pending on the polarity of the respective ferrocene derivatives (7), which were always eluted as the first band of the column. Purification was achieved by recrystallization from ether/*n*-hexane or sublimation at 10^{-3} torr. Yields and data of the compounds thus obtained are shown in Tables I and III.

Ferrocenyl-*N*,*N*,*N′*,*N′*-tetramethylamidinium Hexafluorophosphate (6i). 6,6-Bis(dimethylamino)pentafulvene (**4i**) (0.49 g, 3.0 mmol) was treated with 0.74 g (2.0 mmol) of **5** according to the standard procedure. The dichloromethane solution was concentrated and the residue was triturated with ether. The crude product was collected by filtration and purified by column chromatography on alumina (B II) with acetone as eluent. After the dark red band had been eluted the solution was concentrated. Red-brown plates, mp 157 °C, were obtained upon addition of ether (0.70 g, 81%): ^1H NMR (CD_3COCD_3) 3.45 (s, 6 H, NMe_2), 4.51 (s, 5 H, C_5H_5), 4.99 (s, 4 H, 2–5-H); ^1H NMR ($CDCl_3$) 3.36 (s, 6 H, NMe_2), 4.44 (s, 5 H, C_5H_5), 4.72 (t, $J = 2$ Hz, 2 H, 3,4-H), 4.83 (t, $J = 2$ Hz, 2 H, 2,5-H); MS-FD *m/e* 285 ($C_{15}H_{21}FeN_2^+$); IR (KBr) 1590 (C═N), 830 (P—F); UV (CH_3CN) 236 (4.11), 279 (4.13), 348 (3.25–3.33; concentration dependent), 482 (3.00). Anal. Calcd for $C_{15}H_{21}F_6FeN_2P$ (430.17): C, 41.88; H, 4.92; N, 6.51. Found: C, 41.93; H, 4.92; N, 6.21.

1-(3′-Oxobut-1-enyl)ferrocene (11). 6-(Dimethylamino)pentafulvene (**4a**) (0.36 g, 3.0 mmol) was treated with 0.74 g (2.0 mmol) of **5** according to the standard procedure. The solvent was evaporated and the residue was treated with 100 mL of acetone and 30 mL of 2 N NaOH at reflux temperature for 40 min. The mixture was concentrated and 150 mL of water was added. The aqueous solution was extracted three times with 50 mL of ether. The combined organic layers were washed with water, dried (Na_2SO_4), and concentrated. Chromatography of the residue with elution of the red band gave 0.28 g (55%) of **11** as red-orange crystals, mp 85 °C, identical with authentic material.[19]

C. Reaction of (η^5-Cyclopentadienyl)tris(acetonitrile)ruthenium(II) Hexafluorophosphate (8) with Pentafulvenes. Standard Procedure. A solution of 0.50 mmol (217 mg) of **8** and 0.75 mmol of the appropriate pentafulvene (**4**) in 30 mL of 1,2-dichloroethane was heated to reflux under nitrogen for 14 h. Workup was essentially the same as for the corresponding ferrocenes; vide supra. Yields and data of the ruthenocenes thus obtained are listed in Tables II and III.

Ruthenocenyl-*N*,*N*,*N′*,*N′*-tetramethylamidinium Hexafluorophosphate (9i). 6,6-Bis(dimethylamino)pentafulvene (**4i**) (0.49 g, 3.0 mmol) was treated with 217 mg (0.50 mmol) of **5** according to the standard procedure. After the mixture had been allowed to cool, the solvent was evaporated and the residue was washed with ether. Filtration and recrystallization of the product from acetone/ether yielded 221 mg (93%) of **9i** as red-brown plates, mp 186 °C: ^1H NMR (CD_3COCD_3) 3.42 (s, 6 H, NMe_2), 4.84 (s, 5 H, C_5H_5), 5.11 (t, $J = 2$ Hz, 2 H, 3,4-H), 5.27 (t, $J = 2$ Hz, 2 H, 2,5-H); ^1H NMR ($CDCl_3$) 3.35 (s, 6 H, NMe_2), 4.80 (s, 5 H, C_5H_5), 4.99 (s, 4 H, 2–5-H); MS-FD, *m/e* 331 ($C_{15}H_{21}N_2Ru^+$); IR (KBr) 1590 (C═N), 835 (P—F); UV (CH_3CN) 222 (3.92), 269 (4.25), 360 (3.27), 507 (1.58). Anal. Calcd for $C_{15}H_{21}F_6N_2PRu$ (475.38): C, 37.90; H, 4.45; N, 5.89. Found: C, 38.05; H, 4.51; N, 6.14.

Acknowledgment. We wish to thank the Stiftung Volkswagenwerk and the Fonds der Chemischen Industrie for their support of this work. The Degussa, Wolfgang/Hanau contributed a generous gift of ruthenium trichloride.

Registry No. **4a**, 696-68-4; **4b**, 14469-77-3; **4c**, 30294-52-1; **4d**, 15763-91-4; **4e**, 14749-79-2; (*Z*)-**4f**, 88854-77-7; (*E*)-**4f**, 88854-82-4; **4g**, 61857-27-0; (*Z*)-**4h**, 88854-78-8; (*E*)-**4h**, 88854-83-5; **4i**, 703-24-2; **4j**, 72866-31-0; **4k**, 88854-79-9; **4l**, 88854-80-2; **4m**, 2481-72-3; **5**, 34978-37-5; **6i**, 88854-85-7; **7a**, 12093-10-6; **7b**, 1271-55-2; **7c**, 88854-86-8; **7g**, 88854-87-9; **7h**, 88854-88-0; **7i**, 33135-80-7; **7j**, 88854-89-1; **7k**, 88854-90-4; 8, 88854-92-6; **9i**, 88854-94-8; **10a**, 66507-25-3; **10g**, 88854-95-9; **10h**, 88854-96-0; **10i**, 88854-97-1; **10k**, 88854-81-3; **11**, 12171-14-1; methyl dimethyloxamate, 59571-38-9; triethyloxonium tetrafluoroborate, 368-39-8; lithium *tert*-butylcyclopentadienide, 50356-03-1; sodium cyclopentadienide, 4984-82-1; diethyl carbonate, 105-58-8; (dimethylamino)methoxycarbenium methylsulfate, 34643-89-5.

Syntheses and X-ray Crystal Structures of Highly Dissociated Rhodium(I) Phosphine Complexes Using Very Bulky Phosphine Ligands

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A series of rhodium(I) phosphine complexes has been prepared by treating $[\{RhCl(CO)_2\}_2]$, $[\{RhCl(COD)\}_2]$, and $[\{RhCl(COE)_2\}_2]$ with the bulky phosphines $PX\{CH(SiMe_3)_2\}_2$ (X = Cl, H, or Me). ^{31}P and ^1H NMR and X-ray methods were used to identify the products of these reactions. The olefin complexes are highly dissociated in solution. The molecular structures of $[RhCl(COD)(PCl\{CH(SiMe_3)_2\}_2)]\cdot C_7H_8$ (1), bis-[*trans*-{(cyclooctene)μ-chloro[bis{bis(trimethylsilyl)methyl}phosphine]dirhodium(I)}] (5), and *trans*-$[RhCl(CO)(PH\{CH(SiMe_3)_2\}_2)_2]$ (8) have been determined by X-ray diffraction. The crystal data at 140 K are as follows. 1: $a = 11.158$ (3) Å, $b = 11.930$ (3) Å, $c = 13.132$ (3) Å, $\alpha = 97.24$ (2)°, $\beta = 104.02$ (2)°, $\gamma = 93.82$ (2), $Z = 2$, space group $P\bar{1}$. 5: $a = 11.118$ (5) Å, $b = 16.403$ (9) Å, $c = 17.782$ (11) Å, $\beta = 104.77$ (4)°, $Z = 2$, space group $P2_1/n$. 8: $a = 10.620$ (1) Å, $b = 22.705$ (4) Å, $c = 20.375$ (3) Å, $\beta = 96.00$ (1)°, $Z = 4$, space group $P2_1/n$. For 1 $R = 0.044$, for 5 $R = 0.023$, and for 8 $R = 0.038$. 1 is essentially square planar, Rh–P = 2.287 (1), Rh–Cl = 2.363 (1), and Rh–C = 2.124 (5)–2.253 (5) Å. For 5 the Rh_2Cl_2 core is planar, Rh–Rh = 3.690 (1), Rh–P = 2.203, Rh–Cl = 2.391 (1) and 2.475 (1), and Rh–C = 2.098 (3) and 2.110 (3) Å. Complex 8 is nearly square planar and does not dissociate appreciably in solution. The geometries at phosphorus in the dissociating complexes show no unusual angles or distances. This suggests that the steric effects in these ligands are more subtle than those found in the bulkiest phosphines now known.

Introduction

The catalytic hydrogenation of unsaturated substrates by rhodium(I) phosphine complexes probably involves the presence of three-coordinate intermediates such as $RhCl(P)_2$ (P = phosphine).[1] There are only a few examples of $RhX(P)_2$ complexes in the literature.[2,3] The reaction

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of $P(C_6H_{11})_3$ with $[\{RhCl(COE)_2\}_2]$ was reported to afford $[\{RhCl(P(C_6H_{11})_3)_2\}]$ in equilibrium with its chloro-bridged dimer.[3a] The three-coordinate complex $[RhH\{P(t\text{-}Bu)_3\}_2]$ has been prepared in solution by the reduction of $RhCl_3\cdot 3H_2O$ with Na/Hg in the presence of $P(t\text{-}Bu)_3$.[3b] The complex $[Rh(PPh_3)_2\{N(SiMe_3)_2\}]$ has been isolated by treating $[RhCl(PPh_3)_3]$ with $[LiN(SiMe_3)_2]$.[3c] None of these species has been structurally characterized by X-ray crystallography, with the exception of the related cationic complex $[\{Rh(PPh_3)_3\}^+(ClO_4)^-]$.[2] The geometry at Rh(I) in this complex is best described as distorted T-shape.

We have attempted to prepare and characterize three-coordinate complexes using the very bulky phosphines $PX\{CH(SiMe_3)_2\}_2$, where X = H, Me, Cl,[4] via the reactions

$$[\{RhCl(COD)\}_2] + 4P \rightarrow 2[\{RhCl(P)_2\}] + 2COD \quad (1)$$

$$[\{RhCl(COE)_2\}_2] + 4P \rightarrow 2[\{RhCl(P)_2\}] + 4COE \quad (2)$$

where COD = cyclooctadiene, COE = cyclooctene, and P = $PX\{CH(SiMe_3)_2\}_2$. The reaction products when the $PX\{CH(SiMe_3)_2\}_2$ ligands are employed are quite different from those derived from smaller, more conventional phosphines.[3] The increased steric bulk of these very bulky ligands may account for the differences in reactivity and products obtained.

This work was carried out as part of a systematic study of the reactions of very bulky phosphines and phosphites[5] with various rhodium(I) complexes. ^{31}P and ^{1}H NMR and X-ray diffraction were used in order to determine the structures of the products and their solution equilibria.

Experimental Section

^{1}H and ^{31}P NMR spectra were recorded on a Nicolet NT-200 spectrometer operating at 200 and 81 MHz; $[\{RhCl(COD)\}_2]$,[6] $[\{RhCl(CO)_2\}_2]$,[7] $[\{IrCl(COD)\}_2]$,[8] $[\{RhCl(COE)_2\}_2]$,[9] $PH\{CH(SiMe_3)_2\}_2$, $PCl\{CH(SiMe_3)_2\}_2$, and $PMe\{CH(SiMe_3)_2\}_2$[4] were all prepared by standard literature methods. Triphenylphosphine (Aldrich) was used as purchased. Melting points were determined in capillaries sealed under argon. IR spectra were obtained on a Perkin-Elmer 180 instrument with polystyrene as an external reference. All solvents were freshly distilled from drying agents and degassed three times immediately before use. All manipulations were carried out in a Vacuum Atmospheres Co. Dri-Lab or by using standard Schlenk tube techniques.

(1,5-Cyclooctadiene)chloro[bis{bis(trimethylsilyl)methyl}chlorophosphine]rhodium(I)-Toluene (1). $PCl\{CH(SiMe_3)_2\}_2$ (1.56 g) was added to a toluene (20 mL) solution of $[\{RhCl(COD)\}_2]$ (1.00 g) at 25 °C. The solution was stirred for 12 h and the volatiles removed in vacuo. Toluene (3 mL) and hexane (30 mL) were added, and the mixture was filtered through a Celite padded, medium-porosity filter. The volume was reduced to 10 mL, and the mixture was then filtered again to yield a clear yellow-orange solution. The product crystallized at −20 °C as large yellow-orange plates in 54% yield. The complex was isolated as a toluene adduct. If benzene is used instead of toluene, the product can be recrystallized from hexane or acetone as an adduct-free complex (mp 147–149 °C dec). Traces of free $PCl\{CH(SiMe_3)_2\}_2$ can be removed by multiple recrystallizations. The hexane-insoluble fraction was unreacted $[\{RhCl(COD)\}_2]$, which was recovered by extraction into dichloromethane and subsequent recrystallization. $^{31}P\{^{1}H\}$ NMR (81 MHz, benzene-d_6, relative to external 85% H_3PO_4, ppm) 161.35 (d, J_{Rh-P} = 172.0 Hz); ^{1}H NMR (200 MHz, benzene-d_6, ppm) 5.56, 3.67, 2.27, 1.64 (COD); 0.659, 0.597 ($SiMe_3$).

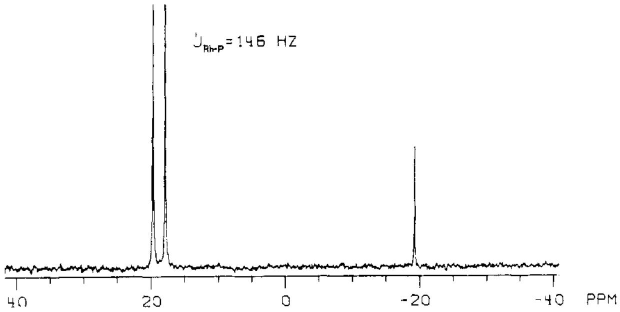

Figure 1. 81-MHz $^{31}P\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 recorded at 21.0 °C.

(1,5-Cyclooctadiene)chloro[bis{bis(trimethylsilyl)methyl}phosphine]rhodium(I) (2). This product was obtained by the procedure described for 1. It was recrystallized from acetone and isolated in 81% yield as yellow-orange crystals. (mp 145–147 °C dec). $^{31}P\{^{1}H\}$ NMR (81 MHz, d^6-benzene-d_6, ppm) −10.16 (d, J_{Rh-P} = 151.2 Hz). ^{1}H NMR (200 MHz, benzene-d_6, ppm) 5.679, 3.196, 2.203, 1.647 (COD); 4.285 (d of t, J_{P-H} = 317.5 Hz, J_{P-CH} = 5.4 Hz, P–H); 1.185, 1.104 (C–H); 0.582, 0.215 ($SiMe_3$).

(1,5-Cyclooctadiene)chloro[bis{bis(trimethylsilyl)methyl}methylphosphine]rhodium(I) (3). This yellow-orange product was isolated in 82% yield by the same method as described for 1: mp 143–146 °C dec; $^{31}P\{^{1}H\}$ NMR (81 MHz, benzene-d_6, ppm) 18.55 (d, J_{Rh-P} = 145.9); ^{1}H NMR (200 MHz, benzene-d_6, ppm) 5.597, 3.251, 2.296, 1.58 (COD), 1.010 (d, J_{P-CMe} = 6.0 Hz, P–Me), 0.628, 0.479 ($SiMe_3$).

Chlorotris(triphenylphosphine)rhodium(I) (4). Benzene (15 mL) was added to 0.50 g of 3. To this stirred solution was added 2 equiv of PPh_3 (0.43 g). The solution was then left to stand for 1 week at 35 °C. Dark maroon crystals were isolated in 57% yield from an orange solution upon cooling: mp 156–157 °C (lit. mp 157 °C); $^{31}P\{^{1}H\}$ NMR (81 MHz, $CDCl_3$, ppm) 48.03 (d of t, J_{Rh-P_1} = 189.1 Hz, $J_{P_1-P_2}$ = 38.0 Hz, P_1 (trans to Cl)), 31.52 (d of d, J_{Rh-P_2} = 141.9 Hz, P_2).

Bis[*trans*-{(cyclooctene)μ-chloro[bis{bis(trimethylsilyl)methyl}phosphine]dirhodium(I)}] (5). $PH\{CH(SiMe_3)_2\}_2$ (1.2 g) was added to a slurry of $[\{RhCl(COE)_2\}_2]$ (1 g) in benzene (20 mL). The solid dissolved to yield an orange solution which precipitated a solid upon warming. Acetone (10 mL) was added and further precipitation occurred. The solvent was removed in vacuo. The solid was washed with acetone (10 mL), and then hexane (30 mL) was added. The mixture was warmed to 50 °C, and a color change to dark red was observed. The solution was filtered warm through a Celite padded, medium-porosity fritted funnel and cooled very slowly to yield the product as large red crystals in 69% yield: mp 155–157 °C dec; $^{31}P\{^{1}H\}$ NMR (81 MHz, $CDCl_3$, ppm) 27.22 (d, J_{Rh-P} = 187.9 Hz); ^{1}H NMR (200 MHz, $CDCl_3$, ppm) 5.623, 2.098, 1.523, 1.337 (COD), 3.48 (br d, J_{P-H} = 334.0 Hz, P–H), 0.471, 0.229 ($SiMe_3$).

***trans*-[Carbonylchlorobis[bis{bis(trimethylsilyl)methyl}phosphine]rhodium(I)] (8).** $PH\{CH(SiMe_3)_2\}_2$ (1.80 g) was added to $[\{RhCl(CO)_2\}_2]$ (1.00 g) in benzene (25 mL). The solution was stirred until CO evolution ceased, and the solvent was removed in vacuo. Hexane (30 mL) was added, and the yellow solution was filtered through a fritted funnel. The solution was concentrated and upon cooling to −30 °C yielded large yellow crystals in 96% yield: mp 171–172 °C; $^{31}P\{^{1}H\}$ NMR (81 MHz, benzene-d_6, ppm) −20.04 (d, J_{Rh-P} = 117.7 Hz); ^{1}H NMR (200 MHz, benzene-d_6, ppm) 5.827 (m, P–H), 0.921 (m, C–H), 0.494, 0.352 (s, $SiMe_3$); IR (CCl_4, cm^{-1}) 2343, 2323 (P–H), 1958 (CO).

Results and Discussion

When a freshly recrystallized sample of **1**, **2**, or **3** was dissolved in benzene, three peaks were observed in the

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$^{31}P\{^1H\}$ NMR spectrum. The peaks were assigned to the rhodium complex (doublet) and the free ligand (see Figure 1). Repeated (four times) recrystallizations of the orange crystals from acetone served only to decrease the concentration of the free ligand slightly to a constant value. The amount of dissociation depends markedly on the phosphine. Expressed as a percentage of total phosphorus content the free ligand was present in the following amounts: X = H, 3%; X = Me, 12%; X = Cl, 32%; at 21 °C. In the case of X = Cl the concentration of free ligand was increased to ca. 45% by heating the sample to 80 °C in C_6D_6. A similar experiment with the complex where X = H resulted in an increase of ligand concentration to ca. 20%. This contrasts with the related 16-electron complexes, $[RhCl(PPh_3)_3]$[1] and $[Pt(PPh_3)_3]$,[10] which show only very small amounts (~0.01%) of free ligand. The extent of dissociation for our complexes is also remarkable in view of the noncrowding coligands Cl^- and COD. We are undertaking a more detailed study of all three cases in order to determine the dissociation constants and dissociation energies of these systems.

^1H NMR confirms the presence of free ligand and also supports the presence of $[\{RhCl(COD)\}_2]$. The addition of 1 excess equiv of phosphine ligand results in the almost complete disappearance of rhodium starting material, while addition of $[\{RhCl(COD)\}_2]$ (1 excess equiv) essentially results in the disappearance of the free ligand. In the light of our results it appears that the equilibrium described in eq 3 is operative.

$$2[RhCl(COD)(PX\{CH(SiMe_3)_2\}_2)] \rightleftharpoons [\{RhCl(COD)\}_2] + 2PX\{CH(SiMe_3)_2\}_2 \quad (3)$$

We have investigated the corresponding iridium systems by treating $[\{IrCl(COD)\}_2]$ with $PX\{CH(SiMe_3)_2\}_2$ (X = H, Me, Cl) to produce $[IrCl(COD)(PX\{CH(SiMe_3)_2\}_2)]$[11] exclusively ($^{31}P$ and ^1H NMR). These systems do not display any observable dissociation of the phosphine ligand at room temperature. When a 1-equiv excess of the free phosphine is added, the only peaks observed are due to the iridium complex and the free phosphine.

When **3** is treated with 2 equiv of PPh_3 in benzene, $[RhCl(PPh_3)_3]$[12] is slowly produced, and signals due to PPh_3 and $PMe\{CH(SiMe_3)_2\}_2$ (−19.38 ppm) appear in the ^{31}P spectrum. We were unable to convert **3** into $[(RhCl(PMe\{CH(SiMe_3)_2\}_2)_3]$ by replacing the COD group with excess $PMe\{CH(SiMe_3)_2\}_2$. In complexes of the type [RhCl(COD)(P)] where the phosphine is less sterically demanding than $PX\{CH(SiMe_3)_2\}_2$ the following reaction is possible:[12,13]

$$[RhCl(COD)(P)] \xrightarrow{+2P} RhCl(P)_3 + COD \quad (4)$$

$$P = PPh_3,\ PPhMe_2,\ \text{or}\ P(n\text{-}Bu)_3$$

The product of eq 4 requires that each phosphine be cis to at least one other phosphine. We believe the large steric bulk of the phosphines $PX\{CH(SiMe_3)_2\}_2$ prohibits the formation of the chlorotris(phosphine)rhodium(I) complex. In fact, when (1,5-cyclooctadiene)(2-methylallyl)rhodium(I) (**6**) (which strongly favors the formation of cis phosphine-substituted products) is treated with excess $PH\{CH(SiMe_3)_2\}_2$, a cyclometalated complex is produced in high yield.[14] Addition of smaller phosphines such as PPh_3 and $HP(C_6H_{11})_2$ to **6** has resulted in the loss of COD to produce a number of four- and five-coordinate rhodium(I) complexes which characteristically have the phosphorus bases arranged in a cis geometry.[15-17]

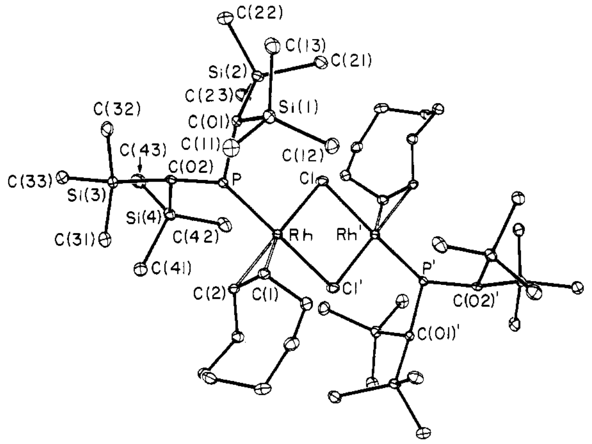

Figure 2. Computer-generated perspective diagram of **5**. The hydrogen atoms have been omitted for clarity.

We also attempted to synthesize three-coordinated rhodium complexes via reaction of phosphine ligands with the more reactive rhodium cyclooctene complex $[\{RhCl(COE)_2\}_2]$. In the case of $PH\{CH(SiMe_3)_2\}_2$ the product obtained was a chloro-bridged dinuclear complex with terminal olefin and phosphine ligands in the trans positions (Figure 2). When the red dimer is dissolved in C_6D_6 or $CDCl_3$, a yellow solution results. The red color can be regenerated by adding excess $PH\{CH(SiMe_3)_2\}_2$. The $^{31}P\{^1H\}$ NMR spectrum of the recrystallized dimer in $CDCl_3$ shows the presence of at least three species in solution. A doublet at 27.22 ppm (J_{Rh-P} = 187.9 Hz, J_{P-H} = 334.0 Hz) was assigned to the dimer; the small doublet at −16.51 ppm (J_{Rh-P} = 153.7 Hz, J_{P-H} = 366.1 Hz) was assigned to either $[RhCl(COE)_2(PH\{CH(SiMe_3)_2\}_2)]$ or *trans*-$[RhCl(COE)(PH\{CH(SiMe_3)_2\}_2)_2]$, and the peak at −70.80 ppm is due to the free phosphine. The ^1H NMR spectrum is complex. The presence of two rhodium phosphine complexes is supported by the identical coupling constants (J_{P-H}) observed in the ^{31}P experiment. We also observe the free phosphine ligand, free cyclooctene, and the precursor $[\{RhCl(COE)_2\}_2]$ in $CDCl_3$. The presence of free phosphine is surprising in view of the short Rh–P bond distance of 2.203 (1) Å (vide infra).

We have also investigated the reactions of $[\{RhCl(CO)_2\}_2]$ with $PX\{CH(SiMe_3)_2\}_2$. The complex *trans*-$[RhCl(CO)(PH\{CH(SiMe_3)_2\}_2)_2]$ (**8**) is the exclusive product when 4 equiv of $PH\{CH(SiMe_3)_2\}_2$ is added to 1 equiv of $[\{RhCl(CO)_2\}_2]$ in benzene (^{31}P NMR, ^1H NMR, X-ray, IR). When freshly recrystallized *trans*-$[RhCl(CO)(PH\{CH(SiMe_3)_2\}_2)_2]$ is dissolved in benzene, it exhibits only a doublet in the $^{31}P\{^1H\}$ NMR spectrum; no free phosphine is observed. When 4 equiv of $PCl\{CH(SiMe_3)_2\}_2$ is added to 1 equiv of $[\{RhCl(CO)_2\}_2]$ in benzene a doublet at 137.32 ppm (J_{Rh-P} = 143.2 Hz) is observed. The complex *trans*-$[RhCl(CO)(P(t\text{-}Bu)_3)_2]$ (**9**) is reported to be in equilibrium with its chloro-bridged dimer bis[*trans*-{(carbonyl)μ-chloro[tris(*tert*-butyl)phosphine]dirhodium(I)}] (**10**). The extent of dissociation for **9** in solution was not reported.[18]

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Table I. Crystallographic Data and Summary of Intensity Data Collection and Structure Refinement for 1, 5, and 8

	1	5	8
formula	$RhC_{22}H_{50}Cl_2PSi_4\cdot C_7H_8$	$Rh_2C_{44}H_{106}Cl_2P_2Si_8$	$RhC_{29}H_{78}OClP_2Si_8$
fw	723.91	1198.68	867.94
cryst system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
T, K	140	140	140
a, Å	11.158 (3)	11.118 (5)	10.620 (1)
b, Å	11.930 (3)	16.403 (9)	22.705 (4)
c, Å	13.132 (3)	17.782 (11)	20.375 (3)
α, deg	97.24 (2)		
β, deg	104.02 (2)	104.77 (4)	96.00 (1)
γ, deg	93.82 (2)		
V, Å^3	1673.8	3135.7	4965.2
Z	2	2 (dimers)	4
d_{calcd}, g cm^{-3}	1.44	1.27	1.16
cryst size, mm	0.21 × 0.22 × 0.27	0.48 × 0.65 × 0.65	0.32 × 0.51 × 0.37
radiation	graphite monochromated Mo Kα (λ = 0.710 60 Å)		
μ, cm^{-1}	8.60	13.49	6.65
scan speed, deg min^{-1}	30	60	60
scan type	ω	ω	ω
scan range, deg	1.7	1.0	1.0
ω background offset, deg	1.5	1.0	1.0
2θ limits, deg	0-50	0-45	0-45
no. of unique data	5885	4096	6374
std reflcns (no decay observed)	(1,−3,3) (0,3,3)	(0,6,0) (2,0,2)	
no. reflcns used in LS ($F > 6\sigma(F)$)	4635	3443	4350
no. parameters	327	474	691
R	0.044	0.023	0.038
R_w	0.048	0.026	0.040
GOF	1.27	1.04	1.06

X-ray Crystallographic Studies

All X-ray data were collected with a Syntex $P2_1$ diffractometer equipped with a locally modified Syntex LT-1 low-temperature device, using a procedure described earlier.[19] Further details are in Table I.

All calculations were carried out on a Data General ECLIPSE computer using the SHELXTL program system. The atomic form factors, including anomalous scattering, were from the "International Tables of Crystallography".[20] The three structures were solved by Patterson and heavy-atom methods, phasing difference electron density maps in consecutive steps.

Large, well-shaped, yellow single crystals of $[RhCl(COD)(PCl\{CH(SiMe_3)_2\}_2)]\cdot[C_7H_8]$ (1) were obtained from a concentrated hexane/toluene solution. After the crystals were removed from the Schlenk tube, they were protected from air contamination by a layer of hydrocarbon oil. A large crystal was cut to a suitable size, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream (140 K). Although the precise stoichiometry was initially unknown the correct structure was found and subsequently refined by least-squares methods, with anisotropic thermal parameters for the non-hydrogen atoms. A disordered toluene is located around ($^1/_2$, $^1/_2$, 0). Most of the 58 H atoms were detected in a difference electron density map; their sites compared well with coordinates calculated according to carbon hybridization. All of the hydrogen atoms in the rhodium complex were included in the refinements with fixed group geometry. The toluene H atoms were not included in any calculations. The refinement converged with R = 0.044 for the 4635 reflections used.

Table II. Atomic Coordinates (and Esd's) for Non-Hydrogen Atoms in Crystalline 1

atom	10^4x	10^4y	10^4z
Rh	1002 (1)	4181 (1)	2417 (1)
Cl(1)	1315 (1)	3020 (1)	926 (1)
Cl(2)	62 (1)	2710 (1)	4429 (1)
P(1)	581 (1)	2505 (1)	2997 (1)
Si(1)	3358 (1)	2557 (1)	4351 (1)
Si(2)	2467 (1)	739 (1)	2299 (1)
Si(3)	−2185 (1)	2366 (1)	1627 (1)
Si(4)	−1310 (1)	226 (1)	2708 (1)
C(1)	1940 (4)	1710 (4)	3357 (4)
C(2)	4051 (5)	3719 (4)	3776 (4)
C(3)	4578 (5)	1582 (5)	4774 (4)
C(4)	3038 (5)	3166 (5)	5627 (4)
C(5)	3068 (5)	−515 (4)	2932 (5)
C(6)	1229 (4)	89 (4)	1113 (4)
C(7)	3747 (5)	1432 (5)	1830 (4)
C(8)	−794 (4)	1579 (4)	2198 (4)
C(9)	−2808 (5)	3174 (5)	2670 (4)
C(10)	−1849 (5)	3327 (5)	702 (4)
C(11)	−3484 (4)	1313 (5)	783 (4)
C(12)	−74 (5)	−428 (4)	3585 (4)
C(13)	−2497 (5)	478 (5)	3486 (5)
C(14)	−1993 (5)	−918 (4)	1558 (5)
C(15)	33 (5)	5198 (4)	3329 (4)
C(16)	−614 (5)	6049 (4)	2697 (4)
C(17)	133 (5)	6550 (4)	1988 (4)
C(18)	902 (5)	5715 (4)	1570 (4)
C(19)	2119 (5)	5619 (4)	2045 (4)
C(20)	2851 (5)	6316 (4)	3074 (4)
C(21)	2191 (5)	6354 (4)	3965 (4)
C(22)	1289 (4)	5299 (4)	3875 (4)

Large, red, single crystals of the chloro-bridged rhodium dimer 5 were obtained from a concentrated hexane solution and handled by the procedure described above. The structure was solved and refined by similar methods to those used for 1. All of the H atoms were located in a difference electron density map and refined isotropically. The structure was refined with isotropic thermal parameters to R = 0.030. The non-hydrogen atoms were then refined with anisotropic thermal parameters. The refinement converged with R = 0.023 for the 3443 reflections used. The structure of 8 was determined by the previously described methods. The non-hydrogen atoms were refined with anisotropic thermal parameters. All 78 of the hydrogen atoms were detected in a difference electron density map and refined isotropically. The refinement converged with R = 0.038 for the 4350 reflections used. The final

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Table III. Atomic Coordinates (and Esd's) for Non-Hydrogen Atoms in Crystalline 5

atom	10^4x	10^4y	10^4z
Rh	599 (1)	812 (1)	4477 (1)
Cl	−115 (1)	662 (1)	5629 (1)
C(1)	233 (3)	1041 (2)	3279 (2)
C(2)	1487 (3)	799 (2)	3560 (2)
C(3)	1976 (3)	3 (2)	3326 (2)
C(4)	2470 (3)	129 (2)	2603 (2)
C(5)	1560 (3)	562 (2)	1933 (2)
C(6)	268 (3)	169 (2)	1654 (2)
C(7)	−791 (3)	589 (2)	1901 (2)
C(8)	−773 (3)	523 (2)	2760 (2)
P	1216 (1)	2087 (1)	4694 (1)
C(01)	315 (2)	2856 (2)	5076 (2)
Si(1)	−1209 (1)	3091 (1)	4333 (1)
C(11)	−913 (3)	3428 (2)	3393 (2)
C(12)	−2283 (3)	2195 (2)	4159 (2)
C(13)	−1940 (3)	4010 (2)	4665 (2)
Si(2)	213 (1)	2851 (1)	6133 (1)
C(21)	−1296 (3)	2470 (2)	6279 (2)
C(22)	391 (3)	3943 (2)	6467 (2)
C(23)	1506 (3)	2279 (2)	6795 (2)
C(02)	2875 (3)	2295 (2)	5178 (2)
Si(3)	3514 (1)	3082 (1)	4594 (1)
C(31)	3434 (3)	2757 (2)	3575 (2)
C(32)	2655 (3)	4065 (2)	4547 (2)
C(33)	5170 (3)	3327 (2)	5074 (2)
Si(4)	3986 (1)	1419 (1)	5565 (1)
C(41)	4819 (3)	1088 (2)	4828 (2)
C(42)	3255 (3)	505 (2)	5891 (2)
C(43)	5163 (3)	1808 (2)	6445 (2)

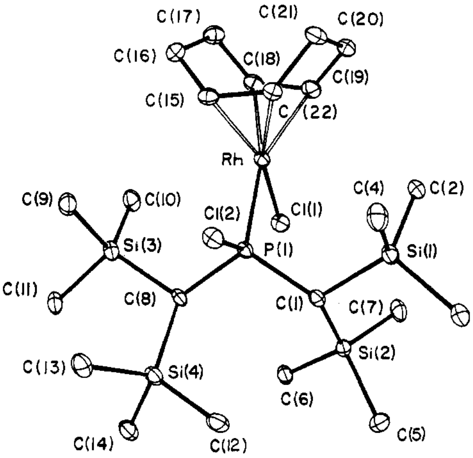

Figure 3. Computer-generated perspective diagram of 1. The hydrogen atoms and toluene have been omitted for clarity.

atomic coordinates for the non-hydrogen atoms in 1, 5, and 8 are listed in Tables II–IV.

Complex 1 exists as a toluene adduct. The approximately square-planar structure is illustrated in Figure 3. The important bond lengths and angles are listed in Table V. The major features of the structure are as follows: (a) the Rh–P bond distance is normal, compared to other Rh–P distances,[21,22] (b) there appears to be an amount of strain within the ligand, as evidenced by the slight elongation of the C–$SiMe_3$ bonds (average 1.921 (5) Å compared to the normal 1.85 Å) and by the wide P–C–Si angles (115–121°),[23,24] (c) the angles at phosphorus are unremarkable, compared with those in other systems,[21,22] (d) the Rh–Cl distance is normal.

Table IV. Atomic Coordinates (and Esd's) for Non-Hydrogen Atoms in Crystalline 8

atom	10^4x	10^4y	10^4z
Rh	3217 (1)	1000 (1)	1927 (1)
Cl(1)	1153 (1)	1415 (1)	1783 (1)
O(1)	5735 (4)	431 (2)	2090 (2)
C(5)	4758 (5)	661 (2)	2024 (3)
P(1)	3696 (1)	1692 (1)	1148 (1)
C(1)	5338 (5)	1907 (2)	1058 (2)
C(2)	2899 (5)	1679 (2)	284 (3)
Si(1)	6350 (1)	1362 (1)	627 (1)
Si(2)	6192 (2)	2307 (1)	1805 (1)
Si(3)	2189 (2)	2424 (1)	48 (1)
Si(4)	1848 (2)	1030 (1)	−24 (1)
C(11)	5453 (5)	690 (3)	330 (3)
C(12)	7776 (5)	1082 (3)	1149 (3)
C(13)	6869 (6)	1763 (3)	−99 (3)
C(21)	6691 (6)	1813 (3)	2512 (3)
C(22)	5159 (6)	2889 (3)	2115 (3)
C(23)	7599 (6)	2686 (3)	1516 (3)
C(31)	3385 (6)	3022 (3)	223 (3)
C(32)	1731 (6)	2441 (3)	−858 (3)
C(33)	807 (6)	2607 (3)	493 (3)
C(41)	2260 (6)	844 (3)	−880 (3)
C(42)	131 (5)	1217 (3)	−79 (3)
C(43)	2030 (6)	342 (3)	483 (3)
P(2)	2436 (1)	376 (1)	2689 (1)
C(3)	3275 (5)	−306 (2)	2962 (3)
C(4)	1803 (5)	665 (2)	3445 (3)
Si(5)	4776 (2)	−231 (1)	3566 (1)
Si(6)	3248 (2)	−913 (1)	2316 (1)
Si(7)	191 (2)	307 (1)	3535 (1)
Si(8)	1880 (2)	1479 (1)	3665 (1)
C(51)	5247 (5)	550 (2)	3749 (3)
C(52)	6196 (6)	−608 (3)	3293 (3)
C(53)	4383 (6)	−581 (3)	4352 (3)
C(61)	1650 (6)	−953 (3)	1831 (3)
C(62)	3508 (6)	−1622 (3)	2782 (3)
C(63)	4434 (6)	−833 (3)	1713 (3)
C(71)	−948 (5)	472 (3)	2803 (3)
C(72)	−468 (6)	561 (3)	4297 (3)
C(73)	335 (5)	−514 (2)	3634 (3)
C(81)	382 (6)	1889 (3)	3404 (3)
C(82)	3202 (6)	1892 (3)	3341 (3)
C(83)	2190 (7)	1494 (3)	4595 (3)

Table V. Selected Bond Distances (Å) and Angles (deg) for 1

(a) Bond Distances			
Rh–Cl(1)	2.363 (1)	Rh–P(1)	2.287 (1)
P(1)–C(8)	1.838 (4)	P(1)–Cl(2)	2.090 (2)
Si(1)–C(1)	1.920 (4)	Si(2)–C(1)	1.923 (5)
C(15)–C(22)	1.401 (7)	C(18)–C(19)	1.368 (7)
(b) Bond Angles			
Cl(1)–Rh–P(1)	85.0 (1)	Cl(1)–Rh–C(15)	157.4 (1)
P(1)–Rh–C(15)	97.0 (1)	Rh–P(1)–Cl(2)	113.7 (1)
Rh–P(1)–C(8)	116.9 (2)	C(1)–P(1)–C(8)	111.8 (2)
Cl(2)–P(1)–C(1)	100.4 (2)	Cl(2)–P(1)–C(8)	97.8 (2)
P(1)–C(1)–Si(1)	115.0 (2)	P(1)–C(1)–Si(2)	121.3 (2)
Si(1)–C(1)–Si(2)	109.9 (2)	Si(3)–C(8)–Si(4)	111.3 (2)

Complex 5 exists as a trans dimer (see Figure 2). The molecule is a rare example of a dimeric rhodium complex containing secondary phosphines.[25] The framework formed by the phosphorus, rhodium, and chlorine atoms is planar, rather than of the folded type. This may be due in part to steric factors, but the finer details of Rh–Rh interactions in such systems remain to be fully understood.[26,27] Most dimeric rhodium systems known to date

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Table VI. Selected Bond Distances (Å) and Angles (deg) for 5

(a) Bond Distances

Rh-Rh′	3.690 (1)	Rh-P	2.203 (1)
Rh-Cl	2.391 (1)	Rh-Cl′	2.475 (1)
Rh-C(1)	2.098 (3)	Rh-C(2)	2.110 (3)
P-C(01)	1.845 (3)	P-C(02)	1.857 (3)
Si(1)-C(01)	1.904 (2)	Si(2)-C(01)	1.911 (3)
C(1)-C(2)	1.413 (4)	P-HP	1.366 (25)

(b) Bond Angles

Cl-Rh-P	96.0 (1)	Cl-Rh-Cl′	81.4 (1)
Rh-Cl-Rh′	98.6 (1)	P-Rh-Cl′	173.0 (1)
Rh-P-C(01)	122.7 (1)	Rh-P-C(02)	118.9 (1)
Si(1)-C(01)-Si(2)	114.7 (2)	P-C(01)-Si(1)	110.7 (1)
C(02)-P-HP	98.5 (10)	Rh-P-HP	106.7 (10)

Table VII. Selected Bond Distances (Å) and Angles (deg) for 8

(a) Bond Distances

Rh-Cl(1)	2.376 (1)	Rh-P(1)	2.345 (1)
Rh-P(2)	2.337 (1)	Rh-C(5)	1.801 (6)
P(1)-C(1)	1.839 (5)	P(1)-C(2)	1.898 (5)
C(5)-O(1)	1.156 (7)	P(2)-H(1)	1.39 (5)

(b) Bond Angles

Cl(1)-Rh-C(5)	177.9 (2)	Cl(1)-Rh-P(1)	85.0 (1)
C(5)-Rh-P(1)	95.9 (2)	Cl(1)-Rh-P(2)	86.4 (1)
Rh-C(5)-O(1)	178.4 (5)	Rh-P(1)-C(1)	121.6 (2)
P(1)-C(2)-Si(4)	120.8 (3)	C(1)-P(1)-C(2)	104.1 (2)

are folded as in [{RhCl(CO)$_2$}$_2$]. This is only the third planar chloro-bridged rhodium(I) complex to be structurally characterized. It is the sole example exhibiting a trans geometry with two different terminal ligands. The planar dimers characteristically have longer Rh···Rh distances (≥3.50 Å) than their folded analogues (<3.20 Å).[28] The Rh···Rh distance in **5** is 3.690 (1) Å. This is longer than in the other two known complexes, [{RhCl(COD)}$_2$] with 3.50 (1) Å and [(PPh$_3$)$_4$Rh$_2$Cl$_2$] with 3.662 (2) Å.[28,29] The Rh–Cl distances in **5** are 2.391 (1) and 2.475 (1) Å. A difference in Rh–Cl bond lengths has also been noted in [(PPh$_3$)$_4$Rh$_2$Cl$_2$] where a trans effect is not operating (Rh–Cl = 2.394 (2) and 2.424 (2) Å).[28] The one long Rh–Cl bond in **5** may explain why the dimer dissociates in solution. Chloro-bridge-splitting reactions, as in eq 3, are well-documented.[4,12,13,18]

As in the mononuclear complex the phosphine ligand appears to be strained internally. The average C–SiMe$_3$ bond distance is 1.907 (3) Å. Some important bond distances and angles for **5** are listed in Table VI. There are many nonbonded contacts in both **1** and **5** which are less than their van der Waals distances. The Cl(1)···P(1) and Cl(1)···Si(2) distances in **1** are 3.142 (3) Å and 3.590 (5) Å, respectively. The Cl···Cl′, Cl···P and Cl···Si(2) distances in **5** are 3.174 (2), 3.415 (2), and 3.697 (3) Å, respectively. The SiMe$_3$ groups in both **1** and **5** are congested and are responsible for many nonbonded interactions with their neighboring groups. It is interesting to note that the complex [IrBr(COD)(PH{CH(SiMe$_3$)$_2$}$_2$)][11] also contains similar nonbonded contacts but does not exhibit any observable dissociation in solution.

The structure of **8** is illustrated in Figure 4. The rhodium atom is in a slightly distorted square-planar environment. The important bond lengths and angles are listed in Table VII. The Rh–P bonds in **8** are longer than in **1** and **5** but are shorter than those in the complex *trans*-[RhCl(CO)(P(*t*-Bu)$_3$)$_2$] (**9**) (average 2.434 (1) Å).[18] The two P–C bonds that are nearest to the chlorine atom are longer than those near the carbonyl group (1.892 (6)–1.842 (5) Å, average). The C(5)–O(1) distance in **8** is 1.156 (7) Å. The previously reported structures of **9** and *trans*-[RhCl(CO)(PPh$_3$)$_2$] (**11**) have displayed shortened C–O distances due to high thermal motion. In fact, the structure of **11** contained a number of peculiar angles and distances that do not agree with the reported spectroscopic data.[30] The structure of **8** is in agreement with all of the spectroscopic data obtained.

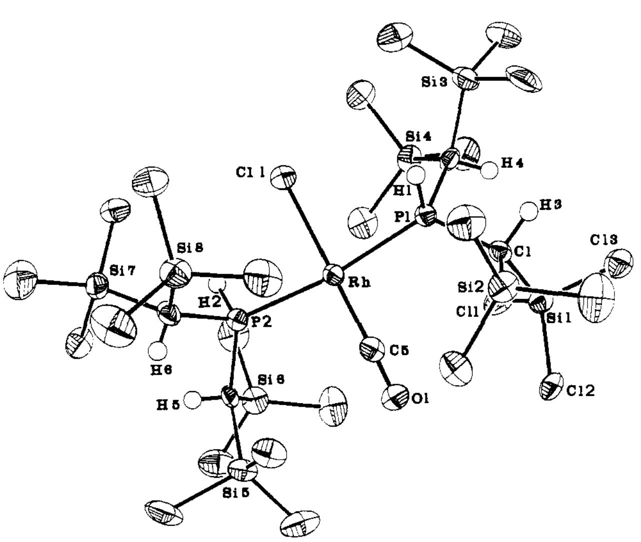

Figure 4. Computer-generated perspective diagram of **8**. The methyl hydrogens have been omitted for clarity.

The cone angles for the phosphines PX{CH(SiMe$_3$)$_2$}$_2$ when bound to a four-coordinate rhodium atom are X = H, 175°; X = Cl, 183°; and X = Me, 195°. Since no crystallographic data was available for PMe{CH(SiMe$_3$)$_2$}$_2$, the cone angle was calculated by assuming similar angles at phosphorus and reasonable methyl geometry and distances (P–C ~ 1.84 Å and C–H ~ 1.0 Å). The cone angles support our view that PH{CH(SiMe$_3$)$_2$}$_2$ and PCl{CH(SiMe$_3$)$_2$}$_2$ are about as bulky as P(*t*-Bu)$_3$ or P(C$_6$H$_{11}$)$_3$, and PMe{CH(SiMe$_3$}$_2$ is even larger.[31,32]

In summary, the most interesting features of the structures described are 3-fold: Firstly, the extent of the dissociation for these 16-electron complexes is remarkable, considering the noncrowding coligands COE, Cl$^-$, and COD. We believe that the size of the phosphine ligands will eventually permit the isolation of three-coordinate rhodium species. Secondly, the fact that X can be readily altered allows control over the degree of dissociation. Finally, the fact that the geometry within one bond away from phosphorus is little changed from typical phosphines suggests that the steric effects of these ligands are more subtle than those in P(*t*-Bu)$_3$ or P(C$_6$H$_{11}$)$_3$. This final point is in agreement with data from other complexes such as [Cr(CO)$_5$Sn{CH(SiMe$_3$)$_2$}$_2$][33] or (P{CH(SiMe$_3$)$_2$}$_2$)$_2$.[4,34] The C–Sn–C and C–P–C angles are fairly small in these species, but the long P–P bond distance in the latter as well as the fact that it dissociates significantly in solution indicate that

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the important interligand steric interactions take place 2–3 bonds distant from the central atom.

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Registry No. 1, 89178-74-5; 2, 89178-75-6; 3, 89178-76-7; 4, 14694-95-2; 5, 89196-39-4; 6, 81177-96-0; 7, 87451-18-1; 8, 87451-19-2; $PCl\{CH(SiMe_3)_2\}_2$, 63429-87-8; $\{RhCl(COD)\}_2$, 12092-47-6; $\{RhCl(COE)_2\}_2$, 12279-09-3; $\{RhCl(CO)_2\}_2$, 14523-22-9; $\{IrCl(COD)\}_2$, 12112-67-3; $PMe\{CH(SiMe_3)_2\}_2$, 70360-01-9; $IrCl(COD)(PH\{CH(SiMe_3)_2\}_2)$, 89178-77-8; $IrCl(COD)(PMe\{CH(SiMe_3)_2\}_2)$, 89178-78-9; $IrCl(COD)(PCl\{CH(SiMe_3)_2\}_2)$, 89178-79-0; $RhCl(COE)_2(PH\{CH(SiMe_3)_2\}_2)$, 89178-80-3; *trans*-$RhCl(COE)(PH\{CH(SiMe_3)_2\}_2)_2$, 89178-81-4.

Supplementary Material Available: Tables of bond distances and angles, structure factors, and calculated hydrogen positional and thermal parameters (90 pages). Ordering information is given on any current masthead page.

Reaction of Mono- and Dilithioferrocene with Octachlorocyclotetraphosphazene. The Crystal and Molecular Structures of $N_4P_4Cl_6[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]_2$ and $N_3P_3Cl_4[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]N_4P_4Cl_7$

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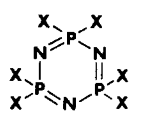
New and unusual derivatives of cyclophosphazenes bearing ferrocene substituents have been synthesized by the reactions of mono- and dilithioferrocene with octachlorocyclotetraphosphazene, $(NPCl_2)_4$, and with equimolar mixtures of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, and $(NPCl_2)_4$. The reactions of monolithioferrocene with $(NPCl_2)_4$ gave $N_4P_4Cl_6[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]_2$ (4) in which the tetrameric ring has contracted to give a cyclic trimer with a phosphorus–nitrogen–phosphorus pendent chain. The two ferrocene units were found to be attached to the terminal phosphorus atom of this chain. The structure of 4 was examined by X-ray diffraction techniques. Crystals of 4 are monoclinic of space group $P2_1/c$ with a = 11.199 (3) Å, b = 22.774 (7) Å, c = 11.504 (7) Å, β = 104.81 (3)°, V = 2837 (4) Å^3, and Z = 4. The structure was refined to discrepancy indices $R = 0.055$ and $R_w = 0.063$. The most striking feature of the molecule is the structure of the pendent chain. Here, the bond angle at nitrogen is unusually wide, being 142.7 (3)°. Also, the single bond between this nitrogen atom and the ring phosphorus (1.54 Å) is significantly shorter than the supposed double bond to the terminal phosphorus atom of the chain (1.57 Å). These observations are compatible with appreciable delocalization within the phosphorus–nitrogen skeleton. The reactions of lithioferrocene with a 1:1 molar mixture of $(NPCl_2)_3$ and $(NPCl_2)_4$ gave the bi(cyclophosphazenes), $N_3P_3Cl_4[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_4X)]N_4P_4Cl_7$ (**5a**, X = H; **5b**, X = Cl). The structure of **5a** was also examined by X-ray diffraction techniques. Crystals of **5a** were triclinic of space group $P\bar{1}$ with a = 12.899 (5) Å, b = 14.206 (3) Å, c = 10.003 (4) Å, α = 99.77 (3)°, β = 105.76 (3)°, γ = 112.99 (2)°, V = 1543 (2) Å^3, and Z = 2. The structure was refined to discrepancy indices $R = 0.053$ and $R_w = 0.061$. The most striking feature of this molecule is the linkage of the cyclic trimeric and tetrameric rings by a P–P bond. This is the first example of a trimer–tetramer bi(cyclophosphazene). Possible mechanisms leading to the formation of these ferrocenylphosphazenes are also discussed.

This investigation is part of an exploration of the reactions of a variety of organometallic reagents with halogenophosphazenes 1–3 (X = halogen).



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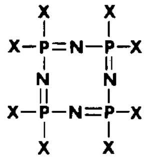

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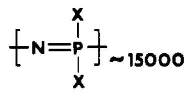

3

Increasing interest exists in the preparation of new cyclic and high polymeric phosphazenes linked to transition-metal organometallic units, partly because such species are prospective catalyst systems or electroactive species. Recently, six methods have been developed to link transition metals to phosphazenes. They are (a) coordination of metals to skeletal nitrogen atoms,[1] (b) coordination of organometallic units to phosphine donors linked to the phosphazene skeleton through aryloxy-spacer groups,[2] (c) attachment of the metal via π-complexing through pendent acetylenic units,[3] (d) metal coordination to phosphazenes that bear *nido*-carborane units,[4] (e) the formation of phosphazenes with direct skeletal phosphorus–transition-metal bonds,[5-7] and (f) linkage of metallocene units to the

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