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Comparisons of Solid-State and Solution Structures of $(R_3P)_2Rh(CO)Cl$ Complexes with Monodentate Phosphole and Phosphine Ligands

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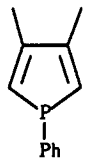
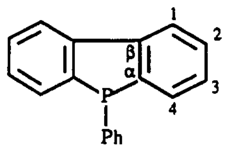
Introduction

$(R_3P)_2Rh(CO)Cl$ complexes have attracted considerable attention. They are catalysts for hydroformylation of alkenes[2] and the nature of the phosphine strongly influences the linear to branched ratio of the aldehyde products. More recently, they have been found to be good catalysts for photolytically promoted C–H bond activation,[3] and their catalytic activity decreases with increasing steric bulk of the phosphine.[4] *trans*-$[(Bu^t)_2PR]_2Rh(CO)X$ complexes exhibit hindered rotation about the Rh–P bond in solution as shown by dynamic ^{31}P NMR studies.[5] $[(t\text{-}Bu)_3P]_2Rh(CO)Cl$ crystallizes as a distinctly non-planar molecule with considerable tetrahedral distortion.[6] $(Ph_3P)_2Rh(CO)Cl$ crystallizes in both monoclinic[7] and triclinic forms,[8] and, also as an orthorhombic CH_2Cl_2 solvate.[9,10]

Phospholes such as 1-phenyl-3,4-dimethylphosphole (DMPP)[11-16] and 1-phenyldibenzophosphole (DBP)[17-21] are phosphorus donors with unusual donor properties. Their



(DMPP)



(DBP)

$(DMPP)_2Rh(CO)Cl$[22] and $(DBP)Rh(CO)_2Cl$[21] complexes have been previously described. The analogs (1-phenylphosphole)$_2$Rh(CO)Cl and (3-methyl-1-phenylphosphole)$_2$Rh(CO)Cl are among the few examples of such complexes[23] that have been reported to exhibit *cis–trans* isomerism. As part of continuing programs of investigation of the structure and properties of transition metal phosphole complexes[12,13,17,20,24-32] and the utility of CP/MAS $^{31}P\{^1H\}$ NMR spectroscopy for solid-state structural determination,[26-39] we now report on the solution and solid-state characterization of four *trans*-$(R_3P)_2Rh(CO)Cl$ complexes. Wu and Wasylishen[40] only recently reported the CP/MAS ^{31}P NMR spectrum of $(Ph_3P)_2Rh(CO)Cl$ at the same time as this study was nearing completion.

Experimental Section

A. **Reagents and Physical Measurements.** All chemicals were reagent grade and were either used as received or synthesized as described below. All solvents, when necessary, were dried by standard procedures and stored over Linde 4Å molecular sieves. All reactions were conducted under a dry nitrogen atmosphere. The phosphines were obtained either from Strem Chemicals or Organometallics, Inc. The $RhCl_3{\cdot}3H_2O$ was used as obtained from Johnson-Matthey. Both 1-phenyldibenzophosphole[41] and 1-phenyl-3,4-dimethylphosphole[42] were prepared by literature methods. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN 37921. Infrared spectra were recorded on a Perkin-Elmer 1800 FT-IR instrument as polyethylene pellets, Nujol mulls on polyethylene thin films, and as solutions in sealed NaCl cells. The solution $^{31}P\{^1H\}$ NMR spectra were recorded at 40.26 MHz on a JEOL FX-100 spectrometer and at 121.56 MHz on a General Electric GN-300 spectrometer as C_6D_6 solutions; except for **1** which was recorded as a $CDCl_3$ solution. The phosphorus chemical shifts were referenced to 85% H_3PO_4 via external PPh_3 ($\delta = -6$ ppm) with shifts to high frequency

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(low field) positive. The solution ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a General Electric GN-300 spectrometer at 300 and 75 MHz respectively. Chemical shifts were referenced to $(CH_3)_4Si$ via internal C_6H_6 (δ ^{1}H = 7.15; δ ^{13}C = 128.0 ppm) or internal $CHCl_3$ (δ ^{1}H = 7.26, δ ^{13}C = 77.0 ppm) with shifts to high frequency (low field) positive. Solid-state cross-polarization magic angle spinning (CP/MAS) ^{31}P{^{1}H} NMR spectra were recorded on a Nicolet NT-150 NMR spectrometer at 60.74 MHz using 20 kHz sweep widths, recycle delay times of 1 to 30 s and proton decoupling fields of 10 G. Between 200 and 300 mg of the compounds were spun at 2.5 to 4.5 kHz in Delrin or Kel-F rotors. The ^{31}P{^{1}H} chemical shifts were referenced to 85% H_3PO_4 via an external sample of solid Ph_3P (δ = –6 ppm). For the solid-state spectra the uncertainties in chemical shifts and coupling constants are estimated to be ±0.5 ppm, ±30 Hz. Conductivity studies were performed with an Industrial Instruments model RC16B2 conductivity bridge utilizing a Yellow Springs Instruments 3400 series conductivity cell ($k = 1.0\ cm^{-1}$).[43]

B. Synthesis. The synthesis of the $(R_3P)_2Rh(CO)Cl$ compounds followed the procedure reported by Chatt and Shaw.[44] Typically, one molar equivalent of $RhCl_3 \cdot 3H_2O$ (~263 mg) was dissolved in 15 mL ethanol. This solution was refluxed under a CO purge for 3h. After the resultant golden-yellow solution was cooled to ambient temperature and placed under a dry nitrogen atmosphere, two molar equivalents of the respective phosphine were added. The reaction mixture was then refluxed for 1 h and allowed to cool gradually to ambient temperature. The resulting yellow precipitate was isolated by filtration, washed with ethanol and vacuum dried at ambient temperature. Yields were typically greater than 80%.

$(DBP)_2Rh(CO)Cl$ (1): mp 154 °C, dec. Conductance (CH_3NO_2, 8.60×10^{-4} M) $\lambda_m = 3.14\ ohm^{-1}\ cm^2\ mol^{-1}$. IR ($CDCl_3$) ν_{CO} 1984 cm^{-1}, (C_6H_6) ν_{CO} 1982, 1960 cm^{-1}, (polyethylene) ν_{CO} 1981, 1972, 1962, 1953 cm^{-1}, (hexachlorobutadiene) ν_{CO} 1981, 1973, 1962, 1956 cm^{-1}, (Nujol) ν_{CO} 1981, 1972, 1963, 1954 cm^{-1}; ν_{RhCl} 302 cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 20.64 (d, $^1J(RhP)$ = 124.95 Hz). ^{1}H NMR ($CDCl_3$) δ 7.24–7.39 (m, 10H, $H_{o,m,p}$), 7.54 (apparent t, $^3J(H_1H_2) = {}^3J(H_2H_3)$ = 7.65 Hz, 4H, H_2), 7.71 (apparent q, $^3J(H_2H_3) = {}^3J(H_3H_4)$ = 7.65 Hz, $|^4J(PH) + {}^6J(PH)|$ = 6.00 Hz, 4H, H_3), 7.92 (apparent d, $^3J(H_1H_2)$ = 7.65 Hz, 4H, H_1), 8.15 (apparent dt, $^3J(H_3H_4)$ = 7.65 Hz, $|^3J(PH) + {}^5J(PH)|$ = 7.20 Hz, 4H, H_4). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 121.38 (T, $|^3J(PC) + {}^5J(PC)|$ = 4.98 Hz, C_1), 128.47 (T, $|^3J(PC) + {}^5J(PC)|$ = 9.81 Hz, C_3), 128.54 (T, $|^3J(PC) + {}^5J(PC)|$ = 11.02 Hz, C_m), 130.59 (s, C_p), 130.97 (s, C_2), 132.49 (T, $|^2J(PC) + {}^4J(PC)|$ = 13.06 Hz, C_o), 133.91 (T, $|^1J(PC) + {}^3J(PC)|$ = 14.42 Hz, C_i), 136.90 (T, $|^1J(PC) + {}^3J(PC)|$ = 50.20 Hz, C_α), 142.57 (T, $|^2J(PC) + {}^4J(PC)|$ = 10.87 Hz, C_β), 186.82 (dt, $^1J(RhC)$ = 74.05, $^2J(PC)$ = 15.40 Hz, CO). Anal. Calcd for $C_{37}H_{26}ClOP_2Rh$: C, 64.72; H, 3.79; Cl, 5.16. Found: C, 64.82; H, 3.82; Cl, 5.65. Recrystallization from CH_2Cl_2 by slow evaporation yielded a CH_2Cl_2 solvate that slowly lost CH_2Cl_2. Anal. Calcd for $C_{37}H_{26}ClOP_2Rh \cdot CH_2Cl_2$: C, 59.15; 4, 3.62; Cl, 13.78. Found: C, 59.41; H, 3.79; Cl, 13.62.

$(DMPP)_2Rh(CO)Cl$ (2): mp 230 °C, dec. Conductance (CH_3NO_2, 1.17×10^{-3} M) $\lambda_m = 5.28\ ohm^{-1}\ cm^2\ mol^{-1}$. IR ($C_6H_6$) ν_{CO} 1973 cm^{-1} (Nujol) ν_{CO} 1947 cm^{-1}, ν_{RhCl} 304, 300 cm^{-1}. ^{31}P{^{1}H} NMR (C_6D_6) δ 32.64 (d, $^1J(RhP)$ = 117.19 Hz). ^{1}HNMR (C_6D_6) δ 1.52 (s, 12H, CH_3), 6.75 (T, $|^2J(PH) + {}^4J(PH)|$ = 33.62 Hz, 4H, H_α), 6.93 (m, 6H, Hm, p), 7.93 (m, 4H, H_o). ^{13}C{^{1}H} NMR (C_6D_6) δ 17.16 (T, $|^3J(PC) + {}^5J(PC)|$ = 11.17 Hz, CH_3), 127.98 (T, $|^1J(PC) + {}^3J(PC)|$ = 46.00 Hz, C_α), 128.53 (T, $|^3J(PC) + {}^5J(PC)|$ = 9.96 Hz, C_m), 129.16 (T, $|^1J(PC) + {}^3J(PC)|$ = 47.55 Hz, C_i), 130.37 (s, C_p), 134.31 (T, $|^2J(PC) + {}^4J(PC)|$ = 13.51 Hz, C_o), 151.28 (T, $|^2J(PC) + {}^4J(PC)|$ = 11.70 Hz, C_β), 187.34 (dt, $^1J(RhC)$ = 67.02, $^2J(PC)$ = 14.64 Hz, CO). Anal. Calcd for $C_{25}H_{26}ClOP_2Rh$: C, 55.34; H, 4.79. Found: C, 55.78; H, 4.93.

$(DPVP)_2Rh(CO)Cl$ (3): mp 150–162 °C. Conductance (CH_3NO_2, 1.08×10^{-3} M) $\lambda_m = 2.26\ ohm^{-1}, cm^2, mol^{-1}$. IR ($C_6H_6$) ν_{CO} 1973 cm^{-1} (Nujol) ν_{CO} 1971, 1950 cm^{-1}, ν_{RhCl}, 304 cm^{-1}. ^{31}P{^{1}H} NMR (C_6D_6) δ 20.31 (d, $^1J(RhP)$ = 124.52 Hz). ^{1}H NMR (C_6D_6) δ 5.66 (m, $^3J(H_aH_b)$ = 9.47, $|^3J(PH) + {}^5J(PH)|$ = 36.56 Hz, 2H, H_b), 5.83 (m, $^3J(H_aH_c)$ = 18.59, $|^3J(PH) + {}^5J(PH)|$ = 24.94 Hz, 2H, H_c), 7.14 (m, 12H, Hm, p), 7.22 (m, 2H, H_a), 7.93 (m, 8H, H_o). ^{13}C{^{1}H} NMR (C_6D_6) δ 128.49 (T, $|^3J(PC) + {}^5J(PC)|$ = 9.06 Hz, C_m), 130.30 (s, C_p), 131.28 (s, C_β), 132.56 (m, $|^1J(PC) + {}^3J(PC)|$ = 46.95 Hz, C_i), 132.57 (T, $|^1J(PC) + {}^3J(PC)|$ = 33.67 Hz, C_α), 134.69 (T, $|^2J(PC) + {}^4J(PC)|$ = 12.02 Hz, C_o), 187.76 (dt, $^1J(RhC)$ = 72.99, $^2J(PC)$ = 16.26 Hz, CO). Anal. Calcd for $C_{29}H_{26}ClOP_2Rh$: C, 58.96; H, 4.40. Found: C, 58.73: H, 4.65.

Table I. Crystallographic Data for **1–3**

	1	**2**	**3**
chem formula	$C_{38}H_{28}Cl_3OP_2Rh$	$C_{25}H_{26}ClOP_2Rh$	$C_{29}H_{26}ClOP_2Rh$
fw	771.9	542.8	590.8
a (Å)	22.122(6)	8.476(2)	8.298(2)
b (Å)	13.241(3)	16.451(4)	9.404(2)
c (Å)	11.963 (3)	9.414 (2)	10.065 (3)
α (deg)			111.25 (2)
β (deg)	90.80 (2)	108.66 (2)	91.13 (2)
γ (deg)			67.57 (2)
V (Å^3)	3504.0 (1.7)	1243.6 (5)	670.2 (2)
Z	4	2	1
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
T (°C)	20 ± 1	20 ± 1	20 ± 1
λ (Å)	0.7107	0.7107	0.7107
ρ_{calc} (g cm^{-3})	1.463	1.449	1.464
μ (cm^{-1})	8.284	9.241	8.638
abs min/max	0.93/1.00	0.97/1.00	0.74/1.25
$R(F)^a$	0.041	0.029	0.040
$R_w(F)^b$	0.063	0.058	0.065

[a] $R(F) = \sum w(|F_o| - |F_c|)^2$ with $\sigma^2(F)^2 = \sigma^2(\text{counts}) + (pI)^2$. [b] $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

$(Ph_3P)_2Rh(CO)Cl$ (4): mp 178 °C, dec. Conductance (CH_3NO_2, 4.36×10^{-4} M) $\lambda_m = 7.57\ ohm^{-1}, cm^2, mol^{-1}$. IR (Nujol) ν_{CO} 1964 cm^{-1}, ν_{RhCl} 302 cm^{-1}. ^{31}P{^{1}H} NMR (C_6D_6) δ 28.22 (d, $^1J(RhP)$ = 126.95 Hz). ^{1}H NMR (C_6D_6) δ 7.10 (m, 18H, H_{mp}), 8.03 (m, 12H, H_o). ^{13}C{^{1}H} NMR (C_6D_6) δ 128.32 (T, $|^3J(PC) + {}^5J(PC)|$ = 13.59 Hz, C_m), 130.14 (s, C_p), 133.80 (T, $|^1J(PC) + {}^3J(PC)|$ = 58.42 Hz, C_i), 135.22 (T, $|^2J(PC) + {}^4J(PC)|$ = 12.61 Hz, C_o). Anal. Calcd for $C_{37}H_{30}ClOP_2Rh$: C, 64.34; H, 4.34. Found: C, 64.19; H, 4.28.

C. X-ray Data Collection and Processing. Yellow crystals of **1** were obtained by slow evaporation of a CH_2Cl_2 solution and light yellow crystals of **2** and **3** were isolated from C_6H_6/hexanes solutions. Crystal data and details of data collection are given in Table I. For each compound, single crystals were cut out from a cluster of crystals and mounted on a rotation-free goniometer head. Systematic searches in reciprocal space with an Enraf-Nonius CAD4-F diffractometer showed that crystals of complexes **1** and **2** belong to the monoclinic system and **3** to the triclinic system.

Quantitative data were obtained at room temperature. The resulting data sets were transferred to a VAX computer, and for all subsequent calculations the Enraf-Nonius SDP/VAX package[45] was used. Three standard reflections measured every 1 h during the entire data collection period showed no significant trends. The raw data were converted to intensities and corrected for Lorentz and polarization factors. Absorption corrections from ψ scans of 4 reflections were applied.

The structures were solved by the heavy atom method. For **2** and **3** the chlorine atom and the CO group are disordered: each atom was refined with a multiplicity of 0.5. After refinement of the heavy atoms, difference-Fourier maps revealed maximas of residual electronic density close to the positions expected for hydrogen atoms. They were introduced in the structure factor calculations by their computed coordinates (CH = 0.95 Å) with isotropic temperature factors such as $B(H) = 1.3\ B_{eqv}(C)$ Å^2 but were not refined. Full least-squares refinements minimizing $\sum\omega(|F_o| - |F_c|)^2$ with $\sigma^2(F)^2 = \sigma^2_{counts} + (pI)^2$ converged to the values given in Table I. Final difference maps revealed no significant maxima (0.43, 0.48 and 0.56 for **1**, **2** and **3** respectively). The scattering factors coefficients and anomalous dispersion coefficients come respectively from parts a and b of ref 46. Selected bond lengths and angles are given in Tables II and III respectively.

Results and Discussion

Structures of the $(R_3P)_2Rh(CO)Cl$ Complexes in Solution. These $(R_3P)_2Rh(CO)Cl$ complexes are all non-electrolytes as shown by their very low conductances[43] in CH_3NO_2 solution.

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Table II. Selected Bond Distances (Å) for **1** ((DBP)$_2$Rh(CO)Cl), **2** ((DMPP)$_2$Rh(CO)Cl), and **3** ((DPVP)$_2$Rh(CO)Cl)

	1	2	3
Rh-Cl	2.372(1)	2.366(4)	2.479(1)
Rh-P1	2.291(1)	2.3131(8)	2.3230(6)
Rh-P2	2.294(1)	2.3131(8)	2.3230(6)
Rh-C	1.824(6)	1.77(1)	1.827(8)
C-O	1.127(6)	1.14(1)	1.44(2)

Table III. Selected Bond Angles (deg) for **1** ((DBP)$_2$Rh(CO)Cl), **2** ((DMPP)$_2$Rh(CO)Cl), and **3** ((DPVP)$_2$Rh(CO)Cl)

	1	2	3
Cl-Rh-P1	89.92(5)	92.0(1)	90.98(5)
Cl-Rh-P2	89.58(5)	92.0(1)	90.98(5)
Cl-Rh-C	178.5(2)	177.4(6)	178.8(1)
P1-Rh-P2	177.91(5)	180.(0)	180.(0)
P1-Rh-C	89.6(2)	91.2(5)	89.7(1)
P2-Rh-C	90.9(2)	91.2(5)	90.2(1)
Rh-C-O	178.9(5)	175.0(9)	171.4(3)

Their far infrared spectra exhibit single ν_{RhCl} vibrations near 300 cm^{-1} as expected,[47] and for **2** $\nu_{Rh^{35}Cl}$ and $\nu_{Rh^{37}Cl}$ were resolved.

The infrared spectra of **2** and **3** in C_6H_6 solution and **1** in $CHCl_3$ solution show single ν_{CO} vibrations in the expected region[44] (~1960 cm^{-1}) while for **1** two ν_{CO} vibrations (1982 and 1960 cm^{-1}) are observed in C_6H_6 but only one (1984 cm^{-1}) is observed in $CDCl_3$. Holah et al.[22] have observed two ν_{CO} vibrations at 1970 and 2060 cm^{-1} for similar (phosphole)$_2$Rh(CO)Cl complexes and attributed these to the presence of *cis* and *trans* isomers. The 2060 cm^{-1} occurs at an unusually high frequency for a neutral monocarbonyl Rh(I) complex and a *cis* geometry for (R$_3$P)$_2$-Rh(CO)X complexes has never been authenticated. The band at 1960 cm^{-1} for **1** in C_6H_6 solution is probably due to a combination of ν_{11} and ν_{19} from the solvent C_6H_6 and not a CO vibration.[48]

If the *cis* and *trans*-(DBP)$_2$Rh(CO)Cl complexes were both present in C_6H_6, then the $^{31}P\{^1H\}$ NMR spectrum in this solvent should exhibit a doublet for the *trans* isomer and two doublets for the *cis* isomer with relative integrated intensities that would represent the relative populations of these two isomers. The $^{31}P\{^1H\}$ NMR spectra of (DBP)$_2$Rh(CO)Cl in both C_6D_6 and $CDCl_3$ show only a single doublet. Similarly, single doublets with ^1J(RhP) ~120 Hz, typical[5,49] of *trans*-bis(phosphine)-rhodium(I) complexes are observed in the $^{31}P\{^1H\}$ NMR spectra of **2**, **3**, and **4** in C_6D_6 solutions. The $^{13}C\{^1H\}$ NMR spectra of all four compounds show second order multiplets for each type of carbon (except for the carbonyl carbon resonance which is a first order doublet of triplets) with line shapes that are typical[50] of two mutually *trans* symmetry equivalent phosphines. Likewise, the second order lineshapes of the ^1H multiplets observed for each compound are typical[50] of two mutually *trans* symmetry equivalent phosphines. Collectively, the spectroscopic data indicate that all four compounds have *trans*-square planar structures with effective C_{2v} symmetry in solution.

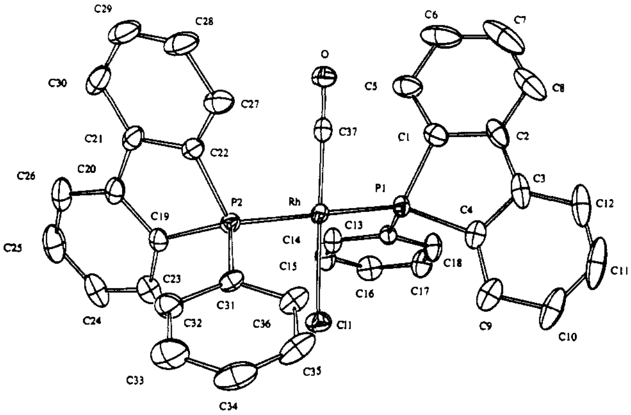

Figure 1. ORTEP drawing of **1** (DBP)$_2$Rh(CO)Cl showing the atom numbering scheme (50% probability ellipsoids). Hydrogen atoms are omitted.

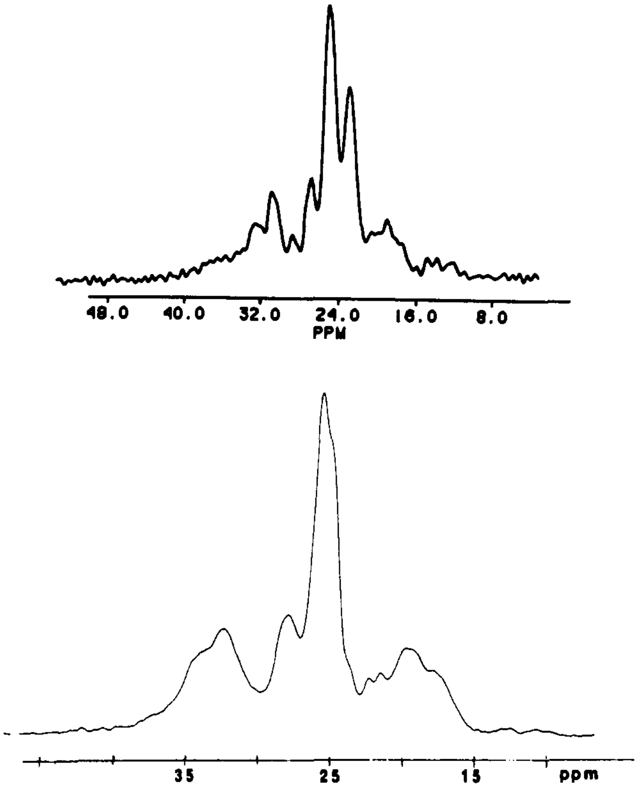

Figure 2. Field dependence of the $^{31}P\{^1H\}$ CP/MAS NMR spectrum of **1** (DBP)$_2$Rh(CO)Cl: 60.74 MHz resolution enhanced spectrum (upper); 161.90 MHz spectrum (lower; we are grateful to Dr. Laima Baltusis of Varian Associates for this spectrum).

Structures of (R$_3$P)$_2$Rh(CO)Cl in the Solid-State. (DBP)$_2$Rh-(CO)Cl (1). The structure of *trans*-(DBP)$_2$Rh(CO)Cl is shown in Figure 1. Bond distances and angles are given in Tables II and III respectively. This complex crystallizes as a CH_2Cl_2 solvate in the $P2_1/n$ space group with four molecules in the unit cell and one in the asymmetric unit with no symmetry. Though the Rh-P distances are essentially equivalent (RhP = 2.291(1), 2.294(1) Å and the complex is rigorously square planar (the sum of the bond angles around Rh is 360°), the two phospholes are not related by symmetry. Thus, the $^{31}P\{^1H\}$ CP/MAS NMR spectrum of this complex is expected[51] to exhibit two resonances due to the two different phosphorus atoms in the asymmetric unit. Each of these resonances should exhibit spin coupling to ^{103}Rh ($I = {}^1/_2$, 100% natural abundance) giving rise to an ABX spin system. The $^{31}P\{^1H\}$ CP/MAS spectra at 60.74 and 161.90 MHz are shown in Figure 2. They consist of two overlapping sets of resonances; the A_2 part of an A_2X (A = ^{31}P, X = ^{103}Rh) spin system δ 24.31 ppm, ^1J(RhP) = 120.3 Hz and a tightly coupled AB part of an ABX spin system. Analysis of the homonuclear ^{31}P J-resolved 2D spectrum,[40,52] shown in Figure 3 yields the parameters $\delta(P_A)$ = 24.96 ppm, $\delta(P_B)$ = 23.07 ppm, $^1J(Rh, P_A)$ = $^1J(Rh, P_B)$ = 120 Hz, $^2J(P_A, P_B)$ = 350 Hz. The A_2X spin

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(52) We are grateful to Mr. Gang Wu and Professor Roderick E. Wasylishen for obtaining this spectrum. The chemical shifts have been increased by 3 ppm as δ^{31}P of solid PPh$_3$ occurs at -9.0 ppm on their spectrometer.

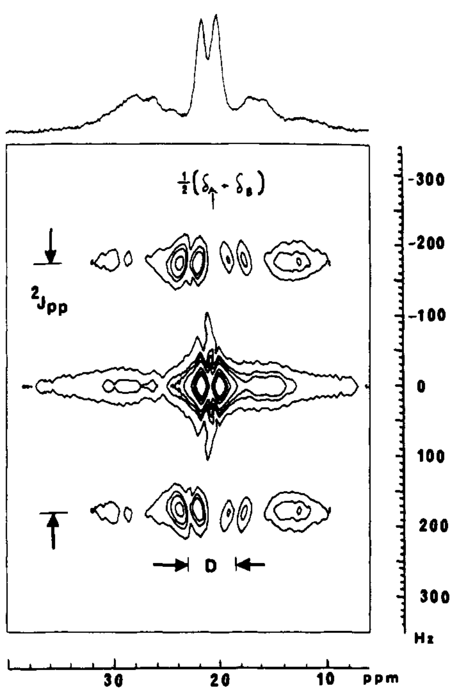

Figure 3. Isotropic part of the 2D *J*-resolved spectrum of **1**, $(DBP)_2Rh(CO)Cl$.[52]

system is probably due to the unsolvated form (CH_2Cl_2 is slowly lost from the crystal lattice) and the ABX spin system to the solvated form for which crystallography shows that the two phospholes are not related by symmetry. Harris et al.[53] and Power and Wasylishen[54] have recently discussed similar phenomena for the $^{31}P\{^1H\}$ CP/MAS spectra of *cis*-$(PPh_3)_2PtCl_2{\cdot}n(CH_2Cl_2)$. For this complex both sets of authors observe three resonances in a 1:1:2 ratio and attribute this to the existence of at least two non-equivalent crystallographic sites in the unit cell. One site has symmetry related phosphines and the other does not. The crystallographic studies involve examination of single crystals whereas the solid-state NMR measurements require bulk samples (typically 200 to 300 mg). For crystals that contain volatile solvents that are readily lost, the solid-state NMR experimental conditions involving rapid spinning, cross polarization and high power decoupling can in some cases promote loss of lattice solvent leading to various degrees of solvation through the bulk sample and more resonances than would be expected on the basis of crystal structure analysis.

The infrared spectra of **1** in the ν_{CO} region are shown in Figure 4. The spectrum of a sample freshly isolated from CH_2Cl_2 shows a prominent ν_{CO} vibration at 1996 cm^{-1} with a shoulder at 1981 cm^{-1}. After heating this sample at 70 °C in a vacuum oven overnight, the infrared spectrum exhibits two prominent vibrations at 1981 and 1955 cm^{-1} with shoulders at 1972 and 1962 cm^{-1}. A sample stored for several weeks under ambient conditions exhibits four roughly equally intense vibrations at 1981, 1972, 1962 and 1953 cm^{-1}. This latter spectrum was obtained on the sample that was used for the CP/MAS $^{31}P\{^1H\}$ NMR spectrum. These spectral results suggest that the solid-state NMR spectrum was obtained on a sample that contained a mixture of solvated and unsolvated forms. For such a mixture only two ν_{CO} vibrations would be expected. The disparity between the number of observed bands and the number expected may be attributed to vibrational coupling within the unit cell and/or reduction of symmetry due to site symmetry effects in the unsolvated form. With four molecules in the unit cell the vibrational coupling mechanism could give rise to four CO vibrations.[55]

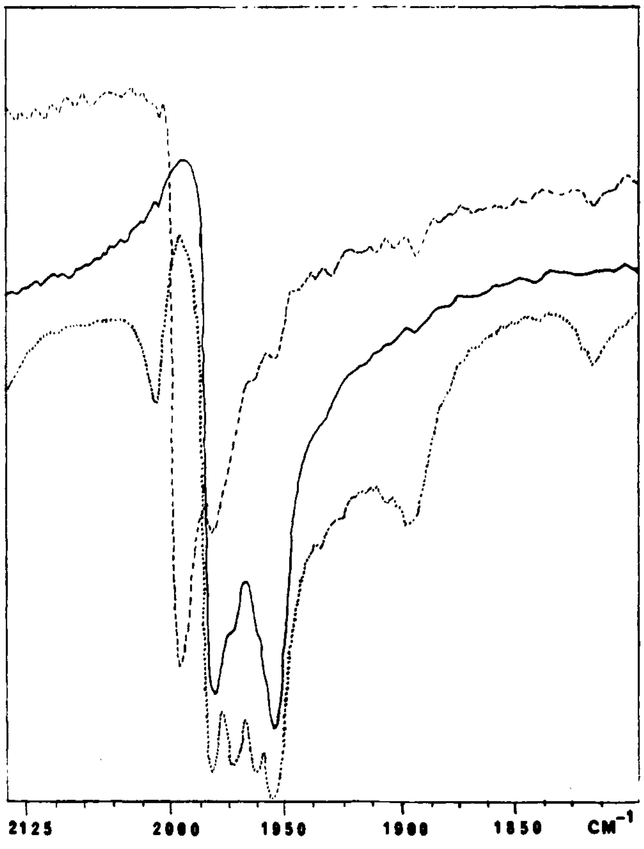

Figure 4. Solid-state infrared spectra in the ν_{CO} region for **1** $(DBP)_2Rh(CO)Cl$: sample freshly isolated from CH_2Cl_2 (- - -); sample vacuum dried at 70 °C overnight (—); sample stored under ambient conditions for about 3 weeks and the sample on which the CP/MAS $^{31}P\{^1H\}$ NMR spectra were obtained (···).

It is interesting to note that Holah et al.[21] reported that $[Rh(CO)_2Cl]_2$ reacts with DBP in CH_3OH to produce $(DBP)Rh(CO)_2Cl{\cdot}CH_3OH$ (ν_{CO} 1988, 1960 cm^{-1}) whereas we find that in CH_3CH_2OH solution the same reactants yield *trans*-$(DBP)_2Rh(CO)Cl$.

$(DMPP)_2Rh(CO)Cl$ (2). Holah et al.[22] have previously isolated $(DMPP)_2Rh(CO)Cl$ from a reaction of $[Rh(CO)_2Cl]_2$ with DMPP in ethanol and assigned it the *trans*-geometry based upon the observation of ν_{RhCl} at 310 cm^{-1}. For this complex we find ν_{CO} at 1969 cm^{-1} in C_6H_6 and at 1947 cm^{-1} in Nujol and ν_{RhCl} at 304 cm^{-1} ($Rh^{35}Cl$) and 300 cm^{-1} ($Rh^{37}Cl$).

The structure of *trans*-$(DMPP)_2Rh(CO)Cl$ is shown in Figure 5. Bond distances and angles are given in Tables II and III respectively. This complex crystallizes in the $P2_1/c$ space group with two molecules in the unit cell. The two RhP distances are required to be equivalent (2.3131 (8) Å), as the structure is disordered with half occupancies for the Cl and CO groups. The coordination geometry is rigorously square planar as the sum of the bond angles around Rh is 360°. The ClRhC angle is not linear (177.4 (6)°); the CO group is tipped slightly toward one phosphorus atom and away from the other but given the disorder this parameter is not well determined. The $^{31}P\{^1H\}$ CP/MAS NMR spectrum exhibits a tightly coupled ABX spin system with the following parameters $\delta(P_A) = 31.6$ ppm, $\delta(P_B) = 33.2$ ppm, $^1J(Rh, P_A) = {}^1J(Rh,P_B) = 100.5$ Hz, and $^2J(P_AP_B) = 346$ Hz (Figure 6). Thus, on the NMR time scale the phosphines are not symmetry equivalent.

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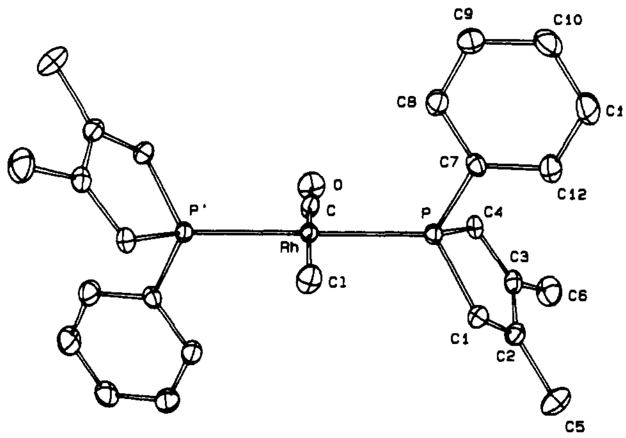

Figure 5. ORTEP drawing of **2**, $(DMPP)_2Rh(CO)Cl$, showing the atom numbering scheme (50% probability ellipsoids). Hydrogen atoms are omitted.

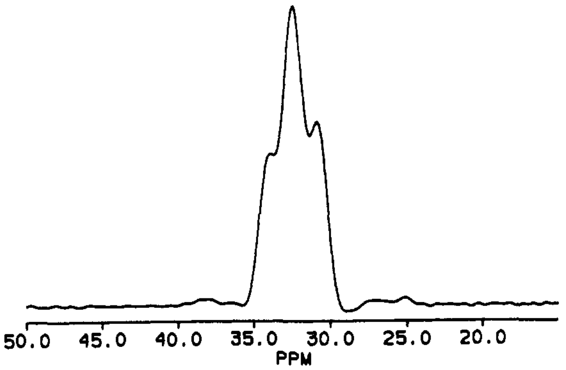

Figure 6. Resolution enhanced 60.74 MHz ${}^{31}P\{{}^1H\}$ CP/MAS NMR spectrum of **2** $(DMPP)_2Rh(CO)Cl$.

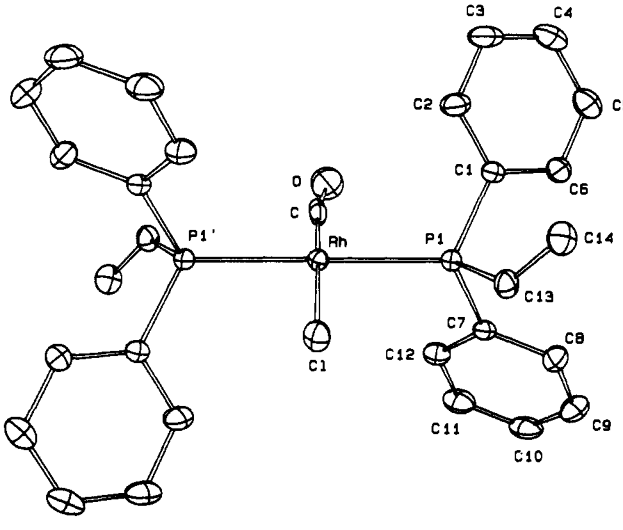

Figure 7. ORTEP drawing of **3**, $(DPVP)_2Rh(CO)Cl$, showing the atom numbering scheme (50% probability ellipsoids). Hydrogen atoms are omitted.

$(DPVP)_2Rh(CO)Cl$ (3). The structure of *trans*-$(DPVP)_2Rh(CO)Cl$ is shown in Figure 7. Bond distances and angles are given in Tables II and III respectively. This complex crystallizes in the $P\bar{1}$ space group with one molecule in the unit cell. The two RhP distances (2.3230 (6) Å) are required to be equivalent, and the molecule is rigorously square planar as the sum of the bond angles around Rh is 360°. The structure is disordered and was refined with half occupancies for the Cl and CO groups with these groups related by a pseudo center of symmetry located at rhodium. Only one ν_{CO} vibration is observed and only one ${}^{31}P$ chemical shift (25.81 d, ${}^1J(RhP) = 95.89$ Hz) is observed consistent with a pseudo center of symmetry at rhodium.

$(Ph_3P)_2Rh(CO)Cl$ (4). This complex crystallizes in three crystalline modifications.[7-10] A triclinic form[8] is yellow and exhibits ν_{CO} at 1965 cm^{-1}. The monoclinic form[7] is dark-orange and exhibits ν_{CO} at 1980 cm^{-1}. Ceriotti et al.[7] isolated a mixture of these two crystalline forms by reaction of $[Rh(CO)_2Cl]_2$ with Ph_3P in ethanol followed by recrystallization from THF/2-propanol. We have isolated yellow crystals of the pure triclinic form by recrystallization from C_6H_6/hexanes. They exhibit ν_{CO} at 1964 cm^{-1} and ν_{RhCl} at 302 cm^{-1}. The triclinic form, and the CH_2Cl_2 solvate[9,10] like *trans*-$(DPVP)_2Rh(CO)Cl$, and *trans*-$(DMPP)_2Rh(CO)Cl$ is disordered[8] with half occupancy of Cl and CO groups and the rhodium atom lies on an inversion center. The two Rh–P bond distances (2.330 (2) Å) are required to be equal and the molecule is rigorously square planar. For it we observe, in agreement with the recent report by Wu and Wasylishen,[40] a tightly coupled ABX spin system with the following parameters: $\delta(P_A) = 32.5$ ppm, $\delta(P_B) = 34.9$ ppm, ${}^1J(RhP_A) = {}^1J(RhP_B) = 125$ Hz, and ${}^2J(P_AP_B) = 360$ Hz (our chemical shifts differ from theirs by 3 ppm).[52] Had either of us isolated a mixture of the monoclinic and triclinic crystalline modifications, the bulk sample would have exhibited two ν_{CO} vibrations and two sets of ${}^{31}P$ CP/MAS resonances.

Three of the four compounds (**2**, **3** and **4**) studied display the same form of Cl and CO half-occupancy disorder in their crystal lattices. In each case the crystallographic results require the rhodium atom to sit at a special position and possess a center of symmetry. The solid-state ${}^{31}P\{{}^1H\}$ CP/MAS spectra of two of these compounds (**2** and **4**), however, show that the phosphorus nuclei in these two compounds are not related by symmetry as ABX spectra are observed for these two compounds. The situation for **3** may be similar and the A_2X spectrum that is observed may be a result of accidental chemical shift equivalence of two symmetry inequivalent phosphines or the two phosphines may be truly symmetry equivalent.[51] The results described herein further illustrate the sensitivity of CP/MAS ${}^{31}P\{{}^1H\}$ NMR spectroscopy[51] for characterization of bulk solids.

The RhP distances for the five $(R_3P)_2Rh(CO)Cl$ complexes that have been investigated crystallographically increase in the following sequence: DBP (2.293 (1) Å av) < DMPP (2.3131 (8) Å) < DPVP (2.3230 (6) Å) < PPh_3 (2.330 (2) Å) < t-Bu_3 (2.434 (1) Å).[6] The ${}^{31}P$ coordination chemical shifts ($\Delta\delta^{31}P = \delta^{31}P(\text{complex}) - \delta^{31}P(\text{ligand})$) increase in the sequence: DPVP (31.11 ppm) < DBP (31.3 ppm) < PPh_3 (34.22 ppm) < DMPP (36.14 ppm). The bond distances generally increase, as expected, with increasing steric bulk of the phosphorus donor but the coordination chemical shifts do not generally increase with decreasing ligand steric bulk. The ${}^2J(PP)$ values, where measurable, are all about 350 Hz, which is in the normal range[56] for *trans*-coupling.

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Supplementary Material Available: For the three structures, listings of crystal and refinement data, atomic coordinates, bond distances and angles, H atom coordinates, and thermal parameters (U) (23 pages). Ordering information is given on any current masthead page. Listings of observed and calculated structure factors (×10) (33 pages) are available from the authors.

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