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Synthesis, structure, and reactivity of ylide rhodium(I) and rhodium(III) complexes *

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Abstract

The olefin(ylide) rhodium(I) complexes $[(L)(^iPr_3PCH_2)RhCl]_2$ (**3**: $L = C_8H_{14}$; **4**: $L = C_2H_4$) have been prepared from $[(L)_2RhCl]_2$ (**1**, **2**) and $CH_2P^iPr_3$ in almost quantitative yield. Upon treatment of **3** and **4** with LiC_5H_5, the half-sandwich type compounds $[C_5H_5Rh(CH_2P^iPr_3)(L)]$ (**5**, **6**) are obtained. Compound **5** ($L = C_8H_{14}$) reacts with carbon monoxide to give $[C_5H_5Rh(CH_2P^iPr_3)(CO)]$ (**7**) and with iodine to give $[C_5H_5Rh(CH_2P^iPr_3)I_2]$ (**8**). Displacement of the olefin ligand also occurs upon treatment of **5** with CH_3I, CH_2I_2 and CH_2ClI, leading to the formation of $[C_5H_5RhCH_2X(CH_2P^iPr_3)I]$ (**9**: X = H; **10**: X = I; **11**: X = Cl). The bis(ylide) rhodium(III) complexes $[C_5H_5Rh(CH_2PR_3)(CH_2P^iPr_3)I]I$ (**12**–**14**), $[C_5H_5Rh(CH_2P^iPr_3)(CH_2AsPh_3)I]I$ (**15**) and $[C_5H_5Rh(CH_2P^iPr_3)(CH_2NEt_3)I]I$ (**16**) are obtained by nucleophilic substitution from **10** upon treatment with PR_3, $AsPh_3$ and NEt_3, respectively. Reaction of **7** with CH_3I or CD_3I give a mixture of **8** and $[C_5H_5RhCX_3(CH_2P^iPr_3)(CO)]I$ (**17a**: X = H; **17b**: X = D). In contrast, treatment of **7** with dimethylsulfate gives only $[C_5H_5RhCH_3(CH_2P^iPr_3)(CO)]SO_4Me$ (**17c**). The X-ray crystal structure of **17c** has been determined. Compound **17c** reacts with P^iPr_3 to give the acetyl(ylide) rhodium(III) complex $[C_5H_5RhCOCH_3(CH_2P^iPr_3)(P^iPr_3)]SO_4Me$ (**18**).

Introduction

Phosphorus ylides are not only classical reagents in organic chemistry but also play an important role as ligands in coordination compounds [1]. Ylide metal complexes are either prepared from preformed ylides and metallic precursors by addition or ligand substitution, or are formed from phosphines and C_1 substrates in the coordination sphere of the metal. They have been the subject of numerous studies in the last twenty years, and there is now good evidence that the central metal atom of an ylide metal complex can come from almost any group of the Periodic Table [1].

Following our work on electron-rich half-sandwich type complexes $[(C_nR_n)ML_2]$ and $[(C_nR_n)MLL']$ which behave like metal bases [2], we recently showed that cyclopentadienylcobalt and -rhodium compounds react with CH_2I_2 and other dihalomethanes to give the complexes $[C_5H_5MCH_2X(L)X]$ or $[C_5H_5MCH_2$-

* In memoriam Professor Piero Pino, one of the pioneers in the field of homogeneous catalysis.

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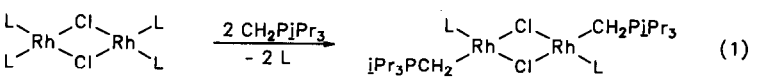
X(L)L′]X, respectively [3]. In both types of products, a carbenoid–metal unit is present, and this is very reactive toward nucleophiles. Taking $[C_5H_5RhCH_2I(PMe_3)I]$ as an example, reaction with pyridine, phosphines, and phosphites leads to the formation of cationic ylide rhodium complexes $[C_5H_5Rh(CH_2L)(PMe_3)I]^+$ whereas with OMe^- or SMe^- neutral compounds of general composition $[C_5H_5RhCH_2EMe(PMe_3)X]$ are obtained [3]. Despite the fact that the Rh–I bond in these ylide and carbenoid rhodium complexes is also prone to nucleophilic attack, our attempts to reduce the cations $[C_5H_5Rh(CH_2L)(PMe_3)I]^+$ to give the corresponding ylide rhodium(I) derivatives were unsuccessful.

We describe here the synthesis of hitherto unknown neutral half-sandwich type compounds $[C_5H_5Rh(CH_2PR_3)(L)]$ and discuss a general route to ylide rhodium(I) and rhodium(III) complexes involving use of the free ylide $CH_2P^iPr_3$ as the starting material. The results of the X-ray crystal structure analysis of $[C_5H_5RhCH_3(CH_2P^iPr_3)(CO)]SO_4Me$ are also reported.

Preparation of ylide rhodium(I) complexes

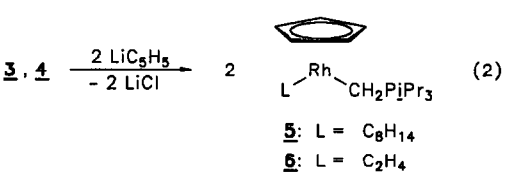
The dinuclear compounds **1** and **2**, which contain fairly labile olefin–rhodium bonds, react with $CH_2P^iPr_3$ in benzene to give a mixture of products. However, when pentane is used as the solvent, a clean reaction occurs to give a yellow precipitate in almost quantitative yield. Although satisfactory elemental analyses of the extremely air-sensitive solids were not obtained, the ^1H NMR spectra leave no doubt that the chloride-bridged complexes **3** and **4** (see eq. 1) are formed. Treatment of **3** and **4** with excess $CH_2P^iPr_3$ does not result in displacement of the second olefin ligand.



(1)

	L
1, 3	C_8H_{14}
2, 4	C_2H_4

The course of the reaction of **3** and **4** with alkali metal cyclopentadienides strongly depends on the reaction conditions. Good yields (65–80%) of the cyclopentadienylrhodium(I) complexes **5** and **6** (see eq. 2) are only achieved if the starting material **3** or **4** is mixed with solid LiC_5H_5 or NaC_5H_5 and, after addition of THF, the suspension is stirred for a short time at room temperature. Compounds **5** and **6** are pale yellow solids, which are as air-sensitive as the chloro-bridged dimers **3** and **4**.

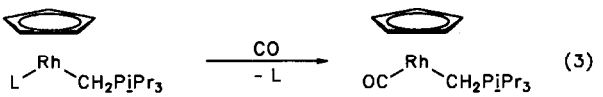


(2)

5: L = C_8H_{14}
6: L = C_2H_4

Displacement of the olefin ligand by CO takes place upon treatment of a benzene solution of **5** with carbon monoxide (see eq. 3). The carbonyl(ylide) complex **7** is isolated as a red air-sensitive oil, which could not be crystallized. The compound is

thermally quite labile and decomposes slowly even when stored at −78°C. In the IR spectrum of 7, the CO stretching band is found at 1880 cm^{-1}; that is at a rather low frequency compared with those for the carbonyl(phosphine) complexes [C_5H_5-Rh(CO)(PR_3)] [4], indicating a higher electron density at the metal center.



(3)

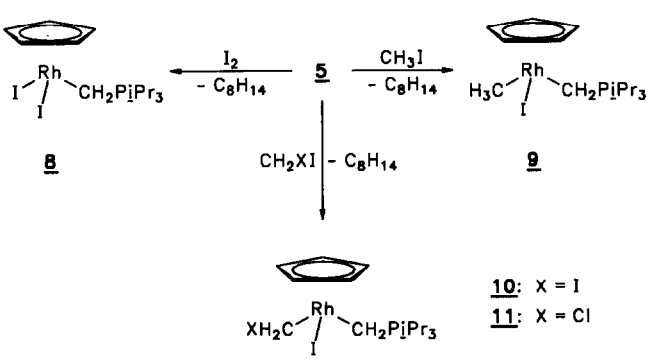
5: L = C_8H_{14} 7

Attempts to substitute the cyclooctene in **5** by phosphines, phosphites or a second ylide ligand were unsuccessful. With acetylene or phenylacetylene, polymerization of the alkyne occurs, and this is accompanied by slow decomposition of the starting material.

Reactions of the ylide complex 5 with electrophiles

Compound **5**, which according to its general composition [C_5H_5MLL'] belongs to the d^8 half-sandwich type complexes mentioned above, reacts under mild conditions with Brønsted acids and other electrophilic substrates. Whereas upon treatment with HBF_4 or CF_3CO_2H/NH_4PF_6, besides the phosphonium salt [$CH_3P^iPr_3$]X (X = BF_4, PF_6), only the bis(cyclooctene) complex [$C_5H_5Rh(C_8H_{14})_2$] is observed, the reactions of **5** with I_2 and CH_3I give cleanly the ylide rhodium(III) compounds [$C_5H_5Rh(CH_2P^iPr_3)I_2$] (**8**) and [$C_5H_5RhCH_3(CH_2P^iPr_3)I$] (**9**) in 96% and 92% yield (see Scheme 1). In both cases, cyclooctene is displaced, and can be detected in the reaction mixture by GLC examination. Compound **8** is an analogue of the previously described ylide rhodium(III) complex [$C_5H_5Rh(CH_2PMe_3)I_2$] that is formed by base-catalyzed rearrangement of the carbenoid isomer [$C_5H_5RhCH_2I(PMe_3)I$] [3]. Attempts to prepare **8** by the same route, with [$C_5H_5RhCH_2I(P^iPr_3)I$] [5] as the starting material, failed.

The dihalomethanes CH_2I_2 and CH_2ClI also react with complex **5** by oxidative addition and concomitant substitution of cyclooctene. The iodomethyl and chloromethyl rhodium(III) compounds **10** and **11** (Scheme 1) are red crystalline solids which can be kept without decomposition under argon. In acetone or dichloromethane solution, however, compound **10** is quite labile, and reacts to give the



Scheme 1

diiodo derivative **8**. The course of this CH_2-elimination can be conveniently monitored by NMR. The most characteristic feature in the ^1H NMR spectra of **10** and **11** is the occurrence of two signals each for the $RhCH_2X$, the $RhCH_2P^iPr_3$, and the $PCH(CH_3)_2$ protons, which is consistent with the chirality of the compounds.

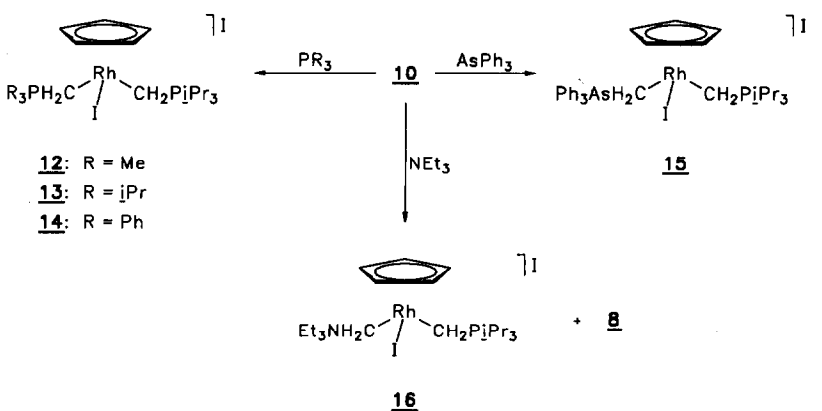
Reactions of the carbenoid rhodium(III) complex 10 with nucleophiles

After our attempts to prepare bis(ylide) rhodium complexes by ligand displacement using **5** or **6** as starting materials failed, we used a different route. Since we recently showed [3,6] that carbenoid metal units such as MCH_2I can be transformed by nucleophilic attack into a MCH_2PR_3 group, we tried to bring about such a conversion with a carbenoid(ylide) metal derivative. Complex **10** was therefore treated with PMe_3, P^iPr_3 and PPh_3, preferably in dichloromethane at $-78°C$, to give the bis(ylide) rhodium(III) compounds **12–14** in almost quantitative yield (Scheme 2). If the reactions are carried out at room temperature the diiodo complex **8** is also formed. Compounds **12–14** are much less air-sensitive than the carbenoid precursor and can be stored under argon for some days without decomposition. They were characterized by elemental analysis, conductivity measurements and ^1H and ^{31}P NMR spectroscopic data.

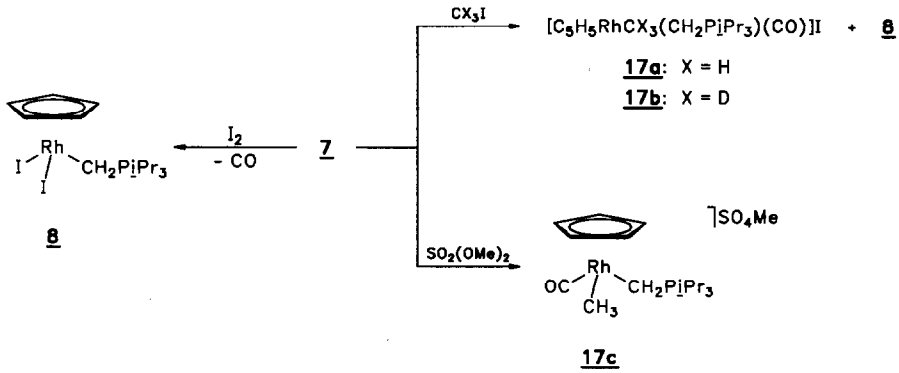
In addition to **12–14**, the related mixed bis(ylide) complexes **15** and **16** can also be prepared (Scheme 2). Again an optimum yield of **15** is only achieved if the reaction time given in the Experimental part is strictly adhered to. Upon treatment of **10** with NEt_3, besides **16** also significant amounts of the diiodo derivative **8** are formed. Owing to the similar solubilities of **8** and **16** in solvents such as CH_3NO_2, $CHCl_3$ etc., attempts to separate the two compounds by crystallization or column chromatography were unsuccessful.

Reactions of the carbonyl(ylide) complex 7 with electrophiles

Not unexpectedly, the behaviour of the carbonyl(ylide) rhodium(I) complex **7** is similar to that of the cyclooctene derivative **5**. Thus the reaction of **7** with an equimolar amount of I_2 leads to quantitative formation of the diiodo rhodium



Scheme 2

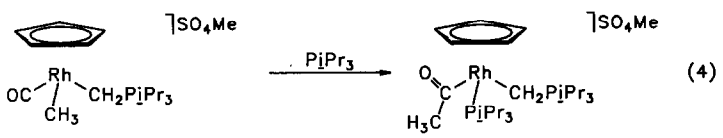


Scheme 3

compound **8**. With methyl iodide, however, a more complicated reaction occurs, to give, besides **8** and $[C_5H_5RhCH_3(CH_2P^iPr_3)(CO)]I$ (**17a**), also the phosphonium salt $[EtP^iPr_3]I$. Analogously, treatment of **7** with CD_3I gives a mixture of **8** and $[C_5H_5RhCD_3(CH_2P^iPr_3)(CO)]I$ (**17b**). The two isotopomers **17a** and **17b** could not be separated from **8** and were characterized from their IR and NMR spectroscopic data.

A clean electrophilic addition occurs if **7** reacts with dimethyl sulfate in benzene (Scheme 3). After crystallization from THF/ether orange crystals are isolated which from their elemental analysis and spectra are shown to be the SO_4Me salt of the cation $[C_5H_5RhCH_3(CH_2P^iPr_3)(CO)]^+$ (**17c**). Although the solid compound is rather stable, it slowly decomposes in CH_3NO_2 or CH_2Cl_2 solution. Pure samples of **17c** are also obtained when the mixture of **17a** and **8** is treated in benzene with dimethyl sulfate, and the crude product worked up as described above.

The expected methyl migration of the metal-bound CH_3 group to the CO ligand does not occur when solutions of **17c** in acetone or nitromethane are treated with NaI; instead, only exchange of the anion and partly formation of the diiodo derivative **8** takes place. Reaction of **17c** with an equimolar amount of P^iPr_3, however, gives the acetyl(ylide) rhodium(III) complex **18**, which is isolated as a bright red oil. It was characterized by elemental analysis and by IR and NMR spectroscopy (eq. 4). The ionic compound is readily soluble not only in acetone and CH_3NO_2, but also in CH_2Cl_2 and THF. We note that other attempts to prepare a rhodium(III) complex containing both P^iPr_3 and $CH_2P^iPr_3$ as ligands, e.g., by reaction of $[C_5H_5RhCH_2I(P^iPr_3)I]$ with P^iPr_3, were unsuccessful [7].



The structure of complex 17c

According to the results of the X-ray diffraction study (see Fig. 1 and Tables 1–3), in the cation of **17c** the metal is pseudooctahedrally coordinated by the

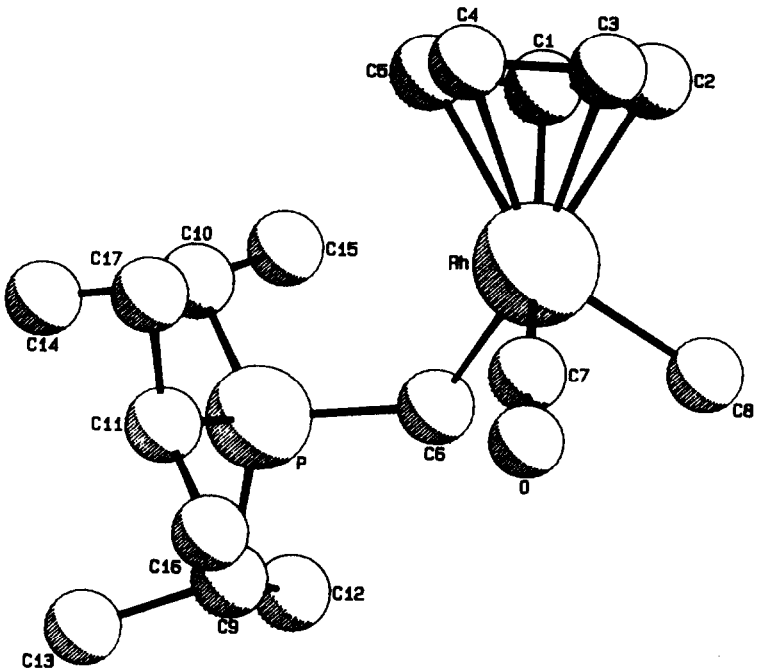


Fig. 1. PLUTO drawing of the cation of **17c** showing the molecular structure and atom numbering. Hydrogen atoms have been omitted for clarity.

cyclopentadienyl ring, the carbonyl ligand, the methyl group and the ylide unit. The five-membered ring is nearly planar and has almost identical C–C distances and C–C–C angles. The Rh–C bond lengths (Rh–CO 1.818(9), Rh–CH_3 2.10(1), Rh–$CH_2P^iPr_3$ 2.126(7) Å) are approximately the same as in other cationic rhodium(III) complexes of this type [3a,d,5,8]. The metal-to-ring carbon distances are also in the usual range for compounds containing the $C_5H_5Rh(CO)$ fragment.

As was found previously for other phosphorus ylide metal complexes [1,3d], the ylide P–CH_2 bond length is somewhat shorter than the P–$CH(CH_3)_2$ distances,

Table 1

Intramolecular bond distances (Å) and bond angles (°) of **17c**

Rh–C(1)	2.23(1)	Rh–C(7)	1.818(9)	O–C(7)	1.13(1)
Rh–C(2)	2.23(1)	Rh–C(8)	2.10(1)	C(1)–C(2)	1.39(2)
Rh–C(3)	2.238(9)	P–C(6)	1.78(1)	C(2)–C(3)	1.40(1)
Rh–C(4)	2.285(8)	P–C(9)	1.835(7)	C(3)–C(4)	1.40(2)
Rh–C(5)	2.27(1)	P–C(10)	1.81(1)	C(4)–C(5)	1.38(1)
Rh–C(6)	2.126(7)	P–C(11)	1.827(8)	C(5)–C(1)	1.40(1)
Rh–C(6)–P	125.7(3)	C(6)–P–C(9)	105.7(4)		
Rh–C(7)–O	178(1)	C(6)–P–C(10)	111.8(5)		
C(6)–Rh–C(7)	90.8(3)	C(6)–P–C(11)	113.2(4)		
C(6)–Rh–C(8)	81.3(4)	C(9)–P–C(10)	113.1(4)		
C(7)–Rh–C(8)	86.7(4)	C(9)–P–C(11)	104.2(4)		
		C(10)–P–C(11)	108.8(5)		

Table 2

Crystallographic data for **17c**

Formula	$C_{18}H_{34}O_5PRhS$
Formula weight	496.42
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
a (Å)	10.014(5)
b (Å)	10.799(5)
c (Å)	12.823(6)
α, (°)	92.33(3)
β, (°)	110.06(2)
γ, (°)	116.57(2)
V, (Å^3)	1133.5
Z	2
d_{calc} (g/cm^3)	1.45
Crystal size (mm)	0.2×0.4×0.5
μ(Mo-K_α) (cm^{-1})	9.2
Data collection instrument	Enraf-Nonius CAD4
Radiation (graphite monochromated)	Mo-K_α (λ 0.7093 Å)
Temperature (°C)	20±1
Scan method	$\omega/2\theta$
2θ(max) (°)	46
No. unique data, total:	3147
with $F_o > 3\sigma(F_o)$:	2965
Number of parameters refined	226
$R(F)$	0.054
$R_w(F)$	0.059
Residual electron density (e/Å^3)	1.56

indicating partial double bond character. Whereas the C–P–C angles differ only slightly from the ideal value expected for tetrahedral coordination, the Rh–C–P angle is opened to 125.7(3)°, which may be a consequence of the presence of the sterically demanding isopropyl substituents. For comparison, the Rh–C–P angle in the cation $[C_5H_5(I)\widehat{RhCH_2PMe_2C_2H_4PMe_2}]^+$ is 118.1° [3d], a value which seems to be typical for phosphorus ylide metal complexes [1].

Experimental

All reactions were carried out under argon and in carefully dried solvents. The starting materials $CH_2P^iPr_3$ [9], **1** [10] and **2** [11] were prepared by published methods. Equivalent conductivity measured in nitromethane; melting points determined by DTA.

*Preparation of [(L)(^{i}Pr$_3$PCH$_2$)RhCl]$_2$ (**3**: L = C$_8$H$_{14}$; **4**: L = C$_2$H$_4$)*

A suspension of 0.5 mmol of **1** (356 mg) or **2** (195 mg) in 10 ml of pentane was treated dropwise with 1.0 mmol (174 mg) of $CH_2P^iPr_3$ at room temperature. After 5 h stirring the dark-red mother liquor was removed and the solid residue repeatedly washed with pentane. The yellow powder obtained was shown by its ^{1}H NMR spectrum to contain traces of $[CH_3P^iPr_3]Cl$. Yield 95% (**3**: 402 mg; **4**: 310 mg). **3**: m.p. (dec) 105°C; ^{1}H NMR (C_6H_6): δ 2.57(m), –CH=CH–; 1.92(m), $-(CH_2)_6-$;

Table 3

Positional parameters for **17c** and their estimated standard deviations [a]

Atom	x	y	z	B (Å^2)
Rh	0.27651(6)	0.32999(6)	0.69975(5)	3.92(1)
S	−0.0034(2)	0.2521(2)	1.2340(2)	6.39(6)
P	−0.0568(2)	0.1992(2)	0.7734(2)	3.73(4)
O	0.4632(7)	0.2530(7)	0.8928(6)	8.5(2)
O1	−0.095(3)	0.116(1)	1.175(1)	33(1)
O2	−0.118(2)	0.275(1)	1.138(1)	37.7(6)
O3	0.142(1)	0.302(2)	1.261(1)	24.7(8)
O4	−0.047(1)	0.274(2)	1.3132(9)	31.2(7)
C1	0.197(1)	0.4448(9)	0.5735(7)	7.4(3)
C2	0.342(1)	0.457(1)	0.5747(8)	8.4(3)
C3	0.466(1)	0.5285(9)	0.6806(8)	7.6(3)
C4	0.403(1)	0.5728(8)	0.7469(8)	6.8(3)
C5	0.241(1)	0.5218(8)	0.6809(8)	7.2(3)
C6	0.0513(7)	0.1727(6)	0.6983(6)	3.9(2)
C7	0.3892(8)	0.2821(8)	0.8198(7)	5.2(2)
C8	0.246(1)	0.1570(9)	0.5950(8)	7.3(3)
C9	−0.2120(8)	0.0209(7)	0.7677(6)	4.6(2)
C10	−0.1446(8)	0.3076(7)	0.7134(9)	6.9(3)
C11	0.0688(9)	0.2778(9)	0.9255(7)	6.5(3)
C12	−0.336(1)	−0.062(1)	0.6495(8)	7.8(3)
C13	−0.293(1)	0.010(1)	0.8513(8)	7.8(3)
C14	−0.251(1)	0.318(1)	0.773(1)	12.0(4)
C15	−0.222(1)	0.270(1)	0.586(1)	11.0(4)
C16	0.148(1)	0.196(1)	0.9820(8)	8.5(4)
C17	0.189(1)	0.435(1)	0.9547(9)	9.4(4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\ [a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\ \gamma)B(1,2) + ac\ (\cos\ \beta)B(1,3) + bc(\cos\ \alpha)B(2,3)]$.

1.11(dd), J(PH) 11.9, J(HH) 7.8 Hz, PCHCH_3; −0.57(dd), J(PH) 11.7, J(RhH) 1.5 Hz, RhCH_2P; signal of PCHCH_3 proton masked by the signal(s) of the cyclooctene protons. **4**: m.p. (dec) 92°C; ^{1}H NMR (C_6H_6): δ 2.97(m), C_2H_4; 1.93(m), PCHCH_3; 0.95(dd), J(PH) 12.2, J(HH) 8.6 Hz, PCHCH_3; −0.47(dd), J(PH) 10.2, J(RhH) 1.4 Hz, RhCH_2P.

Preparation of [$C_5H_5Rh(CH_2P^iPr_3)(C_8H_{14})$] (5)

To a solid mixture of 211.4 mg (0.25 mmol) **3** and 43.2 mg (0.6 mmol) LiC_5H_5 were added 10 ml of THF. The suspension was stirred for 15 min at room temperature, the solvent then removed, and the residue extracted with pentane/benzene (30 ml/10 ml). The extract was evaporated to dryness *in vacuo*, the residue dissolved in 50 ml of pentane, and the solution stored at −78°C to give pale yellow microcrystals. Yield 176 mg (78%); m.p. (dec) 98°C. Found: C, 60.72, H, 9.16; Rh, 22.85. $C_{23}H_{42}PRh$ calc.: C, 61.05; H, 9.36; Rh, 22.74%. MS (70 eV): m/z (I_r) 452 (1; M^+), 342 (29; $M^+ - C_8H_{14}$), 278 (35; $M^+ - CH_2P^iPr_3$), 168 (100; $C_5H_5Rh^+$). ^{1}H NMR (C_6D_6): δ 5.10(d), J(RhH) 0.6 Hz, C_5H_5; 2.74(m), −CH=CH−; 1.76(m), −(CH_2)$_6$−; 0.80(dd), J(PH) 13.8, J(HH) 7.0 Hz, PCHCH_3; −0.71(dd), J(PH) 10.8, J(RhH) 3.4 Hz, RhCH_2P; signal of PCHCH_3 proton not exactly located. ^{31}P NMR (C_6D_6): δ 53.02(d), J(RhP) 3.0 Hz. ^{13}C NMR (C_6D_6): δ 84.09(d), J(RhC) 3.1 Hz,

C_5H_5; 51.14(d), J(RhC) 18.3 Hz, $-CH{=}CH-$; 34.41(s), 33.96(s), 27.52(s), all CH_2 of C_8H_{14}; 22.71(d), J(PC) 43.9 Hz, $PCHCH_3$; 17.41(s), $PCHCH_3$; −26.26(dd), J(PC) 41.1, J(RhC) 13.1 Hz, $RhCH_2P$.

Preparation of $[C_5H_5Rh(CH_2P^iPr_3)(C_2H_4)]$ (6)

This was made as described for **5** but starting from 163 mg (0.25 mmol) **4** and 43.2 mg (0.6 mmol) LiC_5H_5. The pale yellow crystals decompose smoothly even at 0 °C under argon. Yield 60 mg (65%); m.p. (dec) 95 °C. MS (70 eV): m/z (I_r) 370 (3; M^+), 342 (9; $M^+ - C_2H_4$), 196 (3; $M^+ - CH_2P^iPr_3$), 168 (100; $C_5H_5Rh^+$). ^{1}H NMR (C_6D_6): δ 5.16(d), J(RhH) 0.4 Hz, C_5H_5; 2.99(m), 2H of C_2H_4; 1.87(m), $PCHCH_3$; 1.26(m), 2H of C_2H_4; 0.82(dd), J(PH) 13.9, J(HH) 7.0 Hz, $PCHCH_3$; −0.69(dd), J(PH) 10.8; J(RhH) 3.4 Hz, $RhCH_2P$. ^{31}P NMR (C_6D_6): δ 52.51(d), J(RhP) 4.5 Hz. ^{13}C NMR (C_6D_6): δ 82.59(d), J(RhC) 3.0 Hz, C_5H_5; 24.66(d), J(RhC) 17.7 Hz, C_2H_4; 22.70(d), J(PC) 44.6 Hz, $PCHCH_3$; 17.42(s), $PCHCH_3$; −26.27(dd), J(PC) 38.8, J(RhC) 15.1 Hz, $RhCH_2P$.

Preparation of $[C_5H_5Rh(CH_2P^iPr_3)(CO)]$ (7)

A solution of 90.5 mg (0.2 mmol) **5** in 10 ml of benzene was saturated during 30 min with gaseous CO and then stirred for 30 min under a CO atmosphere. Volatile substances were removed *in vacuo* and the dark residue was extracted with benzene. The extract was evaporated to dryness *in vacuo* to give a red oil, which smoothly decomposes even at −78 °C. Yield 63 mg (85%). IR (C_6H_6): ν(CO) 1880 cm^{-1}. MS (70 eV): m/z (I_r) 370 (5; M^+), 342 (12; $M^+ - CO$), 196 (28; $M^+ - CH_2P^iPr_3$), 168 (100; $C_5H_5Rh^+$). ^{1}H NMR (C_6D_6): δ 5.30(d), J(RhH) 0.6 Hz, C_5H_5; 1.91(m), $PCHCH_3$; 0.94(dd), J(PH) 14.1, J(HH) 6.9 Hz, $PCHCH_3$; 0.91(dd), J(PH) ≈ 10, J(RhH) 4.2 Hz, $RhCH_2P$. ^{31}P NMR (C_6D_6): δ 50.75(d), J(RhP) 4.5 Hz. ^{13}C NMR (C_6D_6): δ 201.76(d), J(RhC) 93.8 Hz, CO; 85.95(d), J(RhC) 2.6 Hz, C_5H_5; 22.92(d), J(PC) 45.3 Hz, $PCHCH_3$; 17.72(s), $PCHCH_3$; −27.23(dd), J(PC) 38.6, J(RhC) 27.0 Hz, $RhCH_2P$.

Preparation of $[C_5H_5Rh(CH_2P^iPr_3)I_2]$ (8)

A solution of 45.2 mg (0.1 mmol) **5** in 5 ml of ether was treated dropwise with a solution of 25.4 mg (0.1 mmol) I_2 in 3 ml of ether. A dark-red precipitate was immediately formed, and after stirring of the reaction mixture for 5 min, this precipitate was separated from the mother liquor, repeatedly washed with ether, and dried *in vacuo*. The crude product was recrystallized from CH_2Cl_2/ether to give dark-red microcrystals. Yield 57 mg (96%); m.p. (dec) 167 °C. Found: C, 30.01; H, 4.91; Rh, 17.75. $C_{15}H_{28}I_2PRh$ calc.: C, 30.22; H, 4.73; Rh, 17.26%. MS (70 eV): m/z (I_r) 596 (1; M^+), 469 (12; $M^+ - I$), 422 (10; $M^+ - CH_2P^iPr_3$), 295 (44; $C_5H_5RhI^+$), 168 (60; $C_5H_5Rh^+$). ^{1}H NMR (CD_2Cl_2): δ 5.33(d), J(RhH) 0.5 Hz, C_5H_5; 2.83(m), $PCHCH_3$; 2.45(dd), J(PH) 11.2, J(RhH) 3.9 Hz, $RhCH_2P$; 1.36(dd), J(PH) 14.8, J(HH) 7.2 Hz, $PCHCH_3$. ^{31}P NMR (CD_2Cl_2): δ 39.13(d), J(RhP) 5.8 Hz. ^{13}C NMR ($CDCl_3$): δ 85.71(d), J(RhC) 4.5 Hz, C_5H_5; 22.83(d), J(PC) 43.2 Hz, $PCHCH_3$; 17.85(s), $PCHCH_3$; −26.95(dd), J(PC) 39.7, J(RhC) 19.9 Hz, $RhCH_2P$.

Preparation of $[C_5H_5RhCH_3(CH_2P^iPr_3)I]$ (9)

This was made as described for **8** but starting from 45.2 mg (0.1 mmol) **5** and 6.2 μl (0.1 mmol) CH_3I. Red microcrystals were obtained. Yield 45 mg (92%); m.p.

(dec) 163°C. Found: C, 39.88; H, 6.55; Rh, 20.93. $C_{16}H_{31}IPRh$ calc.: C, 39.70; H, 6.45; Rh, 21.25%. MS (70 eV): *m/z* (I_r) 469 (14; $M^+ - CH_3$), 310 (4; $M^+ - CH_2P^iPr_3$), 295 (42; $C_5H_5RhI^+$), 168 (100; $C_5H_5Rh^+$). ^1H NMR (CD_2Cl_2): δ 4.82(d), *J*(RhH) 0.5 Hz, C_5H_5; 2.25(m), $PCHCH_3$; 1.44(dd), *J*(RhH) 2.6, *J*(PH) 1.3 Hz, $RhCH_3$; 0.99(dd), *J*(PH) 14.3, *J*(HH) 7.2 Hz, $PCHCH_3$; 0.97(dd), *J*(PH) 14.2, *J*(HH) 7.2 Hz, $PCHCH_3$; 0.87(ddd), *J*(PH) 10.8, *J*(RhH) 3.4, *J*(HH) 13.1 Hz, one H of $RhCH_2P$; 0.64(ddd), *J*(PH) 11.2, *J*(RhH) 3.2, *J*(HH) 13.1 Hz, one H of $RhCH_2P$. ^{31}P NMR (CD_2Cl_2): δ 54.49(d), *J*(RhP) 2.9 Hz. ^{13}C NMR ($CDCl_3$): δ 85.59(d), *J*(RhC) 4.4 Hz, C_5H_5; 22.71(d), *J*(PC) 43.4 Hz, $PCHCH_3$; 17.77(s) and 17.72(s), both $PCHCH_3$; −11.82(d), *J*(RhC) 22.3 Hz, $RhCH_3$; −28.87(dd), *J*(PC) 34.2, *J*(RhC) 19.4 Hz, $RhCH_2P$.

*Preparation of $[C_5H_5RhCH_2I(CH_2P^iPr_3)I]$ (**10**)*

A solution of 45.2 mg (0.1 mmol) **5** in 10 ml of ether was treated dropwise with 8.0 μl (0.1 mmol) CH_2I_2. After 15 min stirring, the mixture was worked up as described for **8** to give a dark-red microcrystalline solid. Yield 58 mg (95%); m.p. (dec) 177°C. Found: C, 31.24; H, 4.98; Rh, 17.13. $C_{16}H_{30}I_2PRh$ calc.: C, 31.50; H, 4.96; Rh, 16.87%. MS (70 eV): *m/z* (I_r) 610 (1; M^+), 469 (4; $M^+ - CH_2I$), 436 (3; $M^+ - CH_2P^iPr_3$), 295 (48; $C_5H_5RhI^+$), 168 (100; $C_5H_5Rh^+$). ^1H NMR (CD_2Cl_2, −70°C): δ 5.05(d), *J*(RhH) 0.5 Hz, C_5H_5; 4.65(dd), *J*(RhH) 4.2, *J*(HH) 3.4 Hz, one H of $RhCH_2I$; 3.06(dd), *J*(RhH) 1.8, *J*(HH) 3.4 Hz, one H of $RhCH_2I$; 2.59(m), $PCHCH_3$; 1.52(ddd), *J*(RhH) 3.3, *J*(PH) 11.0, *J*(HH) 13.5 Hz, one H of $RhCH_2P$; 1.31(dd), *J*(PH) 14.6, *J*(HH) 7.1 Hz, $PCHCH_3$; 1.28(dd), *J*(PH) 14.4, *J*(HH) 7.1 Hz, $PCHCH_3$; 0.48(ddd), *J*(RhH) 3.2, *J*(PH) 11.2, *J*(HH) 13.5 Hz, one H of $RhCH_2P$.

*Preparation of $[C_5H_5RhCH_2Cl(CH_2P^iPr_3)I]$ (**11**)*

This was made as described for **10** but starting with 45.2 mg (0.1 mmol) **5** and 7.3 μl CH_2ClI. Red-brown crystals were obtained. Yield 48 mg (93%); m.p. (dec) 168°C. Found: C, 37.00; H, 5.87; Rh, 19.56. $C_{16}H_{30}ClIPRh$ calc.: C, 37.05; H, 5.83; Rh, 19.84%. MS (70 eV): *m/z* (I_r) 518 (1; M^+), 469 (9; $M^+ - CH_2Cl$), 391 (3; $M^+ - I$), 344 (5; $M^+ - CH_2P^iPr_3$), 295 (38; $C_5H_5RhI^+$), 168 (100; $C_5H_5Rh^+$). ^1H NMR (CD_2Cl_2, −70°C); δ 5.56(dd), *J*(RhH) 3.9, *J*(HH) 4.7 Hz, one H of $RhCH_2Cl$; 5.08(d), *J*(RhH) 0.5 Hz, C_5H_5; 3.98(dd), *J*(RhH) 2.1, *J*(HH) 4.7 Hz, one H of $RhCH_2Cl$; 2.61(m), $PCHCH_3$; 1.50(ddd), *J*(RhH) 3.2, *J*(PH) 11.2, *J*(HH) 13.3 Hz, one H of $RhCH_2P$; 1.31(dd), *J*(PH) 14.5, *J*(HH) 7.2 Hz, $PCHCH_3$; 1.29(dd), *J*(PH) 14.3, *J*(HH) 7.2 Hz, $PCHCH_3$; 0.52(ddd), *J*(RhH) 3.1, *J*(PH) 11.3, *J*(HH) 13.3 Hz, one H of $RhCH_2P$.

*Preparation of bis(ylide) complexes $[C_5H_5Rh(CH_2PR_3)(CH_2P^iPr_3)I]I$ (**12–14**)*

A solution of 61 mg (0.1 mmol) **10** in 4 ml of CH_2Cl_2 was treated dropwise at −78°C with a solution of 0.1 mmol PR_3 (R = Me: 10.2 μl; R = ^{i}Pr: 19.2 μl; R = Ph: 26.2 mg) in 1 ml of CH_2Cl_2. After 3 h stirring at −78°C, the solution was warmed to room temperature and the solvent removed *in vacuo*. The oily residue was dissolved in 3 ml of CH_2Cl_2 and ether was slowly added to the solution. The orange-red solid which separated was filtered off, repeatedly washed with ether, and dried *in vacuo*. Yield 87% (**12**), 83% (**13**), 92% (**14**).

12: m.p. (dec) 159°C. Found: C, 33.23; H, 5.83; Rh, 15.27. $C_{19}H_{40}I_2P_2Rh$ calc.:

C, 33.21; H, 5.87; Rh, 14.98%; equiv. conductivity: Λ 65 $cm^2\ \Omega^{-1}\ mol^{-1}$. ^1H NMR ($CDCl_3$): δ 5.28(d), J(RhH) 0.5 Hz, C_5H_5; 2.62(m) PC*H*CH_3; 2.37(ddd), J(RhH) 3.6, J(PH) 11.6, J(HH) 13.1 Hz, one H of $RhCH_2P$; 1.97(dd), J(RhH) 0.8, J(PH) 13.2 Hz, PMe_3; 1.33(dd), J(PH) 11.4, J(HH) 7.2 Hz, PCHC*H*$_3$; 1.31(dd), J(PH) 12.1, J(HH) 7.2 Hz, PCHC*H*$_3$; 0.82(ddd), J(RhH) 2.5, J(PH) 10.4, J(HH) 14.2 Hz, one H of $RhCH_2P'$; 0.65(ddd), J(RhH) 2.5, J(PH) 10.9, J(HH) 14.2 Hz, one H of $RhCH_2P'$; signal of one H of $RhCH_2P$ obscured by signals of phosphane protons. ^{31}P NMR ($CDCl_3$): δ 55.16(dd), J(RhP) 3.2, J(PP) 4.5 Hz, $CH_2P^iPr_3$; 35.13(dd), J(RhP) = J(PP) = 4.5 Hz, CH_2PMe_3.

13: m.p. (dec) 149 °C. Found: C, 38.98; H, 6.80; Rh, 13.06. $C_{25}H_{51}I_2P_2Rh$ calc.: C, 38.98; H. 6.67; Rh, 13.36%; equiv. conductivity: Λ 63 $cm^2\ \Omega^{-1}\ mol^{-1}$. ^1H NMR ($CDCl_3$): δ 5.30(d), J(RhH) 0.4 Hz, C_5H_5; 2.79(m), PC*H*CH_3; 1.77(ddd), J(RhH) 2.9, J(PH) 10.8, J(HH) 13.9 Hz, $RhCH_2P$; 1.39(dd), J(PH) 14.7, J(HH) 7.2 Hz, PCHC*H*$_3$; 1.34(dd), J(PH) 14.6, J(HH) 7.2 Hz, PCHC*H*$_3$; 0.89(ddd), J(RhH) 2.7, J(PH) 11.5, J(HH) 13.9 Hz, $RhCH_2P$. ^{31}P NMR ($CDCl_3$): δ 55.39(d), J(RhP) 2.9 Hz.

14: m.p. (dec) 128 °C. Found: C, 46.67; H, 5.25; Rh, 11.57. $C_{34}H_{45}I_2P_2Rh$ calc.: C, 46.81; H, 5.20; Rh, 11.80%; equiv. conductivity: Λ 66 $cm^2\ \Omega^{-1}\ mol^{-1}$. ^1H NMR ($CDCl_3$): δ 7.5(m), C_6H_5; 4.85(d), J(RhH) 0.4 Hz, C_5H_5; 2.67(m), PC*H*CH_3; 2.34(m), two H of $RhCH_2P/RhCH_2P'$; 2.04(ddd), J(RhH) 2.8, J(PH) 12.4, J(HH) 13.3 Hz, one H of $RhCH_2P'$; 1.35(dd), J(PH) 14.7, J(HH) 7.0 Hz, PCHC*H*$_3$; 1.30(dd), J(PH) 14.6, J(HH) 7.1 Hz, PCHC*H*$_3$; 0.96(ddd), J(RhH) 2.9, J(PH) 12.1, J(HH) 13.3 Hz, one H of $RhCH_2P$. ^{31}P NMR ($CDCl_3$): δ 55.47(dd), J(RhP) 3.0, J(PP) 4.4 Hz, $CH_2P^iPr_3$; 36.72(dd), J(RhP) 3.7, J(PP) 4.4 Hz, CH_2PPh_3.

*Preparation of $[C_5H_5Rh(CH_2P^iPr_3)(CH_2AsPh_3)I]I$ (**15**)*

Analogously as described for **12**–**14**, starting with 61 mg (0.1 mmol) **10** and 30.6 mg (0.1 mmol) $AsPh_3$. A brownish, microcrystalline solid was obtained. Yield 78 mg (85%); m.p. (dec) 132 °C. Found: C, 44.62; H, 5.05; Rh, 10.87. $C_{34}H_{45}AsI_2PRh$ calc.: C, 44.57; H, 4.95; Rh, 11.23%; equiv. conductivity: Λ 59 $cm^2\ \Omega^{-1}\ mol^{-1}$. ^1H NMR ($CDCl_3$): δ 7.5(m), C_6H_5; 5.48(d), J(RhH) 0.5 Hz, C_5H_5; 3.26(dd), J(RhH) 3.2, J(HH) 11.5 Hz, one H of $RhCH_2As$; 3.14(dd), J(RhH) 3.6, J(HH) 11.5 Hz, one H of $RhCH_2As$; 2.64(m), PC*H*CH_3; 2.16(ddd), J(RhH) 2.8, J(PH) 11.5, J(HH) 12.3 Hz, one H of $RhCH_2P$; 1.29(dd), J(PH) 13.4, J(HH) 7.2 Hz, PCHC*H*$_3$; 1.22(dd), J(PH) 13.5, J(HH) 7.2 Hz, PCHC*H*$_3$; 0.82(ddd), J(RhH) 2.6, J(PH) 11.4, J(HH) 12.3 Hz, on H of $RhCH_2P$. ^{31}P NMR ($CDCl_3$): δ 53.72(d), J(RhP) 3.2 Hz. ^{13}C NMR ($CDCl_3$): δ 133.47(s), 132.63(s), 130.35(s), 128.79(s), all C_6H_5; 89.17(d), J(RhC) 4.5 Hz, C_5H_5; 28.83(d), J(RhC) 25.2 Hz, Rh*C*H_2As; 20.40(d), J(PC) 40.2 Hz, P*C*HCH_3; 17.48(s) and 17.40(s), PCH*C*H_3; −3.24(dd), J(RhC) 16.4, J(PC) 22.3 Hz, Rh*C*H_2P.

*Reaction of $[C_5H_5RhCH_2I(CH_2P^iPr_3)I]$ (**10**) with NEt_3*

A solution of 61 mg (0.1 mmol) **10** in 4 ml of CH_2Cl_2 was treated dropwise at −78 °C with 19.0 µl (0.1 mmol) of NEt_3. After being stirred for 4 h, ether (−78 °C) was added to the solution. A red oily precipitate was formed which was separated from the mother liquor and repeatedly washed with ether. The residue was dissolved in 2 ml of THF and pentane was added to the solution. A light brown solid was

isolated which according to the ^1H and ^{31}P NMR spectra contained ca. 70% $[C_5H_5Rh(CH_2P^iPr_3)(CH_2NEt_3)I]I$ (**16**) and ca. 30% **8**. All attempts to separate the two complexes by fractional crystallization or chromatographic techniques failed. Spectroscopic data of **16** are as follows: ^1H NMR ($CDCl_3$): δ 5.21(d), J(RhH) 0.5 Hz, C_5H_5; 3.88(dd), J(RhH) 3.7, J(HH) 11.2 Hz, one H of $RhCH_2N$; 3.62(dd), J(RhH) 3.9, J(HH) 11.2 Hz, one H of $RhCH_2N$; 3.18(dq), $^2J(HH) = {}^3J(HH)$ 7.2 Hz, one H of NCH_2CH_3; 3.14(dq), $^2J(HH) = {}^3J(HH) = 7.2$ Hz, one H of NCH_2CH_3; 2.43(m), $PCHCH_3$; 1.65(ddd), J(RhH) 2.6, J(PH) 11.3, J(HH) 12.5 Hz, one H of $RhCH_2P$; 1.35(t), J(HH) 7.2 Hz, NCH_2CH_3; 1.18(dd), J(PH) 12.8, J(HH) 7.5 Hz, $PCHCH_3$; 1.15(dd), J(PH) 12.8, J(HH) 7.4 Hz, $PCHCH_3$; 0.54(ddd), J(RhH) 2.5, J(PH) 11.2, J(HH) 12.5 Hz, one H of $RhCH_2P$. ^{31}P NMR ($CDCl_3$): δ 53.36(d), J(RhP) 3.0 Hz.

Reaction of $[C_5H_5Rh(CH_2P^iPr_3)(CO)]$ (7) with I_2

A solution of 37 mg (0.1 mmol) **7** in 5 ml of ether was treated dropwise with a solution of 25.4 mg (0.1 mmol) I_2 in 3 ml of ether. A dark-red precipitate was immediately formed, and after 5 min stirring of the mixture it was separated from the mother liquor, repeatedly washed with ether, and dried *in vacuo*. The red solid was shown from its NMR data to be **8**. Yield quantitative.

Reaction of $[C_5H_5Rh(CH_2P^iPr_3)(CO)]$ (7) with CH_3I and CD_3I

A solution of 37 mg (0.1 mmol) **7** in 5 ml of benzene was treated dropwise with a solution of 6.3 μl (0.1 mmol) CH_3I and the mixture stirred for 15 min at room temperature. The solvent was removed *in vacuo* to leave a red oil, which was repeatedly washed with ether and then dissolved in 5 ml of THF. The solution was filtered and the filtrate was concentrated to ca. 2 ml *in vacuo*. A red precipitate was formed, which according to the ^1H NMR spectrum consisted of ca. 70% $[C_5H_5RhCH_3(CH_2P^iPr_3)(CO)]I$ (**17a**) and ca. 30% **8**. Attempts to separate the two complexes by fractional crystallization or column chromatography were unsuccessful. The ^1H NMR spectroscopic data of **17a** are almost the same as those of **17c**.

When the same reaction was carried out with CD_3I, a mixture of $[C_5H_5RhCD_3(CH_2P^iPr_3)(CO)]I$ (**17b**) and **8** (70/30) was obtained. Except for the signal for the $RhCH_3$ protons at δ 0.92, the ^1H NMR spectrum of **17b** is identical to that of **17a**.

Preparation of $[C_5H_5RhCH_3(CH_2P^iPr_3)(CO)]SO_4Me$ (17c)

A solution of 8.5 μl (0.1 mmol) dimethylsulfate in 5 ml of benzene was treated dropwise with a solution of 37 mg (0.1 mmol) **7** in 3 ml of benzene. After 15 min stirring at room temperature, the solvent was removed *in vacuo*, and the orange-red oily residue was extracted with THF. The extract was concentrated to ca. 2 ml and ether was added. After standing for several hours orange microcrystals had separated and were filtered off and repeatedly washed with ether. Yield 51 mg (78%); m.p. (dec) 82°C. Found: C, 43.57; H, 6.99; Rh, 20.47. $C_{18}H_{34}O_5$ PRhS calc.: C, 43.55; H, 6.90; Rh, 20.73%; equiv. conductivity: Λ 65 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR (KBr): ν(CO) 2020, $\nu(SO_4Me)$ 1233, 1228, 1017 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.67(d), J(RhH) 0.4 Hz, C_5H_5; 3.62(s), SO_4Me; 2.59(m) $PCHCH_3$; 2.33(ddd), J(RhH) 3.8, J(PH) 10.5, J(HH) 13.6 Hz, one H of $RhCH_2P$; 1.33(dd), J(PH) 15.2, J(HH) 7.2 Hz, $PCHCH_3$; 1.28(dd), J(PH) 14.8, J(HH) 7.2 Hz, $PCHCH_3$; 0.92(dd), J(RhH)

2.4, J(PH) 0.9 Hz, $RhCH_3$; 0.21(ddd), J(RhH) 2.6, J(PH) 10.7, J(HH) 13.6 Hz, one H of $RhCH_2P$. ^{31}P NMR ($CDCl_3$): δ 52.87(d), J(RhP) 3.5 Hz. ^{13}C NMR ($CDCl_3$): δ 191.46(d), J(RhC) 76.1 Hz, CO; 94.20(d), J(RhC) 2.8 Hz, C_5H_5; 54.00(s), SO_4CH_3; 22.40(d), J(PC) 38.9 Hz, $PCHCH_3$; 17.40(s) and 17.35(s), $PCHCH_3$; −13.53(d), J(RhC) 19.5 Hz, $RhCH_3$; −26.01(dd), J(RhC) = J(PC) = 33.3 Hz, $RhCH_2P$.

Complex **17c** was also obtained when a solution of 0.1 mmol CH_3I or CD_3I and 8.5 μl (0.1 mmol) $(CH_3O)_2SO_2$ in 5 ml of benzene was treated with a solution of 37 mg (0.1 mmol) **7** in 3 ml of benzene. The ^1H NMR spectrum of the isolated product showed only the signals of $[C_5H_5RhCH_3(CH_2P^iPr_3)(CO)]^+$ and SO_4Me^-, and not those of $[C_5H_5RhCD_3(CH_2P^iPr_3)(CO)]^+$.

Preparation of $[C_5H_5RhCOCH_3(CH_2P^iPr_3)(P^iPr_3)]SO_4Me$ (18)

A solution of 49.2 mg (0.1 mmol) **17c** in 3 ml of CH_2Cl_2 was treated with 19.2 μl (0.1 mmol) P^iPr_3. After 12 h stirring at room temperature, the solvent was removed and the oily residue was extracted with THF. The extract was evaporated to dryness *in vacuo* and the residual bright red oil was repeatedly washed with pentane. Yield 51 mg (78%); m.p. (dec) 121°C. Found: C, 49.17; H, 8.72. $C_{27}H_{55}O_5P_2RhS$ calc.: C, 49.39; H, 8.44%; equiv. conductivity: Λ 67 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR (KBr): ν(C=O) 1625, $\nu(SO_4Me)$ 1233, 1228, 1017 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.61(dd), J(RhH) 0.4, J(PH) 1.3 Hz, C_5H_5; 2.62(s), $COCH_3$; 2.51(m), $PCHCH_3$; 1.54(dddd), J(RhH) 4.0, J(PH) 13.9 and 4.0, J(HH) 12.1 Hz, one H of $RhCH_2P$; 1.26(dd) and 1.22(dd), J(PH) 14.2, J(HH) 7.0 Hz, $RhCH_2PCHCH_3$; 1.17(dd) and 1.11(dd), J(PH) 13.7, J(HH) 7.2 Hz, $RhPCHCH_3$; 0.80(dddd), J(RhH) 4.2, J(PH) 12.1 and 4.2, J(HH) 12.1 Hz, one H of $RhCH_2P$. ^{31}P NMR ($CDCl_3$): δ 57.17(dd), J(RhP) = J(PP) 4.5 Hz, $RhCH_2P$; 53.75(dd), J(RhP) 156.3, J(PP) 4.5 Hz, RhP. ^{13}C NMR ($CDCl_3$): δ 235.19(dd), J(RhC) 48.8, J(PC) 13.3 Hz, $RhCOCH_3$; 92.22(dd), J(RhC) 2.8, J(PC) 4.3 Hz, C_5H_5; 53.96(s), SO_4CH_3; 53.06(s), $COCH_3$; 21.68(d), J(PC) 42.5 Hz, $PCHCH_3$; 19.89(d), J(PC) 31.7 Hz, $PCHCH_3$; 17.49(s), 17.41(s), 17.28(s), 17.23(s), all $PCHCH_3$; −21.14(ddd), J(RhC) 26.6, J(PC) 37.3 and 10.7 Hz, $RhCH_2P$.

X-Ray crystallographic study of 17c

Single crystals were grown from acetone/ether at room temperature. Crystal data collection parameters are summarized in Table 2. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied; the minimal transmission was 92.1%. The structure was solved by direct methods (SHELXS-86). Atomic coordinates (See Table 3) and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares. The hydrogen atoms were placed at calculated positions and refined using the riding method. Owing to disorder problems, the methyl carbon atom of the SO_4Me anion could not be exactly located. The final electron density was found at a maximum distance of 1.3 Å from the oxygen atoms and presumably originated from the SO_4Me carbon atom. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-55186, the names of the authors, and the journal citation.

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