$$g_X = g_e(A^2 - B^2 - C^2) - 4KBC \quad (3a)$$

$$g_Y = g_e(A^2 - B^2 + C^2) - 4KAC \quad (3b)$$

$$g_Z = g_e(A^2 + B^2 - C^2) - 4KAB \quad (3c)$$

$$A_{(X)} = P[(D - E)^2 + F^2 - 2(D - E)F \cos 4\varphi]^{1/2} \quad (4a)$$

$$A_{(Y)} = P[(D + E)^2 + F^2 + 2(D + E)F \cos 4\varphi]^{1/2} \quad (4b)$$

$$A_{(Z)} = P[-4KAB - \varkappa(1 - 2C^2) + 2(1 + C^2)/7 + 6(A - B)C/7] \quad (4c)$$

where $D = -2K(A + B)C - (7\varkappa + 1)(A^2 - B^2)/7 - 3(A + B)C/7$, $E = -2K(A - B)C - (7\varkappa - 2)C^2/7 + 3(A - B)C/7$, $F = 3(A + B)^2/7$, $P = g_e g_n \beta_e \beta_n \langle r^{-3} \rangle N^2 = 32.9 \times 10^{-4} N^2$ cm^{-1} (N^2 is a covalency factor),[7,9] $g_e = 2.0023$, $\varkappa = 0.35$,[7] and K is an orbital correction factor.[10]

We see from (4a) and (4b) that $A_{(X)}$ and $A_{(Y)}$ vary with φ. A numerical calculation shows, e.g. for **1**, that the ratio $A_{(X)}/A_{(Y)}$ decreases from 13.0 to 0.22 with increase in φ from 0 to 45°. Such large angular dependence affords a basis for interpreting the observed differences and determining the angle φ with considerable accuracy.[11] In practice, (3a)–(3c) are first solved simultaneously for A, B, C, and K, which are then used to solve (4a) and (4b) for φ and N^2. Finally, φ_g, φ_A, and $A_{(Z)}$ are calculated from (1), (2), and (4c), respectively.[12] The orbital reduction factor k is obtained through the approximation $k = (1 + N^2)/2$. In solving (3a)–(3c), we obtained two different solutions with a reasonable value of K depending upon the sign of the **g** tensor determinant, $g_X g_Y g_Z$. However, the solution from $g_X g_Y g_Z < 0$ is incompatible with the observed $A_{(i)}$ values.[13] Hence, the sign of $g_X g_Y g_Z$ must be positive, which is in agreement with the results from Mössbauer data on cytochromes c_2 and P-450.[14] The calculated results for **1** and **2** are given in Table I, where the principal hf values $A_{i'}$ ($i' = X', Y', Z'$) are also listed.

According to a point-charge-model calculation,[15] the angle φ is expressible as a function of rotational orientation angle of axial ligand(s). For complexes with two equivalent axial ligands (e.g. for **1**), $\varphi = (\varphi_1 + \varphi_2)/2$, where φ_1 and φ_2 are the orientation angles of the two axial ligand planes (e.g. the Fe–O–C planes in **1**). In cases where the field strength of one axial ligand dominates over that of the other (e.g. in **2**), $\varphi \simeq \varphi_1$, where φ_1 is the angle of the axial ligand plane with stronger field (e.g. the Fe–S–C plane in **2**). The values $\varphi = 39.7$ and 11.4° determined for **1** and **2** can be discussed on this basis. On the other hand, X-ray and MO calculation studies have shown that two major factors, namely, steric and electronic effects, influence the axial ligand orientation.[2] The rhombic field orientation is affected similarly and the observed angles are the results of the competition of the two effects.

The parameters φ_g, φ_A, N^2, k, and K/k in Table I cannot be assessed without the hf splitting data. Some of them merit comparison between **1** and **2**. The covalency factor N^2 is found to fall in the range allowable for t_2 orbitals of the type $t_2 = N(d\epsilon - \lambda\psi_{lig})$. The larger value of N^2 for **1** compared with that for **2** is consistent with the general trend of Fe–OR and Fe–SR bonds. By contrast, the value K/k is smaller in **1** than in **2**. Since K/k is a measure of the mixing in of excited $t_2{}^4e$ $^2T_2$,[10] the result is suggestive of the excited states lying higher in **1** than in **2**.

Table I. Summary of Observed and Calculated Results for ^{57}Fe(TPP)(OMe)$_2^-$ (**1**) and ^{57}Fe(TPP)(SEt)(MeOH) (**2**)

	low-spin complex	
	1[a]	**2**
$\lvert g_X \rvert$	1.915	1.958
$\lvert g_Y \rvert$	2.164	2.211
$\lvert g_Z \rvert$	2.491	2.339
$A_{(X)}$/G[b]	6.0	18.2
$A_{(Y)}$/G[b]	16.0	5.5
$A_{(Z)}$/G[b,c]	~9 (9.20)[f]	≲6 (4.78)[f]
$g_X g_Y g_Z$	>0	>0
A	0.99217	0.99647
B	−0.114 76	−0.070 05
C	−0.049 37	−0.046 33
K	1.0945	1.2366
$\varphi = -\varphi_g$/deg[d]	39.66	11.35
φ_A/deg[d]	35.52	6.70
N^2	0.8344	0.6588
k	0.9172	0.8294
K/k	1.1933	1.4910
$A_{X'}/10^{-4}$ cm^{-1} [e]	−16.70	−17.49
$A_{Y'}/10^{-4}$ cm^{-1} [e]	−3.36	1.78
$A_{Z'}/10^{-4}$ cm^{-1} [e]	10.70	5.22

[a] The deuterium-substituted species. See the caption to Figure 1. [b] Normalized by $|g_i|\beta_e$. [c] The line width of g_Z absorption was 2–3 times as broad as those of g_X and g_Y absorptions, which led to less accurate determination of $A_{(Z)}$. [d] The four different angles (e.g. $\pm\varphi$, $90 \pm \varphi$) yield equivalent results. [e] The principal hf values are calculated from $A_{X'} + A_{Y'} = 2PD$, $A_{X'} - A_{Y'} = -2P(E^2 + F^2 + 2EF \cos 4\varphi)^{1/2}$, and $A_{Z'} = A_{(Z)}$. [f] Calculated from (4c). See ref 12.

The present method of hf analysis is of general application to low-spin Fe(III) heme complexes, provided that hf splitting values are experimentally available. For complexes with broad line width, ENDOR spectroscopy would be more suitable. Magnetic Mössbauer spectroscopy can provide a similar electronic characterization. The details have been reported previously.[16]

In sum, it has been demonstrated that a wealth of information is available from the ^{57}Fe hf splitting data. The orientation angle of the rhombic field may serve to probe a delicate electronic and/or structural modulation caused by weak interactions between axial ligands and their surroundings. Further studies of the series of complexes Fe(TPP)(SR)L, where R = *n*-Pr, *n*-Bu, *t*-Bu, C_6H_5, 4-*t*-Bu-C_6H_4, etc. and L = MeOH, RSH, etc., are now in progress, in an attempt to shed light on factors governing the rhombic field orientation.

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(9) The covalency effect is taken into consideration with t_2 orbitals of the type $t_2 = N(d\epsilon - \lambda\psi_{lig})$, where $d\epsilon = d_{yz}, d_{zx}, d_{xy}$.

(10) K is related to an orbital reduction factor k ($= 1 - N^2\lambda^2/2$) through $K \simeq k[1 + 6B(3/E_1 - 1/E_2)] \simeq k(1 + 12B/E)$, where E_1, E_2, or E is the energy of excited $t_2{}^4e$ $^2T_2$ relative to the ground $t_2{}^5$ $^2T_2$. For details, see: Hill, N. J. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 427. Sato, M.; Ohya, T.; Morishima, I. *Mol. Phys.* **1981**, *42*, 475.

(11) A computer simulation that assumes the random orientation of rhombic field has failed to reproduce the observed spectra for both **1** and **2**, implying that there is a preferred orientation angle φ to be determined.

(12) The calculated value $A_{(Z)}$ is used to justify the validity of the crystal field model on which the present analysis is based.

(13) For **1**, $A = 0.614\,33$, $B = -0.579\,93$, $C = -0.535\,04$, and $K = 1.1474$. The calculated hf splittings are $A_{(X)} = 35.15$–35.12 G, $A_{(Y)} = 32.73$–32.70 G, and $A_{(Z)} = 30.81$ G for $\varphi = 0$–$45°$ and $N^2 = 0.8344$, where the values $A_{(i)}$ are normalized by $|g_i|\beta_e$.

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(15) The point-charge approximation is not a good description of the crystal field effect. Nevertheless, we used the approximation to obtain a concrete if rather naive picture of the angular relation between the rhombic field and axial ligand orientations. The angular relation is regarded as zeroth order.

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Biophysics Division
Faculty of Pharmaceutical Sciences
Teikyo University
Sagamiko, Kanagawa 199-01, Japan

Tomoko Otsuka
Toshie Ohya
Mitsuo Sato*

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Cross Polarization Magic Angle Spinning ^{31}P NMR Spectra of Some $(R_3P)_2MCl_2$ (M = Pd, Pt) Complexes

Sir:

We have observed from several detailed investigations[1-3] of the thermodynamics of the cis–trans isomerizations of $(R_3P)_2PdX_2$

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Table I. CPMAS ^{31}P NMR Data of Solid $(R_3P)_2MCl_2$ Complexes with Comparative High-Resolution Solution ^{31}P NMR Data[a]

		CPMAS ^{13}P NMR		solution ^{31}P NMR ($CDCl_3$)	
complex	geometry	δ ($\Delta\nu_{1/2}$, Hz)	$^1J(^{195}Pt-^{31}P)$, Hz	δ	$^1J(^{195}Pt-^{31}P)$, Hz
$(MePPh_2)_2PtCl_2$	cis	16.3 (121), 13.8 (121)	3648, 3662	−2.6	3621
$[PhP(CH{=}CH_2)_2]_2PtCl_2$	cis	8.4 (146), 4.2 (146)	3750, 3447	−4.4	3574
$(DMPP)_2PtCl_2$[b]	cis	21.3 (127), 18.1 (127)	3384, 3179	8.1	3345
$(MePPh_2)_2PdCl_2$	cis	17.2 (80)		19.1 (cis) 7.8 (trans)	
$(Me_2PPh)_2PdCl_2$	cis/trans	25.8 (151), 14.2 (151)		6.6 (cis −5.2 (trans)	
$(DMPP)_2PdCl_2$[b]	cis	40.5 (80), 38.1 (132)		26.4 (cis)	

[a] The preparations of the compounds are given in the references cited in the text. The CPMAS spectra were obtained on a JEOL GX-270 wide-bore spectrometer operating at 6.43 T (^{31}P at 109.25 MHz) using a 40 KHz sweep width, recycle delay time of 6 s, and a proton decoupling field of 10 G. Between 200 and 300 mg of the compounds were spun at 4 KHz in Delrin or Kel-F rotors. All of the CPMAS chemical shifts were referenced to an external sample of PPh_3 ($\delta = -6$ ppm). The errors in chemical shifts are estimated to be ±1 ppm. High-resolution spectra were obtained at 40.26 MHz on a JEOL FX-100 spectrometer operating in the Fourier transform mode. Chemical shifts were referenced to PPh_3 in $CDCl_3$ ($\delta = -6$ ppm) and corrected to 85% phosphoric acid. More positive shifts represent deshielding. The errors in chemical shifts and $^1J(^{195}Pt-^{31}P)$ values are estimated to be ±0.5 ppm and ±10 Hz, respectively. [b] DMPP = 1-phenyl-3,4-dimethylphosphole.

complexes that in general the cis isomers are thermodynamically more stable than the trans isomers unless the steric bulk of the phosphine or halide is quite large. These complexes usually crystallize as the cis isomer, and upon dissolution a temperature- and solvent-dependent equilibrium between the cis and trans isomers is immediately established. The cross polarization magic angle spinning (CPMAS) ^{13}C NMR spectra[4] of $(Me_2PPh)_2PdCl_2$ and $(MePPh_2)_2PdCl_2$ each show two methyl resonances in a 1:1 ratio. On the basis of this observation it was suggested that for these two compounds both the cis and trans isomers were present in the solid state in equal amounts. Since in both cases the crystal structures[5] of the cis isomers show that the phosphines are not in equivalent environments in these molecules, an alternative interpretation of these results is possible.

We have commenced a CPMAS ^{31}P NMR study of the influence of local symmetry on ^{31}P chemical shifts in the solid state and report herein CPMAS ^{31}P NMR data for six complexes of the type $(R_3P)_2MCl_2$, M = Pd, Pt. As shown by X-ray crystallography,[5] all of these complexes are cis in the solid state, and except for $(Me_2PPh)_2PdCl_2$ there is no symmetry element relating the phosphorus atoms in the solid state.

For each of the solid *cis*-$(R_3P)_2PtCl_2$ complexes two ^{31}P resonances separated by 2–4 ppm (Table I) are observed.[6] Figure 1 (supplementary material) shows a typical spectrum. In solution, the ^{31}P chemical shift differences between *cis*- and *trans*-$(R_3P)_2PtCl_2$ are usually about 5 ppm.[7-8] The average values of $^1J(^{195}Pt-^{31}P)$ observed in the solid state are quite close to the values observed for the cis isomers in solution (>3000 Hz), whereas[7] $^1J(^{195}Pt-^{31}P)$ values for *trans*-$(R_3P)_2PtCl_2$ complexes are generally closer to 2500 Hz. Thus, it seems clear for the platinum complexes that the observation of two ^{31}P resonances in the solid state results from small differences in the local environments of the two phosphines within single *cis*-$(R_3P)_2PtCl_2$ molecules and not from a mixture of cis and trans isomers in the solid state. Scalar coupling between these two inequivalent phosphorus nuclei is not observed because it is smaller[9] (generally less than 30 Hz) than the line width (~130 Hz). However, scalar coupling has been recently observed[10] in the CPMAS ^{31}P spectra of distorted tetrahedral mercury(II) phosphine complexes (here $^2J_{P-P}$ = 110–240 Hz).

For $(DMPP)_2PdCl_2$ it is obvious that the two resonances observed in its CPMAS ^{31}P NMR spectrum (supplemental Figure 2) are due to the inequivalence of the two phosphorus nuclei in the cis complex consistent with crystallography and the fact that only the cis isomer is present in solution. In contrast, the CPMAS ^{31}P NMR spectrum of $(Me_2PPh)_2PdCl_2$ shows two resonances separated by 11.6 ppm in roughly a 2:1 intensity ratio (supplemental Figure 3). If the side-band intensities are included, the relative intensities are roughly 1:1. Two ^{31}P resonances separated by 11.8 ppm in a 0.45:0.55 ratio are observed for this complex in $CDCl_3$ at 30 °C. Thus, for this complex, it is possible to argue from the ^{31}P NMR data alone that a roughly 1:1 molar mixture of cis and trans isomers is present in this solid sample. It appears that the two isomers have quite different chemical shift anisotropies. Further work to clarify this is in progress. The CPMAS ^{13}C NMR spectrum[4] of this complex showed two methyl resonances in a 1:1 ratio. The four methyl groups are in equivalent environments[5b] in *cis*-$(Me_2PPh)_2PdCl_2$, and therefore, a mixture of cis and trans isomers in the solid should show only two CPMAS ^{13}C methyl resonances. It seems then that even for this highly crystalline sample, which appears to be cis by infrared spectroscopy (ν_{PdCl_2} at 284 and 306 cm^{-1}), and is cis by X-ray crystallography that both the cis and trans isomers are present in the solid samples studied by NMR. The CPMAS ^{31}P spectrum of crystalline *cis*-$(MePPh_2)_2PdCl_2$ (ν_{PdCl_2} at 293 and 311 cm^{-1}) shows only one ^{31}P resonance ($\nu_{1/2} \sim 80$ Hz), and its CPMAS ^{13}C spectrum shows two ^{13}C methyl resonances. In this case, the X-ray crystal structure shows that the local environments of the phosphorus nuclei are very similar but those of the methyl carbons are quite different. Hence, it appears that this complex is only cis in the solid state.

These and earlier results illustrate clearly that CPMAS spectroscopy is a powerful tool for structure elucidation.

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Supplementary Material Available: 109.25 MHz CPMAS ^{31}P NMR spectra of *cis*-$(DMPP)_2PtCl_2$ (Figure 1), *cis*-$(DMPP)_2PdCl_2$ (Figure 2), and *cis*- + *trans*-$(Me_2PPh)_2PdCl_2$ (Figure 3) (3 pages). Ordering information is given on any current masthead page.

Department of Chemistry **John H. Nelson***
University of Nevada **Jeffrey A. Rahn**
Reno, Nevada 89557

JEOL NMR Applications Laboratory **William H. Bearden**
Peabody, Massachusetts 91960

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