

Therefore the hyperconjugation model, well suited to help in assigning the π spectra of alkyl- and silylacetylenes, does neither prove nor disprove π - d back-bonding in silicon compounds—just as most of the numerous arguments produced favor one or the other.

Experimental Section

Synthesis. Monosilylacetylene²⁰ was prepared from acetylene magnesium bromide and iodasilane in dry, degassed tetrahydrofuran. The reaction product was pumped off and purified by fractionate condensation. The measurement sample was finally obtained by high vacuum line distillation between two baths at -112 and -132° and its purity controlled by ir²¹ and nmr²⁰ as well as molecular weight determination (found 56.8, calcd 56.1).

Disilylacetylene²² can be obtained analogously from acetylene di-Grignard solution in dibutyl ether and bromosilane. The measurement sample was purified from dibutyl ether by fractionate

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condensation at -78 and at -96° from excess bromosilane. Neither by ir and nmr nor by molecular weight determination (found 87.0, calcd 86.2) could any impurities in the measurement sample be detected.

Spectra. The π spectrum of methylacetylene was taken from the literature;⁷ the one of dimethylacetylene has been kindly given to us by Elbel²³ from our group. The π spectra of the silylacetylenes were recorded with a Perkin-Elmer PS 16 and calibrated with argon. The samples have been introduced into the spectrometer carefully avoiding exposition to air.

Calculations. The calculations have been carried out at the UNIVAC 1108 of the computer center of the University of Frankfurt. The modified CNDO/2 version used is described elsewhere.²⁴ In addition the β_A^0 values for the third-period elements have been reduced proportionally to β_{carbon}^0 .²⁴ The π interaction was switched off by setting the corresponding $A(i,j)$ in subroutine SCFCLO equal to zero. Silicon d orbitals can be excluded by either reducing the basis set or by setting all d overlap integrals in subroutine INTEGRL equal to zero. The latter procedure allows alternatively a reduction of the back-bonding by multiplying the d overlap integrals with a factor <1 .

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Triarylphosphine, Hydride, and Ethylene Complexes of Rhodium(I) Chloride

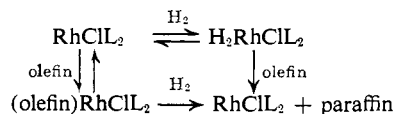
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Abstract: Physical studies, combining molecular weights, ³¹P, ¹³C, and ¹H nmr, infrared, and spectrophotometric measurements, have been made to define the species and rates and equilibria of reactions in solutions containing mixtures of RhCl, triarylphosphines [PPh₃ or P(*p*-tolyl)₃], H₂, ethylene, and cyclohexene. The RhCl₃ complexes do not dissociate to RhCl₂ to a spectroscopically detectable extent but are in equilibrium with the chlorine bridged dimer [RhCl₂]₂. The dimer reacts with H₂ to form H₂[RhCl₂]₂ and is readily cleaved by L or ethylene, but not cyclohexene, to form RhClL₃ or (C₂H₄)RhCl₂. The dimer itself is a good homogeneous hydrogenation catalyst. A species of composition RhCl₂, while not spectroscopically detectable, must be postulated as a kinetic intermediate in order to explain the kinetics of H₂ reaction with solutions of RhCl₃ or of H₂ with cyclohexene in solutions of [RhCl₂]₂.

In 1966 Wilkinson and coworkers reported the rapid homogeneous hydrogenation of olefins catalyzed by RhCl(PPh₃)₃.² They proposed a mechanism shown in Scheme I. Complete dissociation of RhCl(PPh₃)₃ into

Scheme I



RhCl(PPh₃)₂ and PPh₃ was suggested on the basis of an experimental molecular weight about half the theoretical value. (C₂H₄)RhCl(PPh₃)₂ and a compound thought to be H₂RhCl(PPh₃)₂ were isolated from the reactions of RhCl(PPh₃)₃ with C₂H₄ and H₂. A rather insoluble compound with the composition of [RhCl(PPh₃)₂]

(1) Du Pont Resident Research Fellow, June–Aug 1972.

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could be precipitated from solution on standing or heating. The solubility increased under H₂; volume uptake and molecular weight measurements suggested a binuclear tetrahydride.

Several subsequent studies have appeared.³ A preliminary X-ray crystal structure of RhCl(PPh₃)₃ has been reported.⁴ Molecular weight⁵ and ³¹P nmr studies^{6,7} have established that the complex remains largely intact in relatively concentrated solutions. Uv studies⁸ with L = PPh₃ have been interpreted in terms

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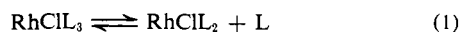
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of equilibrium 1 with a very small value of K_1 . Absor-

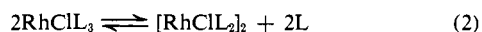


bances at various added ligand concentrations were fitted with $K_1 = 1.4 \times 10^{-4} M$ and an extinction coefficient at infinite dilution of 0.42×10^3 at 410 $m\mu$.

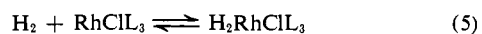
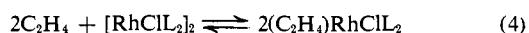
Sacco, Ugo, and Moles⁹ reported isolating the tris-(phosphine) hydride $\text{H}_2\text{RhCl}(\text{PPh}_3)_3$, rather than $\text{H}_2\text{RhCl}(\text{PPh}_3)_2$. Others have disagreed with the proposed simultaneous transfer of both hydrogen atoms to the olefin, based on olefin isomerization¹⁰ and deuteration studies.¹¹ There are also conflicting reports on the effect of ethylene in the hydrogenation system.^{2,12}

Some kinetic data on the reaction of H_2 with $\text{RhCl}(\text{PPh}_3)_3$ and $\text{RhBr}(\text{PPh}_3)_3$ have appeared.¹³ A rather thorough kinetic study of cyclohexene hydrogenation by $\text{RhCl}(\text{PPh}_3)_3$, as a function of Rh, olefin, and phosphine concentrations, has been made,¹⁴ based on H_2 uptake. A review of the literature through 1972 has been made by James.¹⁵

We have combined molecular weights and ^{31}P , ^{13}C , and ^1H nmr, ir, and spectrophotometric studies in order to elucidate the structures of species present in solutions of Rh(I) chloride, H_2 , C_2H_4 , cyclohexene, and PPh_3 or $\text{P}(p\text{-tolyl})_3$. The latter phosphine was preferable because of the greater solubility of its complexes. Equilibrium constants at 25° were measured spectrophotometrically for reactions 2 and 3 and rate and equilib-



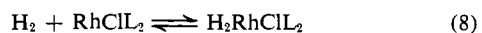
rium constants measured for eq 4–6. The rate of re-



action 7 was determined at various temperatures by



analyzing line shape effects in the ^{31}P nmr spectrum. Reaction 8 is postulated to account for the kinetics of



reaction of H_2 with solutions containing RhCl_3 . Some data are presented on the rates of hydrogenation of cyclohexene and ethylene in toluene at 25° and on the nature of species present under steady-state conditions. Preliminary results of our studies have been communicated earlier.^{16,17}

Experimental Section

Compounds and solutions were prepared and handled under N_2

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or argon atmospheres, using Vacuum Atmospheres, Inc., dryboxes. Melting points were determined in sealed evacuated capillaries on a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 221 spectrometer, using 0.1-mm NaCl microcells from Barnes Engineering, Inc.; a thick-walled NaCl cell (1.4 cm) equipped with an O-ring and pressure gauge was used for solutions under H_2 pressure up to 30 psig. Calibration was with CO gas (2143 cm^{-1}).

Fourier-mode proton noise-decoupled ^{31}P nmr spectra at 36.43 MHz were obtained on a Bruker HFX-90 spectrometer with a Digilab FTS/NMR-3 data system. The 10-mm diameter tubes contained a 3-mm concentric capillary of $\text{CF}_2\text{BrCF}_2\text{Br}$ which provided an ^{19}F lock. A Teflon pressure stem¹⁸ permitted the addition of C_2H_4 or H_2 under pressure. *Caution! The 10-mm thin walled tubes occasionally exploded with 150 psig of H_2 .*

^{13}C nmr spectra at 22.63 MHz were obtained with 10-mm tubes and the same instrument. A solvent mixture of 10% tetramethylsilane (TMS)–90% CD_2Cl_2 provided an internal reference and deuterium lock.

^1H nmr spectra were obtained using 5-mm tubes with the same spectrometer at 90 or at 100 MHz on a Varian HA-100. Chemical shifts were measured with respect to internal TMS and are reported on the τ scale.

The molecular weight of $\{\text{RhCl}[\text{P}(p\text{-tolyl})_3]_2\}_2$ was determined in benzene at 50° by the Singer method¹⁹ using glassware purchased from the Scientific Glass and Apparatus Co. The Rh complex was placed in one arm and $\text{Ni}[\text{P}(\text{OC}_2\text{H}_5)_3]_4$ (mol wt 723) in the other. An absence of dissociation of the nickel complex was established earlier by ^{31}P nmr and uv studies.²⁰ The apparatus was placed in a warm-water bath at 50°, and the volumes were followed with time. As benzene distilled from the Rh side to the Ni side, some Rh solid began to form when equilibrium was nearly reached, ~30 min ($\sim 2.5 \times 10^{-2} M$ complex). Slow volume changes continued as more complex precipitated. Extrapolation back to $t = 0$ gave a molecular weight of 1500 ± 100 , in good agreement with the 1494 g/mol predicted for the dimer.

Solubility of complexes in benzene at ambient temperature (28°) were determined by allowing solutions containing undissolved solid to stand with repeated shaking over a period of 3–4 hr. Solutions containing RhCl_3 complexes contained 0.01 M added phosphine, L, to suppress dimer formation. Solutions saturated with complex were filtered into quartz optical cells of known length and concentrations of complex (below) were determined from previously measured extinction coefficients.

Complex	L = $\text{P}(p\text{-tolyl})_3$	L = PPh_3
RhCl_3	0.16 M	$1.4 \times 10^{-2} M$
$[\text{RhCl}_2]_2$	$1.6 \times 10^{-2} M$	$\sim 3 \times 10^{-5} M$

The measured solubility of $\text{RhCl}(\text{PPh}_3)_3$ of 1.4×10^{-2} mol/l. or 13 g/l. is considerably greater than the 4 g/l. reported in the literature.² The very low solubility of $[\text{RhCl}(\text{PPh}_3)_2]_2$ accounts for the observation that the dimer precipitates from solutions of $\text{RhCl}(\text{PPh}_3)_3$ on standing.

Optical spectra were recorded from 700 to 300 $m\mu$ with a Cary 14 spectrophotometer using serum-capped quartz cells, and the cell compartment was thermostated at 25°. Beer's law in benzene was checked by running solutions of ca. 10^{-2} to $10^{-5} M$ complex in cells of 0.1, 1.0, 10, and 100 mm length, keeping the product of concentration and path length constant. Equilibrium constants for ethylene complex formation were determined by injecting increments of C_2H_4 gas, as described earlier.²¹ Measurements were made with 0.01 M phosphine added to suppress dimer formation. Higher concentrations of added L suppressed formation of $(\text{C}_2\text{H}_4)\text{-RhCl}_2$ as expected from eq 3.

Rates and equilibria of H_2 reactions were determined using the stirred, quartz gas reaction cell shown in Figure 1. Our cell was based on an earlier design by Werneke.²² The cap was sealed with ether resin. Magnetic stirring at the gas–liquid interface was provided from above with the cell chamber (2.5-mm path length) mounted in the light beam of the spectrometer. Mixing experiments with 10 ml of water and Bromophenyl Blue indicator

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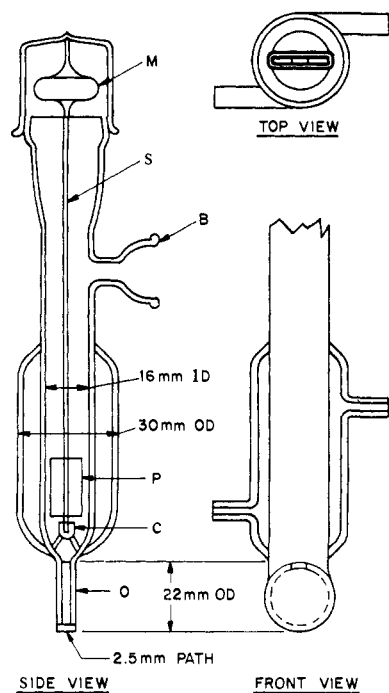


Figure 1. A 2.5-mm gas reaction cell: M, magnet for rotating paddle; S, stirrer shaft; P, Teflon paddle; C, cup for shaft bearing; O, observation cell; B, 19/8 ball joint.

showed that the minimum time required for color homogeneity throughout the reactor (4 sec) was obtained at a stirrer speed of 1800 rpm. This rate was used subsequently in experiments with H_2 in 10 ml of toluene solution. At higher speeds vortexing became severe and communication between the cell chamber and mixing chamber was poor. The mixing chamber was thermostated by circulating water at 25.0° . A similar 20-mm path length gas reaction cell was used in a few cases.

The gas reaction cell was connected by means of an 18/9 ball joint and rubber tubing through a Hoke ball valve to a steel ballast tank fitted with a large precision gauge reading from 30 in. of Hg vacuum to +30 psig. We pressured the quartz cell to +20 psig on several occasions without incident. *Caution! The cell should be shielded when under pressure in case of rupture.* The total volume of the empty system was 256 cm^3 .

The usual procedure in the H_2 reactions was to run an initial spectrum before removing argon with a vacuum pump down to the toluene vapor pressure of 1.1 in. of Hg at 25° . With care this could be done without evaporating more than 1% of the solvent (determined by monitoring the absorbance). For kinetic runs, H_2 could be rapidly added by opening the ball valve between the ballast tank and the cell. Pressure changes were noted and the absorbance changes followed with time at some convenient wavelength, usually $425\text{ m}\mu$ in the case of $RhCl_3$ or $455\text{ m}\mu$ in the case of $[RhCl_2]_2$. For equilibrium measurements it was convenient to leave the ball valve open and leak H_2 into the ballast tank from an external cylinder. Determination of K_5 for the reaction of H_2 with $RhCl[P(p\text{-tolyl})_3]_3$ is illustrated in Table I. $P(p\text{-tolyl})_3$ (0.04 M) was added to suppress dimer formation.

The approach to equilibrium could be followed both by adding H_2 and by removing H_2 from the gas phase with a vacuum pump. In this way rates at several hydrogen pressures could be obtained with one solution. Solutions of $RhCl_3$ with added L were usually cycled 10–15 times, with good reproducibility of rate constants. Solutions of $[RhCl_2]_2$ were much more sensitive to traces of O_2 , changing from clear orange to cloudy brown and giving increased absorbance over the whole 700–300 $m\mu$ range after only a few cycles.

Hydrogenation of Cyclohexene and Ethylene. Hydrogenations were carried out with the gas reaction cell in the spectrometer, following the pressure drop while recording the uv spectrum. Cyclohexene was added to the solutions before H_2 was admitted. Ethylene was admitted as a gas prior to H_2 in some cases and after H_2 in others. In some experiments the rate of H_2 uptake during cyclohexene hydrogenation was measured volumetrically at

Table I. Determination of K_5 for $L = P(p\text{-tolyl})_3$ in Toluene at 25° (0.04 M added L), $H_2 + RhCl_3 \rightleftharpoons H_2RhCl_3$

Gauge reading (in. of Hg vac)	p_{H_2} , in.	$A_{425}(425)^a$	$[H_2RhCl_3]/[RhCl_3]^c$	$K_5, d \text{ in.}^{-1}$
28.9	0.0	0.87		
28.0	0.9	0.435	1.30	1.4
27.0	1.9	0.30	2.85	1.5
25.0	3.9	0.22	5.42	1.4
20.0	8.9	0.16	11.8	1.3
10.0	18.9	0.133	22.3	1.2
0.0	28.9	0.12	37.5	1.3
		(0.10) ^b		Av 1.35 \pm 0.1

^a The absorbance at $425\text{ m}\mu$ at equilibrium. Initially $2.4 \times 10^{-3}\text{ M}$ $RhCl[P(p\text{-tolyl})_3]_3$. ^b Determined by successive approximation to make the calculated K_5 at ~ 1 atm of H_2 equal to the mean K_5 . ^c $[H_2RhCl_3]/[RhCl_3] = [0.87 - A_{425}(425)]/[A_{425}(425) - 0.10]$. ^d $K_5 = [H_2RhCl_3]/[RhCl_3]p_{H_2}$; $1.35 \pm 0.1 (\text{in.})^{-1} \times 29.9 \text{ in. atm}^{-1} = 40 \pm 3 \text{ atm}^{-1}$.

1 atm of pressure using a conventional stirred reactor. Rhodium concentrations were typically $\sim 2 \times 10^{-3}\text{ M}$ in toluene solvent.

Related experiments were carried out at ambient temperature in pressurizable 10-mm nmr tubes, observing ^{31}P nmr spectra after various times. In one such experiment increasing amounts of C_2H_4 (1.3, 2.5, and 5.0 cm^3 total) were added to an orange slurry of 75 mg (0.05 mmol) of $\{RhCl[P(p\text{-tolyl})_3]_2\}_2$ in 2 cm^3 of toluene. With 2.5 cm^3 of C_2H_4 (0.1 mmol) most of the solid dissolved and the spectrum showed $\sim 91\%$ ethylene complex (C_2H_4) $RhCl_2$ and 9% dimer, based on peak heights. With excess C_2H_4 (5.0 cm^3 , 0.2 mmol) all the solid dissolved to give a light orange solution whose spectrum showed complete conversion to the ethylene complex. Slowly adding H_2 up to 50 psig with shaking caused the color to become light red. The spectrum showed $\sim 90\%$ dimer hydride and no remaining ethylene complex. The tube was then chilled in liquid N_2 , evacuated, and charged with 15 cm^3 of C_2H_4 (0.6 mmol). On warming and shaking the solution became light orange and a little solid formed, which redissolved on shaking. Apparently C_2H_4 removed H_2 from the dimer hydride by forming ethane; sparingly soluble dimer precipitated before returning to solution as (C_2H_4) $RhCl_2$, the only species observed in the spectrum of the light orange solution. Adding H_2 to 120 psig and shaking for a few minutes turned the color light red. The spectrum showed no remaining ethylene complex; most of the Rh was present as dimer hydride.

After 5 days the volatiles were vacuum distilled from the nmr tube through cold traps of Dry Ice–Triclene and liquid N_2 . Warming the liquid N_2 trap produced 16.4 cm^3 of gas (1 atm, 25°), corresponding to 82% recovery of the ethylene charged. The infrared spectrum of the gas was identical with that of pure ethane, with no detectable band at 950 cm^{-1} assignable to unreacted C_2H_4 .

Nmr Line Shape Calculations. The temperature-dependent ^{31}P $\{^1H\}$ nmr spectra for solutions of $H_2RhCl[P(C_6H_5)_3]_3$ with and without added $P(C_6H_5)_3$ were calculated using a general computer program, written for intermolecular exchange in first-order spin systems, which sets up an exchange matrix. The data for the program consist of the high-resolution nmr parameters (chemical shifts, coupling constants, and transverse relaxation times) for all of the species participating in the exchange process (H_2RhCl_3 , H_2RhCl_2 and L in this case), their concentrations, the pseudo-first-order reaction rates, and a specification of the reaction process in terms of which spins are exchanged. The program can be used in cases where several exchange processes are taking place simultaneously.

The final expression for the nmr line shape has the same form as the equation given by Sack²³ for exchange of single line spectra between sites of different population.

$$I(\omega) = -\text{Re}\{P \cdot (A - E i\omega)^{-1} \cdot I\}$$

In the above equation $I(\omega)$ is the absorption intensity at angular frequency ω under conditions of slow passage and weak radio-frequency fields. I is the unit vector of dimension equal to the sum of the number of transitions for all of the species participating in the

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exchange process(es). A is a complex non-Hermitian matrix given by $A = \alpha + B$ where α is the exchange matrix and B is a diagonal matrix whose elements are given by $B_{ii} = i\omega_i - 1/T_{2i}$. The ω_i are the transition frequencies in angular frequency units and the T_{2i} are the transverse relaxation times which determine the line widths in the absence of exchange. E is the unit matrix and P is a vector consisting of population weighted transition intensities.

The equation is solved using the numerical method developed by Gordon and McGinnis,²⁴ Binsch,²⁵ and Shirmer, Noggle, and Gaines²⁶ which avoids inverting the matrix $(A - E i\omega)$ by diagonalizing $(A - E i\omega)$ at some particular ω and by using the fact that the transformation which diagonalizes $(A - E i\omega)$ at some particular ω diagonalizes $(A - E i\omega)$ at all ω 's. We have previously discussed the solution of equations of this type²⁷ and have demonstrated the advantages of numerical factoring for the case of mutual exchange. Unfortunately, little or no factoring is possible for the case of intermolecular exchange and the numerical problems increase rapidly with increasing number of spins.

Compounds. Reagent grade solvents benzene, toluene, and CH_2Cl_2 were deoxygenated by bubbling argon in the drybox. Cyclohexene was freshly distilled before use. Research grade C_2H_4 and H_2 were used as received. Triphenylphosphine and tri(*p*-tolyl)phosphine were purified by crystallization from hot ethanol.

Tris(tri-*p*-tolylphosphine)rhodium(I) chloride was prepared by the reaction of 3.89 g (10 mmol) of $[(\text{C}_2\text{H}_5)_2\text{RhCl}]_2$ ²⁸ with 18.3 g (60 mmol) of $\text{P}(p\text{-tolyl})_3$ in 100 ml of toluene. After stirring for 30 min the solution was filtered and 400 ml of petroleum ether was added slowly with stirring. The collected solids were dissolved in a minimum amount of toluene and reprecipitated with petroleum ether. Filtration, washing with petroleum ether, and drying *in vacuo* gave a beige colored product, mp 178–183° dec.

Anal. Calcd for $\text{C}_{63}\text{H}_{63}\text{ClP}_3\text{Rh}$: C, 72.0; H, 6.0; P, 8.8. Found: C, 71.9; H, 6.1; P, 8.9.

Tetrakis(tri-*p*-tolylphosphine)dirhodium(I) dichloride was prepared by the reaction of 2.3 g (6 mmol) of $[(\text{C}_2\text{H}_5)_2\text{RhCl}]_2$ with 7.3 g (24 mmol) of $\text{P}(p\text{-tolyl})_3$ in 150 ml of toluene. The solution was refluxed for 3 hr, cooled, and filtered. About 300 ml of petroleum ether was added with stirring. Filtering, washing with petroleum ether, and drying *in vacuo* gave the product as a beige colored solid, mp 240–243° dec.

Anal. Calcd for $\text{C}_{84}\text{H}_{84}\text{Cl}_2\text{P}_4\text{Rh}_2$: C, 67.5; H, 5.7. Found: C, 67.6; H, 5.7.

Ethylene[bis(tri-*p*-tolylphosphine)]rhodium(I) chloride was prepared from 3.9 g (10 mmol) of $[(\text{C}_2\text{H}_5)_2\text{RhCl}]_2$ and 12.2 g (40 mmol) of $\text{P}(p\text{-tolyl})_3$ in 175 ml of toluene. The solution was heated to reflux and immediately filtered. After cooling to room temperature 300 ml of petroleum ether was slowly added with stirring. Filtration and washing with petroleum ether gave orange solids. These were dissolved in a minimal volume of ethylene-saturated toluene, and ethylene was bubbled through for 30 min. Addition of 300 ml of ethylene saturated petroleum ether gave yellow crystals, which were collected by pressure filtration under ethylene, then dried *in vacuo*, mp 256–259° dec.

Anal. Calcd for $\text{C}_{44}\text{H}_{46}\text{ClP}_2\text{Rh}$: C, 67.2; H, 6.2; Cl, 4.7; P, 8.2. Found: C, 68.1, H, 6.1; Cl, 5.4; P, 8.1.

Carbonyl[bis(tri-*p*-tolylphosphine)]rhodium(I) chloride was prepared by the reaction of CO gas with solid $\{\text{RhCl}[\text{P}(p\text{-tolyl})_3]_2\}_2$. On standing for several weeks, the color of the solid changed from orange to pale yellow, mp 260–263°. The infrared spectrum showed a strong new band at 1972 cm^{-1} (CH_2Cl_2). The ^{31}P spectrum showed less than 5% of the original dimer.

Anal. Calcd for $\text{C}_{43}\text{H}_{42}\text{ClOP}_2\text{Rh}$: C, 66.6; H, 5.5; P, 8.0. Found: C, 66.0; H, 5.5; P, 8.3.

Ethylene[bis(triphenylphosphine)]rhodium(I) chloride² was prepared by the addition of 1.17 g (3 mmol) of $[(\text{C}_2\text{H}_5)_2\text{RhCl}]_2$ to a solution of 3.0 g (11.5 mmol) of PPh_3 in 150 ml of toluene while bubbling ethylene through the solution. Ethylene saturated chloroform (150 ml) was added and the mixture heated until all the solids dissolved. The solution was pressure filtered under ethylene and the filtrate was bubbled with ethylene. After 1.5 hr

the yellow crystal formed were collected and washed with ethylene-saturated petroleum ether. Vacuum drying gave yellow crystals.

Anal. Calcd for $\text{C}_{38}\text{H}_{34}\text{ClP}_2\text{Rh}$: C, 66.0; H, 4.9; Cl, 5.1; P, 9.0. Found: C, 65.8; H, 4.9; Cl, 6.3; P, 9.2.

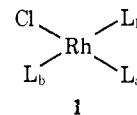
Tris(triphenylphosphine)rhodium(I) chloride was prepared by the literature² method or purchased commercially.

Tetrakis(triphenylphosphine)dirhodium(I) dichloride was prepared from $\text{RhCl}[\text{PPh}_3]_3$ as described in the literature.²

Results and Discussion

As described in the Experimental Section, the compounds $[\text{RhClL}_2]_2$ and RhClL_3 [$\text{L} = \text{P}(p\text{-tolyl})_3$] can be readily prepared by treatment of $[(\text{C}_2\text{H}_5)_2\text{RhCl}]_2$ ²⁸ with phosphine at a L:Rh ratio of 2:1 or 3:1, with elimination of ethylene. $[\text{RhCl}(\text{PF}_3)_2]_2$ has been prepared in a similar way.²⁹ Preparation of the $(\text{C}_2\text{H}_4)\text{RhClL}_2$ complexes merely involves mixing a 2:1 ratio of phosphine to rhodium and crystallization of the product under an ethylene atmosphere. $\text{RhCl}(\text{CO})[\text{P}(p\text{-tolyl})_3]_2$ was prepared nearly pure by exposing a solid sample of $\{\text{RhCl}[\text{P}(p\text{-tolyl})_3]_2\}_2$ to an atmosphere of CO.

Solution Structures. The structures of complexes in solution were established by ^{31}P and ^1H nmr spectra and by isopiestic molecular weight measurements. The proton noise decoupled spectra¹⁶ of the RhClL_3 complexes show a pair of doublets assignable to two equivalent ^{31}P nuclei and a pair of triplets due to the unique P nucleus trans to chloride, consistent with structure 1.^{30,31} The smaller splitting is due to P–P



coupling, the larger to Rh–P coupling. ^{31}P nmr data are given in Table II.

Table II. ^{31}P Nmr Data^a

Compound	δ	$J(\text{Rh-P})$, Hz	$J(\text{P-P})$, Hz
$\text{H}_2\{\text{RhCl}[\text{P}(p\text{-tolyl})_3]_2\}_2$	–51.2 d	195	
	–35.2 d	118	
$\{\text{RhCl}[\text{P}(p\text{-tolyl})_3]_2\}_2$	–49.5 d ^b	196	
$\text{H}_2\text{RhCl}[\text{P}(p\text{-tolyl})_3]_3^c$	–37.0 dd	114	20
	–17.4 dt	90	
$(\text{C}_2\text{H}_5)\text{RhCl}[\text{P}(p\text{-tolyl})_3]_2$	–33.3 d	129	
$\text{RhCl}[\text{P}(p\text{-tolyl})_3]_3$	–46.2 dt	189	38
	–30.2 dd	143	
$(\text{CO})\text{RhCl}[\text{P}(p\text{-tolyl})_3]_2^d$	–27.3 d	124	
$\text{OP}(p\text{-tolyl})_3$	–23.7		
$\text{P}(p\text{-tolyl})_3$	+6.8		
$\text{H}_2\text{RhCl}[\text{PPh}_3]_3^e$	–40.3 dd	114	17.5
	–20.7 dt	90	
$(\text{C}_2\text{H}_4)\text{RhCl}[\text{PPh}_3]_2$	–35.7 d	128	
$\text{RhCl}[\text{PPh}_3]_3$	–48.9 dt	192	37.5
	–32.2 dd	146	
$(\text{CO})\text{RhCl}[\text{PPh}_3]_2^e$	–29.1 d	124	
PPh_3	+5.6		

^a Chemical shifts in ppm from external 85% H_3PO_4 . Spectra were taken at 28° with toluene in the case of $\text{P}(p\text{-tolyl})_3$ or CH_2Cl_2 in the case of PPh_3 , unless noted otherwise. Abbreviations: d, doublet; dd, double doublet; dt, double triplet. ^b At higher resolution further structure is observed as shown in Figure 6. ^c Data at –25° where ligand exchange was slow. ^d In CH_2Cl_2 . ^e Reference 7.

(24) R. G. Gordon and R. P. McGinnis, *J. Chem. Phys.*, **49**, 2455 (1968).

(25) G. Binsch, *J. Amer. Chem. Soc.*, **91**, 1304 (1969).

(26) R. E. Shirmer, J. H. Noggle, and D. F. Gaines, *J. Amer. Chem. Soc.*, **91**, 6240 (1969).

(27) P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Amer. Chem. Soc.*, **93**, 4701 (1971).

(28) R. Cramer, *Inorg. Chem.*, **1**, 722 (1962).

(29) D. A. Clement and J. F. Nixon, *J. Chem. Soc., Dalton Trans.*, 2553 (1972).

(30) The X-ray crystal structure shows that the five heavy atoms are not coplanar.⁴

(31) Letter subscripts on ligands are ordered according to increasing high field shifts of the atoms bonded to Rh, e.g., ^{31}P nuclei in 1.

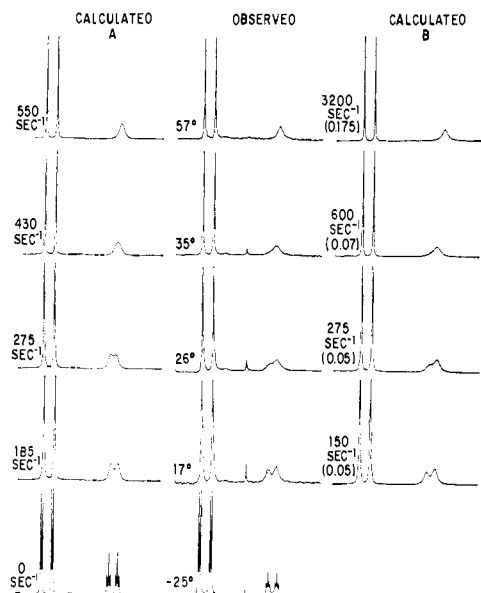


Figure 2. $\{^1\text{H}\} \text{}^{31}\text{P}$ spectra of 0.125 M solutions of $\text{H}_2\text{RhCl}(\text{PPh}_3)_3$ in CH_2Cl_2 under 100 psig of H_2 . Calculated spectra A assume a negligible degree of phosphine dissociation. Spectra B assume that a fraction of the hydride complex was dissociated to H_2RhClL_2 and L . The number in parentheses is $[\text{L}]/[\text{H}_2\text{RhClL}_3]$.

On cooling a 0.125 M solution of $\text{RhCl}[\text{P}(p\text{-tolyl})_3]_3$ in toluene to -95° , much solid crystallized. The ^{31}P spectrum showed, in addition to resonances of RhClL_3 , resonances of free phosphine, phosphine oxide, and an impurity of unknown composition with a spectrum consisting of a doublet ($J(\text{Rh}-\text{P}) = 126 \text{ Hz}$) at -25.4 ppm . On warming to room temperature the RhClL_3 dissolved; resonances of impurity and free phosphine broadened and then disappeared from the spectrum, indicating rapid ligand exchange.³² Resonances of RhClL_3 were still sharp and weak, sharp resonances of $[\text{RhClL}_2]_2$ could be seen at room temperature. On raising the temperature a broad resonance assignable to rapidly exchanging impurity and free phosphine could be seen sharpening and growing in intensity at high field. Dimer resonances grew in intensity but remained sharp. RhClL_3 resonances grew weaker and broadened above 45° .

With a similar solution containing 0.25 M added $\text{P}(p\text{-tolyl})_3$, no dimer resonances were observed at any temperature. The impurity doublet was observable at -95° . At room temperature the spectrum consisted of sharp lines of RhClL_3 and a broad resonance slightly downfield from the free ligand position. Resonances of RhClL_3 broadened above 45° . In the temperature range $45\text{--}70^\circ$, the shape of these lines was independent of the concentration of added phosphine. At 105° the spectrum with 0.25 M added L consisted of two very broad regions assignable to RhClL_3 and impurity + L , respectively. Essentially reversible behavior was observed on cooling; however, at -95° the impurity doublet was more intense than before heating.

We have been unable to identify the impurity but suggest that it may be a Rh(III) -oxygen complex. On pressurizing the above sample to 100 psig with H_2 , the impurity resonance remained unchanged while the

(32) Because of this exchange process the absence of a free phosphine resonance is *not* necessarily good evidence that some is not present in solution.¹⁶

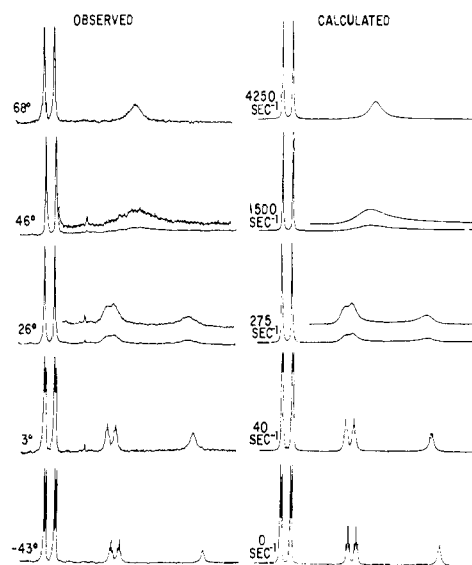
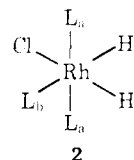


Figure 3. $\{^1\text{H}\} \text{}^{31}\text{P}$ spectra of 0.125 M solutions of $\text{H}_2\text{RhCl}(\text{PPh}_3)_3$ containing 0.0625 M added PPh_3 in CH_2Cl_2 under 100 psig of H_2 . Calculated spectrum assumed that the concentration of free phosphine did not increase with temperature.

RhClL_3 was quantitatively converted to H_2RhClL_3 . Slowly bubbling air through the solution increased the intensity of resonances assigned to impurity and phosphine oxide.

The observed line shape effects permit the following conclusions to be drawn. (1) Dimer formation is enhanced by raising the temperature and suppressed by added phosphine. (2) The rapid exchange of phosphines on RhClL_3 which occurs above 45° does not involve dimer and does not occur by an associative process. (3) Broadening of the free phosphine resonance at room temperature is not due to exchange with RhClL_3 but to exchange with an impurity whose concentration is increased by O_2 . Equation 1 represents a possible pathway for phosphine exchange on RhClL_3 . The impurity is definitely *not* RhClL_2 , however, because it remains on adding a large excess of L and is unreactive toward H_2 .

The proton decoupled ^{31}P spectra of RhClL_3 solutions under 100 psig of H_2 at -25° (Figure 2) show complete conversion to the dihydride H_2RhClL_3 . This A_2BX pattern and the hydride region ^1H nmr spectrum¹⁶ (H_a at τ 19.8, H_b at τ 27.3 with $J(\text{H}_b\text{-P}_b) = 152 \text{ Hz}$ for $\text{H}_2\text{RhCl}(\text{PPh}_3)_2$ in CH_2Cl_2) allow unambiguous assignment of the solution configuration as 2.



The discrepancy between the observed and calculated intensity ratios at -25° is a consequence of the pulsed Fourier mode of operation where the time between pulses was not long compared to the spin lattice relaxation times. The observed spectrum indicates that T_1 of the P nucleus in L_b is longer than in L_a .

Figure 3 shows a series of spectra with added PPh_3 . Broadening of the high field free ligand resonance at -43° , where significant broadening of H_2RhClL_3

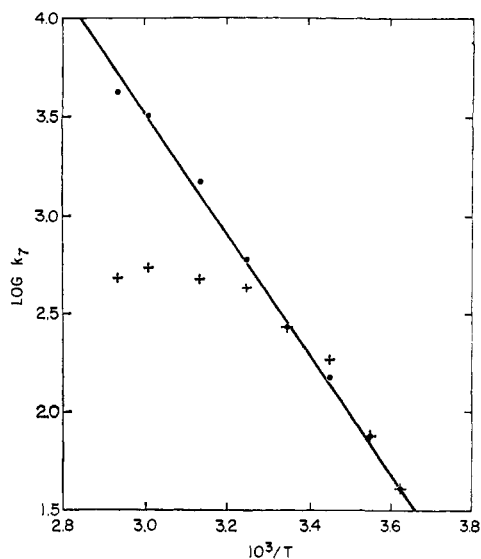


Figure 4. Arrhenius plot for k_7 with $L = \text{PPh}_3$. Points are from fitting spectra with added ligand as in Figure 3. Crosses are from fitting spectra without added ligand and negligible dissociation as in calculated spectra A in Figure 2.

resonances is not observed, is attributed to the same impurity responsible for free ligand broadening in the absence of H_2 . As the temperature is raised, the low field resonances assigned to L_a first broaden and then collapse to become a simple doublet while those of L_b broaden and eventually coalesce with that of free phosphine to form a single line which sharpens on further heating. The calculated spectra assumed that the concentration of free phosphine in solution was not significantly increased by ligand dissociation from $\text{H}_2\text{-RhCl}_3$.

Figure 4 shows an Arrhenius plot, where the points are based on the simulations in Figure 3 (and ones at other temperatures not shown). The straight line corresponds to the expression.

$$k_7 = 10^{12.76} e^{-14.0/RT}$$

$$\Delta G_{300}^\ddagger = 14.0 \text{ kcal/mol}$$

$$\Delta H_{300}^\ddagger = 13.4 \text{ kcal/mol}$$

$$\Delta S_{300}^\ddagger = -2 \text{ eu}$$

The calculated entropy of activation seems small for a dissociative process and may be a consequence of an increased degree of phosphine ligand dissociation of the hydride complex at higher temperatures or to impurity interference with the line shape analysis. Calculated spectra (A) in Figure 2 were based on a rapid and reversible dissociation of L_b from **2** to give a negligible concentration of H_2RhCl_2 by reaction 7. A better



fit of the observed spectra was obtained with calculated spectra (B) where k_7 was fixed at each temperature using Figure 4 and the degree of ligand dissociation allowed to vary with temperature. Ignoring ligand dissociation in Figure 2 gives a poor fit to the Arrhenius plot as shown by the crosses in Figure 4. In view of the complexity of the system any further attempts to obtain accurate values for k_7 and K_7 appear unwarranted. We did not find evidence in the nmr spectra for the paramagnetic Rh(II) reported earlier.^{2,6}

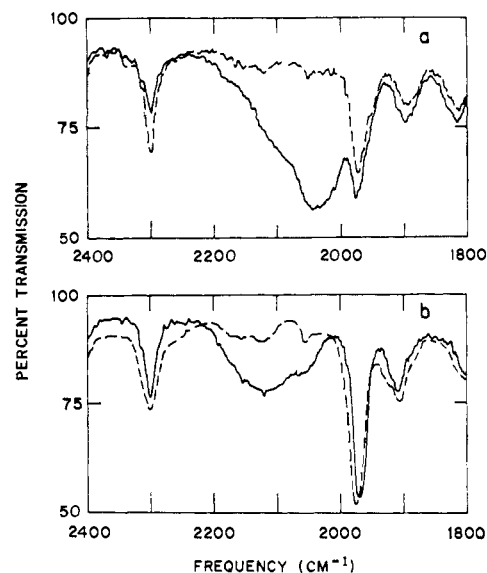


Figure 5. Infrared spectra of ca. 0.01 M CH_2Cl_2 solutions in a 0.1-mm cell under argon (---) and 30 psig of H_2 (—): a, $\text{RhCl}(\text{PPh}_3)_3$; b, $\{\text{RhCl}[\text{P}(p\text{-tolyl})_3]_2\}_2$.

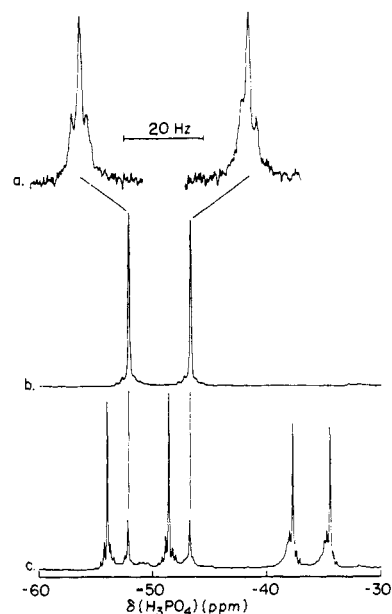


Figure 6. $\{^1\text{H}\} \text{ } ^{31}\text{P}$ spectra of $\{\text{RhCl}[\text{P}(p\text{-tolyl})_3]_2\}_2$ in CH_2Cl_2 : a, at high resolution; b, at normal resolution; c, under H_2 .

The infrared spectrum (Figure 5a) of a CH_2Cl_2 solution of $\text{RhCl}(\text{PPh}_3)_3$ to which H_2 has been added shows a new broad band at 2040 cm^{-1} with a broad shoulder at $\sim 2080 \text{ cm}^{-1}$, assigned to ν_{RhH} .³³ There was no change in the band on adding 1 M PPh_3 . We were unable to find a new band in the region $1200\text{--}800 \text{ cm}^{-1}$ assignable to δ_{RhH} after adding H_2 to solutions of RhCl_3 in benzene or CH_2Cl_2 . The breadth of the ν_{RhH} bands presumably accounts for the markedly different frequencies reported in the literature.

The proton noise decoupled ^{31}P spectrum of $\{\text{RhCl}[\text{P}(p\text{-tolyl})_3]_2\}_2$ is shown in Figure 6. The doublet seen at low resolution indicates that all ^{31}P nuclei are

(33) Osborn, *et al.*,² reported ν_{RhH} at 2099 (m) and 2056 (m) in CH_2Cl_2 with δ_{RhH} at 845 (s). Frequencies in benzene were 2066 (sh), 2051 (m), and 805 (m). Sacco, *et al.*,⁹ reported ν_{Rh} at 2082 and 2012 cm^{-1} in benzene.

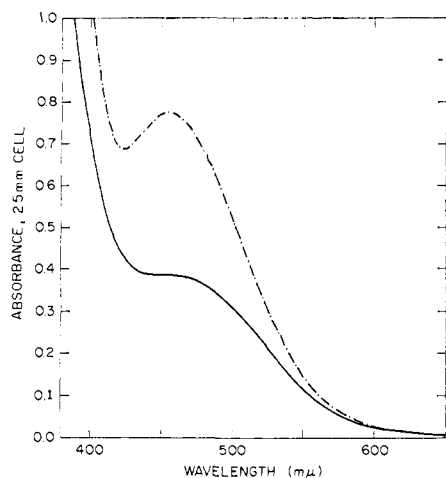
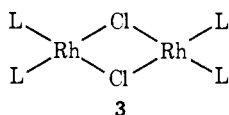


Figure 7. Optical spectra of $1.67 \times 10^{-3} M$ $\{\text{RhCl}[\text{P}(p\text{-tolyl})_3]_2\}$ in toluene under argon (---) and 3 psig of H_2 (—).

chemically equivalent with $J(\text{Rh-P}) = 196$ Hz. At higher resolution some additional splitting is observed, which must be due to coupling of P with more distant Rh or P nuclei. The dimeric nature of the complex is perhaps best shown by the isopiestic molecular weight (1500 ± 100 found *vs.* 1494 calculated for the dimer) and is also indicated by the greatly reduced solubility of the dimer relative to RhCl_3 .

Similar chlorine-bridged dimers of structure 3 have



been established for $[\text{RhCl}(\text{CO})_2]_2$ ^{34a} and $\{\text{P}(\text{O}^i\text{Ph})_3\}_2\text{-Rh}_2\text{Cl}_2(1,5\text{-cyclooctadiene})\}$ ^{34b} by X-ray diffraction and for $[\text{RhCl}(\text{PF}_3)_2]_2$ by mass spectroscopy.³⁵

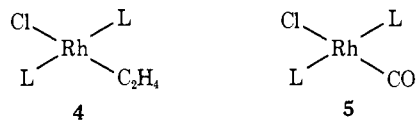
Under H_2 the bottom trace in Figure 6 was obtained, consisting of a strong doublet near that of the original dimer and one of equal intensity with a smaller $J(\text{Rh-P})$ at higher field. Without proton decoupling, components of the lower field doublet appeared as bands with width at half height of ~ 25 Hz due to unresolved aromatic H-P coupling. The higher field doublet consisted of bands of ~ 45 Hz width. We conclude that the dimer hydride has an unsymmetrical structure in which H_2 has added to only one end. Phosphines at that end give rise to the higher field doublet in the ^{31}P spectrum.

Venting H_2 and adding phosphine to the above solution causes rapid dimer cleavage to form monomer hydride and monomer. Only monomeric species are observed if the ratio of added L:Rh exceeds 1:1. No evidence for H_2 addition to the second end of the dimer hydride was seen after a solution of dimer had stood for 24 hr under 150 psig of H_2 . Support for the half hydrogenated dimer is also given by the uv spectrum shown in Figure 7, where 1 atm of H_2 reduces the absorbance at 455 $m\mu$ to about half its original value. Because the ϵ_{455} of H_2RhCl_3 is only $\sim 0.1 \times 10^{-3}$, we conclude that addition of 1 mol of H_2 to the dimer essentially elimi-

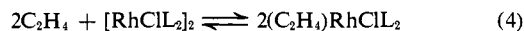
nates the long wavelength electronic absorption of the Rh(III) chromophore while the Rh(I) chromophore spectrum is largely unchanged.

The proton nmr spectrum of $\text{H}_2\{\text{RhCl}[\text{P}(p\text{-tolyl})_3]_2\}_2$ shows a pair of triplets at τ 26.7, $J(\text{Rh-H}) = 22$ and $J(\text{P-H}) = 17$ Hz,³⁶ indicating equivalent hydrogens on a Rh bearing two ^{31}P nuclei. The small value of $J(\text{P-H})$ is consistent with a cis configuration of P and H. The ir spectrum (Figure 5b) shows ν_{RhH} as a broad band centered at ~ 2115 cm^{-1} . No band in the 1200–800- cm^{-1} region assignable to δ_{RhH} was observed.

The complexes $(\text{C}_2\text{H}_4)\text{RhClL}_2$ and $(\text{CO})\text{RhClL}_2$ have ^{31}P spectra consisting of simple doublets with $J(\text{Rh-P}) \sim 125$ Hz, consistent with the equivalent trans P nuclei shown in structures 4 and 5. Structure 4 has been



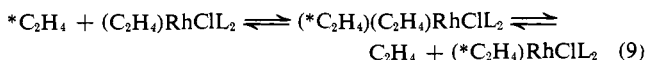
established for $(\text{C}_2\text{F}_4)\text{RhCl}[\text{PPh}_3]_2$ by X-ray diffraction.³⁷ Addition of C_2H_4 (or CO) to solutions of dimer gave ^{31}P resonances of both dimer and $(\text{C}_2\text{H}_4)\text{RhClL}_2$ until the C_2H_4 :dimer ratio reached 2:1. With additional ethylene only the ethylene complex was observed. This indicates a large equilibrium constant for dimer cleavage by reaction 4. Only resonances of dimer were observed



when 2 M cyclohexene or 1-hexene was added to a solution of dimer, indicating markedly reduced coordinating ability of these olefins compared to C_2H_4 or CO.

In a ^{13}C nmr experiment C_2H_4 was added to a solution of $\{\text{RhCl}[\text{P}(p\text{-tolyl})_3]_2\}_2$ in CD_2Cl_2 at ambient temperature. With a C_2H_4 :dimer ratio of less than 2:1 a doublet ($J(\text{Rh-C}) = 16$ Hz) appeared at 44.6 ppm downfield from internal TMS, assigned to coordinated C_2H_4 . The aromatic region showed a new resonance at 140.4 ppm assigned to the para carbon of $(\text{C}_2\text{H}_4)\text{RhCl}[\text{P}(p\text{-tolyl})_3]_2$ in addition to the original para carbon of dimer at 138.5 ppm. With addition of excess C_2H_4 the resonances at 138.5 and 44.6 ppm disappeared. Cooling the solution to -85° gave broad resonances of free and coordinated C_2H_4 at *ca.* 124 and 45 ppm. These observations are consistent with a large value of K_4 and rapid exchange of free and coordinated ethylene in the presence of excess ethylene. The retention of Rh-C coupling with less than 2:1 C_2H_4 :dimer indicates that ethylene exchange by reaction 4 cannot account for the exchange broadening observed in excess ethylene.

In confirmation of this a relatively slow cleavage of dimer by C_2H_4 was found spectrophotometrically (*vide infra*). Exchange with excess ethylene must occur by an associative process as shown in eq 9. An



associative exchange for the 16-electron ethylene com-

(36) A similar spectrum, τ 26.6, $J(\text{Rh-H}) = 20$ and $J(\text{P-H}) = 15$ Hz, has been reported for the triphenylphosphine dimer hydride,² incorrectly formulated as the tetrahydride $\text{H}_4[\text{RhCl}(\text{PPh}_3)_2]_2$.

(37) The heavy atoms and the C_2F_4 mid-point were tetrahedrally distorted from planarity, with the olefin C-C axis perpendicular to the approximate molecular plane.⁴

(34) (a) L. F. Dahl, C. Martell, and D. L. Wampler, *J. Amer. Chem. Soc.*, **83**, 1761 (1961); (b) J. Coetzer and G. Gafner, *Acta Crystallogr., Sect. B*, **26**, 935 (1970).

(35) J. F. Nixon and J. R. Swain, *J. Chem. Soc., Dalton Trans.*, 1044 (1972).

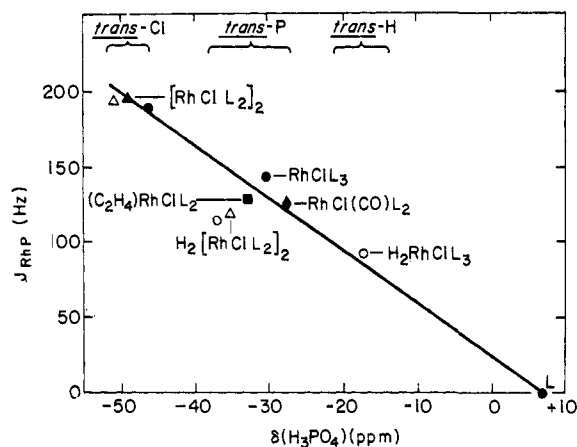
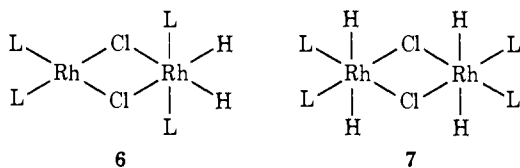


Figure 8. Plot of $J(\text{Rh-P})$ vs. δ taken from $\{^1\text{H}\} ^{31}\text{P}$ data for $\text{L} = \text{P}(p\text{-tolyl})_3$ in toluene at ca. 28° .

plex is expected³⁸ and has also been demonstrated for the 16-electron $(\text{C}_2\text{H}_4)\text{PtL}_2$.²¹

^{31}P nmr data are plotted in Figure 8 for $\text{L} = \text{P}(p\text{-tolyl})_3$ as $J(\text{Rh-P})$ vs. δ . It can be seen from the figure and the known structures 1–5 that values of $J(\text{Rh-P})$ and δ for a given ^{31}P nucleus depend primarily on the nature of the trans ligand, with decreasing $J(\text{Rh-P})$ (increasing δ) in the order trans Cl > P > H. On this basis we conclude that the P ligands in the hydrogen bearing end of $\text{H}_2[\text{RhClL}_2]_2$ are trans to each other and that the structure of the dimer hydride is 6, rather than 7 as originally proposed.²



Spectrophotometric Studies. Spectrophotometric studies were undertaken to confirm the nature of the species in solution and to determine a number of rate and equilibrium constants. Solutions of RhClL_3 do not obey Beer's law, as reported earlier for $\text{L} = \text{PPh}_3$.⁸ On diluting benzene solutions of $\text{RhCl}[\text{P}(p\text{-tolyl})_3]_3$ from 5×10^{-2} to $5 \times 10^{-5} M$, we found a shift in the absorption maximum from ~ 430 to $\sim 450 m\mu$ and a drop in the extinction coefficient from about 1.3 to 1.0×10^3 . On adding phosphine a limiting spectrum with a maximum at 427 ($\epsilon 1.5 \times 10^3$) was obtained with $0.01 M$ or higher added L.

$\{\text{RhCl}[\text{P}(p\text{-tolyl})_3]_2\}_2$ accurately obeys Beer's law over the concentration range 1.6×10^{-2} to $1.6 \times 10^{-4} M$ and the spectrum shows an absorption maximum at $457 m\mu$ ($\epsilon 0.96 \times 10^3$, based on Rh). We conclude that the dimer does not dissociate by reaction 10 to



give a detectable concentration of RhClL_2 even in very dilute solutions. An upper limit of $6 \times 10^{-6} M$ can be set for K_{10} .³⁹

The deviation from Beer's law in solutions of RhClL_3 and the effect of added L can be quantitatively accounted for in terms of the monomer-dimer equilib-

(38) C. A. Tolman, *Chem. Soc. Rev.*, 1, 337 (1972).

(39) Assuming that if 10% of the Rh were present as RhClL_2 , it would have been detected in the $1.6 \times 10^{-4} M$ solution of dimer.

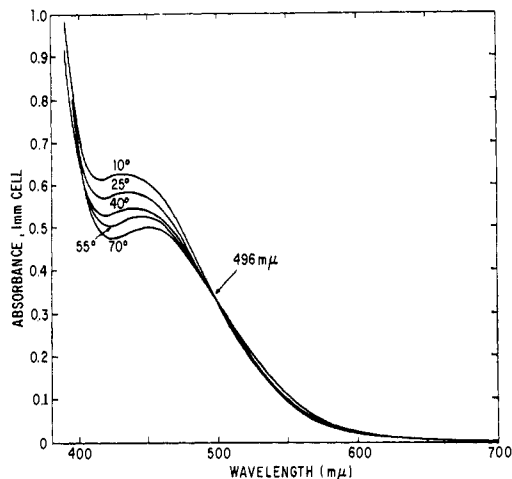


Figure 9. Effect of changing temperature on the optical spectrum of $5.06 \times 10^{-3} M \text{RhCl}[\text{P}(p\text{-tolyl})_3]_3$ in benzene.

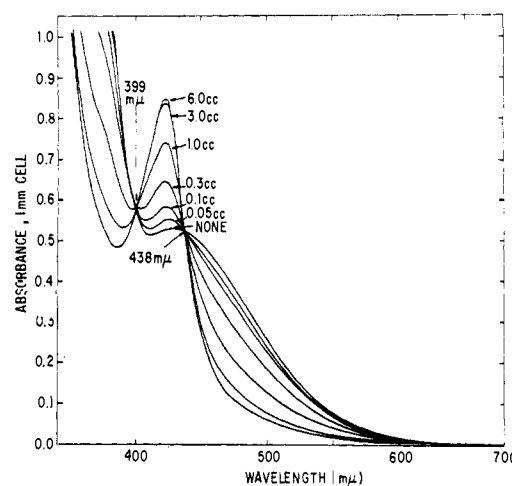
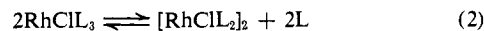
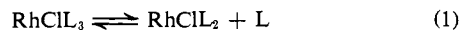


Figure 10. Optical spectra on adding increasing volumes of C_2H_4 gas to 2 cm^3 of $3.82 \times 10^{-3} M \text{RhCl}[\text{P}(p\text{-tolyl})_3]_3 + 0.01 M$ added $\text{P}(p\text{-tolyl})_3$ in benzene at 25° .

rium (2) with $K_2 = 2.5 \pm 0.6 \times 10^{-4} M$ in benzene at 25° .



Arai and Halpern⁸ attributed deviations from Beer's law by $\text{RhCl}(\text{PPh}_3)_3$ and the effects of added PPh_3 to reaction 1. We have found that their data can be



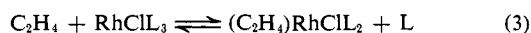
fitted equally well assuming only reaction 2, and obtain $K_2 = 3.3 \pm 0.4 \times 10^{-4} M$ and an extinction coefficient at infinite dilution of 0.8×10^3 at $410 m\mu$. The latter is in much better agreement with our measured value for the p -tolylphosphine dimer (1.0×10^3) than is the value of 0.42×10^3 obtained using eq 1.⁸

Equilibrium 2 can be displaced to the right by heating, indicating that dimer formation is endothermic.⁴⁰ Figure 9 shows the effect of heating a solution of $\text{RhCl}[\text{P}(p\text{-tolyl})_3]_3$ from 10 to 70° .

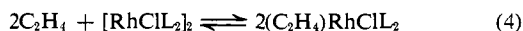
The reaction of C_2H_4 with the RhClL_3 complexes was studied spectrophotometrically. Figure 10 shows opti-

(40) Reaction 2 with $\text{L} = \text{P}(\text{OPh})_3$ is endothermic with $\Delta H = 23$ kcal/mol. This was determined calorimetrically for the reverse reaction by W. Partenheimer and E. F. Hoy, *J. Amer. Chem. Soc.*, **95**, 2840 (1973).

cal spectra obtained on adding increasing amounts of C_2H_4 to a solution containing $RhCl[P(p\text{-tolyl})_3]_3$ and 0.01 M added $P(p\text{-tolyl})_3$. Sharp isosbestic points at 399 and 438 $m\mu$ (lit.² 402 and 434 $m\mu$ for $L = PPh_3$) indicate the presence of two chromophores during the addition, *viz.* $RhClL_3$ and $(C_2H_4)RhClL_2$. Addition of more L displaces the equilibrium to the left, as expected by eq 3.



Addition of C_2H_4 to a solution of $\{RhCl[P(p\text{-tolyl})_3]_2\}_2$ gives a similar series of spectra but with sharp isosbestic points shifted to 393 and 446 $m\mu$. Thus dimer cleavage by C_2H_4 proceeds cleanly according to reaction 4.



Addition of C_2H_4 to a $4 \times 10^{-3} M$ solution of $RhCl[P(p\text{-tolyl})_3]_3$ without added phosphine gives a series of spectra without well-defined isosbestic points. In this case three chromophores are present: $RhClL_3$, $[RhClL_2]_2$, and $(C_2H_4)RhClL_2$.⁴¹

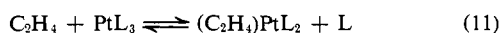
A sample of $(C_2H_4)RhCl[P(p\text{-tolyl})_3]_2$ dissolved in benzene did not give the optical spectrum expected for the ethylene complex but rather one intermediate between the expected spectrum and that of dimer. The purity of the sample was confirmed by the correct ratios of integrated areas of ethylene to ligands in the ¹H nmr spectrum. The curious optical spectrum is a consequence of partial ethylene dissociation accompanied by dimer formation by the reverse of reaction 4. Addition of excess C_2H_4 gave the spectrum expected for $(C_2H_4)RhClL_2$, with the correct $\epsilon_{421} 2.2 \times 10^3$ based on the weight of complex in solution. Electronic spectral data are summarized in Table III.

Table III. Electronic Spectral Data for Complexes in Benzene Solution

Complex ^a	Feature	λ , $m\mu$	$10^3\epsilon$, $cm^{-1} M^{-1}$
$RhClL_3$	Max ^b	427	1.5
$[RhClL_2]_2$	Max	457	0.96
H_2RhClL_3	Isosb ^c	360	3.0
$H_2[RhClL_2]_2$	Sh	455	0.5
$(C_2H_4)RhClL_2$	Max	421 ^d	2.2 ^d
$(CO)RhClL_2$	Max	366	4.2

^a Data are the same for $L = PPh_3$ or $P(p\text{-tolyl})_3$ within the experimental uncertainties of $\pm 2 m\mu$ in wavelength and $\pm 5\%$ in extinction coefficient. ^b The spectrum also shows a shoulder with inflection point at 360 $m\mu$ ($\epsilon 3.0 \times 10^3$) (lit.¹² $\epsilon \sim 6 \times 10^3$). ^c Isosbestic point involving H_2RhClL_3 and $RhClL_3$. ^d Reference 2 reports a band maximum at 416 $m\mu$ with $\epsilon \sim 3 \times 10^3$.

Spectrophotometrically determined equilibrium constants are shown in Table IV. K_3 is 3.4 times as large for $L = P(p\text{-tolyl})_3$ as for PPh_3 . This can be understood in terms of better metal \rightarrow olefin π^* back-donation with the better electron donor $P(p\text{-tolyl})_3$. Equilibrium constants for eq 11 were 0.21 for $L = P(p\text{-tolyl})_3$ and



0.12 for PPh_3 .²¹

Kinetics and equilibria of H_2 reactions were determined with the gas reaction cell shown in Figure 1. Toluene was used as the solvent because of its low

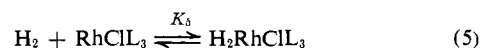
(41) Before C_2H_4 addition a $4 \times 10^{-3} M$ solution of monomer contains $\sim 60\%$ of the Rh as $RhClL_3$, 40% as $[RhClL_2]_2$.

Table IV. Equilibrium Constants Measured Spectrophotometrically at 25°

Equilibrium const	Solvent	$L = P(p\text{-tolyl})_3$	$L = PPh_3$
K_2	Benzene	$2.5 \pm 0.6 \times 10^{-4} M$	$3.3 \pm 0.4 \times 10^{-4} M^a$
K_3	Benzene	1.7 ± 0.25	0.4 ± 0.1
K_4	Benzene	$6.7 \pm 0.8 \times 10^3 M^{-1}$	
K_5	Toluene	$40 \pm 3 atm^{-1 b,c}$	$18 \pm 1 atm^{-1 b}$
K_6	Toluene	$11 \pm 2 atm^{-1}$	

^a Determined by fitting the data of Arai and Halpern⁸ to eq 2. ^b Determined in solutions containing 0.04 M added L . ^c A value of $41 \pm 2 atm^{-1}$ was determined for added $[P(p\text{-tolyl})_3]_3 = 0.1 M$.

vapor pressure. The equilibrium constant for reaction 5 (Tables I and IV) was 2.2 times as large for $L =$



$P(p\text{-tolyl})_3$ as for $L = PPh_3$. The equilibrium for oxidative addition is favored by the better electron donor. The equilibrium constant K_6 for the *p*-tolylphosphine dimer is 3.6 times less than that of the monomer, apparently reflecting a slightly reduced electron density on Rh in the chlorine-bridged dimer. The absence of evidence for formation of a dimer tetrahydride even under forcing conditions (150 psig of H_2 , 18 hr) indicates that the electron-withdrawing action of H_2 addition to one end of the dimer can be transmitted through the chlorine bridge to the other end. An upper limit of $\sim 0.01 atm^{-1}$ can be set on K_{12} with $L = P(p\text{-tolyl})_3$.⁴²



Phosphine was added to the monomer solutions to suppress dimer formation when determining K_5 . As expected, the value of K_5 was independent of $[L]$ and the same value was obtained for added $[P(p\text{-tolyl})_3]_3 = 0.04$ or $0.1 M$.

Kinetic data could be obtained by following the approach of the H_2 reactions to equilibrium. Reactions of H_2 with solutions of $RhClL_3$ containing 0.01 M or more added L or of $[RhClL_2]_2$ gave plots of $\log(A - A_\infty)$ against time which were linear over 4 half-lives (after an initial 0.1 min required for mixing). Values of κ obtained depended on hydrogen pressure, as shown in Figure 11 for the reaction of H_2 with a solution of $RhCl[P(p\text{-tolyl})_3]_3$ containing 0.02 M added phosphine. A value of $K_5 = 40 atm^{-1}$ can be obtained from the ratio of the slope (k_5) to the intercept (k_{-5}), in good agreement with the value in Table IV. A value of k_{-5} could also be determined by following the increase in absorbance after H_2 was removed from the solution by vacuum pump.

Unexpectedly the magnitudes of both the slope and the intercept were dependent on the concentration of added phosphine, as shown by the data in Table V. Increasing phosphine concentration, under conditions where $RhClL_3$ and H_2RhClL_3 were the only detectable Rh species in solution, decreased the rate at which H_2 reacted and decreased the rate at which H_2 could be removed. At each $[L]$ the ratio k_5/k_{-5} remained con-

(42) Assuming that 10% of tetrahydride would have been detected under 10 atm of H_2 .

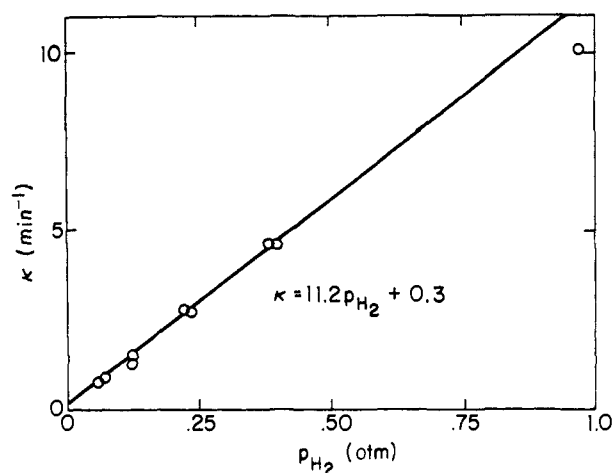


Figure 11. Pseudo-first-order rate constant κ vs. p_{H_2} for the reaction of H_2 with $RhCl[P(p\text{-tolyl})_3]_3$ in toluene at 25° . $P(p\text{-tolyl})_3$ (0.02 M) was added to suppress dimer formation.

Table V. Kinetics of Reaction of H_2 with Rhodium Complexes in Toluene at 25°

Complex	[L], ^a M	Slope, ^b min ⁻¹ atm ⁻¹	Intercept, ^b min ⁻¹
$RhCl[P(p\text{-tolyl})_3]_3$	0.01	19.4	0.4
	0.02	11.2	0.3
	0.04	7.1	0.2
	0.1	3.8	0.1
	0.3	2.1	0.06
	0.3	1.2 ^c	0.015 ^c
$RhCl[PPh_3]_3$	0.04	3.0	0.2
$\{RhCl[P(p\text{-tolyl})_3]_2\}_2$	0.0	1.5	0.12

^a Concentration of added phosphine ligand. ^b Determined from plots of pseudo-first-order rate constant κ against p_{H_2} . ^c Values determined at 15° .

stant. A plot of k_5 against [L] is shown in Figure 12. The data for L = $P(p\text{-tolyl})_3$ are consistent with eq 13

$$k_5 = k_5^\infty + k_8 K_1 / [L] \quad (13)$$

where $k_5^\infty = 1.5 \text{ min}^{-1} \text{ atm}^{-1}$ and $k_8 K_1 = 0.21 \text{ min}^{-1} \text{ atm}^{-1} \text{ M}^{-1}$.

Lowering the temperature from 25 to 15° in one case (added $[P(p\text{-tolyl})_3] = 0.3 \text{ M}$) decreased k_5 by a factor of ~ 2 and k_{-5} by a factor of ~ 4 . Thus k_5 is $\sim 80 \text{ min}^{-1} \text{ atm}^{-1}$ at 15° and ΔH^\ddagger is larger for reductive elimination than for oxidative addition of H_2 (~ 20 vs. ~ 10 kcal/mol).

Comparison of data in Table V for $RhCl[P(p\text{-tolyl})_3]_3$ and $RhCl[PPh_3]_3$, both with [L] = 0.04, shows that the larger K_5 in the case of $P(p\text{-tolyl})_3$ is a consequence of a larger forward rate constant.

The reaction of $\{RhCl[P(p\text{-tolyl})_3]_2\}_2$ with H_2 is rather slow, with $k_6 = 1.5 \text{ atm}^{-1} \text{ min}^{-1}$ at 25° . The reaction rate was shown to be independent of dimer concentration by reducing the concentration from 1.7×10^{-3} to 2.3×10^{-4} and running the reaction in the 20-mm gas reaction cell instead of the 2.5-mm cell. This result shows that dimer hydride formation occurs by a direct reaction, rather than one involving some dissociated species. An absence of spectroscopically detectable $RhClL_2$ was inferred earlier from Beer's law.

The absorbance change observed when H_2 was added to a $\sim 2.5 \times 10^{-3} \text{ M}$ solution of $RhClL_3$ with no

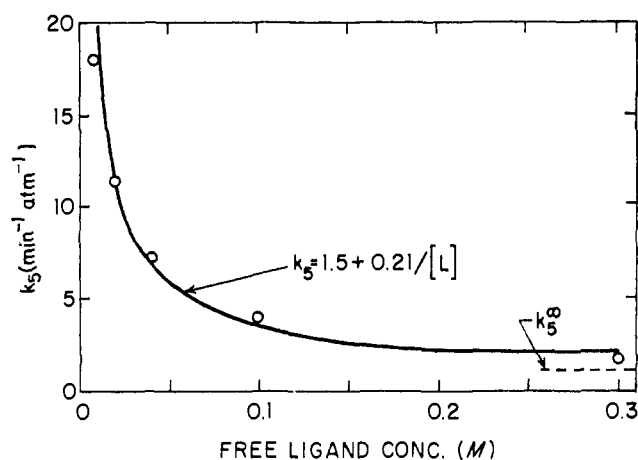
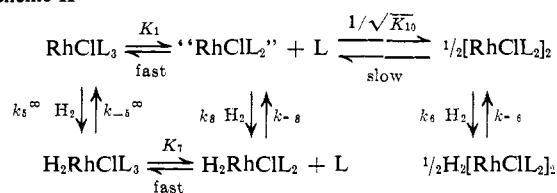


Figure 12. Effect of free phosphine concentration on the forward rate constant in the reaction of H_2 with $RhCl[P(p\text{-tolyl})_3]_3$ in toluene at 25° .

added L was not a simple first-order decay. $A(425)$ fell rapidly during the first minute, followed by a much slower change. Plots of $\log(A - A_\infty)$ vs. time could be fitted with two straight lines, implying parallel reactions with different characteristic rate constants. The smaller κ was the same as that measured in the reaction of H_2 with dimer. The larger κ was $>6 \text{ min}^{-1}$ even at 0.2 atm of H_2 and could not be accurately determined with our apparatus.

The behavior of the H_2 reaction kinetics can be understood by referring to Scheme II.^{43,44} Direct

Scheme II



oxidative addition of H_2 to $RhClL_3$ with rate constant k_5^∞ can be measured at very high added ligand concentrations. At lower [L] but with $[L] \geq 0.01 \text{ M}$ to suppress dimer formation, k_5 is given by eq 13. Since $K_1/\sqrt{K_{10}} = \sqrt{K_2} = 2 \times 10^{-2}$, K_1 must be less than $5 \times 10^{-5} \text{ M}$ and k_8 must be greater than $4 \times 10^3 \text{ min}^{-1}$. In spite of the very low concentration of "RhClL₂," more than 90% of $H_2 RhClL_3$ must form by this path in 0.01 M added L. At lower concentrations of added L a significant fraction of the Rh is present initially as dimer, which reacts with H_2 at a slow rate. The fast and slow descriptions of reactions 1, 7, and 10 in Scheme II are supported by the ³¹P nmr studies described above.

A role for $RhClL_2$ was not expected based on the 16- and 18-electron rule.³⁸ A simple three-coordinate complex would leave the rhodium with only 14 valence electrons. One possibility is that the rule is sometimes invalid for kinetic intermediates. Whitesides⁴⁵ has

(43) A similar scheme has been proposed by Halpern and Wong⁴⁴ who have carried out a kinetic study of the system with L = PPh_3 . We received a preprint of their communication⁴⁴ while our manuscript was in preparation.

(44) J. Halpern and C. S. Wong, *J. Chem. Soc., Chem. Commun.*, 629 (1973).

(45) G. M. Whitesides, J. F. Gaash, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, **94**, 5258 (1972).

Table VI. Hydrogenation of Cyclohexene^a by $2.5 \times 10^{-3} M$ $\text{RhCl}[\text{P}(p\text{-tolyl})_3]_3$ in Toluene at 25°

$10^3[\text{L}]$ added	(atm/min) ^b		$-\Delta A(0.5)^c$	$-\Delta A(1.0)^d$	$(dp(0.5)/dt)/$ $(dp(1.0)/dt)$	$\Delta A(0.5)/\Sigma \Delta A$	% dimer calcd ^e
	$10^2 \times dp(0.5)/dt$	$10^2 \times dp(1.0)/dt$					
0.0	0.77	1.27	0.24	0.17	0.61	0.59	41
0.2	0.77	1.20	0.29	0.16	0.64	0.65	37
0.5	0.70	0.97	0.31	0.12	0.72	0.72	33
2.0	0.37	0.32	0.44	0.055	1.15	0.89	16
5.0	0.2	0.2	0.56	0.05	1.0	0.92	4.2
10.0	0.1	0.1	0.555	0.025	1.0	0.96	1.2

^a Initially 1 M cyclohexene. A 10-cm³ solution in 2.5-mm gas reaction cell with 246 cm³ vapor space. ^b Rate of H₂ pressure drop at 0.5 and 1.0 atm. ^c Decrease in $A(425)$ after adding 0.5 atm of H₂. ^d Decrease in $A(425)$ on increasing p_{H_2} from 0.5 to 1.0 atm. ^e Initial percentage of Rh present as dimer assuming $K_2 = 2.5 \times 10^{-4} M$.

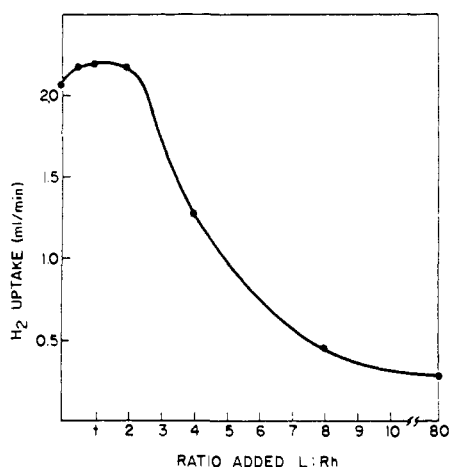


Figure 13. Rate of hydrogen uptake by 10 cm³ of 1 M cyclohexene in toluene at ambient temperature and 1 atm. Various amounts of $\text{P}(p\text{-tolyl})_3$ in a solution of $1.3 \times 10^{-3} M$ Rh added as $\{\text{RhCl}[\text{P}(p\text{-tolyl})_3]_2\}_2$.

presented kinetic evidence for $\text{Pt}(\text{PPh}_3)_2$, though we²¹ were unable to find spectroscopic evidence for its existence in solution. A more attractive (to us) possibility is that "RhCl₂" is actually a 16-electron complex where the extra electron pair is donated by one of the aromatic rings. A precedent for a structure of this type is $(h^3\text{-}4\text{-MeC}_6\text{H}_4\text{CH}_2)(h^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2$.⁴⁶ The suggested participation of an aromatic ring in the rhodium system could be tested by studying the behavior of RhCl_3 complexes where L is a trialkylphosphine. In any case, caution is indicated when applying the 16- and 18-electron rule to the kinetics of reactions involving complexes containing aromatic phosphines.

Cyclohexene Hydrogenation. Early experiments in cyclohexene hydrogenation were carried out at 1 atm pressure, measuring the rate of change of H₂ volume. Some of these results are shown in Figure 13, where the rhodium was charged as $\{\text{RhCl}[\text{P}(p\text{-tolyl})_3]_2\}_2$ and various amounts of $\text{P}(p\text{-tolyl})_3$ were added. The dimer itself is a good catalyst. Small amounts of added phosphine improved the hydrogenation rate while higher concentrations caused marked inhibition.

More detailed studies were carried out at 25° using the 2.5-mm gas reaction cell, where the H₂ pressure could be varied more conveniently and the species present in solution could be monitored by means of their uv spectra. Table VI shows the results of experiments using $\text{RhCl}[\text{P}(p\text{-tolyl})_3]_3$ and added phosphine

(46) F. A. Cotton and M. D. LaPrade, *J. Amer. Chem. Soc.*, **90**, 5418 (1968).

where the rate of H₂ pressure drop at 0.5 and 1.0 atm of H₂ was determined and the absorbance at 425 mμ followed with time. Added phosphine decreased the rate of hydrogenation. At 0.01 M added [L], the rate was only ~1% of that without added L. The effect of increasing H₂ pressure was strongly dependent on [L]. The rates at 0.5 and 1.0 atm became more similar as [L] was increased. This behavior was reflected in the absorbance changes. With increasing [L] the change in absorbance on going to 1.0 atm was less. This behavior can be understood in terms of equilibria 2, 5, and 6. Increasing [L] decreases the fraction of Rh present as dimer. At equilibrium 0.5 atm of H₂ converts ~95% of $p\text{-tolylphosphine}$ monomer to hydride but only ~80% of dimer to hydride. The $\Delta\epsilon_{425}$ is also larger on forming the hydride of the monomer.

The spectrum of $2.5 \times 10^{-3} M$ RhCl_3 in 1 M cyclohexene was the same as in the absence of cyclohexene. Complexes 1, 2, 3, and 6 were the only Rh-containing species detected by ³¹P nmr under conditions of homogeneous hydrogenation of cyclohexene at ambient temperature.

The hydrogenation of cyclohexene by pure dimer was investigated in more detail. Table VII shows results

Table VII. Hydrogenation of Cyclohexene^a by $1.7 \times 10^{-3} M$ $\{\text{RhCl}[\text{P}(p\text{-tolyl})_3]_2\}_2$ in Toluene at 25°

Expt no.	p_{H_2} , atm	$10^2 \times dp/dt^b$ (atm/min)	$-\Delta A(455)^c$	$10^2 \times (dp/dt)/$ (fraction dimer hydride) ^d
1	0.09	0.23	0.025	1.8
2	0.23	0.67	0.055	1.6
3	0.56	1.40	0.05	2.1
4	0.88	1.73	0.02	2.2
5	1.91	2.04	0.02	2.3
6	0.57 ^e	1.08		
7	0.59 ^f	0.13		

^a Initially 1 M cyclohexene. A 10-cm³ solution in a 2.5-mm gas reaction cell with 246 cm³ vapor space. ^b Rate of H₂ pressure drop at pressure indicated. ^c Maximum decrease in $A(455)$ after increasing p_{H_2} . ^d Fraction of dimer as hydride calculated assuming $K_6' = 3.6 \text{ atm}^{-1}$. (See text.) ^e p_{H_2} reduced from ~1.9 atm using a vacuum pump. ^f p_{H_2} reduced to ~0.0 atm using a vacuum pump. Then 0.037 atm of air (0.0073 atm of O₂) was added, followed by ~0.6 atm of H₂.

obtained with one solution at various hydrogen pressures. The rate was nearly first order in p_{H_2} below 0.5 atm but approached zero order at higher pressures. The increases in rate were reflected by dropping $A(455)$, as dimer was converted to dimer hydride under in-

Table VIII. Ethylene Hydrogenation Experiments^a

Expt no.	Complex ^b	10 ³ [Rh], M	P ^o C ₂ H ₄ , ^d atm	P ^o H ₂ , ^d atm	A ₀ (421) ^e	A _∞ (421) ^f	10 ² × dp/dt, ^g (atm/min)
1	[RhClL ₂] ₂	1.4	0.17*	0.64	0.785	0.54	0.07
2	[RhClL ₂] ₂	1.7	0.34*	0.64	0.925	0.71	0.13
3	[RhClL ₂] ₂	1.5	0.31	0.64*	0.18	0.31	0.10
4	RhClL ₃ ^c	1.2	0.17*	0.64	0.585	0.16	0.01
5	RhClL ₃ ^c	1.2	0.34*	0.64	0.635	0.18	0.02
6	RhClL ₃ ^c	1.2	0.33	0.64*	0.09	0.11	0.05

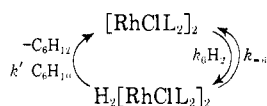
^a Carried out in a 2.5-mm gas reaction cell. A 10-cm³ solution in toluene at 25°. ^b In these experiments L = P(*p*-tolyl)₃. ^c P(*p*-tolyl)₃ (0.01 M) was added to suppress dimer formation. ^d Initial partial pressure of gas above solution. Asterisk indicates which gas was added first. ^e Absorbance at 421 mμ after equilibration with the first gas added. ^f Absorbance at 421 mμ 30 min after the second gas was added. ^g Average rate of pressure drop during the hour after the second gas was added.

creasing hydrogen pressure. The initial spectrum with 1.7×10^{-3} M dimer and 1 M cyclohexene was the same as in the absence of cyclohexene, indicating a negligible tendency to form an olefin complex by bridge splitting.

After each H₂ addition *A*(455) fell with a half-life characteristic of dimer hydride formation, followed by a much slower increase. The slow increase is attributed to reaction of the dimer with traces of O₂ in the system. A similar slow increase was observed in the absence of cyclohexene. Deliberate addition of 0.037 atm of air caused a rapid increase in *A*(455) and decreased the hydrogenation rate at 0.6 atm of H₂ by a factor of 8. Slower reaction with adventitious O₂ accounts for the reduced activity in experiment 6 compared to 3.

The drop in *A*(455) on addition of H₂ to a solution of the dimer is markedly less in the presence of 1 M cyclohexene than in the absence of cyclohexene. It can be concluded that dimer hydride is returned to dimer by cyclohexene so fast that the steady-state concentration of dimer hydride is substantially less than the equilibrium value. Values of $-\Delta A(455)_{\max}$ from Table VII can be used to calculate an approximate apparent dimer hydride formation constant $K_6' = 3.6 \pm 0.3$ atm⁻¹ in 1 M cyclohexene compared to a larger value of $K_6 = 11 \pm 2$ atm⁻¹ (Table IV) with no olefin. This suggests Scheme III. Applying the steady-state treatment gives

Scheme III



eq 14 where [D₀] is the initial concentration of dimer and

$$d[C]/dt = k_6 p_{H_2} [D_0] k' [C] / \{k_6 p_{H_2} + k_{-6} + k' [C]\} \quad (14)$$

[C] is the concentration of cyclohexene; $k' = 0.32$ M⁻¹ min⁻¹.

$$K_6' = k_6 p_{H_2} / \{k_{-6} + k' [C]\} \quad (15)$$

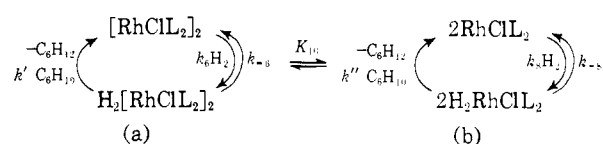
Equation 14 is consistent with the observation that varying the cyclohexene concentration from 0.3 to 2.0 M has essentially no effect on the hydrogenation rate. Equation 14 is inadequate, however, in two respects. The maximum possible rate of hydrogenation is $k_6 p_{H_2} [D_0]$, which at 1.9 atm of H₂ and 1.7×10^{-3} M dimer is 0.48×10^{-2} M min⁻¹. The measured rate (expt no. 5, Table VII) at 1.91 atm is 2.04 atm min⁻¹,⁴⁷

(47) In our system H₂ uptake in units of atm min⁻¹ is equivalent to cyclohexene formation in units of mol l⁻¹ min⁻¹. This is because the vapor space contains 10 mmol of gas at 1 atm and the solution volume is 10 ml.

about four times as large. Equation 14 predicts a reaction rate which is first order in initial dimer concentration. In experiments with 0.3 M cyclohexene and 0.9 atm of H₂, reducing the dimer concentration from 3.5×10^{-3} to 0.9×10^{-3} , a factor of 4, reduced dp/dt by only a factor of about 2.

Scheme IV is a kinetic mechanism⁴⁸ for cyclohexene

Scheme IV



hydrogenation by dimer which appears consistent with the known facts.

The overall hydrogenation rate will be made up of two parts. That from part (a) will be first order in dimer and that from (b) half-order. It appears that ~25% of cyclohexene hydrogenation goes by (a) and ~75% by (b) at 1.7×10^{-3} M {RhCl[P(*p*-tolyl)₃]₂}₂.

Siegel and Ohrt¹⁴ fitted kinetic data on cyclohexene hydrogenation to an assumed mechanism and obtained numerical values for a large number of equilibrium constants. They concluded that the dominant form of the catalyst at high olefin concentrations was (olefin)RhClL₃ while at high hydrogen pressure it was H₂RhClL₂(olefin). Our results suggest that the mechanism fitted is inadequate and that many of the equilibrium constants reported are probably incorrect.

Ethylene Hydrogenation. ³¹P nmr experiments showed that solutions containing ethylene and hydrogen contained (C₂H₄)RhClL₂ (4) in addition to the complexes 1, 2, 3, and 6. One experiment described in the Experimental Section clearly demonstrates that ethylene can be catalytically hydrogenated by {RhCl[P(*p*-tolyl)₃]₂}₂. Complete conversion of ethylene to ethane also occurred in a similar experiment using RhCl[P(*p*-tolyl)₃]₃. These results do not shed light on the rate of the direct reaction of H₂ with (C₂H₄)RhClL₂, in view of the complexity of reversible equilibria in the system. To investigate this question we looked at the hydrogenation of C₂H₄ in the gas reaction cell varying pressures of both gases and their order of addition. The results are summarized in Table VIII.

Addition of increasing pressures of C₂H₄ to a toluene solution of {RhCl[P(*p*-tolyl)₃]₂}₂ gave essentially com-

(48) We use the terms "kinetic mechanism" to denote a mechanism which shows only those steps and species which affect the kinetics of the reaction. Nothing is implied about the existence of intermediate olefin or alkyl complexes.

plete conversion to ethylene complex at 0.17 or 0.34 atm of C_2H_4 . Dimer cleavage was first order in C_2H_4 pressure and first order in dimer with $k_4 = 45 \pm 4 \text{ min}^{-1} \text{ atm}^{-1}$. At steady-state conditions under 0.64 atm of H_2 , spectra showed that a substantial fraction of the Rh remained as ethylene complex. There was a small but measurable rate of pressure drop due to ethylene hydrogenation.

Addition of increasing pressure of C_2H_4 to toluene solutions of $10^{-3} M$ $RhCl[P(p\text{-tolyl})_3]_3$ and $0.01 M$ $P(p\text{-tolyl})_3$ gave rapid equilibration⁴⁹ with $\sim 80\%$ conversion of $RhClL_3$ to ethylene complex with 0.34 atm of C_2H_4 . Steady-state conditions were rapidly achieved after H_2 addition. Spectra showed a predominance of H_2RhClL_3 but some $(C_2H_4)RhClL_2$ was still present. The rate of ethylene hydrogenation was less when most of the Rh was initially present as monomer than when dimer was used.

The much slower hydrogenation of ethylene compared to cyclohexene (*cf.* expt no. 2 Table VIII and expt no. 3 Table VII) indicates that the "hydride route" involving reaction of H_2 (with dimer in this

(49) The half-life on adding the first 0.02 atm of C_2H_4 was ~ 0.6 min.

case) prior to olefin coordination must be much faster than the "unsaturate route" involving oxidative addition of H_2 to a preformed (olefin) $RhClL_2$ complex, in agreement with Wilkinson's original postulate.²

While we do not claim to have a complete mechanism for homogeneous hydrogenation by Wilkinson's catalyst, we hope that our studies have brought that goal closer, particularly with regard to characterizing the species present in solution under hydrogenation conditions. Our work emphasizes the value of breaking complex reaction sequences into simpler steps and of monitoring steady-state concentrations of species during homogeneous catalytic reactions.

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Olefin Complexes of Nickel(0). II. Preparation and Properties of (Olefin)bis(tri-*o*-tolyl phosphite)nickel Complexes

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Abstract: The preparation and properties of (olefin) NiL_2 complexes [$L = P(O\text{-}o\text{-tolyl})_3$] are described where the olefin is maleic anhydride, acrylonitrile, styrene, propylene, 1,5-cyclooctadiene, and tetrafluoroethylene. In the case of tetrafluoroethylene, the complex $(C_2F_4)NiL_2$ was identified in solution but the compound actually isolated was $cyclo\text{-}(C_4F_8)Ni[P(O\text{-}o\text{-tolyl})_3]_2$. Formation of $(C_2F_4)NiL_2$ from NiL_3 occurs *via* an associative reaction with $k_2 = 0.25 \pm 0.025 \text{ sec}^{-1} M^{-1}$ in benzene at 25° . $\Delta H^\ddagger = 6.5 \pm 1 \text{ kcal/mol}$ and $\Delta S^\ddagger = -40 \pm 3 \text{ eu}$. Proton nmr, vibrational, and structural data on these and other transition metal olefin complexes are correlated with the ionization potential of the metal and the degree of metal to olefin π^* back bonding.

Olefin complexes of the transition metals are essential intermediates in a variety of homogeneous catalytic processes and have been studied with increasing interest in recent years. Several review articles have appeared,^{1,2} but there is a shortage of quantitative data.³

Our work was initiated to understand the factors which determine the kinetics and thermodynamics of formation of olefin complexes of zerovalent nickel. Equilibrium studies have since been reported for a series of olefin(dipyridyl)nickel complexes.⁴ The

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kinetics and equilibria of reactions of methyl methacrylate and styrene with $Ni[P(OC_6H_5)_3]_4$ have been investigated.⁵ We have reported the results of studies on ethylene-(triarylphosphine)^{6a} and ethylene-(triethylphosphine)^{6b} complexes of zerovalent Ni, Pd, and Pt.

In part I^{7a} we described the preparation and properties of $(C_2H_4)Ni[P(O\text{-}o\text{-tolyl})_3]_2$. We now report the results of studies on the preparation and characterization in solution of related (olefin) $Ni[P(O\text{-}o\text{-tolyl})_3]_2$ complexes where olefin^{7b} is maleic anhydride, acrylonitrile, styrene, propylene, 1,5-cyclooctadiene, and tetrafluoroethylene. Part III⁸ will describe spectro-

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