2160.7(2)
Z	2	2	2
d_{calcd}, g cm^{-3}	1.433	1.451	1.479
temp, K	173(2)	173(2)	193(2)
μ, mm^{-1}	1.034	0.997	1.112
scan method	φ	ω	ω
2θ(max), deg	50.00	52.74	52.74
total no. of rflns	6781	17545	28637
no. of unique rflns	6781 (R(int) = 0.0000)	4416 (R(int) = 0.0183)	4412 (R(int) = 0.0370)
no. of obsd rflns	5948 ($I > 2\sigma(I)$)	4309 ($I > 2\sigma(I)$)	4084 ($I > 2\sigma(I)$)
no. of rflns used for refinement	6781	4416	4412
no. of params refined	455	234	226
final R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0534, wR2 = 0.1394	R1 = 0.0210, wR2 = 0.0542	R1 = 0.0311, wR2 = 0.0709
R indices (all data)[a]	R1 = 0.0587, wR2 = 0.1420	R1 = 0.0216, wR2 = 0.0546	R1 = 0.0349, wR2 = 0.0726
resid electron density, e Å^{-3}	2.000/−1.529	0.596/−0.342	0.635/−0.267

[a] $w^{-1} = [\sigma^2F_o^2 + (0.0769P)^2 + 6.5760P]$ (**9**), $w^{-1} = [\sigma^2F_o^2 + (0.0295P)^2 + 0.4618P]$ (**15**), and $w^{-1} = [\sigma^2F_o^2 + (0.0334P)^2 + 0.0181P]$ (**18**), where $P = (F_o^2 + 2F_c^2)/3$.

(d, J(RhP) = 185.3 Hz, tBu$_2$P), −144.1 (sept, J(FP) = 708.4 Hz, PF_6). Anal. Calcd for $C_{26}H_{39}F_6P_2Rh$: C, 49.53; H, 6.24. Found: C, 49.24; H, 6.18.

Preparation of [(η^6-2,6-Me$_2$C$_6$H$_3$CH$_2$CH$_2$PtBu$_2$-κP)Rh(HC≡CPh)]PF$_6$ (27). A solution of **23** (93 mg, 0.18 mmol) in acetone (3 mL) was treated with phenylacetylene (0.5 mL, 4.90 mmol) at room temperature. A rapid change of color from light yellow to orange-red occurred. The reaction mixture was stirred for 4 h, which led to the precipitation of an orange solid (probably polyphenylacetylene). The solution was filtered, the filtrate was concentrated to ca. 1 mL in vacuo, and diethyl ether (10 mL) was added. An orange-red solid precipitated, which was filtered, washed twice with diethyl ether (5 mL each) and twice with pentane (5 mL each), and dried. Yield: 106 mg (96%). Mp: 162 °C dec. Λ_M = 117 cm^2 Ω^{-1} mol^{-1}. IR (CH_2Cl_2): ν(≡CH) 3163, ν(C≡C) 1827 cm^{-1}. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.72 (m, 2 H, ortho H of ≡CC$_6$H$_5$), 7.56, 7.25 (both m, 1 H each, meta H of C$_6$H$_3$), 7.45−7.36 (m, 3 H, meta and para H of ≡CC$_6$H$_5$), 5.81 (d, J(RhH) = 3.8 Hz, 1 H, ≡CH), 5.34 (m, 1 H, para H of C$_6$H$_3$), 3.04−2.92 (m, 4 H, PCH$_2$ and PCH$_2$CH_2), 2.85, 2.71 (both s, 3 H each, C$_6$H$_3$(CH_3)$_2$), 1.37, 1.10 (both br d, J(PH) = 13.8 Hz, 9 H each, PCCH$_3$). ^{13}C NMR (100.6 MHz, acetone-d_6): δ 133.2, 129.5, 129.2 (all s, ortho, meta, and para C of ≡CC$_6$H$_5$), 127.7 (d, J(RhC) = 1.9 Hz, ipso C of ≡CC$_6$H$_5$), 122.5 (dd, J(PC) = 4.8, J(RhC) = 3.8 Hz, ipso C of C$_6$H$_3$), 120.1, 119.4 (both s, ortho C of C$_6$H$_3$), 112.9, 110.5 (both s, meta C of C$_6$H$_3$), 96.8 (dd, J(PC) = 12.4, J(RhC) = 1.9 Hz, para C of C$_6$H$_3$), 79.8 (dd, J(RhC) = 16.2, J(PC) = 1.9 Hz, C≡CH), 67.1 (dd, J(RhC) = 14.3, J(PC) = 4.8 Hz, C≡CH), 38.9 (br m, PCCH$_3$), 38.8 (d, J(PC) = 24.8 Hz, PCH$_2$), 29.7, 29.2 (both br s, PCCH$_3$), 27.6 (s, PCH$_2$CH$_2$), 19.6, 19.5 (both s, C$_6$H$_3$(CH_3)$_2$). ^{31}P NMR (162.0 MHz, acetone-d_6): δ 103.2 (d, J(RhP) = 187.5 Hz, tBu$_2$P), −144.1 (sept, J(FP) = 708.4 Hz, PF_6). Anal. Calcd for $C_{26}H_{37}F_6P_2Rh$: C, 49.69; H, 5.93. Found: C, 49.59; H, 5.84.

Preparation of [(η^6-2,6-Me$_2$C$_6$H$_3$CH$_2$CH$_2$PtBu$_2$-κP)Rh(CO)]PF$_6$ (28). A solution of **27** (108 mg, 0.17 mmol) in acetone (120 mL) was irradiated for 3 days with a UV lamp. It was then concentrated to ca. 3 mL in vacuo, and diethyl ether (15 mL) was added. A light yellow solid precipitated, which was filtered, washed with diethyl ether (10 mL) and pentane (10 mL), and dried. Yield: 87 mg (91%). Mp: 154 °C dec. Λ_M = 119 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(CO) 2001 cm^{-1}. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.27 (m, 2 H, meta H of C$_6$H$_3$), 6.33 (m, 1 H, para H of C$_6$H$_3$), 3.20 (m, 2 H, PCH$_2$), 2.95 (m, 2 H, PCH$_2$CH_2), 2.61 (s, 6 H, C$_6$H$_3$(CH_3)$_2$), 1.37 (d, J(PH) = 15.0 Hz, 18 H, PCCH$_3$). ^{13}C NMR (75.5 MHz, acetone-d_6): δ 185.9 (dd, J(RhC) = 91.1, J(PC) = 15.7 Hz, CO), 126.5 (d, J(RhC) = 2.8 Hz, ortho C of C$_6$H$_3$), 121.8 (dd, J(PC) = 5.8, J(RhC) = 3.0 Hz, ipso C of C$_6$H$_3$), 109.9 (dd, J(PC) = J(RhC) = 1.9 Hz, meta C of C$_6$H$_3$), 92.4 (dd, J(PC) = 6.9, J(RhC) = 3.2 Hz, para C of C$_6$H$_3$), 39.6 (d, J(PC) = 21.7 Hz, PCH$_2$), 38.9 (dd, J(PC) = 21.5, J(RhC) = 1.6 Hz, PCCH$_3$), 29.1 (d, J(PC) = 3.7 Hz, PCCH$_3$), 27.7 (s, PCH$_2$CH$_2$), 19.4 (s, C$_6$H$_3$(CH_3)$_2$). ^{31}P NMR (81.0 MHz, acetone-d_6): δ 120.9 (d, J(RhP) = 167.9 Hz, tBu$_2$P), −142.7 (sept, J(FP) = 707.0 Hz, PF_6). Anal. Calcd for $C_{19}H_{31}F_6OP_2Rh$: C, 41.17; H, 5.64. Found: C, 41.20; H, 5.41.

X-ray Structure Determination of Compounds 9, 15, and 18. Single crystals of **9** were grown from benzene at room temperature, those of **15** from a saturated solution in pentane at −10 °C under a CO atmosphere, and those of **18** from dichloromethane at room temperature. Crystal data collection parameters are summarized in Table 1. The data were collected on an IPDS Stoe diffractometer (**9**) and a Bruker Smart Apex diffractometer with a D8 goniometer (**15** and **18**) using monochromated Mo Kα radiation (λ = 0.710 73 Å). Intensity data were corrected by Lorentz and polarization effects, and empirical absorption corrections were applied. The structures of **9** and **18** were solved by direct methods and the structure of **15** by the Patterson method (SHELXS-97).[34] Atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least squares on F^2 (SHELXL-97).[35] The positions of all hydrogen atoms were calculated according to ideal geometry and refined using the riding method, except for H1a, H1b, H2a, H2b, H3a, H3b, H4a,

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and H4b of **9**, which were found in a differential Fourier synthesis.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (Grant SFB 347) and the Fonds der Chemischen Industrie for financial support. Moreover, we gratefully acknowledge support by Mrs. R. Schedl and Mr. C. P. Kneis (elemental analyses and DTA), Mrs. M.-L. Schäfer and Dr. W. Bertermann (NMR measurements), Dr. G. Lange and Mr. F. Dadrich (mass spectra), and BASF AG for gifts of chemicals.

Supporting Information Available: Crystallographic data for **9** and **15** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org. For the corresponding data for **18**, see ref 5.

OM034348P