Half-Sandwich Type Rhodium(I) Complexes with Arenes and Functionalized Arenes $C_6H_5X(CH_2)_nPR_2$ (R = *i*Pr, *t*Bu) as Nonchelating and Chelating Ligands

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A series of arenerhodium(I) complexes $[(\eta^6\text{-arene})Rh(C_8H_{14})(PiPr_3)]PF_6$ (**2**−**6**) were prepared from the highly reactive starting material *cis*-$[Rh(C_8H_{14})(PiPr_3)(acetone)_2]PF_6$ (**1**) and the arene in CH_2Cl_2 in excellent yields. The related ethene compound $[(\eta^6\text{-}C_6H_6)Rh(C_2H_4)(PiPr_3)]PF_6$ (**7**) was obtained by stirring a solution of the corresponding cyclooctene derivative **2** under an ethene atmosphere. Reaction of *cis*-$[Rh(C_8H_{14})_2(acetone)_2]PF_6$ (**10**) with the new alkyldiisopropylphosphines $iPr_2P(CH_2)_nC_6H_5$ (**8**, $n = 2$; **9**, $n = 3$), which were prepared from $HPiPr_2$ and $C_6H_5(CH_2)_nBr$ in the presence of ammonia, in the molar ratio of 1:1 gave the half-sandwich type complexes $[\{\eta^6\text{-}C_6H_5(CH_2)_nPiPr_2\text{-}\kappa\text{-}P\}Rh(C_8H_{14})]PF_6$ (**11**, **12**). They afforded upon treatment with a second equivalent of **8** or **9** the bis(phosphine) compounds $[\{\eta^6\text{-}C_6H_5(CH_2)_nPiPr_2\text{-}\kappa\text{-}P\}\{C_6H_5(CH_2)_nPiPr_2\text{-}\kappa\text{-}P\}Rh]PF_6$ (**13**, **14**). The NMR spectra of **13** and **14** are not temperature-dependent, and therefore a fluxional behavior in solution can be excluded. The cyclooctene ligand of **11** could easily be displaced by ethene, maleicacid anhydride, ethyl propiolate, and triisopropylstibine to generate the substitution products **15**−**18** in 80−90% yield. Similarly, the ethene complex **19** was obtained from **12** and C_2H_4. The even more bulky alkyldi-*tert*-butylphosphines $tBu_2P(CH_2)_nXC_6H_5$ (**20**, $n = 1$, X = CH_2; **21**, $n = 2$, X = O) and their respective olefin and alkyne rhodium(I) complexes **22a**, **23**, and **24** were prepared by using the same methodology as applied for the iPr_2P counterparts. The corresponding triflate $[\{\eta^6\text{-}C_6H_5(CH_2)_2PtBu_2\text{-}\kappa\text{-}P\}Rh(C_8H_{14})]CF_3SO_3$ (**22b**) was obtained from the dimer **25** and the phosphine **20** as starting materials. The molecular structures of **11**, **12**, and **19** were determined by X-ray crystallography.

Introduction

The intention to undertake the work reported in this paper was twofold: First, we were interested to find out whether cationic arenerhodium(I) compounds of the general composition $[(\eta^6\text{-arene})Rh(L)(PiPr_3)]^+$, where L is a labile ligand such as acetone, THF, and cyclooctene, are accessible and, if so, can be used as starting materials for carbene, vinylidene, and allenylidene complexes $[(\eta^6\text{-arene})Rh\{{=}C({=}C)_nR_2\}(PiPr_3)]^+$ ($n = 0$, 1, 2). Second, we were tempted to answer the question whether diisopropylphosphine and di-*tert*-butylphosphine derivatives of the type $R'_2P(CH_2)_nXC_6H_5$ (X = O, CH_2) are able to behave as chelating ligands and thus generate a (possibly solvated) 16-electron rhodium(I) fragment $[\{\eta^6\text{-}C_6H_5X(CH_2)_nPR'_2\text{-}\kappa\text{-}P\}Rh]^+$, which might be more suitable to stabilize a $Rh{=}C({=}C)_nR_2$ linkage than the nonchelating $[(\eta^6\text{-arene})Rh(PiPr_3)]^+$ moiety. We were aware of the fact that various cationic rhodium(I) complexes $[(\eta^6\text{-arene})Rh(L)(L')]^+$ were known,[1] but to the best of our knowledge none of them contain a sterically demanding trialkylphosphine such as $PiPr_3$ and $iPr_2P(CH_2)_nC_6H_5$.

Results and Discussion

1. Arenerhodium(I) Compounds with [Rh(olefin)-($PiPr_3$)]$^+$ as a Molecular Unit. Following our studies on the coordination properties of unsymmetrical chelating ligands of the general formula $R_2P(CH_2)_nPR'_2$ ($n =$ 1, 2, 3; R, R′ = Ph, *i*Pr, Cy, etc.),[2,3] we recently observed that the labile starting material *cis*-$[Rh(C_8H_{14})_2(acetone)_2]PF_6$ reacts with $iPr_2PCH_2PCy_2$ in acetone−benzene or acetone−toluene to give the half-sandwich type complexes $[(\eta^6\text{-arene})Rh(\kappa^2\text{-}iPr_2PCH_2PCy_2)]PF_6$ (arene = C_6H_6, C_6H_5Me).[2] If instead of *cis*-$[Rh(C_8H_{14})_2(acetone)_2]PF_6$ the triisopropylphosphine derivative *cis*-$[Rh(C_8H_{14})(PiPr_3)(acetone)_2]PF_6$ (**1**)[4] is used, the reaction with

(1) (a) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3089−3091. (b) Green, M.; Kuc, T. A. *J. Chem. Soc., Dalton Trans.* **1972**, 832−839. (c) Green, M.; Parker, G. J. *J. Chem. Soc., Dalton Trans.* **1974**, 333−343. (d) Uson, R.; Lahuerta, P.; Reyes, J.; Oro, L. A. *Inorg. Chim. Acta* **1980**, *42*, 75−84. (e) Uson, R.; Oro, L. A.; Foces-Foces, C.; Cano, F. H.; Vegas, A.; Valderrama, M. *J. Organomet. Chem.* **1981**, *215*, 241−253. (f) Uson, R.; Oro, L. A.; Foces-Foces, C.; Cano, F. H.; Garcia-Blanco, S.; Valderrama, M. *J. Organomet. Chem.* **1982**, *229*, 293−304. (g) Valderrama, M.; Oro, L. A. *Can. J. Chem.* **1982**, *60*, 1044−1047. (h) Burch, R. R.; Muetterties, E. L.; Day, V. W. *Organometallics* **1982**, *1*, 188−197. (i) Valderrama, M.; Scotti, M.; Ganz, R.; Oro, L. A.; Lahoz, F. J.; Foces-Foces, C.; Cano, F. H. *J. Organomet. Chem.* **1985**, *288*, 97−107. (j) Bittersmann, E.; Hildenbrand, K.; Cervilla, A.; Lahuerta, P. *J. Organomet. Chem.* **1985**, *287*, 255−263. (k) Bleeke, J. R.; Donaldson, A. J. *Organometallics* **1988**, *7*, 1588−1596.

(2) (a) Wolf, J.; Manger, M.; Schmidt, U.; Fries, G.; Barth, D.; Weberndörfer, B.; Vicic, D. A.; Jones, W. D.; Werner, H. *J. Chem. Soc., Dalton Trans.* **1999**, 1867−1875. (b) Manger, M. Dissertation, Universität Würzburg, 1998.

(3) (a) Fries, G.; Wolf, J.; Pfeiffer, M.; Stalke, D.; Werner, H. *Angew. Chem.* **2000**, *112*, 575−578; *Angew. Chem., Int. Ed.* **2000**, *39*, 564−566. (b) Fries, G. Dissertation, Universität Würzburg, 2000.

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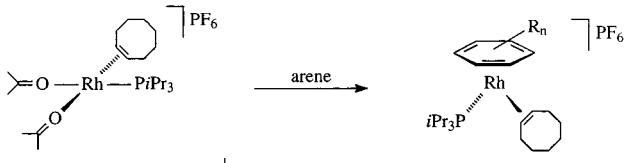
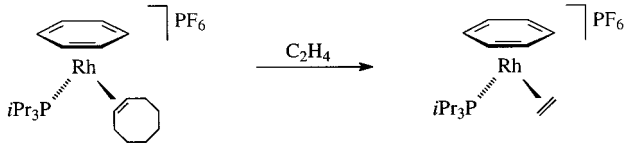
Scheme 1



	arene
2	C_6H_6
3	$C_6H_5CF_3$
4	1.3.5-$C_6H_3(CH_3)_3$
5	$C_6H_5OCH_3$
6	1.3.5-$C_6H_3(OCH_3)_3$

Scheme 2



excess benzene in CH_2Cl_2 as solvent affords the cationic rhodium(I) compound **2** in excellent yield. The analogous complexes **3**−**6** (Scheme 1) were prepared through a similar route. While for the synthesis of **3**, **4**, and **5** the substitution reaction of **1** was carried out in pure $C_6H_5CF_3$, 1,3,5-$C_6H_3Me_3$, or C_6H_5OMe as solvent, the related complex **6** was obtained upon treatment of a suspension of **1** in ether with 1,3,5-trismethoxybenzene. The yield of **3**, **5**, and **6** was 93−98%. The mesitylene derivative **4** could not be isolated analytically pure, as it contained even after repeated recrystallization an impurity, which owing to the ^{1}H NMR spectrum also has one arene and one phosphine ligand coordinated to rhodium.

The half-sandwich type compounds **2**, **3**, **5**, and **6** are yellow, only moderately air-sensitive solids which are readily soluble in polar organic solvents such as CH_2Cl_2 or THF. In nitromethane they exhibit the conductivity of 1:1 electrolytes. While the ^{1}H and ^{13}C NMR spectra of **2**−**6** display the typical signals for the arene, phosphine, and cyclooctene protons and carbon nuclei, the ^{31}P NMR spectra show, apart from the signal for the PF_6^- anion, one resonance which due to phosphorus−rhodium coupling is split into a doublet. In all cases, the coupling constant $^2J(^{31}P^{103}Rh)$ is 181−183 Hz. In the ^{19}F NMR spectrum of **3**, the signal for the fluorine atoms of the CF_3 group appears as a singlet at δ −60.2. It should be mentioned that although compound **3** can be stored under argon at −60 °C for days, in acetone solution in the absence of $C_6H_5CF_3$ the staring material **1** is regenerated.

To find out whether the cyclooctene ligand in **2** can be displaced by another olefin, a degassed solution of **2** in CH_2Cl_2 was brought under an ethene atmosphere. Without cleaving the Rh−C_6H_6 bond, a smooth ligand exchange of C_8H_{14} for C_2H_4 takes place to give the cationic ethenerhodium(I) compound **7** in 89% yield (Scheme 2). The ^{1}H NMR spectrum of **7** exhibits two resonances at δ 3.33 and 2.27 for the "outer" and the "inner" protons of the C_2H_4 unit, indicating that the rotation of the ethene ligand around the Rh−C_2H_4 axis is considerably hindered. Attempts to substitute the cyclooctene moiety in **2** by either an internal or a terminal alkyne failed. Although in each case a reaction occurs, for PhC≡CPh and MeC≡CSiMe$_3$ as well as for HC≡CPh and HC≡CCO$_2$Me as substrates mixtures of products were formed, the NMR spectra of which indicated that presumably a cleavage of both the Rh−C_8H_{14} and the Rh−arene bonds had taken place.

2. Preparation of Chelating Phosphines *i*Pr$_2$P-(CH$_2$)$_n$C$_6$H$_5$. An obvious possibility to prevent a complete elimination of the arene unit in the cationic compounds $[(\eta^6\text{-arene})Rh(L)(P\textit{i}Pr_3)]^+$ is to link the six-membered ring via a $(CH_2)_n$ chain with the phosphorus atom, thus generating a chelate system. Recently, Mirkin et al. reported that upon treatment of $[RhCl(C_8H_{14})_2]_2$ with $AgBF_4$ in THF and subsequent reaction of the intermediate with $Ph_2P(CH_2)_2XC_6H_4R$ (X = CH_2, O), mononuclear rhodium(I) complexes are formed in which the substituted diphenylphosphines can behave as monodentate (*P*-bonded) or chelating ligands.[5] Moreover, Noels and co-workers found that monomeric ruthenium(II) compounds of the general composition $[\{\eta^6\text{-}3.5\text{-}C_6H_3R_2(CH_2)_3PCy_2\text{-}\kappa\text{-}P\}RuCl_2]$ (R = H, CH_3) are accessible, though catalytically less efficient in the ATRP (atom transfer radical polymerization) reaction than the nonchelate counterparts $[(\eta^6\text{-arene})RuCl_2(PCy_3)]$.[6]

A well-known procedure 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), but this method could not be applied for the diisopropylphosphine analogues $\textit{i}Pr_2P(CH_2)_nC_6H_5$. The reason is that, in agreement with earlier work by Issleib and Müller, dialkylphosphides MPR_2 (R = alkyl) upon treatment with alkylhalides R′X undergo a halide−metal exchange which yields via reaction of MPR_2 with the intermediarily formed R_2PX the corresponding diphosphines P_2R_4.[7]

However, we found that a convenient route to prepare the wanted alkyldiisopropylphosphines $\textit{i}Pr_2P(CH_2)_nC_6H_5$ (**8**, n = 2; **9**, n = 3) proceeds via the trialkylphosphonium bromides $[\textit{i}Pr_2PH(CH_2)_nC_6H_5]Br$. These intermediates are obtained by heating a mixture of $HP\textit{i}Pr_2$ and 2-phenylethyl- or 3-phenylpropylbromide for 24 h at 90 °C in the absence of solvent. After cooling, the purified phosphonium bromide was treated with a concentrated aqueous solution of ammonia to give both **8** and **9** as colorless viscous liquids in 89% (**8**) and 78% (**9**) yield (Scheme 3). The new phosphines, which like $P\textit{i}Pr_3$ are quite air-sensitive, were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and by mass spectra. Since **8** and **9** could not be correctly analyzed, these neutral compounds were converted with CH_3I to the corresponding methylphosphonium salts **8a** and **9a**, which are stable solids and gave correct elemental analyses. Typical

(5) (a) Singewald, E. T.; Mirkin, C. A.; Levy, A. D.; Stern, C. L. *Angew. Chem.* **1994**, *106*, 2524−2526; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2473−2475. (b) Singewald, E. T.; Shi, X.; Mirkin, C. A.; Schofer, S. J.; Stern, C. L. *Organometallics* **1996**, *15*, 3062−3069. (c) Singewald, E. T.; Slone, C. S.; Stern, C. L.; Mirkin, C. A.; Yap, G. P. A.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 3048−3056. (d) Slone, C. S.; Mirkin, C. A.; Yap, G. P. A.; Guzei, I. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 10743−10753. (e) Allgeier, A. M.; Mirkin, C. A. *Angew. Chem.* **1998**, *110*, 936−952; *Angew. Chem., Int. Ed.* **1998**, *37*, 894−908.

(6) Delaude, L.; Simal, F.; Demonceau, A.; Noels, A. F. *International Symposium on Organometallics and Catalysis*; Rennes 1999, Abstr. p 1.

(7) Issleib, K.; Müller, D.-W. *Chem. Ber.* **1959**, *92*, 3175−3182.

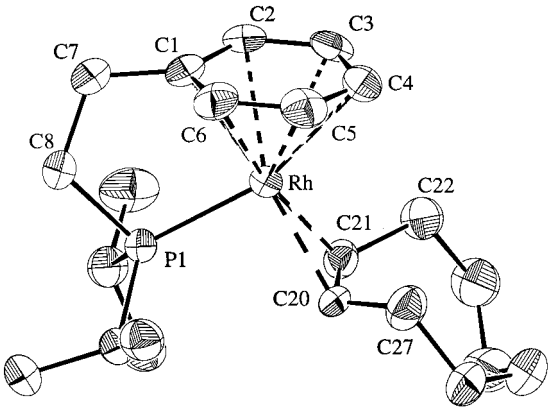
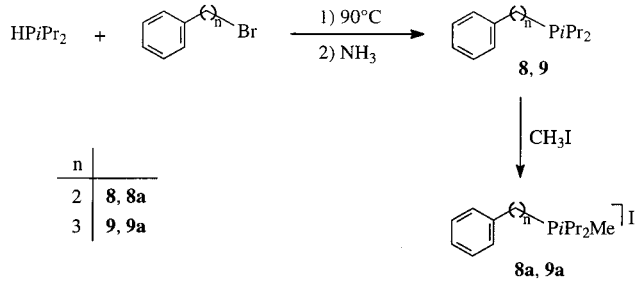


Figure 1. ORTEP drawing of **11**.

Scheme 3



NMR spectroscopic features of **8** and **9** are the two doublets of doublets for the protons of the pairwise anisochronous methyl groups of the isopropyl units and the two or three resonances for the carbon atoms of the bridging CH_2 moieties. All of these ^{13}C NMR resonances are split into doublets, the value of the $^{13}C-^{31}P$ coupling constant being almost the same for the PCH_2 and the PCH_2CH_2 carbon nuclei.

3. Half-Sandwich Type Rhodium(I) Complexes with One or Two *i*Pr$_2$P(CH$_2$)$_n$C$_6$H$_5$ Ligands. The highly reactive bis(acetone)rhodium(I) derivative **10**[8] is an appropriate starting material not only for the synthesis of the above-mentioned compounds $[(\eta^6\text{-arene})\text{-}Rh(\kappa^2\text{-}iPr_2PCH_2PCy_2)]PF_6$ but also for that of the new half-sandwich type complexes **11** and **12** (see Scheme 3). However, the success of the preparation of **11** and **12**, in which *one* alkyldiisopropylphosphine $iPr_2P\text{-}(CH_2)_nC_6H_5$ (n = 2 or 3) is coordinated in a chelating fashion to rhodium, strictly depends on the reaction conditions. After several unsuccessful attempts we found that addition of a diluted solution of **8** in acetone to a highly concentrated solution of **10** in the same solvent at −20 °C affords, after warming to room temperature, the wanted products in nearly quantitative yields. Both **11** and **12** are yellow air-stable solids that are significantly more stable in the crystalline state and in solution than the nonchelate counterparts **2**−**6**. The ^1H and ^{13}C NMR data of **11** and **12** are noteworthy insofar as the signals for the proton and the carbon nuclei of the CH unit *trans* to the *ipso*-C atom of the ring appear at much higher chemical shifts than in the related compounds **3** and **5**.

To compare the stereochemistry of **11** and **12**, the molecular structure of both complexes has been determined by X-ray crystallography. In compound **11** (Figure 1), in which the bridge between the arene and the P*i*Pr$_2$ unit is shorter than in **12**, the six-membered ring possesses a slightly inverse boat conformation, the characteristic feature being that the *ipso*-carbon atom C1 and, to a smaller extent, the carbon atom C4 in *para* position are bent toward the metal center. The consequence is that the distance Rh−C1 is ca. 0.1 Å shorter than the distances Rh−C2 and Rh−C6 (Table 1). The bond lengths Rh−C20 and Rh−C21 as well as the bond angles P1−Rh−C20 and P1−Rh−C21 are nearly identical to those in the nonchelate complex $[(\eta^6\text{-}C_6H_6)Rh\text{-}(C_8H_{14})(PiPr_3)]CF_3SO_3$.[2a]

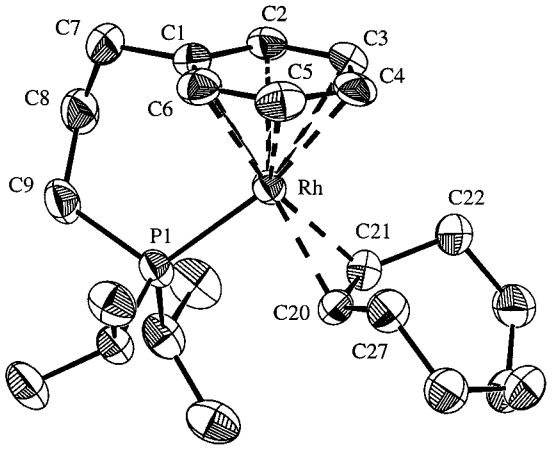


Figure 2. ORTEP drawing of **12**.

Table 1. Selected Bond Distances and Angles with Esd's for Compound 11

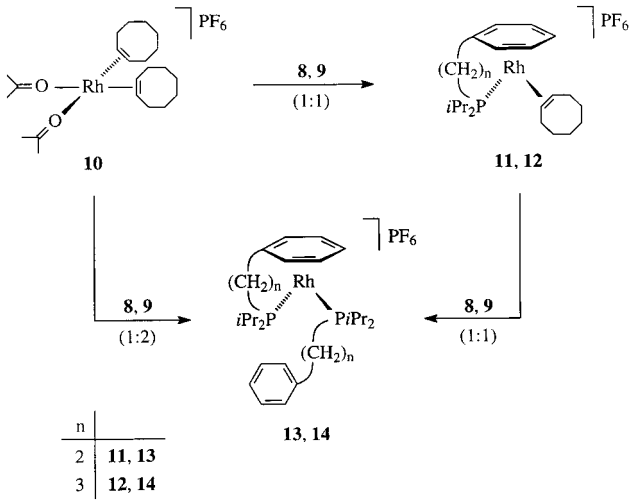
Bond Distances (Å)			
Rh−P1	2.236(1)	Rh−C5	2.377(4)
Rh−C1	2.215(3)	Rh−C6	2.304(3)
Rh−C2	2.308(3)	Rh−C20	2.158(3)
Rh−C3	2.364(3)	Rh−C21	2.138(3)
Rh−C4	2.364(4)	C20−C21	1.403(5)
Bond Angles (deg)			
P1−Rh−C20	92.3(1)	Rh−P1−C8	104.0(1)
P1−Rh−C21	95.9(1)	P1−C8−C7	112.7(3)
Rh−C20−C21	70.2(2)	C8−C7−C1	111.3(3)
Rh−C21−C20	71.7(2)	C7−C1−C2	120.7(4)
C20−C21−C22	122.7(4)	C7−C1−C6	120.3(3)
C21−C20−C27	124.3(3)		

Table 2. Selected Bond Distances and Angles with Esd's for Compound 12

Bond Distances (Å)			
Rh−P1	2.265(1)	Rh−C5	2.355(4)
Rh−C1	2.295(4)	Rh−C6	2.334(4)
Rh−C2	2.330(4)	Rh−C20	2.151(4)
Rh−C3	2.330(4)	Rh−C21	2.127(4)
Rh−C4	2.327(4)	C20−C21	1.403(6)
Bond Angles (deg)			
P1−Rh−C20	86.8(1)	Rh−P1−C9	111.3(1)
P1−Rh−C21	94.3(1)	P1−C9−C8	117.2(3)
Rh−C20−C21	69.9(2)	C9−C8−C7	113.6(4)
Rh−C21−C20	71.8(2)	C8−C7−C1	113.9(4)
C20−C21−C22	122.6(4)	C7−C1−C2	119.5(4)
C21−C20−C27	124.6(4)	C7−C1−C6	121.0(4)

The molecular structure of **12** is shown in Figure 2. Due to the reduced strain in the cyclic Rh−P1−C9−C8−C7−C1 moiety, the arene ring is nearly planar and symmetrically coordinated to the metal center. As a consequence of the steric release, the bond angle Rh−P1−C9 (Table 2) is enlarged by approximately 7° compared with the angle Rh−P1−C8 in compound **11**. The piano stool configuration of the P1,Rh,C20,C21 unit in **12** is slightly distorted, as indicated by the difference between the angles P1−Rh−C20 and P1−Rh−C21 of ca. 8°.

Scheme 4



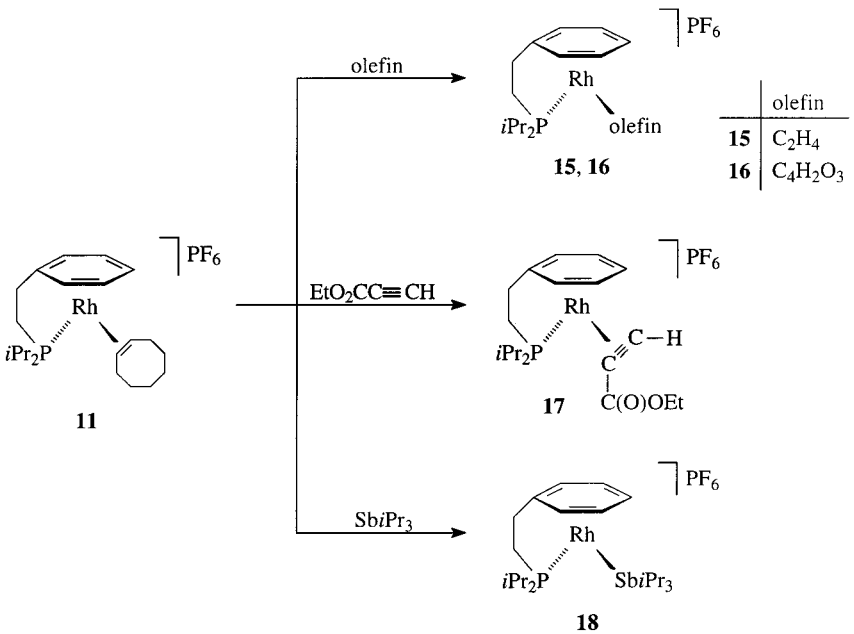
Treatment of **11** and **12** with 1 equiv of the alkyldiisopropylphosphine **8** or **9** leads to a displacement of the cyclooctene and the formation of the substitution products **13** and **14**, respectively (Scheme 4). Both are orange air-sensitive solids which have been characterized by elemental analyses, conductivity measurements, and spectroscopic techniques. The unequal coordination of the two phosphine ligands is best illustrated by the ^{31}P NMR spectra in which two resonances at δ 83.6 and 48.7 (for **13**) and at δ 51.6 and 46.6 (for **14**) appear. In all cases a doublet-of-doublet splitting is observed due to $^{31}P-^{31}P$ and $^{31}P-^{103}Rh$ couplings. On the basis of selectively ^{31}P-decoupled ^{13}C NMR spectra, for both compounds the signal at low field could be assigned to the phosphorus atom of the chelating ligand and the other to the phosphorus atom of the monodentate phosphine. In contrast to the related Ph_2P-containing complex [(η^6-*p*-$FC_6H_4CH_2CH_2CH_2PPh_2$-κ-*P*)(*p*-FC_6H_4-$CH_2CH_2CH_2PPh_2$-κ-*P*)Rh]BF_4 reported by Mirkin,[5b] the ^1H and ^{31}P NMR spectra of **13** are not temperature-dependent, and thus a fluxional behavior in solution can be excluded. Also for compound **14**, an intramolecular exchange of the phenyl groups of the two phosphines in the temperature range between 295 and 363 K does not occur. It should be mentioned that **13** and **14** can equally be obtained by treatment of the bis(acetone)-rhodium(I) species **10** with 2 equiv of the phosphine.

The cyclooctene ligand in the chelate complex **11** is displaced not only by the alkyldiisopropylphosphine **8** but also by ethene, maleicacid anhydride (MAA), ethyl propiolate, and triisopropylstibine (see Scheme 5). These reactions are rather slow, probably due to the fact that the metal center in the 18-electron starting material is significantly shielded. In contrast with the related ethene derivative **7**, the ^1H NMR spectrum of **15** displays at room temperature only one signal (broadened singlet) for the C_2H_4 protons at δ 2.94, which indicates that under these conditions the rotation of the olefin around the $Rh-C_2H_4$ axis is quite fast. The rotation becomes slower by decreasing the temperature, and it is frozen at 230 K. Coalescence is observed at ca. 270 K. We assume that the origin of the low-energy barrier for the rotation of the ethene ligand in **15** compared to **7** lies in steric effects. The relatively short C_2-bridge between the P*i*Pr_2 unit and the arene could lead either to a tilting of the $Rh-C_6H_5X$ axis or to a slippage of the six-membered ring to a more unsymmetrical position, and both of these possibilities would reduce the steric hindrance between the arene and the olefin.

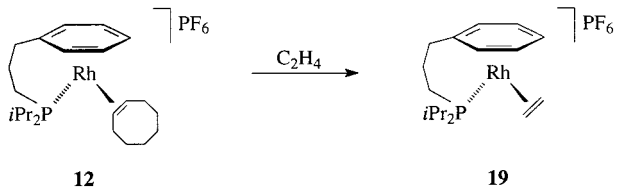
The MAA complex **16** is thermally considerably more stable than the ethene compound **15**, which is probably due to an increase in back-bonding from Rh to MAA compared with C_2H_4. The electron-withdrawing character of the maleic acid anhydride ligand might also be responsible for the difference in the chemical shift of the phosphorus resonance which appears in the ^{31}P NMR spectrum of **15** at δ 93.7 and in that of **16** at δ 102.5.

In contrast with phenylacetylene, which reacts with **11** to give a mixture of products, the reaction of **11** with ethyl propiolate leads to the formation of compound **17** in 83% yield. To the best of our knowledge, **17** is the

Scheme 5



Scheme 6



12 **19**

first arenerhodium(I) half-sandwich type complex containing an alkyne ligand. Typical spectroscopic features of **17** are the ν(C≡C) stretch at 1811 cm^{-1} in the IR spectrum, the signal of the ≡CH proton at δ 5.97 (doublet due to $^1H-^{103}Rh$ coupling) in the ^1H NMR, and the two resonances for the alkyne carbon atoms at δ 82.0 and 73.5 (both doublets of doublets) in the ^{13}C NMR spectrum. Moreover, the appearance of *two* signals for the PCH and *four* signals for the PCH*C*H_3 carbon nuclei indicate a C_1 symmetry of the respective cation and thus the presence of a chiral center at rhodium. The conclusion is that the rotation of the alkyne around the Rh−alkyne bond is severely hindered, as was also found in some cyclopentadienyl and square-planar alkynerhodium compounds.[9] We note that all attempts to rearrange **17** to the corresponding vinylidenerhodium isomer failed.

The preparation of the ethene complex **19** is outlined in Scheme 6. Analogously as for **2** and **11** as starting materials, the reaction of **12** with C_2H_4 is rather slow and in order to obtain a good yield has to be performed in a closed tube at 85 °C in dichloromethane. The ^1H NMR spectrum of **19** displays at room temperature two rather broad resonances at δ 3.28 and 2.45 for the ethene protons, indicating that the rotation around the Rh−C_2H_4 axis is somewhat more hindered than in the C_2-bridged counterpart **15**. At 233 K, the two signals are very sharp, as was found for **15** at 220 K. Under the conditions, where **11** reacts with ethyl propiolate to give **17**, compound **12** is completely inert toward this terminal alkyne.

The molecular structure of **19** is shown in Figure 3. Although the metal−carbon distances Rh−C1 to Rh−C6 differ in the maximum only by 0.045 Å (see Table 3), the arene ring possesses a slightly inverse boat conformation, which, however, is less pronounced than in **11**. The Rh−P bond lengths in **19** [2.251(2) Å] and **12** [2.265(1) Å] are almost identical, and also the bond angles of the Rh,P1,C9,C8,C7 unit in both C_3-bridged compounds are nearly the same. The C_2H_4 ligand in **19** is disordered, and therefore no exact distances between the metal and the ethene carbon atoms could be determined.

The More Bulky Phosphines tBu$_2$P(CH$_2$)$_n$XC$_6$H$_5$ and Their Rhodium(I) Complexes. The methodology for the preparation of the di-*tert*-butylphosphine derivatives **20**, **21** and the corresponding methylphosphonium salts **20a**, **21a** (Scheme 7) followed the routes already developed for the iPr$_2$P counterparts **8**, **9** and **8a**, **9a**, respectively. We note that the temperature for the reaction of HPtBu$_2$ with PhOCH$_2$CH$_2$Br should not exceed 80 °C since otherwise partial decomposition of the functionalized phenyl ether occurs. Similarly to **8** and **9**, also the sterically more demanding phosphines **20** and **21** are colorless oily liquids, which were characterized by mass spectra and common spectroscopic techniques. For the phosphonium salts **20a** and **21a** correct elemental analyses were obtained.

The reactions of **10** with either phosphine **20** or **21** in acetone led to the half-sandwich type complexes **22a** and **23** in 93% and 90% isolated yield (Scheme 8). Both compounds are yellow, slightly air-sensitive solids which in nitromethane reveal the conductivity of 1:1 electrolytes. The anticipated lability of the rhodium−olefin bond in **22a** is illustrated by the substitution reaction with ethyl propiolate, which gives almost quantitatively the alkyne complex **24**. While most of the relevant spectroscopic data of **24** are quite similar to those of **17**, the stability of the tBu$_2$P-containing species in solution and in the solid state is enhanced compared with the iPr$_2$P analogue, probably due to a better shielding of the metal center in **24** by the more bulky *tert*-butyl groups. Attempts to rearrange the alkyne compound **24**

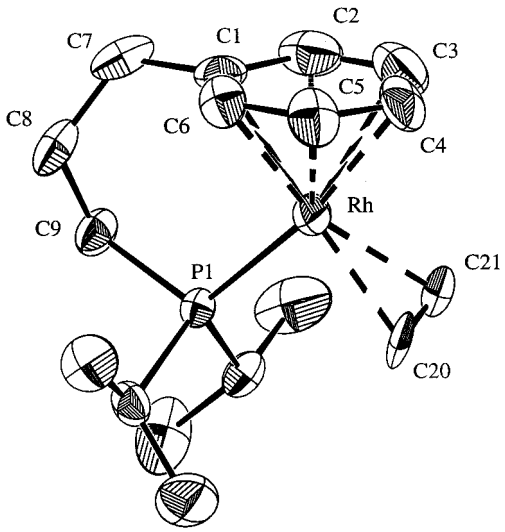
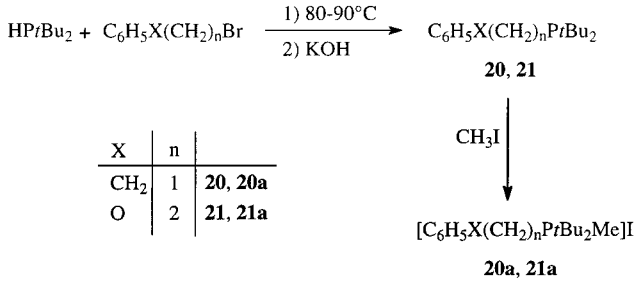


Figure 3. ORTEP drawing of **19**.

Table 3. Selected Bond Distances and Angles with Esd's for Compound 19

Bond Distances (Å)			
Rh−P1	2.251(2)	Rh−C4	2.268(6)
Rh−C1	2.266(6)	Rh−C5	2.304(6)
Rh−C2	2.304(7)	Rh−C6	2.311(6)
Rh−C3	2.296(7)		
Bond Angles (deg)			
Rh−P1−C9	111.5(2)	C8−C7−C1	115.1(5)
P1−C9−C8	118.0(4)	C7−C1−C2	120.2(7)
C9−C8−C7	114.1(6)	C7−C1−C6	120.2(6)

Scheme 7



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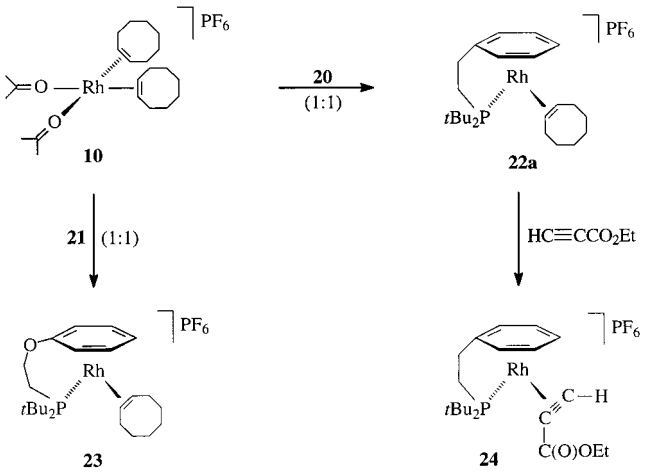
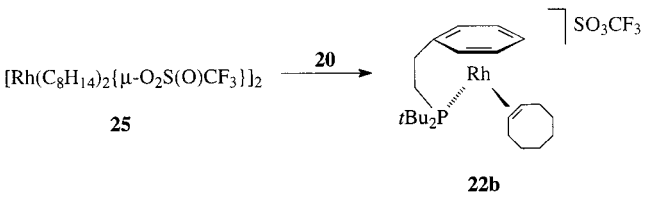
(9) (a) Werner, H.; Wolf, J.; Schubert, U.; Ackermann, K. *J. Organomet. Chem.* **1986**, *317*, 327−356. (b) Werner, H.; Brekau, U. *Z. Naturforsch. Teil B* **1989**, *44*, 1438−1446.

Scheme 8



Scheme 9



either thermally or photochemically to the vinylidene isomer failed. The reaction of **23** with ethyl propiolate proceeds much faster than that of **22a** with the same substrate but yields even at low temperature a mixture of unidentified products.

The synthesis of the cationic chelate complex **22b** with triflate as the counterion, shown in Scheme 9, was an unexpected result. Since we knew that the dimer **25**[10] reacts with 2 equiv of triisopropylphosphine to give the mononuclear species [Rh{κ^2-$O_2S(O)CF_3$}(C_8H_{14})(P*i*Pr_3)], we anticipated that a related compound would be formed upon treatment of **25** with the alkyldi-*tert*-butylphosphine **20**. Instead the ionic product **22b** was isolated in 94% yield. While **22b** is thermally somewhat less stable than the PF_6 salt **22a**, the spectroscopic data as well as the chemical properties of both compounds are quite similar.

Current work in our laboratory is particullarly aimed to explore the potential of the chelating rhodium(I) complexes [{η^6-$RC_6H_4X(CH_2)_n$PR′$_2$-κ-*P*}Rh(L)]$^+$ for catalytic studies. Introducing electron-withdrawing substituents R at the ring should weaken the arene−rhodium bond and thus open the possibility for the coordination and subsequent coupling of reactive substrates. Finally it should be mentioned that all attempts to displace the olefin ligand in **11**, **12**, **15**, or **19** by a carbene C(R)Ph (R = H, Ph) using Ph(R)CN_2 as carbene source failed.

Experimental Section

All experiments were carried out under an atmosphere of argon by Schlenk techniques. Solvents were dried by known procedures and distilled before used. The starting materials **1**,[4] **10**,[8] **25**,[10] HPR_2 (R = *i*Pr, *t*Bu),[11] and Sb*i*Pr_3 [12] were prepared as described in the literature. $C_6H_5(CH_2)_n$Br (n = 2, 3) and $C_6H_5O(CH_2)_2$Br were commercial products from Aldrich. IR spectra were recorded on a Bruker IFS 25 FT and NMR spectra (at room temperature or at the temperature mentioned in the appropriate procedure) on Bruker AC 200 and Bruker AMX 400 instruments. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; br, broadened signal. The conductivity Λ was measured in nitromethane with a Schott Konduktometer CG 851, and melting and decomposition points were determined by DTA. Mass spectra were recorded on a Finnigan 90 MAT instrument.

Preparation of [(η^6-C_6H_6)Rh(C_8H_{14})(P*i*Pr_3)]PF_6 (2). A solution of **1** (651 mg, 1.03 mmol) in 3 mL of CH_2Cl_2 was treated with 3 mL of benzene and stirred for 5 min at room temperature. After the solvent was evaporated in vacuo, the residue was dissolved in 1 mL of CH_2Cl_2 and 7 mL of ether was added to the solution. A yellow solid precipitated, which was separated from the mother liquor, washed with 10 mL of ether, and dried. The solid was recrystallized twice from CH_2Cl_2/ether (1:7), then washed with 7 mL of ether and 7 mL of pentane, and dried: yield 546 mg (89%); mp 89 °C dec. Λ = 73 $cm^2\ \Omega^{-1}\ mol^{-1}$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.67 (s, 6H, C_6H_6), 3.05 (m, 2H, =CH of C_8H_{14}), 2.38 (m, 2H, CH_2 of C_8H_{14}), 1.88 (m, 3H, PC*H*CH_3), 1.70, 1.45 (both m, 10H, CH_2 of C_8H_{14}), 1.26 [dd, J(PH) = 14.1 Hz, J(HH) = 7.3 Hz, 18H, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 105.1 (s, C_6H_6), 68.0 [d, J(RhC) = 13.4 Hz, =CH of C_8H_{14}], 34.1, 32.3, 26.3 (all s, CH_2 of C_8H_{14}), 25.5 [d, J(PC) = 23.8 Hz, P*C*HCH_3], 19.8 (s, PCH*C*H_3). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 63.4 [d, J(RhP) = 183.1 Hz, P*i*Pr_3], −144.3 [sept, J(FP) = 710.6 Hz, PF_6^-]. Anal. Calcd for $C_{23}H_{41}F_6P_2Rh$ (596.4): C, 46.32; H, 6.93. Found: C, 45.95; H, 6.70.

Preparation of [(η^6-$C_6H_5CF_3$)Rh(C_8H_{14})(P*i*Pr_3)]PF_6 (3). A sample of **1** (103 mg, 0.16 mmol) was treated at room temperature with 2 mL of $C_6H_5CF_3$. This led to the formation of an orange solution, from which after a few seconds a yellow solid precipitated. The precipitation was completed by addition of 4 mL of pentane. The mother liquor was decanted, and the yellow solid was washed three times with 5 mL of pentane and dried: yield 106 mg (98%); mp 60 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.77 (m, 1H, *para*-H of $C_6H_5CF_3$), 6.60 (m, 2H, *ortho*-H of $C_6H_5CF_3$), 6.50 (m, 2H, *meta*-H of $C_6H_5CF_3$), 3.26 (m, 2H, =CH of C_8H_{14}), 2.40 (m, 2H, CH_2 of C_8H_{14}), 1.92 (m, 3H, PC*H*CH_3), 1.68, 1.43 (both m, 10H, CH_2 of C_8H_{14}), 1.27 [dd, J(PH) = 14.1 Hz, J(HH) = 7.3 Hz, 18H, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 122.8 [q, J(FC) = 271.8 Hz, CF_3], 115.1 [q, J(FC) = 38.2 Hz, *C*CF_3], 107.4, 103.9, 100.9 (all s, C_6H_5), 71.2 [d, J(RhC) = 14.3 Hz, =CH of C_8H_{14}], 33.9, 32.2, 26.2 (all s, CH_2 of C_8H_{14}), 25.9 [d, J(PC) = 24.8 Hz, P*C*HCH_3], 19.7 (s, PCH*C*H_3). ^{19}F NMR (376.6 MHz, CD_2Cl_2): δ −60.2 (s, CF_3), −73.1 [d, J(PF) = 710.6 Hz, PF_6^-]. ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 63.8 [d, J(RhP) = 180.9 Hz, P*i*Pr_3], −144.3 [sept, J(FP) = 710.6 Hz, PF_6^-]. Anal. Calcd for $C_{24}H_{40}F_9P_2Rh$ (664.4): C, 43.39; H, 6.07. Found: C, 42.40; H, 6.03.

Preparation of [{η^6-1.3.5-$C_6H_3(CH_3)_3$}Rh(C_8H_{14})(P*i*Pr_3)]PF_6 (4). A suspension of **1** (135 mg, 0.21 mmol) in 5 mL of mesitylene was stirred for 1 h at room temperature. After addition of 5 mL of pentane, a yellow solid precipitated. The mother liquor was decanted, and the remaining solid was washed three times with 7 mL of pentane and dried. Owing to the NMR spectra, the solid contained ca. 10% of a P*i*Pr_3-containing impurity, which could not be removed by fractional crystallization. NMR data for **4**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.16 (s, 3H, C_6H_3), 2.79 (m, 2H, =CH of C_8H_{14}), 2.34 (s, 9H, CH_3 of mesitylene), 2.17 (m, 2H, CH_2 of C_8H_{14}), 1.82 (m, 3H, PC*H*CH_3), 1.82, 1.43 (both m, 10H, CH_2 of C_8H_{14}), 1.24 [dd, J(PH) = 13.8 Hz, J(HH) = 7.0 Hz, 18H, PCHC*H*$_3$]. ^{13}C NMR

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(12) Sb*i*Pr_3 was prepared analogously as described for the *n*-propyl derivative: Samaan, S. *Methoden der Organischen Chemie* (*Houben-Weyl*) 4th ed.; 1978; Vol. XIII/8, pp 445−446.

(100.6 MHz, CD_2Cl_2): δ 124.2 (s, *C*CH_3 of mesitylene), 104.4 (s, CH of mesitylene), 60.3 [d, J(RhC) = 15.3 Hz, =CH of C_8H_{14}], 31.8, 31.2, 26.3 (all s, CH_2 of C_8H_{14}), 23.7 [d, J(PC) = 22.9 Hz, P*C*HCH$_3$], 20.8 (s, CH_3 of mesitylene), 19.9 (s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 59.0 [d, J(RhP) = 180.9 Hz, P*i*Pr$_3$], −144.4 [sept, J(FP) = 710.6 Hz, PF_6^-].

Preparation of [(η^6-$C_6H_5OCH_3$)Rh(C_8H_{14})(P*i*Pr$_3$)]PF_6 (5). This compound was prepared as described for **3**, using **1** (111 mg, 0.17 mmol) and 3 mL of $C_6H_5OCH_3$ as starting materials: yellow solid; yield 103 mg (97%); mp 97 °C dec. Λ = 79 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.65 (m, 1H, *para*-H of $C_6H_5OCH_3$), 6.48 (m, 2H, *meta*-H of $C_6H_5OCH_3$), 6.16 (m, 2H, *ortho*-H of $C_6H_5OCH_3$), 3.97 (s, 3H, OCH_3), 3.03 (m, 2H, =CH of C_8H_{14}), 2.18 (m, 2H, CH_2 of C_8H_{14}), 1.91 (m, 3H, PC*H*CH$_3$), 1.57 (m, 10H, CH_2 of C_8H_{14}), 1.26 [dd, J(PH) = 14.1 Hz, J(HH) = 7.0 Hz, 18H, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 150.6 (s, *ipso*-C of $C_6H_5OCH_3$), 104.4 [d, J(RhC) = 2.9 Hz, C_6H_5], 98.4 [d, J(RhC) = 1.9 Hz, C_6H_5], 90.0 (m, C_6H_5), 66.1 [d, J(RhC) = 14.3 Hz, =CH of C_8H_{14}], 56.9 (s, OCH_3), 32.1, 32.0, 26.3 (all s, CH_2 of C_8H_{14}), 25.3 [d, J(PC) = 23.8 Hz, P*C*HCH$_3$], 19.8 (s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 63.0 [d, J(RhP) = 183.1 Hz, P*i*Pr$_3$], −144.4 [sept, J(FP) = 710.6 Hz, PF_6^-]. Anal. Calcd for $C_{24}H_{43}F_6OP_2Rh$ (626.4): C, 46.02; H, 6.92. Found: C, 45.76; H, 6.80.

Preparation of [{η^6-1.3.5-$C_6H_3(OCH_3)_3$}Rh(C_8H_{14})(P*i*Pr$_3$)]PF_6 (6). A suspension of **1** (119 mg, 0.19 mmol) in 5 mL of ether was treated with 1.3.5-$C_6H_3(OCH_3)_3$ (96 mg, 0.57 mmol) and stirred for 30 min at room temperature. After addition of 5 mL of ether, a yellow solid precipitated, which was separated from the mother liquor, washed twice with 5 mL of ether and 5 mL of pentane, and dried: yield 122 mg (93%); mp 72 °C dec. Λ = 79 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.76 (s, 3H, C_6H_3), 3.95 (s, 9H, OCH_3), 2.87 (m, 2H, =CH of C_8H_{14}), 1.95 (m, 2H, CH_2 of C_8H_{14}), 1.88 (m, 3H, PC*H*CH$_3$), 1.72 (m, 2H, CH_2 of C_8H_{14}), 1.43 (m, 8H, CH_2 of C_8H_{14}), 1.27 [dd, J(PH) = 13.5 Hz, J(HH) = 7.0 Hz, 18H, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 149.1 [d, J(RhC) = 1.9 Hz, *C*OCH_3 of $C_6H_3(OCH_3)_3$], 75.4 [s, CH of $C_6H_3(OCH_3)_3$], 60.9 [d, J(RhC) = 17.2 Hz, =CH of C_8H_{14}], 57.5 (s, OCH_3), 31.5, 29.7, 26.4 (all s, CH_2 of C_8H_{14}), 22.8 [d, J(PC) = 22.9 Hz, P*C*HCH$_3$], 19.9 (s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 56.6 [d, J(RhP) = 180.9 Hz, P*i*Pr$_3$], −144.4 [sept, J(FP) = 710.6 Hz, PF_6^-]. Anal. Calcd for $C_{26}H_{47}F_6O_3P_2Rh$ (686.5): C, 45.49; H, 6.90. Found: C, 45.44; H, 6.63.

Preparation of [(η^6-C_6H_6)Rh(C_2H_4)(P*i*Pr$_3$)]PF_6 (7). A solution of **2** (103 mg, 0.17 mmol) in 2 mL of CH_2Cl_2 was degassed in vacuo, cooled to −20 °C, and then brought under an atmosphere of ethene. After warming to room temperature, the solution was layered with 8 mL of ether, which led to the precipitation of a yellow solid. The mother liquor was separated, and the residue was washed with 5 mL of ether and dried. This procedure (dissolvation in CH_2Cl_2, treatment with ethene, precipitation with ether) was repeated three times. The finally obtained yellow solid was washed twice with 5 mL of ether and twice with 5 mL of pentane and then dried in vacuo: yield 79 mg (89%); mp 112 °C dec. Λ = 73 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.73 (s, 6H, C_6H_6), 3.33, 2.27 (both m, 2H each, C_2H_4), 1.83 (m, 3H, PC*H*CH$_3$), 1.22 [dd, J(PH) = 14.1 Hz, J(HH) = 7.0 Hz, 18H, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 104.4 (s, C_6H_6), 40.8 [d, J(RhC) = 14.3 Hz, C_2H_4], 25.3 [d, J(PC) = 23.8 Hz, P*C*HCH$_3$], 19.6 (s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 65.9 [d, J(RhP) = 176.6 Hz, P*i*Pr$_3$], −144.3 [sept, J(FP) = 710.6 Hz, PF_6^-]. Anal. Calcd for $C_{17}H_{31}F_6P_2Rh$ (514.3): C, 39.70; H, 6.08. Found: C, 39.71; H, 6.11.

Preparation of $C_6H_5CH_2CH_2P$*i*Pr$_2$ (8). A mixture of HP*i*Pr$_2$ (12.3 g, 0.10 mol) and 2-phenylethylbromide (12.0 mL, 0.09 mol) was heated under stirring for 24 h at 90 °C. After it was cooled to room temperature, a colorless solid was obtained. This solid was recrystallized from refluxing acetone. The purified intermediate [*i*Pr$_2$PHCH$_2$CH$_2$Ph]Br was washed three times with 60 mL of ether, dried, and dissolved in 25 mL of degassed water. The aqueous solution was layered with 75 mL of ether and then treated, under stirring, dropwise with ammonia (concentrated in water) until the aqueous phase became basic (pH ∼9). After the ethereal phase was separated, it was washed twice with 25 mL of water, then dried with Na_2SO_4, and finally evaporated to dryness in vacuo. The oily residue was distilled in vacuo to give a colorless viscous liquid: yield 17.3 g (89%); bp 68−72 °C (0.05 mbar). ^{1}H NMR (400 MHz, C_6D_6): δ 7.12 (m, 5H, C_6H_5), 2.76 (m, 2H, PhC*H*$_2$), 1.61−1.50 (m, 4H, PCH_2 and PC*H*CH$_3$), 1.02 [dd, J(PH) = 13.5 Hz, J(HH) = 7.0 Hz, 6H, PCHC*H*$_3$], 0.97 [dd, J(PH) = 10.9 Hz, J(HH) = 7.0 Hz, 6H, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, C_6D_6): δ 143.8 [d, J(PC) = 12.4 Hz, *ipso*-C of C_6H_5], 128.7, 128.5, 126.1 (all s, C_6H_5), 35.2 [d, J(PC) = 21.9 Hz, Ph*C*H$_2$], 24.8 [d, J(PC) = 21.0 Hz, PCH_2], 23.7 [d, J(PC) = 14.3 Hz, P*C*HCH$_3$], 20.3 [d, J(PC) = 16.2 Hz, PCH*C*H$_3$], 19.0 [d, J(PC) = 9.5 Hz, PCH*C*H$_3$]. ^{31}P NMR (162.0 MHz, C_6D_6): δ 3.8 (s). MS (70 eV) m/z 222 [34.6, M$^+$], 221 [100, M$^+$ − H], 131 [32.9, CH_2P*i*Pr$_2^+$], 118 [32.5, HP*i*Pr$_2^+$], 105 [55.6, $C_6H_5CH_2CH_2^+$].

Preparation of [$C_6H_5CH_2CH_2P$*i*Pr$_2$Me]I (8a). A solution of **8** (1.33 g, 5.98 mmol) in 25 mL of hexane was treated with CH_3I (377 μL, 6.00 mmol) and stirred for 3 h at room temperature. A colorless solid precipitated, which was separated from the mother liquor, washed three times with 10 mL of ether and twice with 10 mL of pentane, and dried in vacuo: yield 1.97 g (90%); mp 154 °C. ^{1}H NMR (400 MHz, CD_3NO_2): δ 7.30 (m, 5H, C_6H_5), 3.03 (m, 2H, PhC*H*$_2$), 2.76 (m, 2H, PC*H*CH$_3$), 2.58 (m, 2H, PCH_2), 1.87 [d, J(PH) = 12.6 Hz, 3H, PCH_3], 1.41 [dd, J(PH) = 17.0 Hz, J(HH) = 7.3 Hz, 6H, PCHC*H*$_3$], 1.40 [dd, J(PH) = 17.0 Hz, J(HH) = 7.0 Hz, 6H, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, CD_3NO_2): δ 140.9 [d, J(PC) = 14.2 Hz, *ipso*-C of C_6H_5], 130.2, 129.5, 128.4 (all s, C_6H_5), 28.8 [d, J(PC) = 4.1 Hz, Ph*C*H$_2$], 22.5 [d, J(PC) = 46.8 Hz, P*C*HCH$_3$], 19.9 [d, J(PC) = 43.8 Hz, PCH_2], 16.3, 16.2 [both d, J(PC) = 3.1 Hz, PCH*C*H$_3$], 0.8 [d, J(PC) = 50.9 Hz, PCH_3]. ^{31}P NMR (162.0 MHz, CD_3NO_2): δ 42.0 (s). Anal. Calcd for $C_{15}H_{26}IP$ (364.3): C, 49.46; H, 7.19. Found: C, 49.26; H, 6.79.

Preparation of $C_6H_5CH_2CH_2CH_2P$*i*Pr$_2$ (9). The preparation was analogous with that described for **8**, from HP*i*Pr$_2$ (5.82 g, 49.3 mmol) and 3-phenylpropylbromide (6.74 mL, 44.4 mmol). Colorless oil: yield 8.20 g (78%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.22 (m, 5H, C_6H_5), 2.71 (m, 2H, PhC*H*$_2$), 1.90 (m, 2H, PCH_2CH_2), 1.64 (m, 2H, PC*H*CH$_3$), 1.37 (m, 2H, PCH_2), 1.11 [dd, J(PH) = 13.5 Hz, J(HH) = 7.0 Hz, 6H, PCHC*H*$_3$], 1.06 [dd, J(PH) = 10.9 Hz, J(HH) = 6.9 Hz, 6H, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, C_6D_6): δ 142.4 (s, *ipso*-C of C_6H_5), 128.8, 128.6, 126.1 (all s, C_6H_5), 37.8 [d, J(PC) = 11.5 Hz, Ph*C*H$_2$], 30.4 [d, J(PC) = 20.0 Hz, PCH_2 or PCH_2CH_2], 23.7 [d, J(PC) = 14.3 Hz, P*C*HCH$_3$], 21.7 [d, J(PC) = 19.1 Hz, PCH_2 or PCH_2CH_2], 20.3 [d, J(PC) = 16.2 Hz, PCH*C*H$_3$], 19.0 [d, J(PC) = 10.5 Hz, PCH*C*H$_3$]. ^{31}P NMR (162.0 MHz, C_6D_6): δ 2.1 (s). MS (70 eV) m/z 236 (M$^+$).

Preparation of [$C_6H_5CH_2CH_2CH_2P$*i*Pr$_2$Me]I (9a). The preparation was analogous with that described for **8a**, from **9** (1.35 g, 5.72 mmol) and CH_3I (365 μL, 5.80 mmol). Colorless solid: yield 2.01 g (93%); mp 109 °C. ^{1}H NMR (400 MHz, CD_3NO_2): δ 7.25 (m, 5H, C_6H_5), 2.79 (m, 2H, PhC*H*$_2$), 2.65 (m, 2H, PC*H*CH$_3$), 2.27 (m, 2H, PCH_2), 1.97 (m, 2H, PCH_2CH_2), 1.77 [d, J(PH) = 12.6 Hz, 3H, PCH_3], 1.32 [dd, J(PH) = 17.0 Hz, J(HH) = 7.3 Hz, 6H, PCHC*H*$_3$], 1.31 [dd, J(PH) = 17.0 Hz, J(HH) = 7.0 Hz, 6H, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, CD_3NO_2): δ 142.0 (s, *ipso*-C of C_6H_5), 129.9, 129.8, 127.7 (all s, C_6H_5), 37.4 [d, J(PC) = 15.3 Hz, Ph*C*H$_2$], 25.0 [d, J(PC) = 5.0 Hz, PCH_2CH_2], 22.3 [d, J(PC) = 46.8 Hz, P*C*HCH$_3$], 17.6 [d, J(PC) = 46.8 Hz, PCH_2], 16.2, 16.1 [both d, J(PC) = 3.0 Hz, PCH*C*H$_3$], 0.5 [d, J(PC) = 50.9 Hz, PCH_3]. ^{31}P NMR (162.0 MHz, CD_3NO_2): δ 42.3 (s). Anal. Calcd for $C_{16}H_{28}IP$ (378.3): C, 50.80; H, 7.46. Found: C, 50.51; H, 7.20.

Preparation of [(η^6-$C_6H_5CH_2CH_2P$*i*Pr$_2$-κ-*P*)Rh(C_8H_{14})]PF_6 (11). A solution of **10** (194 mg, 0.33 mmol) in 3 mL of

acetone, which was cooled to −20 °C, was treated dropwise over a period of 15 min with an ice-cooled solution of **8** (74 mg, 0.33 mmol) in 20 mL of acetone. After the reaction mixture was warmed to room temperature, the solvent was removed in vacuo. The residue was dissolved in 1 mL of CH_2Cl_2, and after the solution was layered with 7 mL of ether, a yellow solid precipitated. The mother liquor was decanted, the solid was washed three times with 6 mL of ether and twice with 6 mL of pentane, and dried in vacuo: yield 180 mg (94%); mp 182 °C dec. $\Lambda = 75$ cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.98, 6.89 (both m, 2H each, C_6H_5), 5.87 (m, 1H, C_6H_5), 3.43 (m, 2H, =CH of C_8H_{14}), 2.62−2.49 (br m, 4H, PhCH_2 and PCH_2), 2.32 (m, 2H, CH_2 of C_8H_{14}), 2.00 (m, 2H, PCHCH$_3$), 1.85−1.29 (m, 10H, CH_2 of C_8H_{14}), 1.23 [dd, J(PH) = 15.6 Hz, J(HH) = 7.0 Hz, 6H, PCHCH_3], 1.20 [dd, J(PH) = 16.4 Hz, J(HH) = 7.0 Hz, 6H, PCHCH_3]. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 119.3 [dd, J(PC) = 5.4 Hz, J(RhC) = 3.8 Hz; d in ^{13}C{^{31}P}, J(RhC) = 3.8 Hz, *ipso*-C of C_6H_5], 112.0, 102.0 (both s, C_6H_5), 97.7 [d, J(PC) = 9.2 Hz, *para*-C of C_6H_5], 68.0 [d, J(RhC) = 13.3 Hz, =CH of C_8H_{14}], 38.6 [d, J(PC) = 28.5 Hz, PCH_2], 34.3, 32.3, 31.0, 26.3 (all s, CH_2 of C_8H_{14} and PhCH_2], 25.2 [dd, J(PC) = 25.4 Hz, J(RhC) = 2.0 Hz, PCHCH$_3$], 18.9, 17.8 (both s, PCHCH_3). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 92.4 [d, J(RhP) = 185.3 Hz, iPr$_2$P], −144.3 [sept, J(FP) = 710.6 Hz, PF_6^-]. MS (FAB, 2-nitrophenyloctyl ether): m/z 435 (M^+). Anal. Calcd for $C_{22}H_{37}F_6P_2Rh$ (580.4): C, 45.53; H, 6.43; Rh, 17.73. Found: C, 45.18; H, 6.25; Rh, 17.54.

Preparation of [(η^6-$C_6H_5CH_2CH_2CH_2P$*i*Pr_2-*κ*-*P*)Rh(C_8H_{14})]PF_6 (12). The preparation was analogous with that described for **11**, from **10** (340 mg, 0.59 mmol) and **9** (138 mg, 0.59 mmol). Yellow solid: yield 307 mg (88%); mp 187 °C dec. $\Lambda = 80$ cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.85, 6.77 (both m, 2H each, C_6H_5), 5.84 (m, 1H, C_6H_5), 3.18 (m, 2H, =CH of C_8H_{14}), 2.45 (m, 2H, PhCH_2), 2.33 (m, 2H, CH_2 of C_8H_{14}), 1.96−1.83 (br m, 4H, PCH_2 and PCHCH$_3$), 1.72−1.61 (m, 4H, CH_2 of C_8H_{14}), 1.49 (m, 2H, CH_2 of C_8H_{14}), 1.42−1.30 (m, 6H, CH_2 of C_8H_{14} and PCH$_2$CH_2), 1.20 [dd, J(PH) = 15.8 Hz, J(HH) = 7.2 Hz, 6H, PCHCH_3], 1.18 [dd, J(PH) = 14.4 Hz, J(HH) = 6.8 Hz, 6H, PCHCH_3]. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 111.6 [br s; d in ^{13}C{^{31}P}, J(RhC) = 1.9 Hz, C_6H_5], 110.5 [d, J(RhC) = 2.9 Hz, *ipso*-C of C_6H_5], 103.4 [d, J(RhC) = 1.9 Hz, C_6H_5], 98.7 [dd, J(PC) = 8.6 Hz, J(RhC) = 1.9 Hz, *para*-C of C_6H_5], 67.1 [d, J(RhC) = 13.4 Hz, =CH of C_8H_{14}], 34.1, 32.3, 26.2 (all s, CH_2 of C_8H_{14}), 32.1, 25.6 (both s, PhCH_2 and PCH$_2$CH_2), 25.1 [d, J(PC) = 27.7 Hz, PCHCH$_3$], 20.2 (s, PCHCH_3), 17.8 [d, J(PC) = 1.9 Hz, PCHCH_3], 15.8 [d, J(PC) = 27.7 Hz, PCH_2]. ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 54.8 [d, J(RhP) = 178.7 Hz, iPr$_2$P], −144.3 [sept, J(FP) = 710.6 Hz, PF_6^-]. Anal. Calcd for $C_{23}H_{39}F_6P_2Rh$ (594.4): C, 46.48; H, 6.61; Rh, 17.31. Found: C, 46.22; H, 6.67; Rh, 17.06.

Preparation of [(η^6-$C_6H_5CH_2CH_2P$*i*Pr_2-*κ*-*P*)($C_6H_5CH_2CH_2$-*P*i*Pr*$_2$-*κ*-*P*)Rh]PF_6 (13). A solution of **11** (172 mg, 0.30 mmol) in 2 mL of CH_2Cl_2 was treated with **8** (77.8 mg, 0.35 mmol) and stirred for 6 h at room temperature. A change of color from yellow to orange-red occurred. After removal of the solvent in vacuo, the residue was dissolved in 2 mL of acetone, and the solution was treated under stirring with 8 mL of ether. An orange solid precipitated and was washed twice with 5 mL of ether and twice with 5 mL of pentane and dried: yield 189 mg (91%). Alternatively, compound **13** was prepared from **10** (85 mg, 0.15 mmol) and **8** (88.9 mg, 0.40 mmol) in 2 mL of CH_2Cl_2: yield 94 mg (90%); mp 146 °C dec. $\Lambda = 73$ cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2, 295 K): δ 7.30 (m, 2H, C_6H_5), 7.21 (m, 1H, C_6H_5), 7.09 (m, 2H, C_6H_5), 6.91 (m, 4H, C_6H_5), 5.69 (m, 1H, *para*-H of η^6-C_6H_5), 2.75 (m, 2H, PhCH_2), 2.52 (m, 2H, PCH_2), 2.33 (m, 2H, PhCH_2), 2.04−1.78 (m, 6H, PCHCH$_3$ and PCH_2), 1.24 [dd, J(PH) = 16.1 Hz, J(HH) = 7.0 Hz, 6H, PCHCH_3], 1.21 [dd, J(PH) = 14.4 Hz, J(HH) = 7.0 Hz, 6H, PCHCH_3], 1.14 [dd, J(PH) = 16.3 Hz, J(HH) = 7.0 Hz, 6H, PCHCH_3], 1.13 [dd, J(PH) = 15.1 Hz, J(HH) = 6.8 Hz, 6H, PCHCH_3]. ^{1}H NMR (400 MHz, CD_3NO_2, 368 K): δ 7.29 (m, 2H, C_6H_5), 7.20 (m, 3H, C_6H_5), 7.02 (m, 4H, C_6H_5), 5.87 (m, 1H, *para*-H of η^6-C_6H_5), 2.88 (m, 2H, PhCH_2), 2.64 (m, 2H, PCH_2), 2.40 (m, 2H, PhCH_2), 2.17−1.95 (m, 6H, PCHCH$_3$ and PCH_2), 1.31 [dd, J(PH) = 15.8 Hz, J(HH) = 7.0 Hz, 6H, PCHCH_3], 1.28 [dd, J(PH) = 14.1 Hz, J(HH) = 6.9 Hz, 6H, PCHCH_3], 1.25 [dd, J(PH) = 15.9 Hz, J(HH) = 6.9 Hz, 6H, PCHCH_3], 1.21 [dd, J(PH) = 14.7 Hz, J(HH) = 6.8 Hz, 6H, PCHCH_3]. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 141.5 [d, J(P_BC) = 9.5 Hz, *ipso*-C of C_6H_5], 129.1, 127.7, 126.8 (all s, C_6H_5), 113.2 [m; d in ^{13}C{^{31}P}, J(RhC) = 3.8 Hz; dd in ^{13}C{^{31}P$_A$}, J(P_BC) = 7.6 Hz, J(RhC) = 3.8 Hz, *ipso*-C of η^6-C_6H_5], 103.4, 103.2 [both br s; both d in ^{13}C{^{31}P}, J(RhC) = 1.9 Hz, *ortho*/*meta*-C of η^6-C_6H_5], 91.1 [d, J(P_AC) = 8.6 Hz, *para*-C of η^6-C_6H_5], 40.8 [dd, J(P_AC) = 27.7 Hz, J(P_BC) = 2.9 Hz, P_A-CH_2], 31.3 [d, J(P_BC) = 6.7 Hz, PhCH_2], 30.6 (br s, η^6-$C_6H_5CH_2$), 30.0 [m; d in ^{13}C{^{31}P}, J(RhC) = 2.9 Hz, P_BCH_2], 28.1 [d, J(P_BC) = 24.8 Hz, P_BCHCH_3], 26.5 [dd, J(P_AC) = 22.9 Hz, J(RhC) = 2.9 Hz, P_ACHCH_3], 20.1 [d, J(P_AC) = 3.8 Hz, P_ACHCH_3], 19.8, 18.2 (both s, PCHCH_3), 19.2 [d, J(P_BC) = 2.9 Hz, P_BCHCH_3]. ^{31}P NMR (162.0 MHz, CD_2Cl_2, 295 K): δ 83.6 [dd, J(RhP_A) = 202.7 Hz, J(P_BP_A) = 30.5 Hz, iPr$_2$P$_A$], 48.7 [dd, J(RhP_B) = 202.7 Hz, J(P_AP_B) = 30.5 Hz, iPr$_2$P$_B$], −144.4 [sept, J(FP) = 710.6 Hz, PF_6^-]. ^{31}P NMR (162.0 MHz, CD_3NO_2, 368 K): δ 84.4 [dd, J(RhP_A) = 204.9 Hz, J(P_BP_A) = 30.5 Hz, iPr$_2$P$_A$], 49.6 [dd, J(RhP_B) = 204.9 Hz, J(P_AP_B) = 30.5 Hz, iPr$_2$P$_B$], −144.3 [sept, J(FP) = 706.3 Hz, PF_6^-]. For assignment: P_A = ^{31}P nuclei of η^6-$C_6H_5CH_2CH_2P$*i*Pr_2; P_B = ^{31}P nuclei of C_6H_5-CH_2CH_2P*i*Pr_2-*κ*-*P*. MS (FAB, 2-nitrophenyloctyl ether): m/z 547 (M^+). Anal. Calcd for $C_{28}H_{46}F_6P_3Rh$ (692.5): C, 48.57; H, 6.70. Found: C, 48.60; H, 6.55.

Preparation of [(η^6-$C_6H_5CH_2CH_2CH_2P$*i*Pr_2-*κ*-*P*)(C_6H_5-$CH_2CH_2CH_2P$*i*Pr_2-*κ*-*P*)Rh]PF_6 (14). The preparation was analogous with that described for **13**, from **12** (111 mg, 0.19 mmol) and **9** (47 mg, 0.20 mmol) in 2 mL of CH_2Cl_2. Orange solid: yield 126 mg (92%). Alternatively, compound **14** was also prepared from **10** (103 mg, 0.18 mmol) and **9** (90 mg, 0.38 mmol) in 2 mL of CH_2Cl_2: yield 115 mg (89%); mp 134 °C dec. $\Lambda = 76$ cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2, 295 K): δ 7.29 (m, 2H, C_6H_5), 7.22 (m, 1H, C_6H_5), 7.12, 6.80, 6.71 (all m, 2H each, C_6H_5), 5.58 (m, 1H, *para*-H of η^6-C_6H_5), 2.65, 2.31 (both m, 2H each, PhCH_2), 2.10−1.83 (m, 4H, PCHCH$_3$ and PCH_2), 1.72 (m, 2H, PCH$_2$CH_2), 1.54−1.38 (m, 4H, PCHCH$_3$ and PCH_2), 1.25 (m, 2H, PCH$_2$CH_2), 1.17 [dd, J(PH) = 16.3 Hz, J(HH) = 7.2 Hz, 6H, PCHCH_3], 1.13 [dd, J(PH) = 17.3 Hz, J(HH) = 7.2 Hz, 6H, PCHCH_3], 1.05 [dd, J(PH) = 13.0 Hz, J(HH) = 7.0 Hz, 6H, PCHCH_3], 1.04 [dd, J(PH) = 14.1 Hz, J(HH) = 7.0 Hz, 6H, PCHCH_3]. ^{1}H NMR (400 MHz, CD_3NO_2, 363 K): δ 7.31 (m, 2H, C_6H_5), 7.22 (m, 3H, C_6H_5), 6.92, 6.85 (both m, 2H each, C_6H_5), 5.78 (m, 1H, *para*-H of η^6-C_6H_5), 2.71, 2.37 (both m, 2H each, PhCH_2), 2.10 (m, 2H, P_ACHCH_3), 1.97 (m, 2H, P_ACH_2), 1.87−1.69 (m, 4H, $P_BCH_2CH_2$ and P_BCHCH_3), 1.62 (m, 2H, P_BCH_2), 1.37 (m, 2H, $P_ACH_2CH_2$), 1.25 [dd, J(PH) = 15.9 Hz, J(HH) = 7.2 Hz, 6H, PCHCH_3], 1.23 [dd, J(PH) = 17.0 Hz, J(HH) = 7.2 Hz, 6H, PCHCH_3], 1.16 [dd, J(PH) = 12.8 Hz, J(HH) = 6.9 Hz, 6H, PCHCH_3], 1.15 [dd, J(PH) = 13.8 Hz, J(HH) = 7.0 Hz, 6H, PCHCH_3]. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 140.6 (s, *ipso*-C of C_6H_5), 129.0, 128.7, 126.8 (all s, C_6H_5), 104.7 [br s; d in ^{13}C{^{31}P}, J(RhC) = 1.9 Hz, *ortho*/*meta*-C of η^6-C_6H_5], 104.6 (m, *ipso*-C of η^6-C_6H_5), 103.3 [br s; d in ^{13}C{^{31}P}, J(RhC) = 1.9 Hz, *ortho*/*meta*-C of η^6-C_6H_5], 90.5 [d, J(P_AC) = 12.6 Hz, *para*-C of η^6-C_6H_5], 37.1 [d, J(P_BC) = 9.5 Hz, PhCH_2], 33.1 (s, PhCH_2), 28.8 [d, J(P_BC) = 25.8 Hz, P_BCHCH_3], 27.9 [d, J(P_AC) = 24.8 Hz, P_ACHCH_3], 26.2 [m; d in ^{13}C{^{31}P}, J(RhC) = 1.9 Hz, $P_BCH_2CH_2$], 24.8 [m; d in ^{13}C{^{31}P}, J(RhC) = 2.9 Hz, P_BCH_2], 24.3 (s, $P_ACH_2CH_2$), 23.0 [d, J(P_AC) = 4.8 Hz, P_ACHCH_3], 19.1, 19.0 (both s, P_BCHCH_3), 18.2 [d, J(P_AC) = 5.7 Hz, P_ACHCH_3], 14.0 [d, J(P_AC) = 24.8 Hz, P_ACH_2]. ^{31}P NMR (162.0 MHz, CD_2Cl_2, 295 K): δ 51.6 [dd, J(RhP_A) = 200.5 Hz, J(P_BP_A) = 32.7 Hz, iPr$_2$P$_A$], 46.6 [dd, J(RhP_B) = 207.1 Hz, J(P_AP_B) = 32.7 Hz, iPr$_2$P$_B$], −144.4 [sept, J(FP) = 710.6 Hz, PF_6^-]. ^{31}P NMR (162.0 MHz, CD_3NO_2, 363

K): δ 51.6 [dd, $J(RhP_A) = 200.5$ Hz, $J(P_BP_A) = 32.7$ Hz, *i*Pr_2P_A], 47.3 [dd, $J(RhP_B) = 207.1$ Hz, $J(P_AP_B) = 32.7$ Hz, *i*Pr_2P_B], −144.3 [sept, $J(FP) = 706.3$ Hz, PF_6^-]. For assignment: P_A = ^{31}P nuclei of η^6-$C_6H_5CH_2CH_2CH_2PiPr_2$; P_B = ^{31}P nuclei of C_6H_5-$CH_2CH_2CH_2PiPr_2$. Anal. Calcd for $C_{30}H_{50}F_6P_3Rh$ (720.5): C, 50.01; H, 6.99. Found: C, 49.56; H, 6.86.

Preparation of [(η^6-$C_6H_5CH_2CH_2PiPr_2$-κ-*P*)Rh(C_2H_4)]PF_6 (15). A solution of **11** (197 mg, 0.34 mmol) in 2 mL of CH_2Cl_2 was heated under an ethene atmosphere for 1 h at 75 °C. After the solution was cooled to room temperature, 8 mL of ether was added, which led to the precipitation of a yellow solid. The mother liquor was decanted, and the solid was washed with 5 mL of ether and dried. This procedure was repeated twice. Finally, a yellow solid was obtained, which was washed twice with 5 mL of ether and twice with 5 mL of pentane and dried: yield 156 mg (92%); mp 104 °C dec. Λ = 81 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2, 295 K): δ 7.12, 7.02 (both m, 2H each, C_6H_5), 5.58 (m, 1H, C_6H_5), 2.94 (br s, 4H, C_2H_4), 2.68−2.56 (m, 4H, PCH_2 and PhC*H*$_2$), 1.96 (m, 2H, PC*H*CH_3), 1.21 [dd, $J(PH) = 15.8$ Hz, $J(HH) = 7.0$ Hz, 6H, PCHC*H*$_3$], 1.15 [dd, $J(PH) = 17.0$ Hz, $J(HH) = 7.2$ Hz, 6H, PCHC*H*$_3$]. ^{1}H NMR (200 MHz, CD_2Cl_2, 220 K): δ 7.07, 6.93 (both m, 2H each, C_6H_5), 5.52 (m, 1H, C_6H_5), 3.16 (m, 2H, *outer*-H of C_2H_4), 2.64−2.39 (br m, 6H, PCH_2, PhC*H*$_2$ and *inner*-H of C_2H_4), 1.89 (m, 2H, PC*H*CH_3), 1.10 [dd, $J(PH)$ = 15.7 Hz, $J(HH) = 7.0$ Hz, 6H, PCHC*H*$_3$], 1.04 [dd, $J(PH)$ = 16.9 Hz, $J(HH) = 7.3$ Hz, 6H, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 122.0 [dd, $J(RhC) = 4.8$ Hz, $J(PC) = 4.7$ Hz; d in $^{13}C\{^{31}P\}$, $J(RhC) = 4.8$ Hz, *ipso*-C of C_6H_5], 108.9 (s, C_6H_5), 102.8 [d, $J(RhC) = 2.9$ Hz, C_6H_5], 95.4 [dd, $J(PC) = 10.5$ Hz, $J(RhC) = 2.0$ Hz; d in $^{13}C\{^{31}P\}$, $J(RhC) = 2.0$ Hz, *para*-C of C_6H_5], 41.8 [dd, $J(RhC) = 13.4$ Hz, $J(PC) = 1.9$ Hz; d in $^{13}C\{^{31}P\}$, $J(RhC) = 13.4$ Hz, C_2H_4], 40.1 [d, $J(PC) = 27.7$ Hz, PCH_2], 31.3 (s, Ph*C*H$_2$), 24.9 [dd, $J(PC) = 25.7$ Hz, $J(RhC)$ = 1.9 Hz; d in $^{13}C\{^{31}P\}$, $J(RhC) = 1.9$ Hz, P*C*HCH$_3$], 18.7, 17.6 (both s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 93.7 [d, $J(RhP) = 178.7$ Hz, *i*Pr_2P], −144.3 [sept, $J(FP) = 710.6$ Hz, PF_6^-]. Anal. Calcd for $C_{16}H_{27}F_6P_2Rh$ (498.2): C, 38.57; H, 5.46. Found: C, 38.22; H, 4.97.

Preparation of [(η^6-$C_6H_5CH_2CH_2PiPr_2$-κ-*P*)Rh($C_4H_2O_3$)]PF_6 (16). The preparation was analogous with that described for **15**, from **11** (103 mg, 0.18 mmol) and maleic acid anhydride (33.2 mg, 0.36 mmol) in 3 mL of CH_2Cl_2. Yellow solid: yield 85 mg (83%); mp 186 °C dec. Λ = 74 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.64, 7.36 (both m, 2H each, C_6H_5), 5.80 (m, 1H, C_6H_5), 4.24 [dd, $J(PH) = 4.1$ Hz, $J(RhH) = 2.6$ Hz, 2H, =CH of $C_4H_2O_3$], 3.19 [ddd, $J(PH) = 9.7$ Hz, $J(HH)$ = 7.6 Hz, $J(HH) = 7.3$ Hz, 2H, PCH_2], 2.98 [ddd, $J(PH) = 22.6$ Hz, $J(HH) = 7.6$ Hz, $J(HH) = 7.3$ Hz, 2H, PhC*H*$_2$], 2.44 (m, 2H, PC*H*CH_3), 1.36 [dd, $J(PH) = 16.4$ Hz, $J(HH) = 6.8$ Hz, 6H, PCHC*H*$_3$], 1.32 [dd, $J(PH) = 17.2$ Hz, $J(HH) = 7.2$ Hz, 6H, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, d_6-acetone): δ 172.2 (s, C=O of $C_4H_2O_3$), 130.6 [dd, $J(PC) = 5.7$ Hz, $J(RhC) = 4.8$ Hz; d in $^{13}C\{^{31}P\}$, $J(RhC) = 4.8$ Hz, *ipso*-C of C_6H_5], 115.3 (s, C_6H_5), 106.9 [d, $J(PC) = 8.6$ Hz, *para*-C of C_6H_5], 102.8 [d, $J(RhC)$ = 2.9 Hz, C_6H_5], 46.2 [dd, $J(RhC) = 15.3$ Hz, $J(PC) = 2.9$ Hz; d in $^{13}C\{^{31}P\}$, $J(RhC) = 15.3$ Hz, =CH of $C_4H_2O_3$], 39.9 [d, $J(PC)$ = 29.6 Hz, PCH_2], 31.7 (s, Ph*C*H$_2$), 26.1 [d, $J(PC) = 25.8$ Hz, P*C*HCH$_3$], 19.0 (s, PCH*C*H$_3$), 17.7 [d, $J(PC) = 1.9$ Hz, PCH*C*H$_3$]. ^{31}P NMR (162.0 MHz, acetone-d_6): δ 102.5 [d, $J(RhP) = 150.4$ Hz, *i*Pr_2P], −144.2 [sept, $J(FP) = 708.4$ Hz, PF_6^-]. Anal. Calcd for $C_{18}H_{25}F_6O_3P_2Rh$ (568.2): C, 38.05; H, 4.43. Found: C, 37.91; H, 4.63.

Preparation of [(η^6-$C_6H_5CH_2CH_2PiPr_2$-κ-*P*)Rh(HC≡C-CO_2Et)]PF_6 (17). A solution of **11** (126 mg, 0.22 mmol) in 3 mL of CH_2Cl_2 was treated at −20 °C with ethyl propiolate (111 μL, 110 mmol). After warming to room temperature, the reaction mixture was stirred for 12 h, which led to a change of color from yellow to red. Upon addition of 7 mL of ether, a yellow solid precipitated. The mother liquor was decanted, and the solid was washed twice with 5 mL of ether and twice with 5 mL of pentane and dried in vacuo: yield 102 mg (83%); mp 125 °C dec. Λ = 63 cm^2 Ω^{-1} mol^{-1}. IR (CD_2Cl_2): ν(≡CH) 3079, (C≡C) 1808, (C=O) 1700 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.37 (m, 2H, C_6H_5), 7.13, 7.03 (both m, 1H each, C_6H_5), 5.97 [d, $J(RhH) = 3.5$ Hz, 1H, ≡CH], 5.86 (m, 1H, C_6H_5), 4.30 [dq, $J(HH) = 7.0$ Hz, $J(PH) = 2.6$ Hz, 2H, OC*H*$_2$CH$_3$], 2.83−2.71 (m, 4H, PCH_2 and PhC*H*$_2$), 1.92 (m, 2H, PC*H*CH_3), 1.36 [t, $J(HH) = 7.0$ Hz, 3H, OCH_2CH_3], 1.22 (m, 6H, PCHC*H*$_3$), 1.13 [dd, $J(PH) = 17.0$ Hz, $J(HH) = 7.0$ Hz, 6H, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, CD_2Cl_2, 233 K): δ 158.6 [d, $J(RhC) = 1.9$ Hz, C=O], 125.4 [dd, $J(PC) = 5.7$ Hz, $J(RhC) = 3.8$ Hz; d in $^{13}C\{^{31}P\}$, $J(RhC) = 3.8$ Hz, *ipso*-C of C_6H_5], 113.2, 112.3 (both s, C_6H_5), 101.8 [d, $J(PC) = 11.5$ Hz, *para*-C of C_6H_5], 100.8, 99.7 [both d, $J(RhC) = 2.9$ Hz, C_6H_5], 82.0 [dd, $J(RhC) = 15.3$ Hz, $J(PC)$ = 3.8 Hz; d in $^{13}C\{^{31}P\}$, $J(RhC) = 15.3$ Hz, C≡*C*H], 73.5 [dd, $J(RhC) = 17.2$ Hz, $J(PC) = 4.8$ Hz; d in $^{13}C\{^{31}P\}$, $J(RhC)$ = 17.2 Hz, *C*≡CH], 62.4 (s, O*C*H$_2$CH$_3$), 37.6 [d, $J(PC) = 28.6$ Hz, PCH_2], 31.3 (s, Ph*C*H$_2$), 24.8 [d, $J(PC) = 26.7$ Hz, P*C*HCH$_3$], 24.7 [d, $J(PC) = 27.7$ Hz, P*C*HCH$_3$], 17.5, 17.3, 17.1, 17.0 (all s, PCH*C*H$_3$), 13.8 (s, OCH_2CH_3). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 95.9 [d, $J(RhP) = 170.0$ Hz, *i*Pr_2P], −144.4 [sept, $J(FP)$ = 710.6 Hz, PF_6^-]. Anal. Calcd for $C_{19}H_{29}F_6O_2P_2Rh$ (568.3): C, 40.16; H, 5.14. Found: C, 39.85; H, 4.88.

Preparation of [(η^6-$C_6H_5CH_2CH_2PiPr_2$-κ-*P*)Rh(Sb*i*Pr_3)]PF_6 (18). A solution of **11** (150 mg, 0.26 mmol) in 3 mL of CH_2Cl_2 was treated with Sb*i*Pr_3 (107 μL, 0.52 mmol) and stirred for 8 h at room temperature. A change of color from yellow to red occurred. The solution was evaporated to dryness in vacuo, and the oily residue was washed twice with 5 mL of pentane and then dissolved in 3 mL of acetone. After the solution was layered with 7 mL of ether, a light red solid precipitated. The mother liquor was decanted, and the solid was washed with 5 mL of ether and twice with 5 mL of pentane and dried: yield 152 mg (81%); mp 114 °C dec. Λ = 71 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.88, 6.81 (both m, 2H each, C_6H_5), 5.74 (m, 1H, C_6H_5), 2.58 [ddd, $J(PH) = 8.8$ Hz, $J(HH) = 7.6$ Hz, $J(HH) = 7.3$ Hz, 2H, PCH_2], 2.39 [ddd, $J(PH) = 19.4$ Hz, $J(HH) = 7.6$ Hz, $J(HH) = 7.3$ Hz, 2H, PhC*H*$_2$], 2.15 [sept, $J(HH) = 7.3$ Hz, 3H, SbC*H*CH_3], 1.81 (m, 2H, PC*H*CH_3), 1.30 [d, $J(HH) = 7.3$ Hz, 18H, SbCHC*H*$_3$], 1.16 [dd, $J(PH) = 15.0$ Hz, $J(HH) = 6.9$ Hz, 6H, PCHC*H*$_3$], 1.14 [dd, $J(PH) = 17.3$ Hz, $J(HH) = 7.3$ Hz, 6H, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 110.8 [dd, $J(PC) = 5.4$ Hz, $J(RhC)$ = 4.8 Hz; d in $^{13}C\{^{31}P\}$, $J(RhC) = 4.8$ Hz, *ipso*-C of C_6H_5], 101.6 (s, C_6H_5), 100.5 [d, $J(RhC) = 3.1$ Hz, C_6H_5], 88.4 [dd, $J(PC)$ = 9.2 Hz, $J(RhC) = 2.0$ Hz; d in $^{13}C\{^{31}P\}$, $J(RhC) = 2.0$ Hz, *para*-C of C_6H_5], 39.9 [d, $J(PC) = 26.5$ Hz, PCH_2], 31.0 (s, Ph*C*H$_2$), 27.2 [dd, $J(PC) = 26.4$ Hz, $J(RhC) = 2.0$ Hz; d in $^{13}C\{^{31}P\}$, $J(RhC) = 2.0$ Hz, P*C*HCH$_3$], 21.6 (s, SbCH*C*H$_3$), 21.0 [d, $J(RhC) = 3.0$ Hz, PCH*C*H$_3$], 20.3 [d, $J(PC) = 4.1$ Hz, PCH*C*H$_3$], 18.2 (s, Sb*C*HCH$_3$). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 99.8 [d, $J(RhP) = 180.9$ Hz, *i*Pr_2P], −144.4 [sept, $J(FP)$ = 710.6 Hz, PF_6^-]. Anal. Calcd for $C_{23}H_{44}F_6P_2RhSb$ (721.2): C, 38.31; H, 6.15. Found: C, 38.19; H, 6.39.

Preparation of [(η^6-$C_6H_5CH_2CH_2CH_2PiPr_2$-κ-*P*)Rh(C_2H_4)]PF_6 (19). The preparation was analogous with that described for **15**, from **12** (143 mg, 0.24 mmol). Reaction conditions: 1.5 h at 85 °C, repeating the procedure four times. Yellow solid: yield 97 mg (79%); mp 180 °C dec. Λ = 73 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.05, 6.90 (both m, 2H each, C_6H_5), 5.45 (m, 1H, C_6H_5), 3.28 (br s, 2H, *exo*-H of C_2H_4), 2.52 (m, 2H, PhC*H*$_2$), 2.45 (br s, 2H, *endo*-H of C_2H_4), 2.01−1.76 (m, 4H, PCH_2 and PC*H*CH_3), 1.32 (m, 2H, PCH_2CH_2), 1.15 [dd, $J(PH) = 14.6$ Hz, $J(HH) = 6.8$ Hz, 6H, PCHC*H*$_3$], 1.13 [dd, $J(PH) = 16.2$ Hz, $J(HH) = 7.0$ Hz, 6H, PCHC*H*$_3$]. ^{1}H NMR (400 MHz, CD_2Cl_2, 233 K): δ 7.01, 6.84 (both m, 2H each, C_6H_5), 5.44 (m, 1H, C_6H_5), 3.21 (m, 2H, *exo*-H of C_2H_4), 2.46 (m, 2H, PhC*H*$_2$), 2.33 (m, 2H, *endo*-H of C_2H_4), 1.94−1.68 (m, 4H, PCH_2 and PC*H*CH_3), 1.25 (m, 2H, PCH_2CH_2), 1.08 [dd, $J(PH) = 14.9$ Hz, $J(HH) = 6.9$ Hz, 6H, PCHC*H*$_3$], 1.06 [dd, $J(PH) = 16.4$ Hz, $J(HH) = 7.1$ Hz, 6H, PCHC*H*$_3$]. ^{13}C NMR

(100.6 MHz, CD_2Cl_2): δ 112.3 [d, J(RhC) = 2.9 Hz, *ipso*-C of C_6H_5], 108.7 [d, J(RhC) = 1.9 Hz, C_6H_5], 104.3 [d, J(RhC) = 2.9 Hz, C_6H_5], 96.3 [dd, J(PC) = 10.5 Hz, J(RhC) = 1.9 Hz; d in $^{13}C\{^{31}P\}$, J(RhC) = 1.9 Hz, *para*-C of C_6H_5], 39.9 [dd, J(RhC) = 13.3 Hz, J(PC) = 1.9 Hz; d in $^{13}C\{^{31}P\}$, J(RhC) = 13.3 Hz, C_2H_4], 31.9, 26.2 (both s, PCH_2CH_2 and $PhCH_2$), 25.0 [d, J(PC) = 27.7 Hz, $PCHCH_3$], 19.7, 17.6 (both s, $PCHCH_3$), 15.4 [d, J(PC) = 27.6 Hz, PCH_2]. ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 56.0 [d, J(RhP) = 172.2 Hz, iPr_2P], −144.3 [sept, J(FP) = 710.6 Hz, PF_6^-]. Anal. Calcd for $C_{17}H_{29}F_6P_2Rh$ (512.3): C, 39.86; H, 5.71. Found: C, 39.58; H, 5.43.

Preparation of $C_6H_5CH_2CH_2PtBu_2$ (20). A mixture of $HPtBu_2$ (7.4 g, 50.7 mmol) and 2-phenylethylbromide (6.2 mL, 45.7 mmol) was heated under stirring for 4 days at 90 °C. After the reaction mixture was cooled to room temperature, a colorless oily liquid was obtained. The liquid was dissolved in 30 mL of degassed water, and the solution was washed five times with 20 mL of ether. The aqueous solution was layered with 80 mL of ether and then treated under stirring with KOH until the aqueous phase became basic (pH ∼9). The ethereal phase was separated, washed three times with 20 mL of water, and then dried with Na_2SO_4. The solvent was removed in vacuo, and the residue was distilled to give a colorless oily liquid: yield 9.7 g (85%); bp 77−78 °C (0.04 mbar). ^1H NMR (200 MHz, $CDCl_3$): δ 7.24 (m, 5H, C_6H_5), 2.82 (m, 2H, $PhCH_2$), 1.67 (m, 2H, PCH_2), 1.15 [d, J(PH) = 10.6 Hz, 18H, $PCCH_3$]. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 143.7 [d, J(PC) = 14.8 Hz, *ipso*-C of C_6H_5], 128.4, 128.1, 125.9 (all s, C_6H_5), 36.7 [d, J(PC) = 24.0 Hz, $PhCH_2$], 31.4 [d, J(PC) = 20.3 Hz, $PCCH_3$], 29.7 [d, J(PC) = 13.9 Hz, $PCCH_3$], 23.8 [d, J(PC) = 21.3 Hz, PCH_2]. ^{31}P NMR (81.0 MHz, $CDCl_3$): δ 30.4 (s). MS (70 eV) m/z 251 ($M^+ + H$).

Preparation of $[C_6H_5CH_2CH_2PtBu_2Me]I$ (20a). The preparation was analogous with that described for **8a**, from **20** (1.38 g, 5.52 mmol) and CH_3I (350 μL, 5.60 mmol). Colorless solid: yield 1.99 g (92%); mp 174 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 7.35 (m, 5H, C_6H_5), 3.19 (m, 2H, $PhCH_2$), 2.52 (m, 2H, PCH_2), 2.20 [d, J(PH) = 11.7 Hz, 3H, PCH_3], 1.53 [d, J(PH) = 15.0 Hz, 18H, $PCCH_3$]. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 138.9 [d, J(PC) = 12.0 Hz, *ipso*-C of C_6H_5], 129.0, 128.5, 127.2 (all s, C_6H_5), 33.9 [d, J(PC) = 38.8 Hz, $PCCH_3$], 29.6 [d, J(PC) = 4.6 Hz, $PhCH_2$], 27.2 (s, $PCCH_3$), 18.9 [d, J(PC) = 39.8 Hz, PCH_2], 1.8 [d, J(PC) = 45.3 Hz, PCH_3]. ^{31}P NMR (81.0 MHz, $CDCl_3$): δ 47.8 (s). Anal. Calcd for $C_{17}H_{30}IP$ (392.3): C, 52.05; H, 7.71. Found: C, 51.83; H, 7.56.

Preparation of $C_6H_5OCH_2CH_2PtBu_2$ (21). The preparation was analogous with that described for **20**, from $HPtBu_2$ (4.49 g, 30.7 mmol) and $PhOCH_2CH_2Br$ (5.56 g, 27.6 mmol). Reaction conditions: 3 days at 80 °C. Colorless oily liquid: yield 8.20 g (81%). ^1H NMR (400 MHz, C_6D_6): δ 7.13, 6.91 (both m, 2H each, C_6H_5), 6.84 (m, 1H, C_6H_5), 4.07 (m, 2H, PCH_2CH_2), 1.85 (m, 2H, PCH_2), 1.01 [d, J(PH) = 11.2 Hz, 18H, $PCCH_3$]. ^{13}C NMR (100.6 MHz, C_6D_6): δ 159.4 (s, *ipso*-C of C_6H_5), 129.8, 120.8, 114.9 (all s, C_6H_5), 69.0 [d, J(PC) = 5.8 Hz, PCH_2CH_2], 31.1 [d, J(PC) = 21.0 Hz, $PCCH_3$], 29.6 [d, J(PC) = 14.3 Hz, $PCCH_3$], 22.2 [d, J(PC) = 21.9 Hz, PCH_2]. ^{31}P NMR (162.0 MHz, C_6D_6): δ 19.4 (s). MS (70 eV) m/z 267 ($M^+ + H$).

Preparation of $[C_6H_5OCH_2CH_2PtBu_2Me]I$ (21a). The preparation was analogous with that described for **8a**, from **21** (400 mg, 1.50 mmol) and CH_3I (95 μL, 1.52 mmol). Colorless solid: yield 541 mg (88%); mp 138 °C. ^1H NMR (200 MHz, CD_3NO_2): δ 7.32 (m, 2H, C_6H_5), 7.00 (m, 3H, C_6H_5), 4.45 (m, 2H, PCH_2CH_2), 2.82 (m, 2H, PCH_2), 1.96 [d, J(PH) = 12.1 Hz, 3H, PCH_3], 1.51 [d, J(PH) = 15.7 Hz, 18H, $PCCH_3$]. ^{13}C NMR (50.3 MHz, CD_3NO_2): δ 158.8 (s, *ipso*-C of C_6H_5), 131.0, 123.1, 115.7 (all s, C_6H_5), 63.3 [d, J(PC) = 5.9 Hz, PCH_2CH_2], 34.8 [d, J(PC) = 38.3 Hz, $PCCH_3$], 26.8 (s, $PCCH_3$), 18.5 [d, J(PC) = 44.8 Hz, PCH_2], 0.3 [d, J(PC) = 47.4 Hz, PCH_3]. ^{31}P NMR (81.0 MHz, CD_3NO_2): δ 49.3 (s). Anal. Calcd for $C_{17}H_{30}OIP$ (408.3): C, 50.01; H, 7.41. Found: C, 49.67; H, 7.28.

Preparation of $[(\eta^6\text{-}C_6H_5CH_2CH_2PtBu_2\text{-}\kappa\text{-}P)Rh(C_8H_{14})]PF_6$ (22a). A solution of **10** (1.00 g, 1.73 mmol) in 3 mL of acetone was treated at −20 °C dropwise over a period of 25 min with an ice-cooled solution of **20** (474 mg, 1.73 mmol) in 10 mL of acetone. After the reaction mixture was warmed to room temperature, the solution was concentrated to ca. 3 mL in vacuo and then treated with 12 mL of ether. A yellow solid precipitated, which was separated from the mother liquor, washed three times with 7 mL of ether and twice with 7 mL of pentane, and dried: yield 983 mg (93%); mp 144 °C dec. Λ = 93 $cm^2\ \Omega^{-1}\ mol^{-1}$. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.01, 6.86 (both m, 2H each, C_6H_5), 5.69 (m, 1H, C_6H_5) 3.91 (m, 2H, =CH of C_8H_{14}), 2.66, 2.55 (both m, 2H each, $PhCH_2$ and PCH_2), 2.33 (m, 2H, CH_2 of C_8H_{14}), 1.71−1.33 (m, 10H, CH_2 of C_8H_{14}), 1.31 [d, J(PH) = 13.8 Hz, 18H, $PCCH_3$]. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 118.4 [dd, J(PC) = 4.8 Hz, J(RhC) = 3.8 Hz; d in $^{13}C\{^{31}P\}$, J(RhC) = 3.8 Hz, *ipso*-C of C_6H_5], 111.6 (s, C_6H_5), 103.6 [d, J(RhC) = 1.9 Hz, C_6H_5], 95.0 [dd, J(PC) = 9.5 Hz, J(RhC) = 1.9 Hz; d in $^{13}C\{^{31}P\}$, J(RhC) = 1.9 Hz, *para*-C of C_6H_5], 69.2 [d, J(RhC) = 13.4 Hz, =CH of C_8H_{14}], 40.1 [d, J(PC) = 24.8 Hz, PCH_2], 37.2 [dd, J(PC) = 15.3 Hz, J(RhC) = 1.9 Hz; d in $^{13}C\{^{31}P\}$, J(RhC) = 1.9 Hz, $PCCH_3$], 34.0, 32.3, 31.2 and 26.3 (all s, CH_2 of C_8H_{14} and $PhCH_2$), 30.4 [d, J(PC) = 2.9 Hz, $PCCH_3$]. ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 96.0 [d, J(RhP) = 189.6 Hz, tBu_2P], −144.3 [sept, J(FP) = 710.6 Hz, PF_6^-]. Anal. Calcd for $C_{24}H_{41}F_6P_2Rh$ (608.4): C, 47.38; H, 6.79; Rh, 16.91. Found: C, 47.44; H, 6.54; Rh, 16.86.

Preparation of $[(\eta^6\text{-}C_6H_5CH_2CH_2PtBu_2\text{-}\kappa\text{-}P)Rh(C_8H_{14})]CF_3SO_3$ (22b). A solution of **25** (230 mg, 0.24 mmol) in 10 mL of ether was treated at −70 °C dropwise with a cooled (−20 °C) solution of **20** (134 mg, 0.54 mmol) in 3 mL of ether. Almost instantaneously, a yellow solid precipitated, which was separated from the mother liquor, washed three times with 5 mL of ether and three times with 5 mL of pentane, and dried: yield 280 mg (94%); mp 117 °C dec. Λ = 73 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR ($CH_2Cl_2$): $\nu(O_3S)$ 1242 and 1031, $\nu(CF_3)$ 1158 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.08, 6.87 (both m, 2H each, C_6H_5), 5.70 (m, 1H, C_6H_5), 3.90 (m, 2H, =CH of C_8H_{14}), 2.69 [ddd, J(PH) = 9.3 Hz, J(HH) = 7.2 Hz, J(HH) = 6.8 Hz; dd in $^1H\{^{31}P\}$, J(HH) = 7.2 Hz, J(HH) = 6.8 Hz, 2H, PCH_2], 2.57 [ddd, J(PH) = 19.4 Hz, J(HH) = 7.2 Hz, J(HH) = 6.8 Hz; dd in $^1H\{^{31}P\}$, J(HH) = 7.2 Hz, J(HH) = 6.8 Hz, 2H, $PhCH_2$], 2.33 (m, 2H, CH_2 of C_8H_{14}), 1.70−1.30 (m, 10H, CH_2 of C_8H_{14}), 1.32 [d, J(PH) = 13.8 Hz, 18H, $PCCH_3$]. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 121.3 [q, J(FC) = 321.4 Hz, CF_3], 118.7 [dd, J(PC) = 4.8 Hz, J(RhC) = 3.8 Hz; d in $^{13}C\{^{31}P\}$, J(RhC) = 3.8 Hz, *ipso*-C of C_6H_5], 111.6, 103.6 (both s, C_6H_5), 95.0 [dd, J(PC) = 9.5 Hz, J(RhC) = 1.9 Hz; d in $^{13}C\{^{31}P\}$, J(RhC) = 1.9 Hz, *para*-C of C_6H_5], 69.0 [d, J(RhC) = 12.4 Hz, =CH of C_8H_{14}], 40.1 [d, J(PC) = 24.8 Hz, PCH_2], 37.2 [d, J(PC) = 16.2 Hz, $PCCH_3$], 34.0, 32.3, 31.2, 26.2 (all s, CH_2 of C_8H_{14} and $PhCH_2$), 30.4 [d, J(PC) = 3.8 Hz, $PCCH_3$]. ^{19}F NMR (188.3 MHz, CD_2Cl_2): δ −78.7 (s). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 96.0 [d, J(RhP) = 189.9 Hz]. Anal. Calcd for $C_{25}H_{41}F_3O_3PSRh$ (612.5): C, 49.02; H, 6.75; S, 5.23. Found: C, 48.81; H, 6.46; S, 5.29.

Preparation of $[(\eta^6\text{-}C_6H_5OCH_2CH_2PtBu_2\text{-}\kappa\text{-}P)Rh(C_8H_{14})]PF_6$ (23). The preparation was analogous with that described for **11**, from **10** (197 mg, 0.34 mmol) and **21** (91 mg, 0.34 mmol). Yellow solid: yield 192 mg (90%); mp 122 °C dec. Λ = 102 $cm^2\ \Omega^{-1}\ mol^{-1}$. ^1H NMR (400 MHz, CD_2Cl_2): δ 6.90, 6.79 (both m, 2H each, C_6H_5), 5.51 (m, 1H, C_6H_5), 4.43 (m, 2H, PCH_2CH_2), 4.01 (m, 2H, =CH of C_8H_{14}), 2.34 (m, 2H, CH_2 of C_8H_{14}), 1.76−1.36 (m, 12H, CH_2 of C_8H_{14} and PCH_2), 1.32 [d, J(PH) = 13.8 Hz, 18H, $PCCH_3$]. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 129.2 [d, J(RhC) = 2.9 Hz, *ipso*-C of C_6H_5], 112.2, 97.6 (both s, C_6H_5), 91.9 [dd, J(PC) = 8.6 Hz, J(RhC) = 3.8 Hz; d in $^{13}C\{^{31}P\}$, J(RhC) = 3.8 Hz, *para*-C of C_6H_5], 69.4 (s, PCH_2CH_2), 66.4 [d, J(RhC) = 14.3 Hz, =CH of C_8H_{14}], 37.8 [dd, J(PC) = 16.2 Hz, J(RhC) = 1.9 Hz; d in $^{13}C\{^{31}P\}$, J(RhC) = 1.9 Hz, $PCCH_3$], 33.6, 32.3, 26.3 (all s, CH_2 of C_8H_{14}), 31.1 [d, J(PC) = 2.9 Hz, $PCCH_3$], 15.2 [d, J(PC) = 21.9 Hz, PCH_2]. ^{31}P NMR (162.0

Table 4. Crystallographic Data for 11, 12, and 19

formula	$C_{22}H_{37}F_6P_2Rh$ (**11**)	$C_{23}H_{39}F_6P_2Rh$ (**12**)	$C_{17}H_{29}F_6P_2Rh$ (**19**)
fw	580.37	594.39	512.25
cryst size, mm^3	0.22 × 0.18 × 0.17	0.19 × 0.15 × 0.14	0.18 × 0.16 × 0.15
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
cell dimens	5000 reflns,	5000 reflns,	25 reflns,
determn	$2° < \theta < 25°$	$2° < \theta < 25°$	$10° < \theta < 15°$
a, Å	13.403(1)	13.436(2)	8.749(2)
b, Å	9.945(1)	9.7565(8)	17.578(4)
c, Å	18.974(2)	20.086(2)	13.270(3)
β, deg	99.89(1)	104.02(1)	92.91(3)
V, $Å^3$	2491.5(5)	2554.7(5)	2038.1(7)
Z	4	4	4
d_{calc}, $g·cm^{-3}$	1.547	1.530	1.669
temp, K	173(2)	173(2)	193(2)
μ, mm^{-1}	0.866	0.847	1.047
scan method	Φ	Φ	Ω/ϕ
2θ(max), deg	50	50	50
total no. of reflns	25 465	21 382	4505
no. of unique reflns	4290	4506	3584
	[*R*(int) = 0.0719]	[*R*(int) = 0.0562]	[*R*(int) = 0.0275]
no. of obsd reflns [$I > 2\sigma(I)$]	3463	3539	2620
no. of reflns used for refinement	4290	4506	3584
no. of params refined	285	331	276
final *R* indices	$R_1 = 0.0386$,	$R_1 = 0.0413$,	$R_1 = 0.0484$
[$I > 2\sigma(I)$]	$wR_2 = 0.1010$[a]	$wR_2 = 0.1046$[a]	$wR_2 = 0.1027$[a]
R indices (all data)	$R_1 = 0.0465$,	$R_1 = 0.0535$,	$R_1 = 0.0761$,
	$wR_2 = 0.1052$[a]	$wR_2 = 0.1105$[a]	$wR_2 = 0.1207$[a]
extinction coeff	0.0053(7)	0.0031(5)	
resid electron density, e $Å^{-3}$	0.784/−0.647	0.683/−1.409	0.615/−0.668

[a] $w^{-1} = [\sigma^2F_o^2 + (0.0764P)^2 + 0.0000P]$ (**11**), $w^{-1} = [\sigma^2F_o^2 + (0.0773P)^2 + 0.0000P]$ (**12**), $w^{-1} = [\sigma^2F_o^2 + (0.0452P)^2 + 6.7551P]$ (**19**), where $P = (F_o^2 + 2F_c^2)/3$.

MHz, CD_2Cl_2): δ 47.1 [d, J(RhP) = 185.3 Hz, *t*Bu_2P], −144.3 [sept, J(FP) = 710.6 Hz, PF_6^-]. Anal. Calcd for $C_{24}H_{41}F_6OP_2Rh$ (624.4): C, 46.16; H, 6.62. Found: C, 46.07; H, 6.38.

Preparation of [(η^6-$C_6H_5CH_2CH_2P$*t*Bu_2-κ-*P*)Rh(HC≡C-CO_2Et)]PF_6 (24). The preparation was analogous with that described for **17**, from **22a** (110 mg, 0.18 mmol) and ethyl propiolate (92 μL, 0.90 mmol). Yellow solid: yield 98 mg (91%); mp 136 °C dec. Λ = 81 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR ($CH_2Cl_2$): ν(≡CH) 3042, ν(C≡C) 1811, ν(C═O) 1700 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.41, 7.30, 7.13, 7.03 (all m, 1H each, C_6H_5), 6.07 [d, J(RhH) = 3.5 Hz, 1H, ≡CH], 5.61 (m, 1H, C_6H_5), 4.30 [dq, J(HH) = 7.0 Hz, J(PH) = 1.6 Hz, 2H, OCH_2CH_3], 2.88−2.70 (m, 4H, PCH_2 and PCH_2CH_2), 1.35 [t, J(HH) = 7.0 Hz, 3H, OCH_2CH_3], 1.26 [d, J(PH) = 14.6 Hz, 9H, $PCCH_3$], 1.23 [d, J(PH) = 14.6 Hz, 9H, $PCCH_3$]. ^{13}C NMR (100.6 MHz, CD_2Cl_2, 233 K): δ 158.8 [d, J(RhC) = 1.9 Hz, C═O], 125.9 [dd, J(PC) = 5.7 Hz, J(RhC) = 3.8 Hz; d in $^{13}C\{^{31}P\}$, J(RhC) = 3.8 Hz, *ipso*-C of C_6H_5], 113.5 [d, J(RhC) = 1.9 Hz, C_6H_5], 112.7 (s, C_6H_5), 103.2, 102.1 [both d, J(RhC) = 2.9 Hz, C_6H_5], 100.7 [d, J(PC) = 11.4 Hz, *para*-C of C_6H_5], 81.1 [dd, J(RhC) = 15.3 Hz, J(PC) = 3.8 Hz; d in $^{13}C\{^{31}P\}$, J(RhC) = 15.3 Hz, C≡*C*H], 72.5 [dd, J(RhC) = 17.2 Hz, J(PC) = 3.8 Hz; d in $^{13}C\{^{31}P\}$, J(RhC) = 17.2 Hz, *C*≡CH], 62.9 (s, OCH_2CH_3), 39.9 [d, J(PC) = 25.8 Hz, PCH_2], 37.2 [d, J(PC) = 17.2 Hz, $PCCH_3$], 37.1 [d, J(PC) = 16.2 Hz, $PCCH_3$], 32.2 (s, PCH_2CH_2), 29.5 [d, J(PC) = 1.9 Hz, $PCCH_3$], 29.3 [d, J(PC) = 2.9 Hz, $PCCH_3$], 14.3 (s, OCH_2CH_3). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 109.5 [d, J(RhP) = 176.6 Hz, *t*Bu_2P], −144.3 [sept, J(FP) = 710.6 Hz, PF_6^-]. Anal. Calcd for $C_{21}H_{33}F_6O_2P_2Rh$ (596.3): C, 42.30; H, 5.58. Found: C, 42.48; H, 5.26.

X-ray Structural Determination of Compounds 11, 12, and 19. Single crystals were grown by diffusion of ether into a concentrated solution of **11**, **12**, and **19** in acetone at room temperature. The data were collected from a shock-cooled crystal protected by an oil drop[13] on a Stoe IPDS diffractometer (**11**, **12**) and an Enraf-Nonius CAD4 diffractometer (**19**) using monochromated Mo Kα radiation (λ = 0.71073 Å). Crystal data collection parameters are summarized in Table 4. Intensity data were corrected by Lorentz and polarization effects, and for **19** an empirical absorption correction was applied (Ψ-scan method, minimum transmission 80%). The structures were solved by direct methods (SHELXS-97).[14] Atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least squares on F^2 (SHELXL-97).[15] The ethene ligand in **19** was found layer disordered. Two geometrically independent positions were found and refined anisotropically with restraints (SIMU, DELU) and the occupancy factors 0.50:0.50. In **12** and **19** also the PF_6^- ion was found disordered (occupation factors 0.82:0.12 (**12**) and 0.83:0.17 (**19**)). The positions of all hydrogen atoms were calculated according to ideal geometry and refined by using the riding method.

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Supporting Information Available: Tables of data collection parameters, bond lengths and angles, positional and thermal parameters, and least-squares planes for **11**, **12**, and **19**. This material is available free of charge via the Internet at http://pubs.acs.org.

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