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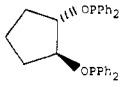
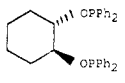


XIX



XX

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Soluble (Chlorosilyl)phosphine and Siloxyphosphine Complexes of Rhodium(I)

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A number of soluble (chlorosilyl)phosphine complexes of rhodium(I) which are capable of being polymerized into poly(siloxyphosphine)–rhodium(I) species have been synthesized and characterized. They are $L_2'Rh(CO)Cl$, L'_3RhCl, L''_3RhCl, and $L'_4Rh_2Cl_2$ (L′ = $Cl_3Si(CH_2)_2P(C_6H_5)_2$, L″ = $Cl_3Si(CH_2)_8P(C_6H_5)_2$). Soluble siloxyphosphine–rhodium(I) complexes $LRh(NBD)Cl$, $L_2Rh(CO)Cl$, L_3RhCl, and $L_4Rh_2Cl_2$ (NBD = norbornadiene, L = $[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2$) have also been synthesized and characterized and their reactions with gaseous H_2, CO, and HCl as well as their catalytic behavior in hydrogenation reactions have been studied. These complexes were prepared to serve as study models for their polymeric counterparts.

Introduction

There is currently a considerable interest in the problem of "heterogenizing" homogeneous catalysts by attaching transition-metal complexes to insoluble supports.[1] These supports are usually polystyrene and related polymers or inert materials such as silica and glass. In our laboratories we are interested in utilizing silicones as supports since these are potentially more inert than traditional organic polymers and also, if necessary, can be modified more easily than other inorganic supports.

Two methods are available for producing metal centers anchored to an insoluble matrix in such a way that there is a good likelihood of multiple attachment. These are exemplified in the present context of our aim of combining silicones with phosphine derivatives of rhodium(I) as follows: a preformed (chlorosilyl)phosphine–rhodium(I) complex could be attached to a polymeric support[2] or it could be hydrolytically polycondensed to a poly(siloxyphosphine)–rhodium(I) macro compound.[3] In the latter case if the starting monomeric complex is well characterized and if the "heterogenization" process does not change appreciably the environment of the metal center, it should be possible to produce a polymer with well-defined catalytic sites.

This work describes the synthesis and characterization of some (chlorosilyl)phosphine complexes of rhodium(I) which

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are capable of being polymerized into poly(siloxyphosphine)–rhodium(I) compounds. A number of soluble siloxyphosphine–rhodium(I) complexes are also described. These were synthesized to serve as study models for their polymeric counterparts.

Experimental Section

Techniques and Instrumentation. In all synthetic work and for the manipulation of oxygen- and/or moisture-sensitive compounds Schlenk tubes and filters under a nitrogen atmosphere and a drybox under helium were used.

Infrared spectra were recorded on Perkin-Elmer Model 457 and 225 spectrophotometers. ^1H and ^{31}P (^1H decoupled) NMR spectra were measured with a Varian XL-100 spectrometer. The solvent was C_6D_6 unless otherwise indicated. Chemical shifts are given in parts per million downfield from external Me_4Si for ^1H spectra and upfield from external 85% H_3PO_4 for ^{31}P spectra.

Low-resolution mass spectra were determined on Varian/MAT CH4B and AEI MS902 mass spectrometers.

Thin-layer chromatography was done on Eastman chromatogram sheets of 13181 silica gel with fluorescent indicator no. 6060.

Column chromatography was done on Florisil (100–200 mesh). The solvents and Florisil were deoxygenated prior to use. Column preparation and product elution and collection were done under nitrogen. Gas–liquid chromatography was performed by using an Aerograph Model A-90-P gas chromatograph equipped with a 2 m long column (internal diameter 4.5 mm). The column packing used to separate the vinylsiloxanes was 10% FFAP on Chromosorb W-AW, 60/80 mesh. The gas (He) flow rate was 15 mL/min, and the column temperature was 150 °C.

Ultraviolet irradiation reactions were done with a 200-W mercury lamp (Hanovia S-654 A36) in thick-walled Pyrex Carius tubes which were cooled by a stream of air.

Microanalyses for C, H, and Cl were performed by P. Borda of the microanalytical laboratory, Chemistry Department, University of British Columbia, and microanalyses for Rh, P, and Si by Alfred Bernhardt Mikroanalytisches Laboratorium.

Preparation of Vinylsiloxanes. Chlorotrimethylsilane (108 g, 1 mol) and methylvinyldichlorosilane (72 g, 0.5 mol) dissolved in 200 mL of diethyl ether were added slowly to 400 mL of water at such a rate as to maintain the reaction temperature at 6–10 °C. The reaction vessel was cooled in an ice–salt–water bath.

The mixture was next stirred for 1 h while the temperature was allowed to increase to 20 °C. The ether layer was separated and washed with water, and the solvent was flash evaporated, leaving 84.3 g of a colorless oil. The presence of at least three major components in the product mixture was detected by GLC.

Three fractions, all colorless liquids, were separated by repeated distillation at a reduced pressure:

(a) First fraction, identified as $(CH_3)_3SiOSi(CH_3)_3$: bp 35–37 °C (74 mm) [lit.[4] bp 100.1 °C (757 mm)]; 3.7 g; mass spectrum *m/e* 162 (M^+); ^1H NMR 0.07 (s, $Si(CH_3)_3$). Anal. Calcd for $C_6H_{18}OSi_2$: C, 44.4; H, 11.1. Found: C, 44.0; H, 10.9.

(b) Second fraction, identified as $[(CH_3)_3SiO]_2Si(CH_3)(CH{=}CH_2)$: bp 100 °C (77 mm) [lit.[5] bp 164–166 °C (760 mm)]; 34 g (27.5% yield); mass spectrum *m/e* 248 (M^+); ^1H NMR 0.10 (s, 18 H, $Si(CH_3)_3$), 0.12 (s, 3 H, $Si(CH_3)$), 5.9 (m, 3 H, $Si(CH{=}CH_2)$). Anal. Calcd for $C_9H_{24}O_2Si_3$: C, 43.6; H, 9.8. Found: C, 43.6; H, 9.7.

(c) Third fraction, identified as $(CH_3)_3Si[OSi(CH_3)(CH{=}CH_2)]_3OSi(CH_3)_3$: bp 122–124 °C (77 mm); 5.5 g; mass spectrum *m/e* 420 (M^+); ^1H NMR 0.10 (s, 18 H, $Si(CH_3)_3$), 0.13 (s, 9 H, $Si(CH_3)$), 5.9 (m, 9 H, $Si(CH{=}CH_2)$). Anal. Calcd for $C_{15}H_{36}O_2Si_3$: C, 42.9; H, 8.6. Found: C, 42.9; H, 8.8.

Higher siloxy polymers (bp >140 °C (1 × 10^{-3} mm), 40.2 g) remained in the still pot.

Preparation of Phosphine Ligands. All phosphine ligands were prepared by ultraviolet irradiation of a mixture of diphenylphosphine (1 mol) and the appropriate vinylsilane (1.2 mol).

In a typical reaction 12 g (64.5 mmol) of diphenylphosphine and 19.2 g (77.5 mmol) of $[(CH_3)_3SiO]_2Si(CH_3)(CH{=}CH_2)$ were introduced into a Carius tube which had previously been evacuated and then filled with nitrogen. The mixture was degassed on the vacuum line. The tube was closed and irradiated with a mercury lamp for 48 h, while continuously shaken. When the reaction was completed, the products were transferred into a nitrogen-filled distillation apparatus. Distillation yielded an air-sensitive, colorless liquid identified as $[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2$: bp 142 °C ($10^{-3}$ mm); 71.4% yield; mass spectrum *m/e* 434 (M^+); ^1H NMR 0.11 (s, 18 H, $Si(CH_3)_3$), 0.08 (s, 3 H, $Si(CH_3)$), 0.60 (m, 2 H, $SiCH_2$), 2.09 (m, 2 H, PCH_2), 7.38 (m, 10 H, $P(C_6H_5)_2$); ^{31}P NMR 9.14 (s). Anal. Calcd for $C_{21}H_{35}O_2PSi_3$: C, 58.1; H, 8.1. Found: C, 57.9; H, 8.2.

The following were prepared in the same way.

$(CH_3)_3Si(CH_2)_2P(C_6H_5)_2$: bp 128 °C (1 × 10^{-3} mm); 79.6% yield; mass spectrum *m/e* 286 (M^+); ^1H NMR 0.14 (s, 9 H, $Si(CH_3)_3$), 0.68 (m, 2 H, $SiCH_2$), 2.48 (m, 2 H, PCH_2), 7.40 (m, 10 H, $P(C_6H_5)_2$); ^{31}P NMR 10.32 (s). Anal. Calcd for $C_{17}H_{23}PSi$: C, 71.4; H, 8.4. Found: C, 71.6; H, 8.4.

$Cl_2(CH_3)Si(CH_2)_2P(C_6H_5)_2$: bp 142 °C (1 × 10^{-3} mm); 86.2% yield; mass spectrum *m/e* 326 (M^+); ^1H NMR 0.83 (s, 3 H, $Si(CH_3)$), 1.29 (m, 2 H, $SiCH_2$), 2.33 (m, 2 H, PCH_2), 7.45 (m, 10 H, $P(C_6H_5)_2$); ^{31}P NMR 10.38 (s). Anal. Calcd for $C_{15}H_{17}Cl_2PSi$: C, 55.2; H, 5.2; Cl, 21.5. Found: C, 55.4; H, 5.4; Cl, 21.2.

$Cl_3Si(CH_2)_2P(C_6H_5)_2$: bp 142 °C (1 × 10^{-3} mm) [lit.[6,7] bp 142–144 °C (1 × 10^{-1} mm)]; 85.6% yield; mass spectrum *m/e* 347 (M^+); ^1H NMR 1.63 (m, 2 H, $SiCH_2$), 2.35 (m, 2 H, PCH_2), 7.45 (m, 10 H, $P(C_6H_5)_2$); ^{31}P NMR 10.35 (s). Anal. Calcd for $C_{14}H_{14}Cl_3PSi$: C, 48.4; H, 4.0; Cl, 30.6. Found: C, 48.6; H, 4.0; Cl, 30.4.

$Cl_3Si(CH_2)_8P(C_6H_5)_2$: bp 210–215 °C (6.5 × 10^{-1} mm) [lit.[6,7] bp 218–221 °C (5 × 10^{-1} mm)]; 30.6% yield; mass spectrum *m/e* 431 (M^+); ^1H NMR 1.42 (m, 14 H, $Si(CH_2)_7$), 2.30 (m, 2 H, PCH_2), 7.36 (m, 10 H, $P(C_6H_5)_2$); ^{31}P NMR 16.08 (s). Anal. Calcd for $C_{20}H_{26}Cl_3PSi$: C, 55.6; H, 6.0; Cl, 24.7. Found: C, 56.1; H, 6.3; Cl, 24.6.

Preparation of (NBD){[$(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2$}RhCl. (Bicyclo[2.2.1]hepta-2,5-diene)di-μ-chloro-dirhodium, $[(NBD)RhCl]_2$ (0.461 g, 1.0 mmol), was introduced into a Schlenk tube and suspended in 8 mL of dichloromethane. A solution of $[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2$ (0.868 g, 2.0 mmol) in 8 mL of dichloromethane was gradually introduced with a syringe. The tube contents were stirred with a magnetic bar at room temperature for 1 h.

The reaction mixture was separated by column chromatography, using acetone/petroleum ether (bp 40–60 °C) (15% (v/v)), and the main product eluted as a yellow band. It was recrystallized from petroleum ether at −75 °C, giving 1 g (75.0% yield) of yellow solid: mass spectrum *m/e* 664 (M^+); ^1H NMR 0.08 (s, 3 H, $Si(CH_3)$), 0.12 (s, 18 H, $Si(CH_3)_3$), 1.40 (m, 2 H, $SiCH_2$), 2.30 (m, 2 H, PCH_2), 7.23 (m, 10 H, $P(C_6H_5)_2$), 1.40 (m, 2 H, CH_2 (NBD)), 3.03 (m, 2 H, *CH* (NBD) trans to Cl), 3.72 (m, 2 H, *CH* (NBD)), 5.23 (m, 2 H, *CH* (NBD) trans to P); ^{31}P NMR −31.45 (d, J(Rh–P) = 171.6 Hz). Anal. Calcd for $C_{28}H_{43}ClO_2PRhSi_2$: C, 50.6; H, 6.5; Cl, 5.4. Found: C, 50.8; H, 6.6; Cl, 5.3.

Preparation of {[$(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2$}$_2$Rh(CO)Cl. To a degassed solution of 0.389 g (1.0 mmol) of $[Rh(CO)_2Cl]_2$ in 8 mL of benzene was added a solution of 1.736 g (4.0 mmol) of $\{[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2\}$ in 8 mL of benzene. The mixture was refluxed for 4 h under nitrogen until ν(C≡O) of the starting material disappeared. The solution was cooled to room temperature. The desired yellow product precipitated out upon addition of ethyl alcohol. TLC using an acetone/petroleum ether mixture (1:9 (v/v)) as the eluent indicated the presence of only one component: 1.25 g (60.0% yield); mp 39–44 °C; mass spectrum *m/e* 450 (M^+) (probe not heated), *m/e* 1034 (M^+) (probe temperature 300 °C); IR ν(C≡O) 1968 cm^{-1}; ^1H NMR 0.14 (s, 6 H, $Si(CH_3)$), 0.18 (s, 36 H, $Si(CH_3)_3$), 0.70–1.50 (m) and 2.96 (m) (total 8 H, relative intensities 2:1, CH_2CH_2), 7.16 (m) and 7.97 (m) (total 20 H, relative intensities 2:1, $P(C_6H_5)_2$); ^{31}P NMR −29.44 (s), −29.65 (d, J(Rh–P) = 124.6 Hz), relative intensities vary from 1:5 to 2:7 for different preparation batches. Anal. Calcd for $C_{43}H_{70}ClO_5P_2RhSi_6$: C, 49.9; H, 6.8; Cl, 3.4. Found: C, 50.3; H, 6.8; Cl, 3.2.

{[$(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2$}$_3$RhCl was similarly prepared from 4.557 g (105 mmol) of the phosphine and 0.681 g (17.5 mmol) of $(C_2H_4)_4Rh_2Cl_2$ in benzene (120 mL, 1 h, 20 °C). The product was a viscous, dark red oil: 4.75 g (94.0% yield); ^1H NMR 0.07 (s, 21 H, $Si(CH_3)$ and $Si(CH_3)_3$), 0.72 (m, 2 H, $SiCH_2$), 1.48 (m, 2 H, PCH_2), 7.88 (m, 10 H, $P(C_6H_5)_2$), and 0.18 (s, 42 H, $Si(CH_3)$ and $Si(CH_3)_3$), 1.12 (m, 4 H, $SiCH_2$), 2.72 (m, 4 H, PCH_2), 7.06 (m, 20 H, $P(C_6H_5)_2$); ^{31}P NMR −29.75 (dd, J(P–P) = 39.0 Hz, J(Rh–P) = 140.0 Hz), −44.97 (dt, J(P–P) = 39.0 Hz, J(Rh–P) = 188.0 Hz), −29.92 (s), relative intensities 20:10:1; IR (neat) ν(Rh–Cl) 260 (w)

cm^{-1}. Anal. Calcd for $C_{63}H_{105}ClO_6P_3RhSi_9$: C, 52.5; H, 7.3; Cl, 2.5; Rh, 7.2; P, 6.5. Found: C, 52.2; H, 7.3; Cl, 2.6; Rh, 6.9; P, 6.3.

$\{[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2\}_4Rh_2Cl_2$ was similarly prepared by reaction of $(C_2H_4)_4Rh_2Cl_2$ (0.487 g, 1.25 mmol) with $[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2$ (2.172 g, 5.00 mmol) in 50 mL of refluxing benzene (3 h). The product was obtained as a very viscous dark red oil: 2.34 g (93.0% yield); ^1H NMR 0.12 (s, 84 H, $Si(CH_3)$ and $Si(CH_3)_3$), 1.00 (m, 8 H, $SiCH_2$), 2.14 (m, 8 H, PCH_2), 7.22 (m) and 7.90 (m) (total 40 H, relative intensities 2:1, $P(C_6H_5)_2$); ^{31}P NMR −47.02 (d, J(Rh–P) = 196.5 Hz); IR(neat) ν(Rh–Cl) 225 (m) cm^{-1}. Anal. Calcd for $C_{84}H_{140}Cl_2O_8P_4Rh_2Si_{12}$: C, 50.1; H, 7.0; Cl, 3.5; Rh, 10.2; P, 6.2. Found: C, 50.5; H, 7.2; Cl, 3.8; Rh, 10.1; P, 6.4.

$[Cl_3Si(CH_2)_2P(C_6H_5)_2]_2Rh(CO)Cl$ was similarly prepared from the phosphine (1.400 g, 4.0 mmol) and $(CO)_4Rh_2Cl_2$ (0.389 g, 1.0 mmol) in refluxing benzene (16 mL, 4 h). The product precipitated out of the solution upon addition of petroleum ether. The complex, an oxygen- and moisture-sensitive yellow solid, was purified by reprecipitation with petroleum ether out of a benzene solution: 1.65 g (96.0% yield); mp 52–75 °C; IR (C_6D_6) ν(C≡O) 1970 (s) cm^{-1}; ^{31}P NMR −30.00 (d, J(Rh–P) = 127.5 Hz); ^1H NMR 1.92 (m, 4 H, $SiCH_2$), 2.98 (m, 4 H, PCH_2), 7.10 (m) and 7.74 (m) (total 20 H, relative intensities 3:2, $P(C_6H_5)_2$). Anal. Calcd for $C_{29}H_{28}Cl_7OP_2RhSi_2$: C, 40.0; H, 3.3; Cl, 28.9; Rh, 12.0; P, 7.2. Found: C, 40.4; H, 3.3; Cl, 28.6; Rh, 12.1; P, 7.1.

$[Cl_3Si(CH_2)_2P(C_6H_5)_2]_3RhCl$ and $[Cl_3Si(CH_2)_8P(C_6H_5)_2]_3RhCl$. The former was prepared from 0.934 g (2.4 mmol) of $Cl_3Si(CH_2)_2P(C_6H_5)_2$ dissolved in 4 mL of benzene and 0.156 g (0.4 mmol) of $(C_2H_4)_4Rh_2Cl_2$ in 8 mL of benzene (1 h). The orange product was obtained by evaporating the solution to dryness under vacuum: 0.900 g (95.3% yield); mp 170–210 °C dec; ^{31}P NMR −28.53 (dd, J(P–P) = 39.9 Hz, J(Rh–P) = 136.2 Hz), −42.97 (dt, J(Rh–P) = 187.1 Hz, J(P–P) = 40.0 Hz), −25.88 (dd, J(Rh–P) = 97.6 Hz, J(P–P) = 26.4 Hz), −39.49 (dt, J(Rh–P) = 142.3 Hz, J(P–P) = 25.4 Hz), −49.34 (s), −48.77 (s), −44.37 (s), −43.89 (s); ^1H NMR 1.38 (m) 1.96 (m), 2.71 (m), and 4.12 (m) (total 12 H, CH_2CH_2), 7.06 (m), 7.74 (m), and 8.36 (m) (total 30 H, $P(C_6H_5)_2$), relative intensities 1:3:1:1:10:4:1, −13.96 (m, Rh–H); IR (C_6D_6) ν(Rh–H) 2095 (w) cm^{-1}; IR (Nujol) ν(Rh–H) 2095 (w), ν(Rh–Cl) 260 (w), 280 (w) cm^{-1}. Anal. Calcd for $C_{42}H_{42}C_{10}P_3RhSi_3$: C, 42.7; H, 3.6; Cl, 30.1; P, 7.9; Rh, 8.7. Found: C, 42.4; H, 3.7; Cl, 29.8; P, 7.7; Rh, 8.9.

In a similar reaction $[Cl_3Si(CH_2)_8P(C_6H_5)_2]_3RhCl$ was obtained: 93.2% yield; mp 147–172 °C; ^{31}P NMR −26.25 (dd, J(Rh–P) = 139.2 Hz, J(P–P) = 39.9 Hz), −40.94 (dt, J(Rh–P) = 188.0 Hz, J(P–P) = 40.1 Hz), −34.55 (m), −30.06 (m), −25.35 (m), −22.86 (m), −22.30 (m), relative intensities of dd plus dt to the rest of the peaks 4:1; ^1H NMR 1.05 (m), 1.93 (m), 2.45 (m), and 3.93 (m) ($(CH_2)_8$), 7.05 (m), 7.87 (m), and 8.35 (m) ($P(C_6H_5)_2$), relative intensities 72:10:5:1:20:9:1, −14.32 (m, Rh–H); IR (C_6D_6) ν(Rh–H) 2090 (m), 2170 (sh) cm^{-1}; IR (Nujol) ν(Rh–H) 2090 (m), 2170 (sh), ν(Rh–Cl) 260 (w), 280 (w) cm^{-1}. Anal. Calcd for $C_{60}H_{78}Cl_{10}P_3RhSi_3$: C, 50.2; H, 5.4; Cl, 24.8; Rh, 7.2; P, 6.5. Found: C, 50.5; H, 5.7; Cl, 24.4; Rh, 7.3; P, 6.5.

The preparation of $[Cl_3Si(CH_2)_2P(C_6H_5)_2]_3RhCl$ was repeated in glassware pretreated with trimethylchlorosilane. The spectra showed the following pattern: ^{31}P NMR −42.67 (dt, J(Rh–P) = 186.8 Hz, J(P–P) = 39.8 Hz), −28.27 (dd, J(Rh–P) = 140.4 Hz, J(P–P) = 39.3 Hz), −40 (m), −37 (m), −27 (m), −24 (m), relative intensities of the dt and dd to all multiplets 5:2; ^1H NMR 1.46 (m), 1.90 (m), 2.72 (m), and 4.16 (m) (total 12 H, CH_2CH_2), 7.04 (m), 7.72 (m), and 8.36 (m) (total 30 H, $P(C_6H_5)_2$), relative intensities 2:2:2:1:13:5:trace, −14.00 (m, Rh–H); $\{^{31}P\}^1H$ NMR no change in the downfield region, −14.00 (d, J(Rh–H) = 10 Hz); IR (C_6D_6) ν(Rh–H) 2095 (w) cm^{-1}.

$[Cl_3Si(CH_2)_2P(C_6H_5)_2]_4Rh_2Cl_2$. In the usual way 0.695 g (2.0 mmol) of $Cl_3Si(CH_2)_2P(C_6H_5)_2$ and 0.195 g (0.5 mmol) of $(C_2H_4)_4Rh_2Cl_2$ in 15 mL of benzene were refluxed for 3 h. An orange product was obtained by evaporating the filtered solution to dryness in vacuo: 0.76 g (91.0% yield); decomposition at 210–230 °C; ^{31}P NMR −72.22 (m), −68.77 (m), −46.91 (m), −43.95 (m), −26.67 (m), −24.20 (m), all of approximately the same intensities; ^1H NMR 1.4 (m), 2.2 (m), 3.3 (m), and 3.8 (m) (total 16 H, CH_2CH_2), 7.1 (m), 7.6 (m), 7.9 (m), and 8.3 (m) (total 40 H, $P(C_6H_5)_2$), relative intensities 6:6:3:1:30:6:2:2, −15.72 (dt, J(Rh–H) = 14 Hz, J(P–H) = 18 Hz), −13.95 (m), relative intensities 4:1, Rh–H; IR (C_6D_6) ν(Rh–H) 2090 (m); IR (Nujol) ν(Rh–H) 2090 (m), ν(Rh–Cl) 290 (w, br), 265 (w, br) cm^{-1}. Anal. Calcd for $C_{56}H_{56}C_{14}P_4Rh_2Si_4$: C, 40.3; H, 3.4; Cl, 29.8; Rh, 12.4; P, 7.4. Found: C, 40.4; H, 3.5; Cl, 29.5; Rh, 12.4; P, 7.2.

Reaction of $\{[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2\}_3RhCl$ with H_2. The complex was dissolved in deuterated benzene in an NMR tube, under nitrogen. The NMR tube was connected to a constant-pressure gas-uptake apparatus. The solution was degassed by the freeze-and-thaw method and hydrogen was introduced (760 mm). The color of the solution slowly changed from dark red to yellow. The NMR and IR spectra of the solution were recorded: ^1H NMR −8.5 (m), −10.1 (m), −17.9 (m), relative intensities 1:1:2, Rh–H; $\{^{31}P\}^1H$ NMR −9.3 (m, partly decoupled), −17.9 (d, J(Rh–H) = 23 Hz), relative intensities 1:1, Rh–H; ^{31}P NMR −41.03 (dd, J(P–P) = 20 Hz, J(Rh–P) = 110 Hz), −20.17 (dt, J(P–P) = 20 Hz, J(Rh–P) = 90 Hz), −29.92 (s), relative intensities 16:8:1; IR (C_6D_6) ν(Rh–H) 2075 (s), 2160 (sh) cm^{-1}.

The solvent was then evaporated in vacuo. The complex was redissolved in deuterated benzene in the same NMR tube. The NMR and IR spectra of the solution showed signals due to the original Rh(I) complex only. Repeating the hydrogenation step gave a solution with the same spectroscopic properties as those of the originally hydrogenated compound.

Reaction of $\{[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2\}_4Rh_2Cl_2$ with H_2. A similar procedure was followed. After the first hydrogenation, the NMR and IR spectra showed the following pattern (Figure 2): ^1H NMR −16.1 (m), −17.8 (m), −19.8 (t, J(P–H) = 24 Hz), −20.1 (dt, J(Rh–H) = 24 Hz, J(P–H) = 16 Hz) (all Rh–H); $\{^{31}P\}^1H$ NMR −16.1 (d, J(Rh–H) = 15 Hz), −17.8 (d, J(Rh–H) = 15 Hz), −19.8 (s), −20.1 (d, J(Rh–H) = 24 Hz); ^{31}P NMR −48.76 (s), −43.95 (s), −41.85 (s), −38.88 (s), −49.38 (s), −44.56 (s), −42.22 (s), −39.50 (s), −29.62 (s), −21.26 (m), −19.04 (m), relative intensities 83:74:100:70:24:27:25:25:20:27:25; IR (C_6D_6) ν(Rh–H) 2102 (s), 2165 (sh) cm^{-1}.

After removal of hydrogen by pumping, NMR and IR spectra of the solution were recorded. Only signals due to the original Rh(I) complex were present.

On hydrogenation the spectra showed the same pattern as the originally hydrogenated complex.

Reaction of $\{[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2\}_4Rh_2Cl_2$ with CO. An analogous procedure indicated that after 24 h the reaction appeared to be complete, and spectral analysis was performed. The spectra showed patterns characteristic of $\{[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2\}_2Rh(CO)Cl$: ^{31}P NMR −29.81 (d, J(Rh–P) = 124.7 Hz), −30.00 (s), relative intensities 30:1; ^1H NMR 0.19 (s, 42 H, $Si(CH_3)$ and $Si(CH_3)_3$), 1.15 (m, 4 H, $SiCH_2$), 2.98 (m, 4 H, PCH_2), 7.16 (m) and 8.00 (m) (total 20 H, relative intensities 3:2, $P(C_6H_5)_2$); IR (C_6D_6) ν(C≡O) 1965 (vs) cm^{-1}.

Reaction of $\{[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2\}_3RhCl$ with CO. The procedure was the same as for the di-μ-chloro-bis(phosphine)dirhodium. After the reaction had finished, the NMR and IR spectra showed the following patterns: ^{31}P NMR (C_6D_6, 35 °C) −30 to −3 (m), −29.94 (s); ^{31}P NMR [$(CD_3)_2CO$, −60 °C] −47 to −13 (m); ^1H NMR (C_6D_6) 0.18 (s, 63 H, $Si(CH_3)$ and $Si(CH_3)_3$), 1.05 (m, 6 H, $SiCH_2$), 2.71 (m, 6 H, PCH_2), 7.13 (m) and 7.85 (m) (total 30 H, relative intensities 3:2, $P(C_6H_5)_2$); IR (C_6D_6) ν(C≡O) 1965 (vs) cm^{-1}.

Reaction of $\{[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2\}_2Rh(CO)Cl$ with $\{[(CH_3)_3SiO]_2(CH_3)Si(CH_3)Si(CH_2)_2P(C_6H_5)_2\}$. The free phosphine ($3.8 \times 10^{-2}$ g, 8.8×10^{-2} mmol) and the complex (9.1×10^{-2} g, 8.8×10^{-2} mmol) were dissolved in C_6D_6 in an NMR tube: ^{31}P NMR −20 to −3 (m), −29.41 (s), relative intensities 4:1.

Reaction of $\{[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2\}_3RhCl$ with HCl(g). An NMR tube with the solution of the complex in benzene was connected to a modified constant-pressure gas-uptake apparatus equipped with Teflon stopcocks.

The solution was degassed and HCl(g) was introduced (760 mm), resulting in the immediate precipitation of a yellow, insoluble solid.

The precipitate was filtered, washed with benzene, dried in a stream of nitrogen for 8 h, and finally dried in vacuo for 1 h. The product was a noncrystalline pale yellow solid, insoluble in benzene, toluene, acetone, dichloromethane, 1,2-dichloroethane, petroleum ether, dimethyl sulfoxide, dimethylacetamide, and carbon disulfide: IR (Nujol) ν(Rh–H) 2110 (m), ν(Rh–Cl) 253 (m), 273 (w) cm^{-1}. Anal. Found: C, 53.7; H, 7.3; Cl, 9.5.

Hydrogenation of Styrene with Siloxyphosphine Complexes. The reactions were carried out in a constant-pressure gas-uptake apparatus at 35 °C and 760 mmHg of hydrogen pressure. The complex (3.0

$\times 10^{-3}$ mmol, based on Rh(I) atoms) and styrene (3.1×10^{-2} g, 3.0 $\times 10^{-1}$ mmol) were dissolved in 3 mL of benzene.

Percentage conversion as a function of time was recorded and the results are shown in Figure 3.

Discussion and Results

Ligand Synthesis. A convenient method for the preparation of phosphines R_2PR' is the addition of compounds with phosphorus–hydrogen bonds, e.g., R_2PH, to molecules containing carbon–carbon double bonds. Such reactions can be base catalyzed[8] or free-radical initiated.[9,10]

In this work (chlorosilyl)- and siloxyphosphines were prepared in good yields in the UV-induced reactions between diphenylphosphine and some vinyl- and octenylsilanes (eq 1).

$$(C_6H_5)_2PH + R'(R'')_2Si(CH_2)_nCH{=}CH_2 \rightarrow R'(R'')_2Si(CH_2)_{n+2}P(C_6H_5)_2 \quad (1)$$

$n = 0$, $R' = R'' = CH_3$

$n = 0$, $R' = CH_3$, $R'' = Cl$

$n = 0$, $R' = CH_3$, $R'' = OSi(CH_3)_3$ (L)

$n = 0$, $R' = R'' = Cl$ (L')

$n = 6$, $R' = R'' = Cl$ (L'')

The two trichlorosilyl derivatives have been described before.[6,7] The mass spectra of all products correspond with the appropriate molecular weights; no peaks of m/e values higher than those calculated for the parent ion M^+ are found. The $\{^1H\}^{31}P$ NMR spectra of each phosphine contain only one single peak in the region +9 to +16 ppm. The lack of any peaks due to $CHC\mathit{H}_3$ moieties in the ^1H NMR spectra confirms the addition of phosphorus to the terminal carbon atom only. The spectra of the (trimethylsilyl)- and (methyldichlorosilyl)phosphines show single resonances for the $Si(CH_3)$ groups at 0.14 and 0.83 ppm, respectively. The two different types of methyl groups in the siloxyphosphine are responsible for two different single peaks at 0.08 and 0.11 ppm with relative intensities 1:6 for $Si(CH_3)$ and $Si(CH_3)_3$, respectively. The same compound shows two unresolved multiplets of equal intensity which can be assigned to the $C\mathit{H}_2C\mathit{H}_2$ moiety. A partially ^{31}P-decoupled spectrum shows a noticeable difference in the pattern of the multiplet centered at 0.60 ppm. The multiplet centered at 2.09 ppm is not affected. It has been reported[11,12] that $J(P\text{–}C\text{–}C\text{–}H)$ is greater than $J(P\text{–}C\text{–}H)$. Thus the upfield multiplet can be attributed to $SiCH_2$ protons and the downfield one to PCH_2 protons. The spectra of all the other phosphines show two multiplets due to the $Si(CH_2)_n\mathit{P}$ protons in the region 0.60–2.48 ppm. The multiplet at higher field is attributed to the $Si(CH_2)_n$ group and that at lower field to the PCH_2 protons on the basis of the assignment made for the siloxyphosphine.

The precursor to the siloxyphosphine L, 1,1,1,3,5,5,5-heptamethyl-3-vinyltrisiloxane, has been prepared previously via cohydrolysis of trimethylchlorosilane with diethoxymethylvinylsilane.[5] In this work, in order to simplify the procedure, we prepared the compound in 28% yield by cohydrolysis of two chlorosilanes in a large excess of water, eq 2. The ^1H NMR spectra of both vinylsiloxanes are almost

$$(CH_2{=}CH)Si(CH_3)Cl_2 + 2ClSi(CH_3)_3 \xrightarrow{H_2O} (CH_3)_3SiOSi(CH_3)(CH{=}CH_2)OSi(CH_3)_3 + (CH_3)_3SiOSi(CH_3)_3 + (CH_3)_3SiO[Si(CH_3)(CH{=}CH_2)]_3OSi(CH_3)_3 + \text{higher polymers} \quad (2)$$

identical, the only difference being, as expected, the relative proportions of the peak areas associated with the particular groups. The two singlets at 0.10 and 0.12 ppm are attributed to the $Si(CH_3)_3$ and $Si(CH_3)$ moieties, respectively. The unresolved multiplet centered at 5.9 ppm is assigned to the vinyl protons.

It is of interest that the volatile fractions $(CH_3)_3SiO[Si(CH_3)(CH{=}CH_2)]_nOSi(CH_3)_3$ contain only two compounds with $n = 1$ and 3; no compound with $n = 2$ is produced. The compound with $n = 3$ has not been previously described.

Synthesis of the Complexes. All the rhodium(I) complexes were prepared from rhodium(I) precursors by well-established procedures.[13–17] The siloxyphosphine complexes analyze well and the mass spectra of LRh(NBD)Cl and $L_2Rh(CO)Cl$ (L = $[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2$) match the predicted molecular weights.

The silicon-methyl region of all the ^1H NMR spectra is potentially the most informative as to the coordination state around the metal center since the chemical shifts and the relative intensities of the peaks due to the $SiCH_3$ and $Si(CH_3)_3$ moieties of the free ligand may change on coordination. In LRh(NBD)Cl the chemical shifts and the area ratio of the silicon-methyl peaks are the same as in the free phosphine.[17] This is also found in the spectrum of the carbonyl complex $L_2Rh(CO)Cl$ where the two trans phosphines are equivalent; the peaks are shifted slightly downfield from those of the free phosphine.

The pattern changes for the tris(phosphine) L_3RhCl and the tetrakis(phosphine) $L_4Rh_2Cl_2$ chlororhodium complexes. The latter, which has four equivalent phosphines, shows only one singlet in the silicon-methyl region at 0.12 ppm. The area of the peak accounts for all 42 protons in the $SiCH_3$ and $Si(CH_3)_3$ groups. For the tris(phosphine) complex L_3RhCl the silicon-methyl region has two singlets at 0.18 and 0.07 ppm of relative intensity 2:1. However, again there is no difference in the chemical shifts of the $SiCH_3$ and $Si(CH_3)_3$ protons.

The ^{31}P NMR spectra of the complexes are, as anticipated, similar to those reported[16,19] for the triarylphosphine analogues where it is known[20,21] that $J(M\text{–}P)$ values are larger when the phosphorus atom is trans to a ligand with low trans-influencing properties, such as halides, than when it is trans to a ligand of higher trans influence, such as PR_3, H, or CO. This is seen in the present results where the phosphines which are trans to Cl in the tetrakis(phosphine) compound have higher $J(Rh\text{–}P)$ values, 196.5 Hz, than is found in the carbonyl complex, 124.6 Hz, where the two phosphines are trans to each other.

In the tris(phosphine) complex the phosphine trans to Cl gives a double triplet at lower field, −44.97 ppm, and has a higher coupling constant, $J(Rh\text{–}P) = 188$ Hz, than the two phosphines trans to each other which give a double doublet at −29.75 ppm and have $J(Rh\text{–}P) = 140$ Hz. Thus the coupling constants for the siloxyphosphine complexes are very similar to those reported[16] for Wilkinson's $[(C_6H_5)_3P]_3RhCl$ complex. The ^{31}P NMR spectra of $L_2Rh(CO)Cl$ and L_3RhCl show singlets at −29.44 and −29.92 ppm, respectively. The downfield position[12] and lack of coupling suggest that they are due to the presence of the phosphine oxide. In fact the mass spectrum of the carbonyl chloride run at ambient temperature shows the presence of the oxide.

It has been found[22,23] that $(C_6H_5)_3P{=}O$ is produced in the reactions of $[(C_6H_5)_3P]_3RhCl$, $[(C_6H_5)_3P]_4Rh_2Cl_2$, and $[(C_6H_5)_3P]_2Rh(CO)Cl$ with molecular oxygen. Since neither ^{31}P NMR nor the mass spectra of the free siloxyphosphine, L, indicate the presence of the phosphine oxide, it seems that the oxide is formed from the phosphine and traces of molecular oxygen during the preparation of the complexes. The reaction is catalyzed by some intermediate rhodium species present in the reaction mixture.

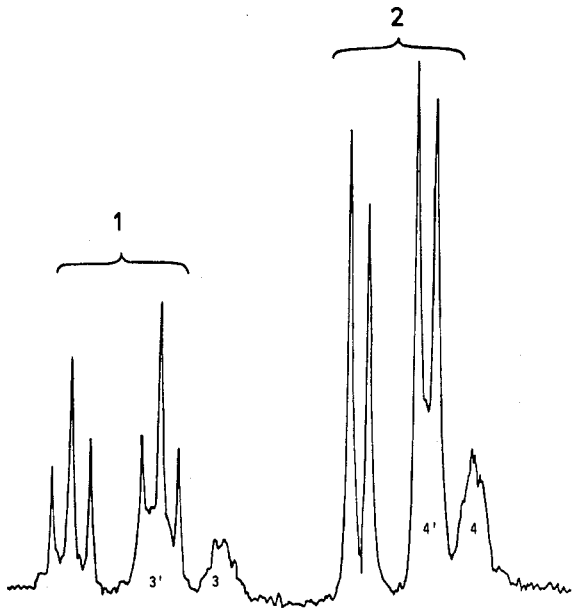


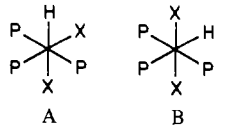
Figure 1. ^{31}P NMR spectrum of the product mixture obtained in the preparation of L'_3RhCl.

The (chlorosilyl)phosphine complexes become insoluble after evaporation of the reaction solvent. This is most likely because of polymerization caused by the presence of traces of moisture. Consequently, in order that the NMR spectra could be recorded immediately after formation of the complexes, the preparations were carried out in deuteriobenzene.

The spectroscopic results for $L'_2Rh(CO)Cl$ ($L' = Cl_3Si(CH_2)_2P(C_6H_5)_2$) parallel those for the siloxyphosphine analogue $L_2Rh(CO)Cl$. The IR carbonyl stretching frequency at 1970 cm^{-1} (in C_6D_6) is almost identical with that of the siloxyphosphine complex (1968 cm^{-1}). The ^{31}P NMR chemical shift and the J(Rh–P) values are also very similar: −30.00 ppm and J(Rh–P) = 127.5 Hz compared with −29.65 ppm and J(Rh–P) = 124.6 Hz. No peak assignable to a phosphine oxide is observed.

The microanalytical results (C, H, Cl, P, Rh) for $L'_2Rh(CO)Cl$ and the other (chlorosilyl)phosphine complexes agree well with the calculated values. However, this is rather meaningless for the others in view of the fact that the NMR spectra show that a mixture of compounds is produced. The number and the amount of side products can be decreased if the reaction vessels are pretreated with $(CH_3)_3SiCl$. This deactivates the free OH groups on the glass surface. Thus, it is likely that the impurities are produced by the partial hydrolysis, possibly followed by an oxidative addition of the liberated HCl to the rhodium(I) centers.

As an example, the ^{31}P NMR spectrum of the products obtained during the attempted preparation of $[Cl_3Si(CH_2)_2P(C_6H_5)_2]_3RhCl$, L'_3RhCl, is shown in Figure 1. It contains a double triplet 1 and a double doublet 2, with coupling constants J(Rh–P) of 186.8 and 140.4 Hz, respectively, and J(P–P) about 40 Hz. There are four multiplets, 3 and 4 and 3′ and 4′ (buried under the larger peaks), which could possibly consist of at least one other set of a double triplet and a double doublet. (They show a greater intensity and have a very definite double doublet and double triplet pattern in the spectrum of the batch prepared in unpretreated glassware.) The principal sets 1 and 2 are probably due to the required complex L'_3RhCl since this pattern is to be expected for the square-planar structure. However, an analogous pattern would also be expected from the HCl adduct L'_3RhHCl_2 which for related complexes has been reported[24,25] to exist in two possible isomeric forms A and B.



The ^1H NMR spectrum of the same product mixture which gives the ^{31}P NMR spectrum in Figure 1 shows that a hydrido complex[26] is the minor component. It probably is the HCl adduct A with cis chlorine atoms since the high-field ^1H NMR spectrum has an unresolved multiplet at −14 ppm whose spectral width is about 65 Hz. This multiplet collapses to a doublet, J(Rh–P) = 10 Hz, on phosphorus decoupling which indicates the presence of only one of the two possible HCl adducts. The isomeric HCl adducts can be differentiated[25] by their J(P–H) values, cis chlorine atoms having smaller values (ca. 10–20 Hz) than trans (ca. 200 Hz). Thus, on the basis of the spectral width of the hydride proton multiplet (65 Hz), the cis structure A is preferred.

The presence of the HCl adduct is also seen in the IR spectrum where there is a band assignable to a Rh–H stretching frequency[27,28] at 2095 cm^{-1} and two weak bands in the ν(Rh–Cl) region at 280 and 260 cm^{-1}. Since the M–Cl stretching frequencies are strongly influenced by the nature of the ligand trans to chlorine[29–31] but only slightly affected by cis ligands, a mixture of a L'_3RhCl complex and its HCl adduct could contain two, rather than the expected three, ν(Rh–Cl) bands. The frequencies due to ν(Rh–Cl) for Cl trans to P would be very similar or the same for the two compounds. The chlorine trans to H in the L'_3RhHCl_2 complex should give rise to another band at a slightly lower frequency.[32] On the basis of this argument, ν(Rh–Cl) at 260 cm^{-1} is assigned to Cl trans to H, and ν(Rh–Cl) at 280 cm^{-1} is assigned to Cl trans to P in both L'_3RhCl and L'_3RhHCl_2.

The spectra of the products obtained in the preparation of L''_3RhCl ($L'' = Cl_3Si(CH_2)_8P(C_6H_5)_2$) and $L'_4Rh_2Cl_4$ also indicate that a mixture of compounds is produced. The desired complex L''_3RhCl is the main product, however. The presence of ν(Rh–H) and ν(Rh–Cl) IR bands as well as hydride ^1H NMR peaks (spectral width ca. 70 Hz) shows that the major impurity (~20%) is most likely a similar HCl adduct.

No one major product is obtained in the attempted syntheses of $L'_4Rh_2Cl_4$. Instead a number of compounds are produced in roughly equal yields as indicated by the relative intensities of the peaks in the ^{31}P NMR spectrum. Judging by the presence of hydride peaks in the ^1H NMR spectrum and by ν(Rh–H) and ν(Rh–Cl) IR bands, an HCl adduct(s) is formed. Unfortunately, there are no data concerning HCl adducts of $P_4Rh_2Cl_2$ complexes for comparison. The high-field ^1H NMR spectrum contains a multiplet at about −14 ppm and a double triplet at −15.72 ppm of relative intensities 1:4. The small spectral width of the multiplet (ca. 40 Hz) and the small J(P–H) value of the double triplet (18 Hz) indicate that both the different types of rhodium hydride protons are cis to P. However, no definite structures can be assigned to the products of this reaction.

Reactions of the Complexes with Gaseous H_2, CO, and HCl. Both $[(C_6H_5)_3P]_3RhCl$ and $[(C_6H_5)_3P]_4Rh_2Cl_2$ are known[15,16] to be powerful hydrogenation catalysts. The chemical reactivity of their siloxyphosphine analogues is of particular interest in this work. The analogues were prepared because they would have steric and electronic properties similar to those of the polymeric siloxane compounds which were to be prepared at a later stage and studied as hydrogenation catalysts. Unfortunately, the reactivity of the (chlorosilyl)phosphine complexes which are the precursors to the polymeric siloxane complexes could not be studied due to their extreme hydrolytic instability.

Hydrogen adds oxidatively to the chlorotris(phosphine)-rhodium[15,16,33,34] and to the di-μ-chloro-tetrakis(phosphine)-

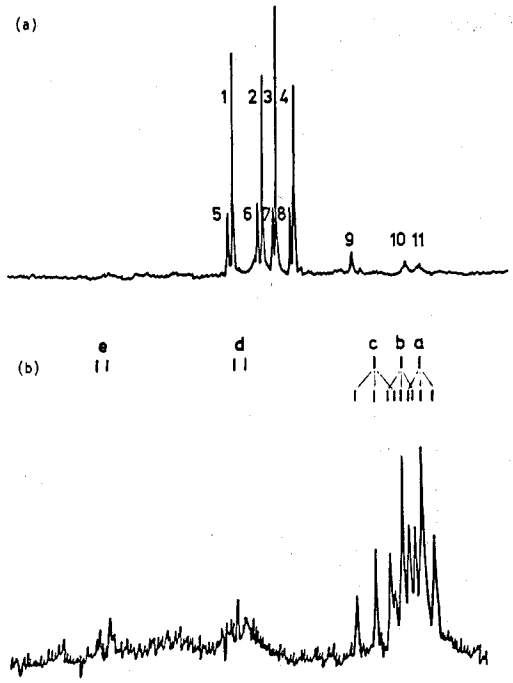
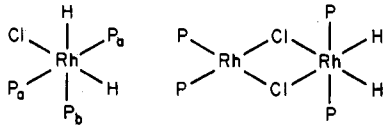


Figure 2. (a) ^{31}P NMR and (b) high-field ^{1}H NMR spectra of the hydrogenated complex $L_4Rh_2Cl_2$.

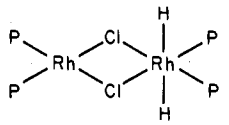
dirhodium[16] complexes, producing compounds with structures C and D, respectively. The reaction of L_3RhCl with H_2 was



C D

monitored with IR, ^{1}H NMR, and ^{31}P NMR spectroscopy and proved to be completely reversible at 25 °C. The molecular structure of the 1:1 adduct is identical with that of C, judging by its IR spectrum (ν(Rh–H) 2075 and 2160 cm^{-1}) and ^{1}H and ^{31}P NMR spectra. Both ^{1}H and ^{31}P NMR spectra have chemical shifts and patterns similar to those for the H_2 adduct of Wilkinson's complex.[15,34] The high-field ^{1}H NMR spectrum contains three peaks at −8.5, −10.1, and −17.1 ppm with relative intensities 1:1:2. Upon partial phosphorus decoupling the more intense peak collapses into a doublet and the two smaller peaks into one multiplet, the ratio of their integrated areas being 1:1. The ^{31}P NMR spectrum contains a double doublet due to phosphorus P_a, at −41.03 ppm, and a double triplet due to phosphorus P_b, at −20.17 ppm. The singlet due to siloxyphosphine oxide which is observed in the spectrum of the starting complex is also present in that of the product.

Hydrogen uptake by the complex $L_4Rh_2Cl_2$ is also reversible at 25 °C. The ^{31}P and the high-field ^{1}H NMR spectra of the H_2 adduct are shown in Figure 2. The four resonances[35] 1–4 in the ^{31}P NMR spectrum can be assigned[16] to the two doublets of a species with the structure D. This is confirmed by the double triplet a and b in the high-field ^{1}H NMR spectrum at −20.1 ppm, J(Rh–H) = 24 Hz and J(P–H) = 16 Hz, which collapses to a doublet on phosphorus decoupling. The assignment of the rest of the spectrum is more difficult since very little help is available from the literature. The four ^{31}P NMR peaks of lower intensity, 5–8, which look like a shadow of peaks 1–4, could possibly be assigned to an isomer E of the complex D. Such a structure would call for a double triplet in the high-field ^{1}H NMR spectrum. Only one triplet c is observed at −19.8 ppm; there is the possibility that its "twin" triplet is buried under the large peaks of the double triplet a–b. However, so far no transition-metal complex with two H atoms



E

trans to each other has been reported.

Alternatively, the remaining ^{31}P peaks can be assigned to a mixture of $L_4Rh_2Cl_2$ and L_3RhH_2Cl with the small singlet 9 being due to the siloxyphosphine oxide. The ^{1}H NMR contains two small multiplets e and d at −16.1 and −17.8 ppm, each of which forms a doublet on partial phosphorus decoupling. The one at −17.8 ppm can be assigned to the more intense one in the L_3RhH_2Cl spectrum. The small multiplet at −16.1 ppm cannot be assigned. However, the reversibility of the hydrogenation seems to rule out the production of L_3RhH_2Cl.

Although a precise assignment of all the complexes formed cannot be made unequivocably, the spectra show that complex D (P = L) is the main product of hydrogenation of the complex $L_4Rh_2Cl_2$.

Both $[(C_6H_5)_3P]_3RhCl$ and $[(C_6H_5)_3P]_4Rh_2Cl_2$ react with electron-donor species. The reactivity of $[(C_6H_5)_3P]_3RhCl$ is probably due to the ease of P_2RhCl formation in solution.[15,36] Its reaction with CO, reported[15] to be irreversible, produces the *trans*-$P_2Rh(CO)Cl$ complex only. The same compound is obtained when $P_4Rh_2Cl_2$ is treated with CO via a bridge-splitting reaction.

The IR spectra of the solutions of both the siloxyphosphine complexes L_3RhCl and $L_4Rh_2Cl_2$ exposed to CO contain a strong band at 1965 cm^{-1} which is identical with the ν(C≡O) of the $L_2Rh(CO)Cl$ complex described above. The product obtained from $L_4Rh_2Cl_2$ has a ^{31}P NMR spectrum identical with that of $L_2Rh(CO)Cl$.

The ^{31}P NMR spectrum of the solution obtained from L_3RhCl treated with CO shows a very broad multiplet from −30 to −3 ppm (plus a siloxyphosphine oxide singlet at −29.94 ppm) instead of the doublet at −29.81 expected for the *trans*-$L_2Rh(CO)Cl$ complex and the singlet at +9.14 due to the displaced phosphine. The spectrum recorded in deuterioacetone at −60 °C has a similar downfield-shifted multiplet. The proton NMR signals at 35 °C are also broad with no separate set of peaks for the complex and the free phosphine. The broadening of the signals is most likely due to ligand exchange between the carbonyl complex and the released free phosphine, since the same features are seen in the spectra of a deliberately prepared mixture.

As described above, HCl(g) adds oxidatively to P_3RhCl to give a rhodium(III) complex. There are two possible structures A and B for the product P_3RhHCl_2. Isomer A exhibits an IR ν(Rh–H) band[27,28] around 2100–2200 cm^{-1} and two ν(Rh–Cl) bands[24,25,32,37] in the 225–290-cm^{-1} region. The Rh–H stretches in the isomers B give rise to peaks at lower frequencies[25,28] 1960–1990 cm^{-1}. The ν(Rh–Cl) region shows only one band[25,32] at a frequency higher than that for A, 320–330 cm^{-1}, characteristic of Cl trans to Cl.

Upon reaction with HCl(g) both soluble siloxyphosphine complexes L_3RhCl and $L_4Rh_2Cl_4$ give solid products insoluble in common solvents. The presence of two ν(Rh–Cl) bands (273 and 253 cm^{-1}) and the position of the ν(Rh–H) band well above 2000 cm^{-1} (2110 cm^{-1}) suggest formation of an adduct of structure A in the reaction of L_3RhCl with HCl. The product of the reaction with the tetraphosphine complex also shows two IR ν(Rh–Cl) bands at 255 and 275 cm^{-1} and one ν(Rh–H) at 2100 cm^{-1}, but its structure cannot be determined on the basis of these data.

The addition of HCl is partly reversible for both the adducts and, upon pumping the HCl(g) off, the peaks due to the Rh–H

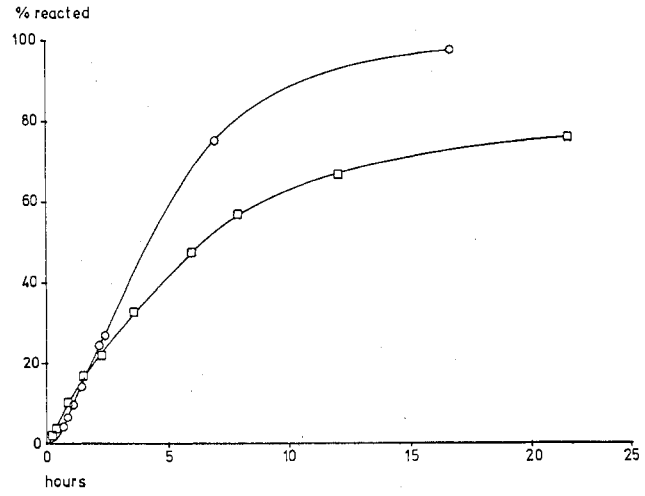


Figure 3. Hydrogenation of styrene in benzene in the presence of L_3RhCl and $L_4Rh_2Cl_2$: (○) L_3RhCl; (□) $L_4Rh_2Cl_2$. Reaction conditions: temperature 35 °C, 3 mL of benzene, 3.0×10^{-3} mmol of complex as Rh(I), 3.0×10^{-1} mmol of styrene.

and Rh–Cl stretching frequencies diminish and the yellow color of the adducts (characteristic of rhodium(III)) changes to orange (characteristic of rhodium(I)).

The formation of insoluble solids in these reactions is probably due to acid-catalyzed siloxane-linkage rearrangements[38-41] followed by polymerization.[42] The microanalytical values (C, H, Cl) found for the products do not fit any reasonable formulation. They are especially high in chlorine and may indicate strong chemisorption of HCl.

The Siloxyphosphine Complexes L_3RhCl and $L_4Rh_2Cl_2$ as Hydrogenation Catalysts. The two siloxyphosphine complexes were tested as to their ability to catalyze hydrogenation of styrene. The results (Figure 3) show that both the complexes are effective catalysts, the reaction rate being higher for the tris(phosphine) complex than for the tetrakis(phosphine) one.

Both $[(C_6H_5)_3P]_3RhCl$ and $[(C_6H_5)_3P]_4Rh_2Cl_2$ have been described as good hydrogenation catalysts,[15,16] although it is generally believed that the dimer is considerably less active. The siloxyphosphine analogues also show no dramatic difference in catalytic ability between the two compounds.

Since the soluble siloxyphosphine complexes discussed here proved to be hydrogenation catalysts, it is expected that the (chlorosilyl)phosphine analogues after being polymerized to poly(siloxyphosphine) macro compounds would also exhibit catalytic activity. In fact, the catalytic activity of the polymeric complexes has already been investigated and will be discussed in future publications.

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Registry No. (NBD){$[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2$}RhCl, 71393-66-3; {$[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2$}$_2$Rh(CO)Cl, 71393-67-4; {$[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2$}$_3$RhCl, 71393-68-5; {$[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2$}$_4Rh_2Cl_2$, 71393-69-6; $[Cl_3Si(CH_2)_2P(C_6H_5)_2]_2Rh(CO)Cl$, 71425-18-8; $[Cl_3Si(CH_2)_2P(C_6H_5)_2]_3RhCl$, 52563-05-0; $[Cl_3Si(CH_2)_8P(C_6H_5)_2]_3RhCl$, 52633-23-5; $[Cl_3Si(CH_2)_2P(C_6H_5)_2]_4Rh_2Cl_2$, 71393-70-9; {$[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2$}$_3$RhCl$(H)_2$, 71393-71-0; {$[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2$}$_4Rh_2Cl_2(H)_2$, 71393-72-1; {$[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2$}$_3RhCl_2(H)$, 71393-73-2; $[(CH_3)_3SiO]_2(CH_3)Si(CH_2)_2P(C_6H_5)_2$, 71382-90-6; $(CH_3)_3Si(CH_2)_2P(C_6H_5)_2$, 27840-95-5; $Cl_2(CH_3)Si(CH_2)_2P(C_6H_5)_2$, 4145-76-0; $Cl_3Si(CH_2)_2P(C_6H_5)_2$, 4145-77-1; $Cl_3Si(CH_2)_8P(C_6H_5)_2$, 52217-68-2; $(CH_3)_3SiOSi(CH_3)_3$, 107-46-0; $[(CH_3)_3SiO]_2Si(CH_3)(CH{=}CH_2)$, 5356-85-4; $(CH_3)_3Si[OSi(CH_3)(CH{=}CH_2)]_3OSi(CH_3)_3$, 16545-47-4; chlorotrimethylsilane, 75-77-4; methylvinyldichlorosilane, 124-70-9; diphenylphosphine, 829-85-6; $[(NBD)RhCl]_2$, 12257-42-0; $[Rh(CO)_2Cl]_2$, 14523-22-9; $(C_2H_4)_4Rh_2Cl_2$, 12081-16-2.

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