ORGANOMETALLICS

Metal basicity. 63. Novel ylide-type rhodium complexes containing a six-membered [cyclic] RhCH2PR2CH2PR2 ring

Helmut. Werner, Lothar. Hofmann, Wilfried. Paul, and Ulrich. Schubert

Organometallics, **1988**, 7 (5), 1106-1111• DOI: 10.1021/om00095a014 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

together with appropriate cut of light filters ($\lambda \geq 320$ nm). The beam was focused on the center of the microwave cavity.

Acknowledgment. Dr. W. Kaim is thanked for stimulating discussions and for his critical reading of the manuscript.

Registry No. $Re(CO)_3$(*i*-Pr-DAB)′, 113110-69-3; $Re(CO)_3$(*t*-Bu-DAB)′, 113110-70-6; $Re(CO)_3$(*p*-Tol-DAB)′, 113110-71-7; $Re(CO)_3$(*i*-Pr-PyCa)′, 113110-72-8; $Re(CO)_3$(phen)′, 113110-73-9; $Mn(CO)_3$(*t*-Bu-DAB)′, 96455-75-3; $(PPh_3)Re(CO)_3$(*t*-Bu-DAB), 113110-74-0; $(P(OPh)_3)Re(CO)_3$(*t*-Bu-DAB), 113110-75-1; $(P(OMe)_3)Re(CO)_3$(*t*-Bu-DAB), 113110-76-2; (Pyridine)$Re(CO)_3$(*t*-Bu-DAB), 113110-77-3; (*t*-Bu)N(O′)$Re(CO)_3$(*p*-Tol-DAB), 113110-78-4; (*t*-Bu)N(O′)$Re(CO)_3$(*t*-Bu-DAB), 113110-79-5; (*t*-Bu)N(O′)$Re(CO)_3$(*i*-Pr-PyCa), 113110-80-8; (*t*-Bu)N(O′)$Re(CO)_3$(phen), 113132-25-5; (*t*-Bu)N(O′)$Re(CO)_3$(bpy′), 113110-81-9; (*t*-Bu)N(O′)$Mn(CO)_3$(*i*-Pr-PyCa), 113110-82-0; (*t*-Bu)N(O′)$Mn(CO)_3$(phen), 113132-26-6; (*t*-Bu)N(O′)$Mn(CO)_3$(bpy′), 113132-27-7.

Novel Ylide-Type Rhodium Complexes Containing a Six-Membered $\overline{RhCH_2PR_2CH_2CH_2PR_2}$ Ring[1]

Helmut Werner,* Lothar Hofmann, Wilfried Paul, and Ulrich Schubert

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg, Germany

Received August 20, 1987

The chelate rhodium(I) complexes $C_5H_5Rh[1,2\text{-}C_2H_4(PR_2)_2]$ (**2**, R = Ph; **3**, R = Me) have been prepared from $[L_2RhCl]_2$ (L = C_2H_4, C_8H_{14}), the diphosphine (dppe or dmpe), and MC_5H_5 (M = Na, Tl). Compounds **2** and **3** react with CH_2I_2 by oxidative addition to give the (iodomethyl)rhodium(III) compounds $[C_5H_5RhCH_2I(1,2\text{-}C_2H_4(PR_2)_2)]I$ (**4a**, **5a**) which have been converted by reaction with NH_4PF_6 to the more stable PF_6 salts **4b** and **5b**. Whereas **4b** is completely inert in nitromethane solution, **5b** on addition of NEt_3 isomerizes quantitatively to give the metallaheterocycle $[C_5H_5(I)\overline{RhCH_2PMe_2CH_2CH_2PMe_2}]PF_6$ (**7**). The corresponding dicationic derivative $[C_5H_5(PMe_3)\overline{RhCH_2PMe_2CH_2CH_2PMe_2}](PF_6)_2$ (**8**) is obtained by ligand exchange. The molecular structure of **7** has been determined by X-ray analysis. Compound **7** crystallizes in the space group $P2_1/n$ with $a = 848.2$ (2) pm, $b = 1489.5$ (4) pm, $c = 1594.6$ (4) pm, and $\beta = 103.17$ (2)°. The six-membered ring in the cation of **7** adopts a chair conformation. Complex **7** has also been prepared from $C_5H_5RhCH_2I[P(OMe)_3]I$ and dmpe in the presence of NH_4PF_6. In contrast, the analogous (iodomethyl)rhodium compound $C_5H_5RhCH_2I(PMe_3)I$ reacts with dmpe (and NH_4PF_6) to produce a dinuclear-bridged species which presumably has the composition $\{[C_5H_5(PMe_3)(I)Rh]_2(\mu\text{-}CH_2PMe_2CH_2CH_2PMe_2CH_2)\}(PF_6)_2$ (**9**). The cobalt complexes C_5H_5Co(dmpe) (**12**), $[C_5H_5(CO)Co]_2(\mu\text{-dmpe})$ (**13**), $C_5H_5Co(CO)(\eta^1\text{-dppm})$ (**14**), and $[C_5H_5CoCOCH_3(\eta^2\text{-dppm})]I$ (**15**) also have been prepared by using either $C_5H_5Co(PMe_3)_2$ or $C_5H_5Co(CO)_2$ as starting material.

Introduction

We have recently shown that cyclopentadienylcobalt and -rhodium complexes of general composition C_5H_5MLL' (where L = PR_3 and L′ = PR_3, $P(OR)_3$, CO, C_2H_4, etc.) are *metal bases* and react not only with Brønsted acids and alkyl iodides but also with CH_2I_2 and other dihalomethanes by oxidative addition.[2] The two types of products obtained, $[C_5H_5MCH_2X(L)L']X$ and $[C_5H_5MCH_2X(L)X]$, contain a carbenoid–metal fragment that proved to be very reactive toward nucleophiles. Using the neutral (iodomethyl)rhodium complex 1 as an example, the results summarized in Scheme I illustrate that the course of the nucleophilic attack on the C–X bond of the $RhCH_2X$ unit is strongly dependent on the nature of the nucleophile used. Whereas with pyridine, phosphines, and phosphites cationic ylide rhodium compounds are formed,[3] treatment of 1 with SH^-, SeH^-, or TeH^- gives, probably via a $RhCH_2EH$ intermediate, the corresponding thio-, seleno-, and telluroformaldehyde complexes.[4] The hydroxide ion, however, in presence of a phase-transfer catalyst, reacts with 1 in a different way, producing the isomer $[C_5H_5Rh(CH_2PMe_3)I_2]$ which is not accessible by other routes.[3,4]

It was this unexpected isomerization that led us to investigate the mechanism and scope of this reaction in more detail. During these studies we observed that also the ionic carbenoid complexes $[C_5H_5RhCH_2I(PMe_3)_2]PF_6$ and $[C_5H_5RhCH_2I(PR_3)L]PF_6$ isomerize thermally or in the presence of NEt_3 to produce ylide rhodium compounds of composition $[C_5H_5Rh(CH_2PMe_3)(PMe_3)I]PF_6$ and $[C_5H_5Rh(CH_2PR_3)(L)I]PF_6$.[5] Kinetic studies for PR_3 = PMe_3 and L = $P(OMe)_3$ revealed a distinct dependence of the rate of isomerization on the NEt_3 concentration and suggested an intramolecular exchange mechanism similar to that known for dyotropic rearrangements. The question that seemed to be most interesting to us, however, was whether carbenoid complexes having a *chelate* ligand coordinated to the metal would behave similarly and would thus open a synthetic route to cyclic ylide-type transition-metal complexes. It is worth mentioning that more recently Weber et al., using a different approach to this target, prepared five- and six-membered ylide-chelate chromium compounds by the reaction of $Cr(CO)_5[CH_2S(O)Me_2]$ with $CH_2(ER_2)_2$ and $1,2\text{-}C_2H_4(ER_2)_2$ (E = P, As), respectively.[6] A short communication describing some

---

[1] Part 63 of the series "Metal Basicity". For part 62, see: Dziallas, M.; Höhn, A.; Werner, H. *J. Organomet. Chem.* **1987**, *330*, 207.

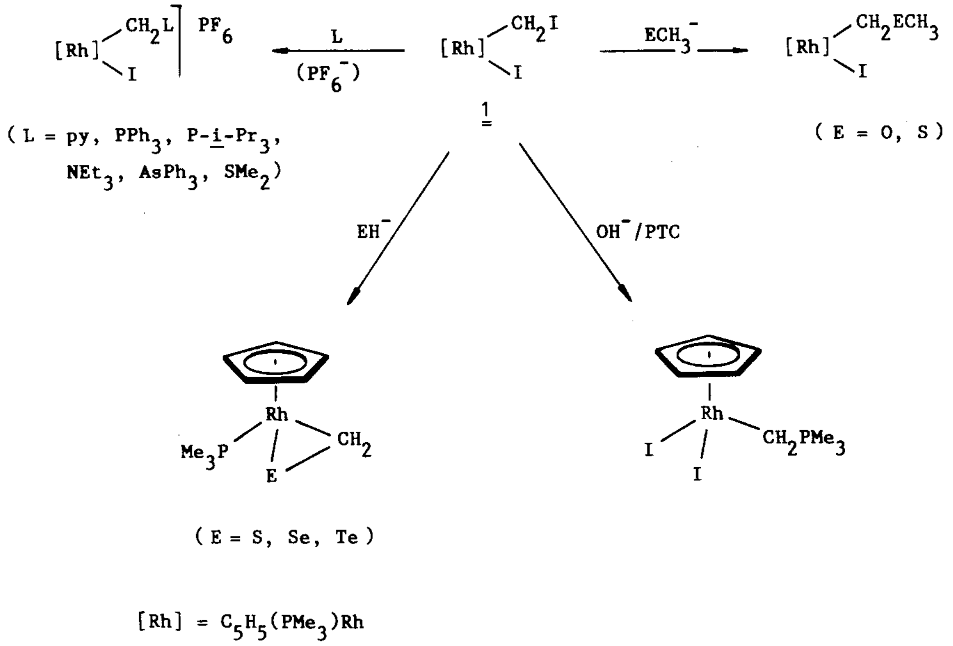
[2] Werner, H. *Angew. Chem.* **1983**, *95*, 932; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 927.

[3] (a) Werner, H.; Feser, R.; Paul, W.; Hofmann, L. *J. Organomet. Chem.* **1981**, *219*, C29. (b) Werner, H.; Paul, W.; Feser, R.; Zolk, R.; Thometzek, P. *Chem. Ber.* **1985**, *118*, 261.

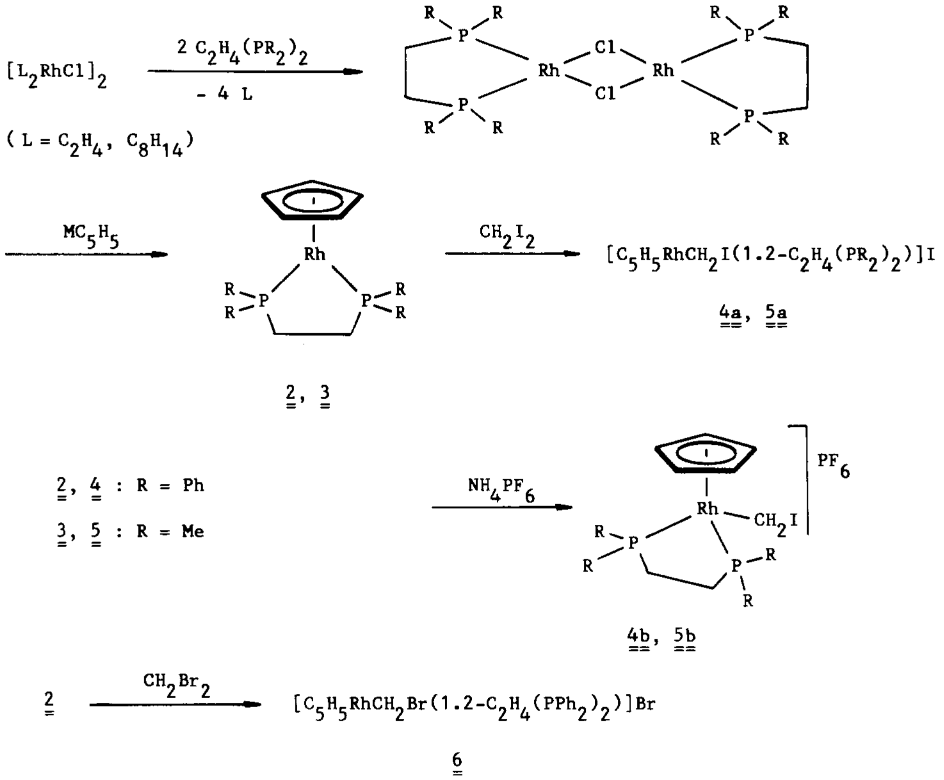
[4] (a) Paul, W.; Werner, H. *Angew. Chem.* **1983**, *95*, 333; Angew. *Chem., Int. Ed. Engl.* **1983**, *22*, 316; *Angew. Chem. Suppl.* **1983**, 396. (b) Werner, H.; Paul, W.; Knaup, W.; Wolf, J.; Müller, G., manuscript to be submitted.

[5] Werner, H.; Hofmann, L.; Feser, R.; Paul, W. *J. Organomet. Chem.* **1985**, *281*, 317.

Scheme I



Scheme II



preliminary results of our work has already appeared.[7]

Results

Rhodium Complexes. The synthesis of the cyclopentadienylrhodium(I) complexes $C_5H_5Rh[1,2\text{-}C_2H_4(PR_2)_2]$ (**2**, R = Ph; **3**, R = Me) followed the same route that was previously used to prepare the nonchelate compounds $C_5H_5Rh(PR_3)_2$[8] and $C_5H_5Rh[P(OR)_3]_2$.[9] For an increase in the yield, the dinuclear chloro-bridged intermediates $\{[1,2\text{-}C_2H_4(PR_2)_2]RhCl\}_2$ are not isolated but are treated directly in solution with TlC_5H_5 or NaC_5H_5, respectively. Faraone et al. have independently reported the preparation of **2**,[10] starting with $C_5H_5Rh(CO)_2$ and displacing the CO ligands by 1,2-bis(diphenylphosphino)ethane (dppe) at higher temperatures.

The reactions of **2** and **3** with CH_2I_2 proceed smoothly and give the (iodomethyl)rhodium complexes $[C_5H_5RhCH_2I(1,2\text{-}C_2H_4(PR_2)_2)]I$ (**4a**, R = Ph; **5a**, R = Me)

---

(6) (a) Weber, L.; Wewers, D.; Meyer, W.; Boese, R. *Chem. Ber.* **1984**, *117*, 732. (b) Weber, L.; Wewers, D. *Chem. Ber.* **1984**, *117*, 1103. (c) Weber, L.; Wewers, D. *Organometallics* **1985**, *4*, 841.

(7) Werner, H.; Hofmann, L.; Paul, W. *J. Organomet. Chem.* **1982**, *236*, C 65.

(8) Werner, H.; Feser, R.; Buchner, W. *Chem. Ber.* **1979**, *112*, 834.

(9) Neukomm, H.; Werner, H. *Helv. Chim. Acta* **1974**, *57*, 1067.

(10) Faraone, F.; Bruno, G.; Schiavo, S. L.; Tresoldi, G.; Bombieri, G. *J. Chem. Soc., Dalton Trans.* **1983**, 433.

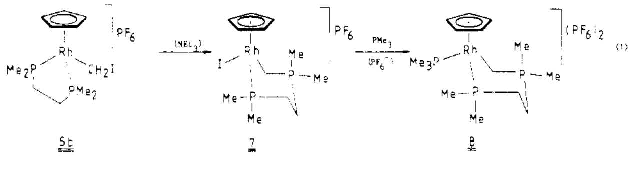
Table I. ^{1}H NMR Data of Compounds 2–9, 12, and 13 (δ; Internal TMS; *J* and *N* in Hz)[a]

compd	$\delta(C_5H_5)$	$J(PH)$	$J(RhH)$	$\delta(PR_2)$	$J(PH)/N$	$\delta(MCH_2)$	$J(PH)$	$J(RhH)$	$\delta(PC_2H_4P)$
2	5.20 (d, br)[b]		0.8	7.54 (m)					2.32 (dd)[c]
3	5.49 (dt)	0.7	0.7	1.44 (dvt)[d]	9.5				1.18 (dd)[e]
4b	5.76 (dt)	1.3	0.3	7.88 (m)		2.09 (dt)	12.5	1.3	2.99 (m)
5b	5.45 (dt)	1.4	0.5	1.68 (d) 1.48 (d)	12.4 12.4	2.53 (dt)	5.4	1.7	1.95 (m)
6	5.80 (dt)	1.0	0.4	7.72 (m)		2.13 (dt)	11.5	1.1	2.93 (m)
7	5.61 (dd)	3.2	0.5	*f*		*g*			2.00 (m)
8	5.97 (t, br)[h]	2.3		1.60 (br)[i]		*g*			2.05 (m)
9	5.63 (dd)	2.5	0.4	*j*		*g*			2.40 (m)
12	4.78 (t)	1.1		1.38 (vt)	9.4				1.39 (m)[k]
13	4.70 (t)	0.7		1.10 (vt)	8.2				1.43 (m)

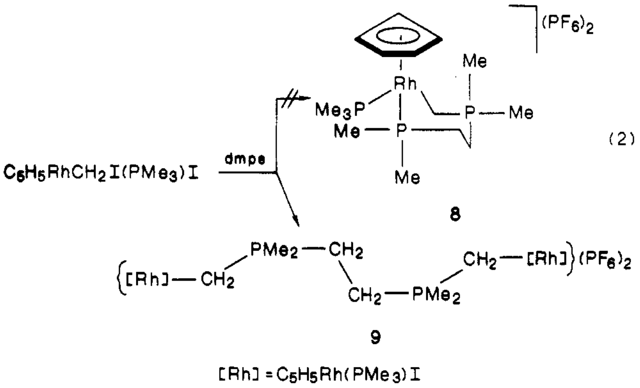
[a] Spectra of **2**, **5b**, and **7** in acetone-d_6, of **3**, **12**, and **13** in benzene-d_6, of **4b**, **6**, and **9** in nitromethane-d_3, and of **8** in dimethyl-d_6 sulfoxide. Abbreviations used: s, singlet; d, doublet; t, triplet; m, multiplet; vt, virtual triplet. [b] $J(PH)$ not resolved; after $^1H\{^{31}P\}$ decoupling sharp doublet. [c] $J(PH) = 17.7$, $J(RhH) = 1.3$ Hz. [d] $J(RhH) = 1.2$ Hz. [e] $J(PH) = 17.6$, $J(RhH) = 1.2$ Hz. [f] Four signals for the four different PCH_3 groups: δ 1.83 (d), $J(PH) = 11.5$ Hz; δ 1.81 (d), $J(PH) = 11.5$ Hz; δ 1.80 (d), $J(PH) = 14.0$ Hz; δ 1.77 (d), $J(PH) = 14.0$ Hz. [g] Signal could not be exactly located. [h] PMe_3 and PMe_2CH_2 units are virtually equivalent; broadening probably due to conformational exchange of PMe_3 between axial and equatorial positions. [i] Broadening probably due to overlap of PMe_3 and PMe_2 signals; $\delta(RhCH_2PMe_2)$ 1.80 (d), $J(PH) = 13.2$ Hz. [j] $\delta(PMe_3)$ 1.82 (dd), $J(PH) = 11.0$, $J(RhH) = 0.8$ Hz; $\delta(RhCH_2PMe_2)$ 1.98 (d), $J(PH) = 12.1$ Hz. [k] Spin system not analyzed, $J(PH) = 14.2$ Hz.

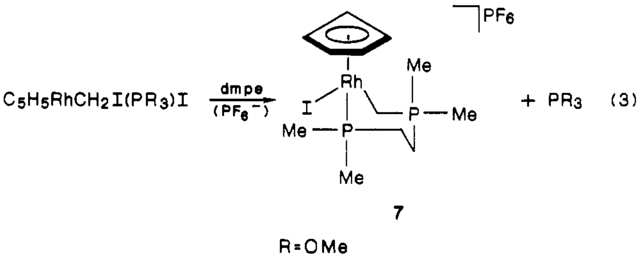
in good yield. Whereas **4a** has been isolated, **5a** was converted directly with NH_4PF_6 to the more stable PF_6 salt **5b**. Both **4a** and **5b** (as well as **5a**) are light brown, moderately air-stable solids that have been characterized by elemental analysis, conductivity measurements, and NMR spectroscopic data (see Table I). Expectedly, CH_2Br_2 is much less reactive toward **2** than CH_2I_2, and, therefore, the preparation of **6** requires a much longer reaction time (30 h at 25 °C) than that of **4a**. By following the reaction by ^{1}H NMR spectroscopy, some line broadening is observed which indicates that possibly small quantities of paramagnetic side products are formed. It has already been found in our laboratory that on treatment of $C_5H_5Rh(PMe_3)_2$ with secondary and tertiary alkyl halides, besides the expected products $[C_5H_5Rh(PMe_3)_2R]^+$, the corresponding bromo- and iodorhodium cations $[C_5H_5Rh(PMe_3)_2X]^+$ are produced which also probably originate from a radical-type mechanism.[2,11]

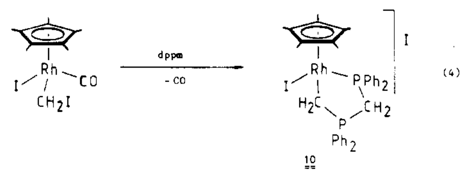
Whereas **4b** is completely inert in nitromethane solution and does not react even in the presence of NaOH to form a six-membered metallaheterocycle, the analogue **5b** on addition of NEt_3 isomerizes quantitatively to give **7**. The reaction can be easily monitored by ^{1}H NMR spectroscopy where during the rearrangement a characteristic change in both the C_5H_5 and the PMe_2 proton region is observed. On the basis of the ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic data (see Table I and Experimental Section) we assume that complex **7** has the same chairlike conformation also in solution which is found in the crystal.



The Rh–I bond in the cation of **7** is rather labile, and therefore **7** readily reacts with PMe_3 to produce the dicationic derivative **8**. In contrast to **7** which is orange-red, **8** is a bright yellow crystalline solid which in nitromethane behaves as a 1:2 electrolyte. Various attempts to prepare the metallaheterocycle **8** by an independent route starting with $C_5H_5RhCH_2I(PMe_3)I$ and $1,2-C_2H_4(PMe_2)_2$ (dmpe) and substituting both iodides by the diphosphine remained unsuccessful. A red, crystalline product, **9**, has been isolated which besides PF_6^- contains two phosphorus and one iodine per rhodium atom and for which the structure shown in eq 2 is tentatively assigned. It seems worth mentioning that on treatment of the trimethyl *phosphite* derivative $C_5H_5RhCH_2I(PR_3)I$ (R = OMe) with dmpe complex **7** also is obtained which means that now two independent synthetic pathways are available for this metallaheterocycle.







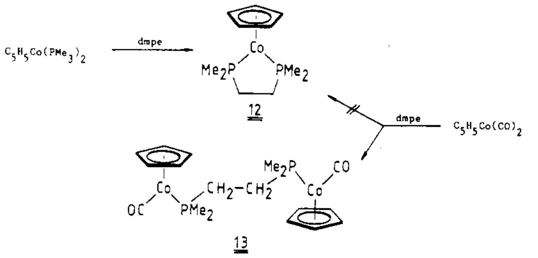
To the best of our knowledge, besides the chromium chelates $(CO)_4\overline{CrCH_2PR_2(CH_2)_2P}R_2$ recently described by Weber and Wevers,[6c] the rhodium compounds **7** and **8** are the first examples[7] of ylide-type transition metal complexes containing a MCPCCP six-membered ring in which the metal-bound carbon atom is *unsubstituted*. Oosawa[12] as

---

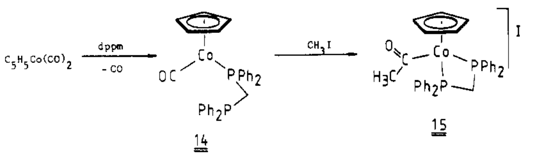
(11) Feser, R. Dissertation, Universität Würzburg, 1981.

(12) Oosawa, Y.; Urabe, H.; Saito, T.; Sasaki, Y. *J. Organomet. Chem.* **1976**, *122*, 113.

Scheme III



Scheme IV



well as Schmidbaur et al.[13] previously reported the preparation of palladium derivatives containing a MCPCCP six-membered ring but in these compounds the ylidic carbon atom carries at least one substituent. We recently prepared the five-membered metallaheterocycle **10** which like **8** also has a $RhCH_2PR_2$- unit from $C_5Me_5RhCH_2I(CO)I$ and $CH_2(PPh_2)_2$ (dppm) according to eq 4 by a consecutive displacement process.[14]

Cobalt Complexes. The chelate compound C_5H_5Co(dppe) (**11**) had originally been prepared by Rinze[15] and more recently in our laboratory by treating the heterometallic dinuclear complex $[C_5H_5(PMe_3)Co(\mu\text{-}CO)_2Mn(CO)C_5H_4Me]$ with dppe.[16] During the present investigation the synthesis of C_5H_5Co(dmpe) (**12**), i.e., the cobalt analogue of **3**, was first tried by reaction of $C_5H_5Co(CO)_2$ and dmpe, but this method only gives the bridged species $[C_5H_5(CO)Co]_2(\mu\text{-dmpe})$ (**13**) (Scheme III) in 80% yield. Compound **12** can be obtained, however, by using the bis(trimethylphosphine) complex $C_5H_5Co(PMe_3)_2$ as starting material and displacing the monodentate PMe_3 ligands by the chelating diphosphine. Like $C_5H_5Co(PMe_3)_2$,[17] **12** forms dark brown, very air-sensitive crystals that are very soluble in hydrocarbon solvents. C_5Me_5Co(dmpe), the ring-substituted counterpart of **12**, has been prepared recently by Green et al.[18] from $[C_5Me_5Co(\mu\text{-}CO)]_2$ and dmpe and the electronic structure studied by photoelectron spectroscopy.

Various attempts to obtain a carbenoid cobalt compound from **12** and CH_2I_2 or CH_2ClI failed. The strikingly different behavior between **3** and **12** toward dihalomethanes is in agreement with our previous observations[19] that the preparation of cobalt complexes of the general type $[C_5H_5CoCH_2X(L)X]$ or $[C_5H_5CoCH_2X(L)L']X$ is much more difficult than that of the rhodium analogues. It should be mentioned that **13** also does not react with CH_2I_2 or CH_2Br_2 in benzene to give a stable Co–CH_2X- or Co–CH_2PMe_2-containing product.

In contrast to the reaction of $C_5H_5Co(CO)_2$ with dmpe, which produces the dinuclear compound **13**, treatment of the cyclopentadienylcobalt dicarbonyl with $CH_2(PPh_2)_2$ (dppm) leads to the formation of the mononuclear complex $C_5H_5Co(CO)(\eta^1\text{-dppm})$ (**14**) (Scheme IV). This new compound in which only one phosphorus atom of the diphosphine is linked to the metal again is not a suitable precursor for the synthesis of a carbenoid or ylide-type product. It reacts, however, with methyl iodide to give

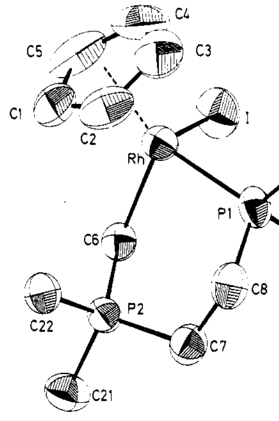


Figure 1. A drawing of the cation of **7** showing the molecular structure and atom numbering. Hydrogen atoms have been omitted for clarity.

Table II. Relevant Bond Distances (pm) and Bond Angles (deg) for 7

Bond Distances			
Rh–I	267.4 (1)	P(1)–C(8)	182.4 (7)
Rh–P(1)	225.9 (2)	P(1)–C(11)	183.7 (6)
Rh–C(1)	223.3 (6)	P(1)–C(12)	179.5 (7)
Rh–C(2)	217.6 (7)	C(7)–C(8)	152.9 (9)
Rh–C(3)	221.2 (8)	P(2)–C(6)	176.2 (6)
Rh–C(4)	220.8 (10)	P(2)–C(7)	179.2 (6)
Rh–C(5)	221.5 (9)	P(2)–C(21)	179.7 (6)
Rh–C(6)	212.1 (5)	P(2)–C(22)	178.6 (6)

Bond Angles			
I–Rh–C(6)	88.6 (2)	P(1)–C(8)–C(7)	114.1 (4)
I–Rh–P(1)	95.64 (4)	P(2)–C(7)–C(8)	115.0 (5)
P(1)–Rh–C(6)	87.6 (2)	C(6)–P(2)–C(7)	110.4 (3)
Rh–P(1)–C(8)	113.5 (2)	C(6)–P(2)–C(21)	111.3 (3)
Rh–P(1)–C(11)	118.5 (2)	C(6)–P(2)–C(22)	113.1 (3)
Rh–P(1)–C(12)	115.0 (3)	C(21)–P(2)–C(22)	106.8 (3)
C(11)–P(1)–C(12)	102.7 (3)	P(2)–C(6)–Rh	118.1 (3)

Table III. Positional Parameters for the Non-Hydrogen Atoms and Their Estimated Standard Deviation for $[(C_5H_5)(I)RhCH_2PMe_2CH_2CH_2PMe_2]PF_6$ (7)

atom	x/a	y/b	z/c
Rh	0.39879 (6)	0.29086 (3)	0.42200 (3)
I	0.64223 (6)	0.30244 (3)	0.56153 (3)
C(1)	0.4093 (10)	0.2840 (5)	0.2835 (4)
C(2)	0.2789 (9)	0.3343 (5)	0.2929 (4)
C(3)	0.3347 (13)	0.4113 (5)	0.3402 (5)
C(4)	0.5013 (14)	0.4051 (6)	0.3640 (5)
C(5)	0.5475 (10)	0.3267 (7)	0.3294 (5)
C(6)	0.3980 (7)	0.1499 (4)	0.4404 (3)
C(7)	0.0642 (7)	0.1271 (4)	0.4561 (4)
C(8)	0.0261 (8)	0.2276 (4)	0.4496 (4)
P(1)	0.1997 (21)	0.29922 (9)	0.49432 (9)
C(11)	0.2460 (9)	0.2686 (5)	0.6089 (4)
C(12)	0.1078 (10)	0.4080 (4)	0.4942 (5)
P(2)	0.21563 (18)	0.09130 (9)	0.40121 (8)
C(21)	0.2415 (9)	−0.0273 (4)	0.4200 (4)
C(22)	0.1377 (8)	0.1055 (4)	0.2882 (4)
P(3)	0.8403 (2)	0.4967 (1)	0.2199 (1)
F(1)	0.7688 (8)	0.5252 (4)	0.2992 (3)
F(2)	0.7908 (6)	0.5895 (3)	0.1791 (4)
F(3)	0.8887 (6)	0.4030 (3)	0.2646 (3)
F(4)	0.6698 (5)	0.4571 (3)	0.1775 (3)
F(5)	1.0084 (6)	0.5364 (4)	0.2634 (4)
F(6)	0.9071 (8)	0.4658 (4)	0.1444 (4)

---

[13] Holy, N.; Deschler, U.; Schmidbaur, H. *Chem. Ber.* **1982**, *115*, 1379.

[14] Paul, W.; Werner, H. *Chem. Ber.* **1985**, *118*, 3032.

[15] Rinze, P. V. Dissertation, Universität Marburg, 1970. For an improved method see: Koelle, U.; Ohst, S. *Inorg. Chem.* **1986**, *25*, 2689.

[16] Juthani, B. Dissertation, Universität Würzburg, 1980. The synthesis of 11 starting with the (Co–Mn) complex is very similar to that of various $C_5H_5Co(PMe_3)L$ compounds; see: Leonhard, K.; Werner, H. *Angew. Chem.* **1977**, *89*, 656; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 649.

[17] Werner, H.; Hofmann, W. *Chem. Ber.* **1977**, *110*, 3481.

[18] Dudeney, N.; Green, J. C.; Grebenik, P.; Kirchner, O. N. *J. Organomet. Chem.* **1983**, *252*, 221.

[19] Hofmann, L.; Werner, H. *J. Organomet. Chem.* **1985**, *289*, 141.

after metathetical exchange with NH_4PF_6 the stable PF_6 salt $[C_5H_5CoCOCH_3(dppm)]PF_6$ (**15**). We assume that the electrophilic alkyl halide primarily attacks the basic metal center to form the cationic intermediate $[C_5H_5CoCH_3(CO)(\eta^1\text{-dppm})]^+$ which quickly rearranges by methyl group migration to give the final product. There is precedence for such a reaction sequence insofar as the trimethylphosphine compound $C_5H_5Co(CO)(PMe_3)$ also reacts with CH_3I in pentane to produce first $[C_5H_5CoCH_3(CO)(PMe_3)]I$ which on dissolving in acetone is transformed into the acetyl complex $[C_5H_5CoCOCH_3(PMe_3)I]$.[20]

The Structure of Complex 7. According to the X-ray structure determination (see Figure 1 and Tables II and III), in the cation of **7** the metal is pseudooctahedrally coordinated by the cyclopentadienyl ring, the iodide atom, and the chelating ylide-type ligand. The bond angles at the rhodium atom are almost the same as in $[C_5H_5Rh(CH_2NC_5H_5)(PMe_3)I]PF_6$,[3b] particularly the P–Rh–C angles are identical in both compounds. The chelating ligand in **7**, therefore, does not induce geometrical distortions at the metal. The rhodium-to-ligand bond distances are in the usual range for complexes containing the $C_5H_5(PMe_3)Rh$ fragment. As has been previously observed for compounds of this type with π-donating ligands,[3b,21,22] the Rh–C(C_5H_5) distance trans to this ligand is shorter than the other Rh–C(C_5H_5) bond lengths.

The six-membered ring in the cation of **7** adopts a chair conformation. The atoms Rh, P(1), C(7), and P(2) are approximately coplanar, and C(6) and C(8) are equidistant above and below this plane. Within the metallaheterocycle the small C(6)–Rh–P(1) angle (87.6 (2)°) is compensated by opening the other angles up to 118.1° (Rh–C(6)–P(2)). Compared with known P–C(sp^3) distances, the "ylide" P(2)–C(6) bond length is slightly shortened, a phenomenon which is also found in complexes which contain open-chain ylide-type ligands.[23]

Experimental Section

All reactions were carried out under an atmosphere of purified nitrogen by using Schlenk tube techniques. The starting materials $[(C_2H_4)_2RhCl]_2$,[24] $[(C_8H_{14})_2RhCl]_2$,[25] $[C_5H_5RhCH_2I(PR_3)I]$ (R = Me, OMe),[3,5] $C_5H_5Co(CO)_2$,[26] $C_5H_5Co(PMe_3)_2$,[17] PMe_3,[27] and dmpe[28] were prepared by published methods. The other diphosphines, dppe and dppm, were commercial products. NMR spectra were recorded on a Varian EM 360 L (^1H), a Bruker WH 90 FT (^{13}C and ^{31}P), and a Bruker Cryospec WM 400 (^{13}C) spectrometer, IR spectra on a Perkin-Elmer 457 spectrometer, and mass spectra on a Varian MAT CH 7 instrument (70 eV). Conductivity measurements were carried out in CH_3NO_2, melting points were determined by DTA.

Preparation of $C_5H_5Rh(dppe)$ (2). A solution of $[(C_2H_4)_2RhCl]_2$ (509 mg, 1.31 mmol) in 25 mL of THF was treated with dppe (1043.6 mg, 2.62 mmol) and stirred for 2.5 h at 60 °C. After the solution was cooled to room temperature, TlC_5H_5 (705.8 mg, 2.62 mmol) was added to the solution which was stirred for another 24 h. The solution was filtered, and the filtrate was dried in vacuo. The residue was dissolved in 15 mL of benzene, and the solution was chromatographed on Al_2O_3 (neutral, activity grade IV). After the eluant benzene was removed, a red-brown, crystalline solid was obtained: yield 1.0 g (67%); mp 163 °C dec. Anal. Calcd for $C_{31}H_{29}P_2Rh$: C, 65.73; H, 5.16; Rh, 18.17; M_r, 566.43. Found: C, 65.78; H, 4.96; Rh, 17.96; M_r, 566 (MS). ^{31}P NMR (C_6D_6): δ 80.76 (d), J(PRh) = 220.3 Hz.

Preparation of $C_5H_5Rh(dmpe)$ (3). A suspension of $[(C_8H_{14})_2RhCl]_2$ (718 mg, 1.00 mmol) in 30 mL of THF was treated dropwise with dmpe (370 μL, 335 mg, 2.20 mmol) and stirred for 2 h at room temperature. NaC_5H_5 (264 mg, 3.00 mmol) was then added to the solution which was stirred for 3 h. After removal of the solvent in vacuo, the residue was repeatedly extracted (three times) with 50 mL of pentane. The pentane solution was filtered, concentrated to ca. 10 mL, and cooled to −78 °C. Orange-red, air-sensitive crystals were obtained: yield 324 mg (54%); mp 54 °C dec. Anal. Calcd for $C_{11}H_{21}P_2Rh$: C, 41.53; H, 6.65; Rh, 32.35; M_r, 318.14. Found: C, 41.33; H, 6.64; Rh, 31.97; M_r, 318 (MS). ^{31}P NMR (C_6D_6): δ 48.7 (d), J(PRh) = 217.3 Hz.

Preparation of $[C_5H_5RhCH_2I(dppe)]I$ (4a). A solution of **2** (98.0 mg, 0.17 mmol) in 5 mL of ether was treated with CH_2I_2 (0.2 mL, 2.5 mmol) and stirred for 90 min at room temperature. The brown precipitate was filtered, repeatedly washed with ether and pentane, and dried in vacuo: yield 94 mg (65%); mp 167 °C dec; Λ = 65 $cm^2\ \Omega^{-1}\ mol^{-1}$. Anal. Calcd for $C_{32}H_{31}I_2P_2Rh$: C, 46.07; H, 3.75; Rh, 12.33. Found: C, 46.39; H, 4.25; Rh, 12.20. **4a** was converted into the PF_6 salt **4b** with NH_4PF_6 in acetone. The ^1H NMR spectra of **4a** and **4b** were virtually identical. **4b**: ^{31}P NMR (CD_3NO_2) δ 72.81 (d), J(PRh) = 138.5 Hz.

Preparation of $[C_5H_5RhCH_2I(dmpe)]PF_6$ (5b). A solution of **3** (159 mg, 0.50 mmol) in 20 mL of pentane was treated dropwise with CH_2I_2 (60 μL, 201 mg, 0.75 mmol) at 0 °C. After the solution was stirred for 20 min, the precipitate was separated, washed with ether, and dissolved in 3 mL of methanol. After excess NH_4PF_6 (ca. 300 mg) was added to the methanol solution, it was stirred for 10 min and then treated with 20 mL of ether. A yellow-brown precipitate was formed, which was filtered, repeatedly washed with ether, and recrystallized from acetone/ether: yield 227 mg (75%); Λ = 92 $cm^2\ \Omega^{-1}\ mol^{-1}$. Anal. Calcd for $C_{12}H_{23}F_6IP_3Rh$: C, 23.86; H, 3.84; Rh, 17.04. Found: C, 24.11; H, 3.85; Rh, 17.36. ^{31}P NMR (acetone-d_6): δ 54.4 (d), J(PRh) = 137.0 Hz.

Preparation of $[C_5H_5RhCH_2Br(dppe)]Br$ (6). **6** was prepared analogously as described for **4a**, starting with **2** (109 mg, 0.19 mmol) and CH_2Br_2 (0.2 mL, 2.9 mmol). After the solution was stirred for 30 h at room temperature, a brown solid was isolated; yield 57 mg (45%). The compound was characterized by the ^1H NMR spectrum (Table I).

Preparation of $[C_5H_5(I)\overline{RhCH_2PMe_2CH_2CH_2P}Me_2]PF_6$ (7). (a) A solution of **5b** (121 mg, 0.20 mmol) in 2 mL of acetone was treated with 0.3 mL of NEt_3 and stirred for 3 h at 50 °C. After the solution was cooled to room temperature, 20 mL of ether was added to the solution. An orange-red precipitate was formed, which was filtered, repeatedly washed with ether, and recrystallized from acetone/ether: yield 109 mg (90%); Λ = 89 $cm^2\ \Omega^{-1}\ mol^{-1}$. Anal. Calcd for $C_{12}H_{23}F_6IP_3Rh$: C, 23.86; H, 3.84; Rh, 17.04. Found: C, 23.92; H, 4.20; Rh, 17.19. ^{31}P NMR (CD_3NO_2): δ 9.5 (dd), J(RhP) = 137.0, J(PP) = 26.8 Hz, Rh*P*Me_2; δ 28.6 (dd), J(RhP) = 3.0, J(PP) = 26.8 Hz, CH_2*P*Me_2.

(b) A solution of $[C_5H_5RhCH_2I(P(OMe)_3)I]$ (140 mg, 0.25 mmol) in 5 mL of benzene was treated dropwise with dmpe (31 μL, 38 mg, 0.25 mmol) and stirred for 1 h at room temperature. The precipitate was filtered, repeatedly washed with ether, and dried in vacuo. It was dissolved in 3 mL of methanol and treated with NH_4PF_6 to give the PF_6 salt analogously as described for **5b**; yield 125 mg (83%).

Preparation of $[C_5H_5(PMe_3)\overline{RhCH_2PMe_2CH_2CH_2P}Me_2](PF_6)_2$ (8). A solution of **7** (121 mg, 0.20 mmol) in 2 mL of nitromethane was treated with PMe_3 (42 μL, 23 mg, 0.30 mmol) and stirred for 2 h at room temperature. A color change from red to bright yellow occurred. After 20 mL of ether had been added to the solution, a light yellow precipitate was formed, which was filtered, repeatedly washed with ether, and recrystallized from nitromethane/ether. The solid was dissolved in 3 mL of methanol and converted to **8** analogously as described for **5b**: yield 119 mg (85%); Λ = 85 $cm^2\ \Omega^{-1}\ mol^{-1}$. Anal. Calcd for $C_{15}H_{32}F_{12}P_5Rh$:

---

(20) Spencer, A.; Werner, H. *J. Organomet. Chem.* **1979**, *171*, 219.

(21) Werner, H.; Wolf, J.; Schubert, U. *Chem. Ber.* **1983**, *116*, 2848.

(22) Werner, H.; Heiser, B.; Schubert, U.; Ackermann, K. *Chem. Ber.* **1985**, *118*, 1517.

(23) (a) Stein, J.; Fackler, J. P.; Paparizos, C.; Chen, H.-W. *J. Am. Chem. Soc.* **1981**, *103*, 2192. (b) Barnett, B. L.; Krüger, C. *J. Cryst. Mol. Struct.* **1972**, *2*, 271.

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

(25) van der Ent, A.; Onderdelinden, L. *Inorg. Synth.* **1973**, *14*, 92.

(26) Rausch, M. D.; Genetti, R. A. *J. Org. Chem.* **1970**, *35*, 3888.

(27) Wolfsberger, W.; Schmidbaur, H. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 149.

(28) Butter, S. A.; Chatt, J. Inorg. *Synth.* **1974**, *15*, 185.

(29) Günther, H. *NMR-Spektroskopie*; Georg Thieme Verlag: Stuttgart, 1983.

C, 25.80; H, 4.62; Rh, 14.74. Found: C, 25.62; H, 4.63; Rh, 14.65. ^{31}P NMR (DMSO-d_6): ABMX spin system (see ref 29) where A and B represent the ^{31}P nuclei directly bound to Rh, M represents the second ^{31}P nucleus in the six-membered ring, and X represents the ^{103}Rh nucleus; δ(A) 9.9, δ(B) 8.8, δ(M) 30.4; $J(P_AP_B) = 42.8$, $J(P_AP_M) = 10.7$, $J(RhP_A) = 130.7$, $J(P_BP_M) = 30.4$, $J(RhP_B) = 130.8$, $J(RhP_M) = 5.2$ Hz. The ^{31}P NMR data have been supported by a computer analysis.

Preparation of $\{[C_5H_5(PMe_3)IRh]_2(\mu\text{-}CH_2PMe_2CH_2CH_2PMe_2CH_2)\}(PF_3)_2$ (9). A solution of $[C_5H_5RhCH_2I(PMe_3)I]$ (102 mg, 0.20 mmol) in 5 mL of benzene was treated dropwise with dmpe (37 μL, 33 mg, 0.22 mmol) and stirred for 2 h at room temperature. After 20 mL of ether had been added, the red precipitate was filtered, repeatedly washed with ether, and dried in vacuo. It was dissolved in 5 mL of methanol and treated with NH_4PF_6 to give the PF_6 salt as described for **5b**. After recrystallization from nitromethane/ether, a red, microcrystalline powder was obtained: yield 103 mg (85%); $\Lambda = 172$ cm^2 Ω^{-1} mol^{-1}. Anal. Calcd for $C_{24}H_{44}F_{12}I_2P_6Rh_2$: C, 23.82; H, 3.66; Rh, 17.01. Found: C, 24.38; H, 3.88; Rh, 17.42.

Preparation of $C_5H_5Co(dmpe)$ (12). A solution of $C_5H_5Co(PMe_3)_2$ (276 mg, 1.00 mmol) in 5 mL of toluene was treated dropwise with dmpe (183 μL, 165 mg, 1.10 mmol) and stirred for 1 h at 45 °C under slightly reduced pressure (ca. 50 Torr). After the solution was cooled to room temperature, the solvent was removed in vacuo and the residue worked up analogously as described for **3**. Dark brown, air-sensitive crystals were obtained: yield 132 mg (48%); mp 74 °C dec. Anal. Calcd for $C_{11}H_{22}CoP_2$: C, 48.19; H, 7.72; Co, 21.50; M_r, 274.14. Found: C, 48.53; H, 7.55; Co, 21.20; M_r, 274 (MS).

Preparation of $[C_5H_5(CO)Co]_2(\mu\text{-dmpe})$ (13). A solution of $C_5H_5Co(CO)_2$ (360 mg, 2.00 mmol) in 10 mL of hexane was treated dropwise with dmpe (167 μL, 150 mg, 1.00 mmol) and stirred for 3 h at room temperature. A deep red crystalline precipitate was formed, which was filtered, repeatedly washed with cold pentane, and dried in vacuo: yield 363 mg (80%); mp 108 °C dec. Anal. Calcd for $C_{18}H_{26}Co_2O_2P_2$: C, 47.60; H, 5.77; Co, 25.95; M_r, 454.19. Found: C, 47.69; H, 6.02; Co, 26.20; M_r, 454 (MS). IR (pentane): ν(CO) 1930 cm^{-1}.

Preparation of $C_5H_5Co(CO)(\eta^1\text{-dppm})$ (14). A solution of $C_5H_5Co(CO)_2$ (90 mg, 0.50 mmol) in 3 mL of benzene was treated with dppm (192 mg, 0.50 mmol) and stirred for 3 h at 60 °C. After cooling to room temperature, 20 mL of ether was added to the solution. A red-brown precipitate was formed, which was filtered, repeatedly washed with ether, and recrystallized from benzene/pentane (1:10) to give red-brown, air-stable crystals: yield 148 mg (55%); mp 124 °C dec. Anal. Calcd for $C_{31}H_{27}CoOP_2$: C, 69.41; H, 5.07; Co, 10.98. Found: C, 69.35; H, 4.94; Co, 11.00. IR (benzene): ν(CO) 1955 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.23 (m), C_6H_5; δ 4.78 (d), J(PH) = 1.0 Hz, C_5H_5; δ 3.35 (dd), J(PH) = J(P′H) = 8.4 Hz, CH_2.

Preparation of $[C_5H_5CoCOCH_3(dppm)]PF_6$ (15). A solution of **14** (107 mg, 0.20 mmol) in 2 mL of benzene was treated with CH_3I (62 μL, 142 mg, 1.00 mmol) and stirred for 5 h at room temperature. After 20 mL of ether was added to the solution, an orange-yellow precipitate was formed, which was filtered and repeatedly washed with ether. It was dissolved in 5 mL of methanol and transformed with NH_4PF_6 into the PF_6 salt analogously as described for **5b**. Recrystallization from nitromethane/ether gave orange-yellow crystals: yield 66 mg (47%); $\Lambda = 82$ cm^2 Ω^{-1} mol^{-1}. Anal. Calcd for $C_{32}H_{30}CoF_6OP_3$: C, 55.19; H, 4.34; Co, 8.46. Found: C, 55.09; H, 3.85; Co, 8.49.

X-ray Structure Analysis of 7. Crystals of **7** were obtained by diffusion of ether into a concentrated solution of **7** in acetone. A crystal (0.3 × 0.25 × 0.25 mm) was mounted on a Syntex $P2_1$ automatic four-circle diffractometer. Mo Kα radiation ($\lambda = 71.069$ pm, graphite monochromator) was used for all measurements. Centering and refinement of 25 reflections from different parts of the reciprocal space resulted in the following unit-cell parameters: $a = 848.2$ (2) pm, $b = 1489.5$ (4) pm, $c = 1594.6$ (4) pm, $\beta = 103.17$ (2)°, and $V = 1962 \times 10^6$ pm^3. By systematic absences space group $P2_1/n$ was established; d(calcd) = 2.03 g/cm^3 (Z = 4). Diffraction intensities were measured in an ω-scan mode (scan range 0.9°); the scan rate varied as a function of maximum peak intensity from 1.0 to 29.3 cm^{-1}. Background radiation was measured on each side of the reflection center for half of the total scan time. Two reference reflections measured every 50 reflections showed no significant deviation in their intensity. A total of 3663 independent reflections were collected ($2° \leq 2\theta \leq 51°$). Intensity data were corrected for Lorentz and polarization effects; an empirical absorption correction was applied ($\mu = 27.3$ cm^{-1}). The structure was solved by the heavy-atom method (Syntex XTL). The positions of the hydrogen atoms were taken from difference Fourier maps or calculated according to ideal geometry. Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares with all structure factors included. Final $R = 0.051$ and $R_w = 0.055$ ($1/w = \sigma(F_o)$). The final positional parameters of the non-hydrogen atoms are given in Table III.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support, Mrs. Dr. G. Lange and Mr. F. Dadrich for the mass spectra, Dr. W. Buchner and Dr. J. Wolf for NMR measurements, and Mrs. U. Neumann and Mrs. R. Schedl for the elemental analyses. Support by Degussa AG (Hanau) and HM-Leasing (Heidelberg) through gifts of chemicals and instruments is gratefully acknowledged.

Registry No. **2**, 84330-24-5; **3**, 84330-23-4; **4a**, 113160-71-7; **4b**, 84578-41-6; **5b**, 84578-43-8; **6**, 113180-33-9; **7**, 84330-26-7; **8**, 84330-28-9; **9**, 113160-73-9; **12**, 113160-74-0; **13**, 113160-75-1; **14**, 113160-76-2; **15**, 113160-78-4; $[(C_2H_4)_2RhCl]_2$, 12081-16-2; $[(C_8H_{14})_2RhCl]_2$, 12279-09-3; $[C_5H_5RhCH_2I(P(OMe)_3)I]$, 97688-35-2; $[C_5H_5RhCH_2I(PMe_3)I]$, 80215-92-5; $C_5H_5Co(PMe_3)_2$, 63413-01-4; $C_5H_5Co(CO)_2$, 12078-25-0; TlC_5H_5, 34822-90-7; NaC_5H_5, 4984-82-1.

Supplementary Material Available: A table of the atomic coordinates and temperature parameters for all atoms (2 pages); a listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.