Table III. Root-Mean-Square Amplitudes of Vibration (Å) for $Cs_2LiFe(CN)_6$ for Neutron and X Ray[2]

	Neutron	X ray
Li	0.156 (21)	0.167 (12)
Cs	0.185 (4)	0.216 (1)
Fe	0.125 (5)	0.131 (2)
C(max)	0.189 (3)	0.188 (5)
C(min.)	0.120 (8)	0.153 (8)
N(max)	0.272 (3)	0.272 (6)
N(min.)	0.135 (5)	0.153 (8)

Table II contains a comparison of bond distances for the neutron and x-ray studies. No peculiarities are noted. The structure is held together by the Li–N bond which agrees well with the sum of the crystal radii for Li and N of 2.1 Å.[12] The Cs atom seems to merely fill space and balance charge in the structure. The high thermal parameter of Cs would indicate that the hole containing it is too large. This is borne out by the fact that the distance between the Cs and nitrogen is 3.805 (1) Å, which is significantly larger than the sum of the crystal radii for Cs and N, 3.24 Å.[12] The C–N bond of 1.146 (3) seems to be an invariant distance in both the x-ray[2] and neutron refinements. In Table III a compilation of the root-mean-square amplitudes of vibration (Å) for both x rays and neutrons can be seen. Table IV compares observed and calculated crystal structure factors.

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Registry No. $Cs_2LiFe(CN)_6$, 37164-29-7.

Supplementary Material Available: Table of crystal structure factors (1 page). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada V8W 2Y2

Ligand Properties of *cis*-(Diphenylphosphinito)-(hydroxydiphenylphosphine)platinum and -palladium Complexes

K. R. Dixon* and A. D. Rattray

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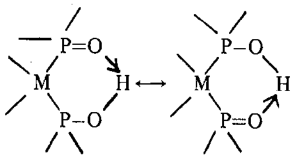
Complexes in which there is the possiblity of a cis arrangement of one diphenylphosphinito[1] and one hydroxydiphenylphosphine ligand are known to exist as a symmetrical hydrogen bonded system of the type:



This was originally established by us on the basis of infrared evidence[3] and has since been confirmed by an x-ray diffraction study[4] of $[Pd_2(SCN)_2\{(PPh_2O)_2H\}_2]$. The reactivity of this type of system is of interest since if the proton can be replaced by other Lewis acids then a chelate ligand system somewhat analogous to acetylacetone is produced. Moreover, the overall result is a ligand bridging between "soft" and "hard" metal centers. The results described in the present note show that such proton replacement reactions are easily achieved and of general occurrence and suggest that the new ligand system will form a wide range of complexes analogous to the acetylacetonates. The presence of the spin $^1/_2$ phosphorus nucleus is of great assistance in structural studies and, in cases where the "hard" metal center is paramagnetic, the complexes can yield valuable data regarding the extent of electron delocalization.

Prior to our work, Austin reported reactions of BF_3 with $[PtCl_2(PPh_2OH)_2]$ and $[Pt\{PO(OCH_3)_2\}_2\{POH(OCH_3)_2\}_2]$ which yielded products similar to ours although the structures were not definitely established.[5] More recently, this type of reaction has been noted by Roundhill and co-workers,[2] who prepared three "BF_2 capped" complexes including one of those described below, namely $[Pt\{(PPh_2O)_2BF_2\}_2]$.

Results and Discussion

Our most detailed studies have been carried out using the complex, $[PtCl(PEt_3)\{PPh_2O)_2H\}]$,[3] and Figure 1 shows the proton-decoupled ^{31}P NMR spectrum of this complex. Corresponding peak assignments and numerical data are collected in Table I, which also shows the proposed structure of the complex. The spectrum basically consists of two pairs of doublets, X and Z, centered at 129.0 and 64.5 ppm, respectively, and a triplet (Y) at 82.7 ppm. Each set of resonances is accompanied by satellites (X′, Y′ and Z′ in Figure 1) due to coupling to ^{195}Pt ($I = {}^1/_2$, relative abundance = 33.8%) and the assignments shown in Table I may be established on the basis of the platinum–phosphorus coupling constants. These are expected to be larger trans to Cl than trans to P and larger for phosphines having electron-withdrawing substituents (i.e., $PPh_2O > PEt_3$). This assignment then gives $J(P–P)trans \gg J(P–P)cis$, which is the expected order. The appearance of the P_Y resonance as a triplet must be caused by overlap of peaks resulting from the very similar values of $J(P_X–P_Y)$ and $J(P_Y–P_Z)$, since a "deceptively simple" or "virtually coupled" X triplet is not expected in the ABX spin system for cases where $(\delta(A) - \delta(B)) > J(AB)$ (equivalent to $(\delta(X) - \delta(Z)) > J(P_X–P_Z)$ in the present complex).

Treatment of $[PtCl(PEt_3)\{(PPh_2O)_2H\}]$ with boron trifluoride etherate or with fluoroboric acid yields a colorless, crystalline solid analyzing as $[PtCl(PEt_3)\{(PPh_2O)_2BF_2\}]$ (see Table II). The ^{31}P NMR spectrum of this product (see Table I) is very similar to that shown in Figure 1 except for downfield shifts of all resonances, consistent with the introduction of an electron-withdrawing group and broadening of the P_Y and P_Z resonances caused by additional coupling to ^{10}B, ^{11}B, and ^{19}F. The ^{19}F NMR spectrum is a broad ($W_{1/2} \sim 27$ Hz) single resonance showing some poorly resolved fine structure,[6] and the chemical shift (137.3 ppm upfield from $CFCl_3$) indicates the fluorine is bound to boron (cf. BF_4^- at 147.5 ppm).[7] The compound $[PtCl(PEt_3)\{(PPh_2O)_2BF_2\}]$ is a nonelectrolyte in

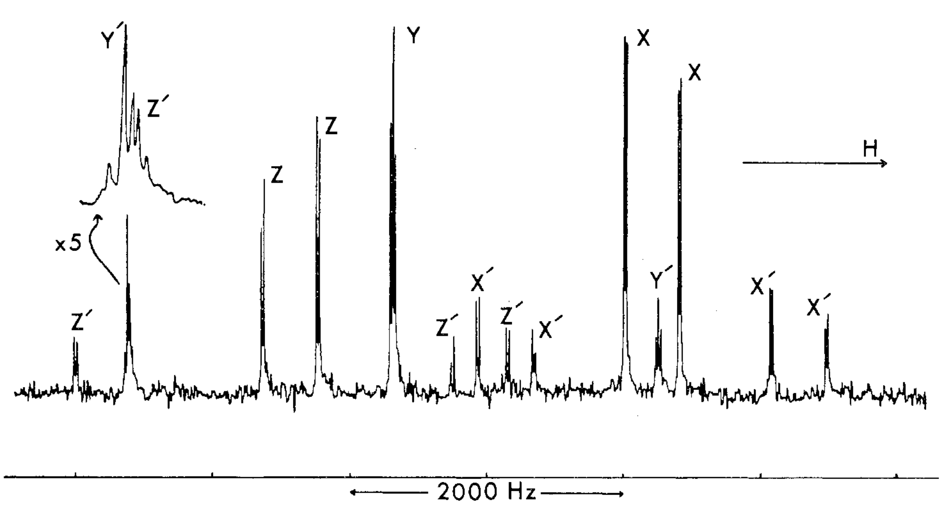
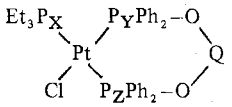


Figure 1. Proton decoupled, ^{31}PNMR spectrum of $[PtCl(PEt_3)\{(PPh_2O)_2H\}]$, recorded at 40.5 MHz. Peak labels correspond to the assignments given in Table I and in the text.

Table I. ^{31}PNMR Data for Complexes



	Chemical shifts[a]			Coupling constants, Hz[b]					
Q	$\delta(P_X)$	$\delta(P_Y)$	$\delta(P_Z)$	$J(Pt\text{-}P_X)$	$J(Pt\text{-}P_Y)$	$J(Pt\text{-}P_Z)$	$J(P_X\text{-}P_Y)$	$J(P_Y\text{-}P_Z)$	$J(P_X\text{-}P_Z)$
H	129.0	82.7	64.5	2129	3833	2726	17	21	397
BF_2	127.0	73.3	59.3	2139	3882	2654	17	*c*	393
$SiMe_3$[d]	126.5	82.2	58.4	2151	3960	2766	19	21	412

[a] Measured in ppm upfield from an external $P(OMe)_3$ reference capillary. [b] See Experimental Section for comments on likely accuracy. [c] Not resolved. Peaks are broadened by additional coupling to ^{10}B, ^{11}B, and ^{19}F. [d] The formulation is not completely certain (see Discussion section).

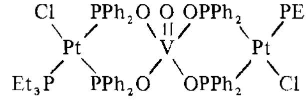
nitromethane and an osmometric molecular weight measurement in dibromoethane gave no evidence of dissociation. These observations clearly support a structure derived from the hydrogen-bonded system by simple replacement of the proton by a BF_2 group and there is no evidence to suggest an ionic structure such as $[PtCl(PEt_3)\{(PPh_2O)_2(BF)\}][F]$ as has been discussed previously for some related complexes.[5]

As we have described previously,[3,8] hydrogen bonded M-P-O--H--O-P systems are typified by infrared absorption due to ν(P–O) ~ 1000 cm^{-1}, very broad absorptions in the 1200–1600 and 700–800 cm^{-1} regions, and a strong absorption at 330 cm^{-1}. In the particular case of $[PtCl(PEt_3)\{(PPh_2O)_2H\}]$ the 1000 cm^{-1} region is complicated by absorption due to the triethylphosphine ligand but comparison with spectra of other triethylphosphineplatinum complexes suggests that a band at 1010 cm^{-1} may be assigned to ν(P–O). The other features typical of the hydrogen-bonded system are found at 1300–1400 (broad), 800 (broad), and 330 cm^{-1}. The last three absorptions are absent from the infrared spectrum of $[PtCl(PEt_3)\{(PPh_2O)_2BF_2\}]$ and bands at 1060, 1005, and 890 cm^{-1} may be assigned to the –P–O–BF$_2$–O–P– system.[9] Most probably the three bands are due respectively to vibrations which are primarily ν(B–F), ν(P–O), and δ(O–B–O), but any such assignment must be very tentative in the absence of a proper vibrational analysis. The other principal areas of infrared absorption are those normally found in ethyl- and phenylphosphine complexes (i.e., 700–800 and 500–550 cm^{-1}). Thus the infrared spectrum, especially the strong absorption ca. 890 cm^{-1}, provides a ready means of identification of $M(PPh_2O)_2BF_2$ systems, and using this criterion we have demonstrated that the BF_2 capping reaction occurs with all the $M(PPh_2O)_2H$ complexes described in our previous work.[3,8]

A selection of typical products has been fully characterized and details are included in Table II.

The reaction of $[PtCl(PEt_3)\{(PPh_2O)_2H\}]$ with $SiClMe_3$ was more complicated. Removal of volatile materials after a 15-min reaction time in acetone solution gave a sticky, white solid lacking the characteristic infrared absorptions of the hydrogen-bonded system and having a new broad, weak absorption at 920 cm^{-1}. The ^{31}P NMR spectrum of this product is given in Table I and is very similar to those of $[PtCl(PEt_3)\{(PPh_2O)_2H\}]$ and $[PtCl(PEt_3)\{(PPh_2O)_2BF_2\}]$. It is therefore probable that the initial product is $[PtCl(PEt_3)\{(PPh_2O)_2SiMe_3\}]$ analogous to the known acetylacetonate, $[Si(acac)Me_3]$.[10] However, we have been unable to confirm this formulation since longer reaction times or attempted purification procedures gave gradual formation of very insoluble products. This process may involve formation of high molecular weight species such as an analogue of $[Si(acac)_3{}^+]$.[11] Similar problems were encountered with a variety of related reactions, for example, $[Pt_2Cl_2\{(PPh_2O)_2H\}_2]$ with $SiMe_2Cl_2$, $SiCl_4$, $SnCl_4$, or $TiCl_4$, but in each case infrared evidence indicated that the initial reaction is elimination of HCl and coordination of the oxygens to the metal or metalloid.

A further example of the analogy with acetylacetone is provided by reaction of $[PtCl(PEt_3)\{(PPh_2O)_2H\}]$ with $[VO(acac)_2]$. Acetylacetone is eliminated and the pale green complex



is formed.[12] Infrared and molecular weight measurements on

Table II. Characterization Data

Complex	Mp, °C	% C		% H		Mol wt[a]		IR spectra,[b] cm^{-1}			
		Calcd	Found	Calcd	Found	Calcd	Found	ν(B–F)	ν(P–O)	δ-(O–B–O)	ν(M–Cl)
$PtCl(PEt_3)\{(PPh_2O_2BF_2\}$	234–237	45.0	45.1	4.4	4.5	800	819	1060	1005	890	297
$PdCl(PEt_3)\{(PPh_2O)_2BF_2\}$	220–225	50.7	50.6	4.9	4.8	711	737	1055	1000	880	297
$PtCl(PPh_3)\{(PPh_2O)_2BF_2\}$	240–250	53.4	53.2	3.7	3.9	944	904	1055	1010	887	293
$PtCl(PHPh_2)\{(PPh_2O)_2BF_2\}$	255–265	49.8	49.4	3.6	3.8	868	855	1040	1010	888	293[c]
$Pt\{(PPh_2O)_2BF_2\}_2$	315–320	52.5	52.4	3.7	3.8			1030	1010	880	
$Pd_2Cl_2\{(PPh_2O)_2BF_2\}_2$	260 dec	48.6	49.1	3.4	3.4	1186	1123	1065	1010	870	260
$Pd_2Br_2\{(PPh_2O)_2BF_2\}_2$	230 dec	45.2	45.0	3.2	3.3	1275	1218	1065	1010	870	
$Pt_2(PPh_2O)_2\{(PPh_2O)_2BF_2\}_2$	310–315	51.0	50.2	3.6	3.7			1050	1000 970	895	
$\{PtCl(PEt_3)(PPh_2O)_2\}_2VO$	270–275	45.7	46.1	4.5	4.6	1573	1695		1010[d]		285

[a] Determined osmometrically in dibromomethane. Where values are not quoted the complexes were too insoluble for accurate measurement. [b] Nujol mulls. Only characteristic frequencies are included (see Discussion section). All bands are "strong" except for ν(M–Cl) and ν(P–H) which are both "weak". The assignments are those considered most probable but have not been rigorously established. [c] ν(P–H) = 2380 cm^{-1}. [d] Broad, poorly resolved absorption which includes ν(P–O) and ν(V–O).

this complex (Table II) are consistent with the above formulation and addition of aqueous HCl to an acetone solution of the complex regenerates $[PtCl(PEt_3)\{(PPh_2O)_2H\}]$ and a pale blue solution containing the $[VO(H_2O)_5]^{2+}$ ion. The formulation was confirmed by electronic absorption spectra in the visible region and by electron spin resonance spectroscopy.

The crystal field spectra of oxovanadium(IV) species normally show three principal bands in the visible region; for example, $[VO(acac)_2]$ in $CHCl_3$ has absorptions at 400, 595, and 675 nm.[13] In $[\{PtCl(PEt_3)(PPh_2O)_2\}_2VO]$ in CH_2Cl_2 solution, the 400-nm region is obscured by the tail of intense charge transfer absorption in the ultraviolet and the two longer wavelength bands are each shifted toward the red, occurring at 670 nm (ϵ = 34) and 790 nm (ϵ = 46), respectively. The ESR spectrum of $[\{PtCl(PEt_3)(PPh_2O)_2\}_2VO]$ in CH_2Cl_2 solution showed an eight-line spectrum as expected for a single d electron coupled to ^{51}V ($I = {}^7/_2$, relative abundance = 99.8%). The isotropic g factor and hyperfine splitting for the complex are $g = 1.975 \pm 0.005$ and $a_V = 105 \pm 5$ G, respectively, compared with ranges of 1.9664–1.9704 and 101.2–108.2 G for $[VO(acac)_2]$ in a variety of solvents.[14] The line widths of corresponding lines in the studied complex and $[VO(acac)_2]$ are 46.3 ± 1 and 10 ± 1 G, respectively. The higher line widths in the platinum complex are not likely to be due to relaxation processes, since variation of solvent or concentration caused little change, and the effect is probably due to unresolved hyperfine structure resulting from coupling to ^{31}P nuclei ($I = {}^1/_2$, relative abundance = 100%). If this interpretation is correct, it indicates appreciable delocalization of the vanadium d electron onto the ligands.

Experimental Section

^{31}P NMR spectra were recorded at 40.486 MHz on a JEOL PFT-100 Fourier transform spectrometer using $P(OMe)_3$ as external reference and C_6D_6 as external lock. For a 10 kHz sweep 8192 data points were used, giving resolution of 2.44 Hz, and the data are therefore subject to uncertainties of this magnitude. Protons were decoupled by broad-band ("noise") irradiation at the appropriate frequencies.

$[PtCl(PEt_3)\{(PPh_2O)_2H\}]$ and other complexes containing the $(PPh_2O)_2H$ ligand system were prepared as previously described.[3,8] All reactions were conducted in an atmosphere of dry nitrogen using solvents dried by Type 4A molecular sieves. The products listed in Table II were stable under normal atmospheric conditions.

$[PtCl(PEt_3)\{(PPh_2O)_2BF_2\}]$. Boron trifluoride diethyl etherate (42 μl, 0.334 mmol) was added dropwise to a stirred suspension of $[PtCl(PEt_3)\{(PPh_2O)_2H\}]$ (0.250 g, 0.332 mmol) in acetone (15 ml) at 25 °C. A clear solution resulted which was stirred for 20 min and then evaporated under reduced pressure to ca. 3 ml. Diethyl ether (15 ml) and hexane (30 ml) were added to precipitate *the complex* as colorless crystals (0.215 g, 0.269 mmol) which were recrystallized from dichloromethane by careful addition of diethyl ether.

Similar procedures were employed for the other "BF_2 capped" products listed in Table II and reactions using concentrated aqueous HBF_4 instead of $BF_3 \cdot OEt_2$ also gave the same products. Procedures involving silicon, tin, and titanium compounds were also similar.

$[\{PtCl(PEt_3)(PPh_2O)_2\}_2VO]$. $[PtCl(PEt_3)\{(PPh_2O)_2H\}]$ (0.66 g, 0.87 mmol) was added to a solution of $[VO(acac)_2]$ (0.115 g, 0.43 mmol) in dichloromethane (30 ml) at 25 °C. The initially pale blue solution became pale green and after stirring for 10 min was evaporated under reduced pressure to 10 ml and added to chilled, stirred diethyl ether (100 ml) at 0 °C to precipitate *the complex* as a green powder (0.61 g, 0.39 mmol).

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Registry No. $PtCl(PEt_3)\{(PPh_2O)_2BF_2\}$, 60746-14-7; $PdCl(PEt_3)\{(PPh_2O)_2BF_2\}$, 60746-15-8; $PtCl(PPh_3)\{(PPh_2O)_2BF_2\}$, 60746-16-9; $PtCl(PHPh_2)\{(PPh_2O)_2BF_2\}$, 60746-17-0; $Pt\{(PPh_2O)_2BF_2\}_2$, 55012-61-8; $Pd_2Cl_2\{(PPh_2O)_2BF_2\}_2$, 60746-18-1; $Pd_2Br_2\{(PPh_2O)_2BF_2\}_2$, 60746-19-2; $Pt_2(PPh_2O)_2\{(PPh_2O)_2BF_2\}_2$, 60788-80-9; $\{PtCl(PEt_3)(PPh_2O)_2\}_2VO$, 60746-20-5; $PtCl(PEt_3)\{(PPh_2O)_2H\}$, 60746-21-6; $PtCl(PEt_3)\{(PPh_2O)_2SiMe_3\}$, 60746-22-7; $VO(acac)_2$, 3153-26-2; $BF_3 \cdot OEt_2$, 109-63-7; ^{31}P, 7723-14-0.

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