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# Anisotropies of the $^{31}$P Chemical Shift and $^{31}$P–$^{195}$Pt Indirect Spin–Spin Coupling in Platinum(II) Phosphines

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The $^{31}$P solid-state NMR spectra of a series of *cis-* and *trans-*platinum(II) bis(phosphine) complexes, $Pt(PR_3)_2Cl_2$ (R = phenyl, cyclohexyl, ethyl), have been obtained with and without magic-angle spinning. The $^{31}$P CPMAS spectra of these solid compounds are discussed in light of the results from crystallographic diffraction studies. The static spectra have been interpreted to provide more detailed information about the nature of the $^{31}$P chemical shielding and $^{31}$P–$^{195}$Pt indirect spin–spin ($J$) coupling in these compounds. Only one of the three principal components of the $^{31}$P chemical shift tensor is found to be responsible for the "coordination shift". Anisotropies of well over 1000 Hz are found to exist in the $J$ coupling between $^{31}$P and $^{195}$Pt in these complexes, indicating that the Fermi contact mechanism is not the sole spin–spin coupling mechanism. This observation indicates that previous interpretations of the values of $J_{iso}$ in these compounds based solely on the s character of bonding orbitals are probably not valid.

## Introduction

Since the first applications of NMR spectroscopy, and specifically $^{31}$P, to the field of inorganic chemistry, much interest has been placed on the possibility that this technique could identify very fundamental features of structure and bonding in metal complexes.[1-5] It was quickly recognized that the magnitude of coupling constants among $^{31}$P nuclei, and between $^{31}$P and metal nuclei, provided a quick and effective probe of the stereochemistry of these compounds. The classic example of this was the difference in $^1J_{iso}(^{31}P,^{195}Pt)$ in square-planar platinum(II) bis(phosphine) complexes, where cis geometry led to values of about 3500 Hz for this coupling and trans geometry resulted in $J_{iso}$ values of approximately 2500 Hz. The ease and reliability of $^{31}$P NMR spectroscopy in providing data to assign structure made it the first practical alternative to crystallography in structure determination and has had much to do with the advances in inorganic chemistry over the last 25 years. Many examples exist in the literature today where the only evidence of molecular structure comes from NMR spectral data.[6-9]

Another contribution to inorganic chemistry has been realized with the development of solid-state NMR techniques, which can supply information complementary to the results of diffraction experiments.[10,11] Ambiguities in symmetry elements, and hence space groups, in the crystal lattice sometimes occur in the analysis of a single-crystal diffraction pattern. If the corresponding sample is available for a solid-state NMR experiment, these ambiguities sometimes can be resolved by comparing the number of isotropic signals observed in a CPMAS experiment with the number expected on the basis of the crystal structure.[12] Where isochronous signals due to magnetically nonequivalent nuclei occur in the MAS experiment, it may be possible to identify differences in the overall chemical shift tensor from static spectra.[13] Chemical-exchange effects in solution NMR spectroscopy generally can be overcome by obtaining the NMR spectrum of a solid sample. Increased access to solid-state NMR facilities in recent years has allowed researchers to correlate crystallographic features to those of solid-state NMR spectra, especially the isotropic chemical shift and the chemical shift tensor.[14]

Due to the importance of $J_{iso}$ in providing structural data, significant effort has been expended to understand the origins of indirect spin–spin coupling and the influences on its observed values.[15] A completely general theory of electron-mediated interactions between nuclear spins in molecules was first presented by Ramsey.[16] Three distinct mechanisms were identified for the indirect spin–spin coupling between two nuclear spins A and B: the electron orbital mechanism, $J^o$, the spin–dipolar mechanism, $J^{sd}$, and the Fermi contact mechanism, $J^{Fc}$. Also, there is a cross-term between the latter two mechanisms, $J^{sd-Fc}$, which does not contribute to the isotropic value of $J$, but can in principle contribute to the **J** tensor. Thus, the **J** tensor may be expressed as arising from the sum of four terms:

$$\mathbf{J} = J^o + J^{sd} + J^{Fc} + J^{sd-Fc} \qquad (1)$$

McConnell[17] and Pople and Santry[18] presented approximate formulas involving the LCAO–MO coefficients for each of the isotropic terms in eq 1. This work was followed by an important contribution from Buckingham and Love,[19] who examined the complete indirect spin–spin coupling tensor using LCAO–MO theory. In particular, formulas for the anisotropy in the **J** tensor were given and the results of the MO calculations for a number of simple molecules were presented. In linear molecules, the **J** coupling tensor has only two independent components, one of which lies along the A–B bond axis, $J_\parallel$, and the other which is perpendicular to this axis, $J_\perp$. Thus the anisotropy in **J** is defined as

$$\Delta J = J_\parallel - J_\perp \qquad (2)$$

and the isotropic value is defined as

$$J_{iso} = \tfrac{1}{3}(J_\parallel + 2J_\perp) \qquad (3)$$

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Calculations of $J$ and $\Delta J$ where A and B are first-row elements led to a number of important conclusions:[19] (1) $J^{\mathrm{Fc}}$ is completely isotropic ($\Delta J^{\mathrm{Fc}} = 0$) and makes the largest contribution to $J_{\mathrm{iso}}$. (2) In general, $J^{\mathrm{o}}$ and $J^{\mathrm{sd}}$ contribute to both $J_{\mathrm{iso}}$ and $\Delta J$. These terms are most important when there is multiple bonding between atoms A and B. (3) As already mentioned, the isotropic value of $J^{\mathrm{sd-Fc}}$ is zero; however, this term was found to make significant contributions to calculated values of $\Delta J$ involving first-row elements.

It seems that the results of these early theoretical calculations[18,19] led experimentalists to rationalize measured coupling constants in terms of the Fermi contact mechanism alone. In fact, there are hundreds of publications in which this assumption is made. Generally, an attempt is then made to rationalize the results using expressions such as the following:[18]

$$^{1}J_{\mathrm{A-B}} = -\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}\frac{\hbar}{2\pi}\left(\frac{256\pi^2}{9}\beta^2\right)|s_{\mathrm{A}}(0)|^2|s_{\mathrm{B}}(0)|^2 \times \sum_{i}^{\mathrm{occ}}\sum_{j}^{\mathrm{unocc}} {}^{3}\Delta E_{i\rightarrow j}{}^{-1}c_{is_{\mathrm{A}}}c_{js_{\mathrm{A}}}c_{js_{\mathrm{B}}}c_{is_{\mathrm{B}}} \quad (4)$$

where the magnetogyric ratio of the two nuclei are given by $\gamma_{\mathrm{n}}$ (n = A, B), $\beta$ is the Bohr magneton, $s_n(0)$ is the magnitude of the valence s orbital at nucleus n, $^{3}\Delta E_{i\rightarrow j}$ is the triplet excitation energy between occupied ($i$) and unoccupied ($j$) molecular orbitals, and the coefficients $c$ describe the contributions of the s atomic orbitals of the two nuclei to the occupied and unoccupied molecular orbitals. The summation is carried out over all occupied and unoccupied molecular orbitals. Equation 4 assumes that $^{1}J_{\mathrm{A-B}}$ depends only on the Fermi contact mechanism; the contributions from other mechanisms are neglected.

The larger value of $J$(Pt,P) in cis square-planar Pt(II) bis(phosphine) complexes compared to the corresponding trans complexes is generally rationalized using eq 4 or simplifications of this expression. The current consensus[7] appears to be that the differences in $^{1}J_{\mathrm{iso}}(^{31}\mathrm{P},^{195}\mathrm{Pt})$ for cis and trans isomers of Pt($\mathrm{PR_3}$)$_2$Cl$_2$ complexes are due to the trans influence.[20] Significant evidence has been provided indicating that a phosphine ligand has a strong trans influence compared to that of a chlorine atom. In the trans isomers of the platinum(II) bis(phosphine) complexes, this is believed to weaken the P–Pt bond, relative to the cis isomers, where the P–Pt bond is trans to a chlorine. This has also been used to explain the variations in bond lengths observed for the square-planar platinum(II) complexes.[20] The bond weakening reduces the metal s character, which, in a Fermi contact interpretation, results in a smaller isotropic $J$ coupling constant.[6] Unfortunately there is no simple way of proving that the Fermi contact mechanism completely dominates and that this interpretation is correct. Reliable ab initio calculations are a theoretical challenge for the simplest diatomics; thus calculations on large molecules of general interest to inorganic chemists would appear to be many years away! Experimentally, one can, in principle, measure the anisotropy in spin–spin coupling constants. We have recently shown that this is most easily accomplished in cases where one has an isolated heteronuclear spin pair which possesses large $J$ couplings and weak dipolar couplings in the solid state.[21-23] If the **J** tensor is found to be anisotropic, the implication is that mechanisms other than the Fermi contact must be operative.

We have examined the classic examples of geometry-dependent $J$ couplings, the platinum(II) bis(phosphines), using solid-state $^{31}$P NMR spectroscopy. These compounds have been investigated previously by $^{31}$P MAS NMR spectroscopy,[24-27] but only in terms of the isotropic values of the $^{31}$P chemical shift and $^{31}$P,$^{195}$Pt $J$ coupling in the solid state. Static and magic-angle spinning (MAS) NMR spectra have been analyzed to characterize the $^{31}$P chemical shift tensors in these complexes, to identify the presence of anisotropy in the **J** tensor, and, where possible, to determine the value of $\Delta J$ accurately. A detailed description of the procedure used to analyze the $^{31}$P NMR spectra is provided in the hope that inorganic chemists will be encouraged to carry out measurements of $\Delta J$ in related systems.

## Analysis of Spin $^{1}/_{2}$ NMR Line Shapes from Solid Powder Samples

**A. Spectra Obtained from Nonspinning Samples.** The NMR line shape for a spin $^{1}/_{2}$ nucleus, such as $^{31}$P, that is adjacent to a metal M, such as platinum, will depend on the orientation-dependent chemical shielding interaction, as well as any coupling that may exist to the adjacent isotopes of M possessing spin. Where both spin-active and -inactive isotopes of M are present, the $^{31}$P NMR line shape will consist of components with weighted intensities corresponding to the natural abundance of each of the magnetically active and inactive isotopes of M. In the case of platinum, $^{195}$Pt has spin $^{1}/_{2}$ and is 33.8% naturally abundant, while the remaining naturally-occurring isotopes of platinum do not possess nuclear spin. The presence of a large isotropic $J$ coupling constant simplifies this situation by separating the "satellites" (where $m_{\mathrm{Pt}} = +^{1}/_{2}$ or $-^{1}/_{2}$) from the uncoupled center band, arising from $^{31}$P nuclei adjacent to platinum isotopes other than $^{195}$Pt. The line shape of the uncoupled center band will be completely dominated by the anisotropic (orientation-dependent) $^{31}$P chemical shielding interaction. The satellite line shapes are sensitive to the anisotropic chemical shielding and direct dipolar and indirect spin–spin interactions, as well as their relative orientations.[28-30] The overall $^{31}$P NMR powder line shape (and relative intensities, $\rho(m)$) can be described by

$$\nu_{\mathrm{P}}(\theta,\phi) = \nu_{\sigma}(\theta,\phi) - m_{\mathrm{Pt}}[\nu_{\mathrm{DJ}}(\theta,\phi) - {}^{1}J_{\mathrm{iso}}(^{31}\mathrm{P},^{195}\mathrm{Pt})]$$

$$\begin{aligned}\rho(\mathrm{m}_{\mathrm{Pt}}) &= 0.169 \text{ for } m_{\mathrm{Pt}} = +\tfrac{1}{2}, -\tfrac{1}{2} \\ &= 0.662 \text{ for } m_{\mathrm{Pt}} = 0\end{aligned} \quad (5)$$

where

$$\nu_{\sigma}(\theta,\phi) = \nu_0[1 - (\sigma_{11}\sin^2\theta\cos^2\phi + \sigma_{22}\sin^2\theta\sin^2\phi + \sigma_{33}\cos^2\theta)] \quad (6)$$

$$\nu_{\mathrm{DJ}} = R_{\mathrm{eff}}[3(\sin\beta\sin\theta\cos(\alpha - \phi) + \cos\beta\cos\theta)^2 - 1] \quad (7)$$

$$\nu_0 = \frac{\gamma_{\mathrm{P}}B_0}{2\pi} \quad (8)$$

and

$$\begin{aligned}R_{\mathrm{eff}} &= R_{\mathrm{DD}} - \tfrac{1}{3}\Delta J(^{31}\mathrm{P},^{195}\mathrm{Pt}) \\ &= \frac{\gamma_{\mathrm{P}}\gamma_{\mathrm{Pt}}\hbar}{2\pi r_{\mathrm{PtP}}{}^{3}}\frac{\mu_0}{4\pi} - \tfrac{1}{3}(J_{\parallel} - J_{\perp})\end{aligned} \quad (9)$$

The direct dipolar coupling constant, $R_{\mathrm{DD}}$, depends on the inverse cube of the internuclear separation; if this separation is known from other techniques (e.g., X-ray or neutron diffraction), it can be calculated. The principal components of the $^{31}$P chemical shielding tensor, $\sigma_{ii}$, $i$ = 1–3, are reported most commonly as chemical shifts, $\delta_{ii}$, with respect to a reference such as 85% $\mathrm{H_3PO_4}$(aq). The convention is maintained that $\delta_{11}$ and $\delta_{33}$ denote the shifts of the least shielded and most shielded principal com-

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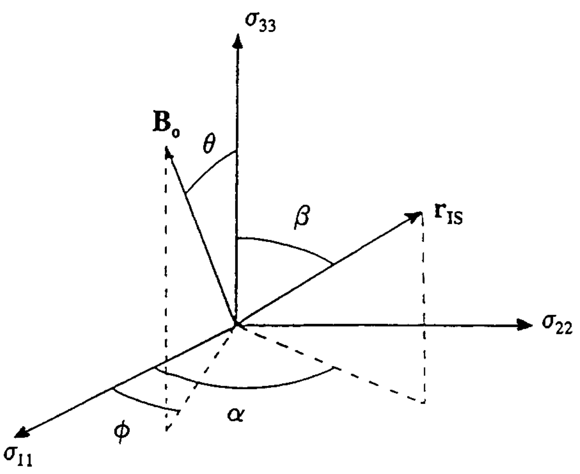

**Figure 1.** Definition of the Euler angles $\alpha$ and $\beta$, relating $\sigma$ and $r_{IS}$, and the orientation angles $\theta$ and $\phi$, relating $\sigma$ and $B_0$.

ponents, respectively. The equations above assume that J is axially symmetric and that $J_{\parallel}$ lies along the P–Pt bond. The angles $\theta$ and $\phi$ orient the molecule in the laboratory frame, in this case, the magnetic field. As the chemical shielding tensor will be fixed in its orientation with respect to the molecule, these angles can be used to orient the magnetic field vector, $B_0$, in the chemical shielding tensor. In a powder sample, these angles assume all possible values.[12] The Euler angles $\alpha$ and $\beta$ describe the orientation of the $^{31}$P chemical shielding tensor with respect to the P–Pt dipolar vector, or equivalently, the P–Pt bond, as shown in Figure 1. Thus these Euler angles fix the orientation of the $^{31}$P chemical shielding tensor in the molecular frame. The spin state of the platinum nuclei, $m_{Pt}$, is $\pm^1/_2$ for $^{195}$Pt and zero for all other Pt isotopes.

Theoretical spectra resulting from the interactions important in this study are presented in Figure 2. The $^{31}$P solution or solid-state MAS NMR spectrum of a phosphorus–platinum spin pair appears as shown in Figure 2a, due to isotropic $J$ coupling and chemical shielding. The addition of $^{31}$P anisotropic chemical shielding broadens the central feature as well as the satellites, as in Figure 2b. Finally, the total $^{31}$P NMR line shape is given in Figure 2c, which includes the effects of anisotropic dipolar coupling and anisotropic $J$ coupling, as well as the interactions described for the previous two spectra. The last spectrum is typical of the experimental spectra encountered in this analysis. The splittings indicated in Figure 2c result from the combined effects of the isotropic $J$ coupling constant, $J_{iso}(^{31}\mathrm{P},^{195}\mathrm{Pt})$, and the effective dipolar coupling between $^{31}$P and $^{195}$Pt, given by $R_{eff}$. They are analyzed to obtain information on the orientation and strength of the effective dipolar coupling, using the following relationships:

$$\begin{aligned} \Delta\nu_{11} &= |J_{iso} - R_{eff}(3\sin^2\beta\cos^2\alpha - 1)| \\ \Delta\nu_{22} &= |J_{iso} - R_{eff}(3\sin^2\beta\sin^2\alpha - 1)| \qquad (10) \\ \Delta\nu_{33} &= |J_{iso} - R_{eff}(3\cos^2\beta - 1)| \end{aligned}$$

Once the splittings are obtained from the experimental spectra, there are only three equations with six unknowns: the values of the angles $\alpha$ and $\beta$ and the signs and magnitudes of $J_{iso}$ and $R_{eff}$. The signs of the splittings are not available from the NMR spectrum (note the absolute value symbols in eq 10). Of the six unknowns, $J_{iso}$ can be obtained independently from MAS spectra; its sign is also known from previous solution NMR studies of platinum(II) phosphines.[31] Although that still leaves three equations with four unknowns, orientation information can often be obtained by inspection of the ratios of the splittings. It is common to find one element of a chemical shift tensor aligned along or close to the dipolar vector, especially for fairly symmetric species such as the platinum(II) phosphine complexes. This situation reveals itself by yielding ratios of 1:1:−2 for the three splittings once $J_{iso}$ has been subtracted from their values. The component of the $^{31}$P chemical shift tensor that corresponds to the greatest splitting due to $R_{eff}$ alone is the one which lies along the P–Pt bond. This fixes the angles $\alpha$ and $\beta$, allowing further analysis to determine the magnitude and sign of $R_{eff}$. Estimates of the parameters based on the splittings were used to generate calculated spectra using eq 5, and these estimates were fine-tuned to match the overall experimental $^{31}$P NMR line shapes.

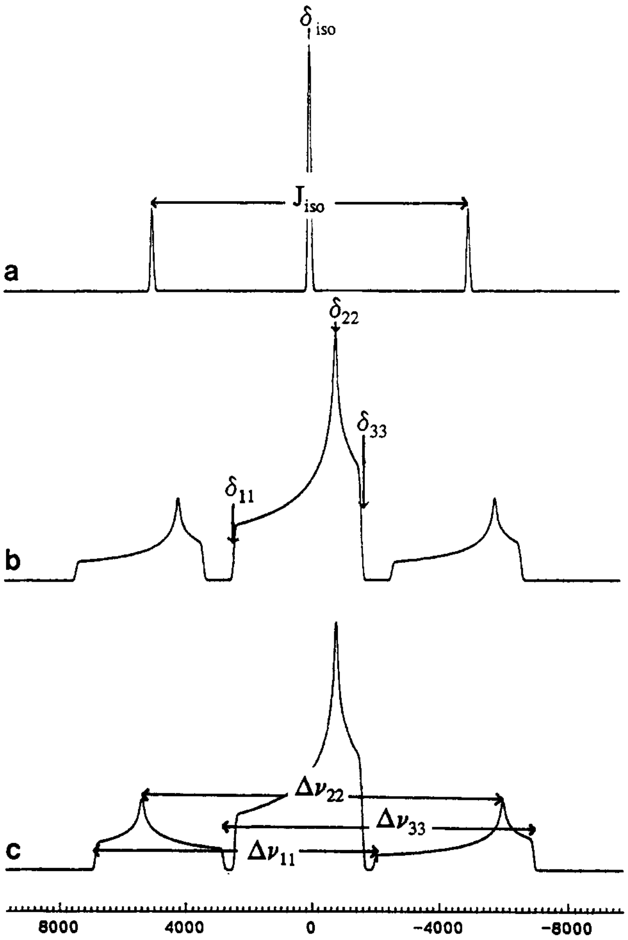

**Figure 2.** Calculated NMR spectra for a $^{31}$P nucleus of an M–P heteronuclear spin pair, including the interactions of (a) isotropic $J(^{31}\mathrm{P},\mathrm{M})$ coupling alone, (b) isotropic $J$ coupling and $^{31}$P chemical shielding, and (c) isotropic $J(^{31}\mathrm{P},\mathrm{M})$ coupling, $^{31}$P chemical shielding, and $^{31}$P–M direct dipolar and anisotropic $J$ couplings. The nucleus M has one spin $^1/_2$ isotope (40%), while the remaining isotopes do not possess a magnetic moment.

**B. Recovering Anisotropic Information from Slow-Spinning MAS Spectra.** Analysis such as that outlined above becomes difficult whenever there is more than one crystallographically distinct nucleus that contributes to the observed NMR spectrum in a given sample. This can be due to the presence of lattice sites in the unit cell that are not related by symmetry or to the fact that there is more than one type of crystal in the bulk powder sample. Whichever is the case, interpretation of the resulting powder spectra becomes difficult, as it may be unclear which spectral features correspond to which site. When such circumstances arose in this work, slow magic-angle spinning experiments were applied to allow resolution of the spectral features of each site. A judicious choice of spinning speed allows one to completely resolve the spinning sidebands of one site from the others. For spin $^1/_2$ nuclei, the powder NMR spectrum due to each independent site can be reconstructed from the spinning sidebands using a technique developed by Herzfeld and Berger.[32] The critical frequencies of the reconstructed powder patterns are analyzed in the same fashion as that outlined in the preceding section.

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**Table I.** Phosphorus-31 NMR Spectral Parameters for the Platinum(II) Phosphines from Magic-Angle Spinning NMR Spectra[a]

| compd | $\delta_{iso}$ | $^1J_{iso}(^{31}P,^{195}Pt)$, Hz |
|---|---|---|
| *trans*-$Pt(PPh_3)_2Cl_2$ | 21.6 | 2624 |
| *trans*-$Pt(PCy_3)_2Cl_2$ | 14.6 | 2420 |
| *trans*-$Pt(PEt_3)_2Cl_2$ | 13.2 | 2392 |
| *cis*-$Pt(PPh_3)_2Cl_2$ | 12.7 | 3727 |
|  | 10.9 | 3910 |
|  | 7.8 | 3596 |
| *cis*-$Pt(PCy_3)_2Cl_2$ | 14.8 | 3565 |
| *cis*-$Pt(PEt_3)_2Cl_2$[b] | 9.3 | 3448 |

[a] Errors in $\delta_{iso}$ are ±0.3 ppm and in $J_{iso}$ are ±25 Hz. [b] Average of two signals observed with MAS at 2.5 kHz; these signals are believed to be due to $^{31}$P sites related by a mirror plane (see text).

Once this is performed for all the sites that are present in the NMR spectra, the overall multisite static powder NMR line shape is calculated, using the parameters derived independently for each site from the slow-MAS spectra, as well as properly weighting their respective contributions to the NMR spectrum. Comparison of this calculated line shape to the original multisite powder line shape provides a final check on the precision of both the Herzfeld–Berger fitting and the resulting NMR parameters derived for each site. While this approach may increase the error, it is often the only way to obtain this information when there are overlapping line shapes due to more than one crystallographic site.

## Experimental Section

All compounds were obtained from Aldrich Chemical Co., with the exception of the cis and trans complexes of $Pt(PCy_3)_2Cl_2$, which were kindly provided by Dr. A. M. Nicholas. These compounds proved pure upon initial acquisition of their spectra, so no further purification was performed, except where noted otherwise in the next section.

All $^{31}$P solution NMR spectra were obtained at 293 K at a frequency of 146.1 MHz on a Nicolet NT360 NMR spectrometer and referenced with respect to external 85% $H_3PO_4$(aq). Phosphorus-31 90° pulse widths were 25 μs, with acquisition times of 106.5 ms, during which 16384 data points were collected. All $^{31}$P solid-state NMR spectra were obtained at 293 K on a Bruker MSL-200 NMR spectrometer, operating at 81.033 MHz for $^{31}$P. Cross-polarization was used in the acquisition of all spectra, with $^1$H 90° pulses of 3.6–4.0 μs. Contact times for polarization transfer were typically 3 ms, except that for *trans*-$Pt(PEt_3)_2Cl_2$, which was 300 μs. Contact times were optimized on spinning samples. Recycle delays of 10–20 s were used. Acquisition times for static and spinning samples were 41 ms, during which 4096 data points were collected. Zero-filling to twice this amount of data points was applied prior to Fourier transformation. Magic-angle spinning was performed in a Bruker double-air-bearing MAS probe using zirconia rotors, with spinning rates up to 6 kHz. All spectra were referenced with respect to 85% $H_3PO_4$(aq) at 0 ppm; this was accomplished using an external sample of $NH_4H_2PO_4$(s), which has a shift of +0.81 ppm with respect to the reference.

All calculated spectra were generated using a Fortran-77 program developed in this laboratory incorporating the POWDER interpolation routine of Alderman, Solum, and Grant.[33] Calculations were performed on an 80286/287 microcomputer.

## Results

**A. MAS Spectra.** The isotropic values of the $^{31}$P chemical shift ($\delta_{iso}$) and the $^{31}$P,$^{195}$Pt indirect spin–spin coupling ($^1J_{iso}(^{31}P,^{195}Pt)$) for the cis and trans complexes, given in Table I, follow the trends noted previously from solution NMR spectra, most notable in the values of $J_{iso}$.[3,7,34] In general, $J_{iso}$ is near 3500 Hz in the cis complexes and approximately 2500 Hz in the trans complexes. One aspect of the solid-state NMR study that was not possible to observe in solution NMR studies was the correspondence of crystallographic symmetry to the number of signals observed in the $^{31}$P MAS spectra.[10] This was especially apparent in the cis complexes, where, in general, the crystal symmetry for the two phosphine ligands of one complex renders each crystallographically distinct. As a consequence, more than one signal was observed in MAS spectra while only one signal would be observed in solution for a given cis complex. However, in the trans complexes, the crystal symmetry generally places the platinum at a center of symmetry, which makes the two phosphorus nuclei equivalent in the solid as well as in solution. Such features have been noted previously,[11] although for some compounds there has been substantial variation in the results available in the literature.

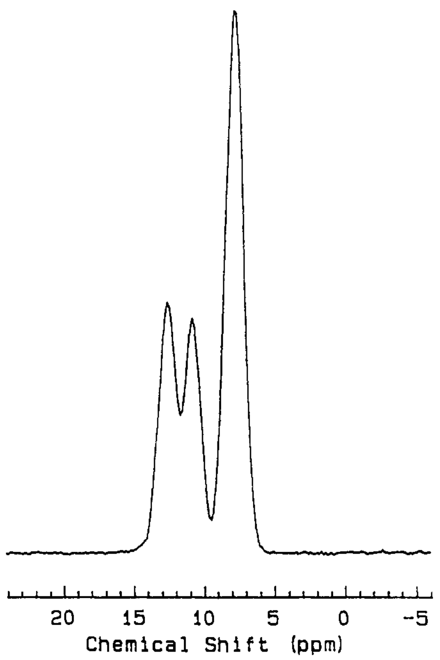

**Figure 3.** Phosphorus-31 CPMAS spectrum of *cis*-$Pt(PPh_3)_2Cl_2$ at a spinning rate of 4.0 kHz. Note the presence of three isotropic signals at 12.7, 10.9, and 7.8 ppm.

One example was the $^{31}$P MAS spectra observed for *trans*-$Pt(PPh_3)_2Cl_2$. Previously, two closely spaced $^{31}$P signals were attributed to this complex in the $^{31}$P MAS spectra of a mixture of trans and cis isomers, with isotropic shifts of 20.9 and 19.0 ppm.[24] However, in the spectra obtained here, only one signal corresponding to the isotropic chemical shift was observed, at 21.6 ppm, with a line width of less than 80 Hz (1.0 ppm). One possible explanation for this difference was the presence of different crystal forms in the two samples that were studied. If the structure of this complex followed the trend of other *trans*-bis(phosphine)platinum(II) complexes, one might expect that the two phosphorus centers would be equivalent and only one $^{31}$P signal would be observed. Unfortunately, no crystal structure has been reported for this compound, so this discrepancy cannot be resolved.

Another case is that of *cis*-$Pt(PPh_3)_2Cl_2$, which has been reported to have two components, but with much different isotropic shifts, of 12.9 and 8.6 ppm,[24] 12.6 and 7.8 ppm,[35] and 7.9 and −4.1 ppm,[27] in each of the three studies. A commercial sample of this compound yielded a $^{31}$P MAS spectrum with three distinct signals, at 12.7, 10.9, and 7.8 ppm, with relative intensities of 1:1:2 (see Figure 3). The peak with double intensity possessed satellites (also with double intensity) that had line widths approximately equal to those observed for the other two sites, indicating that these were probably not two isochronous signals but were due to two $^{31}$P nuclei at crystallographically identical sites in the crystal lattice. This was the first observation of three $^{31}$P signals for this compound. Variation of the contact time did not change the relative intensities of the three signals. The $^{31}$P solution NMR spectrum of this compound in dichloromethane contained only a single $^{31}$P signal with $^{195}$Pt satellites, with $\delta_{iso}$ = 14.5 ppm and $J_{iso}$ = 3679 Hz, in excellent agreement with previous solution data,[24] indicating that the multiple signals in the solid-state spectrum were due to crystallographic effects. Recrystallization of the complex from

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**Table II.** Phosphorus-31 Solid-State NMR Spectral Parameters for the Platinum Phosphines[a]

| compd | $\delta_{11}$ | $\delta_{22}$ | $\delta_{33}$ | $\Delta\sigma$ | $\eta_\sigma$ | $R_{\text{eff}}$, Hz | $\Delta J$, Hz |
|---|---|---|---|---|---|---|---|
| *trans*-$Pt(PPh_3)_2Cl_2$ | 85 | −7 | −13 | 95 | 0.09 | 242 | 1865 |
| *trans*-$Pt(PCy_3)_2Cl_2$ | 90 | −6 | −40 | 113 | 0.45 | 288 | 1602 |
| *trans*-$Pt(PEt_3)_2Cl_2$ | 96 | 1 | −58 | 125 | 0.71 | 353 | 1536 |
| *cis*-$Pt(PPh_3)_2Cl_2$ | 89 | −10 | −41 | 115 | 0.41 | 183 | 2184 or 3282 |
|  | 86 | −18 | −35 | 113 | 0.23 | 255 | 1968 or 3498 |
|  | 58 | 3 | −37 | 75 | 0.80 | 232 | 2037 or 3429 |
| *cis*-$Pt(PCy_3)_2Cl_2$ | 78 | −11 | −23 | 95 | 0.19 |  |  |
| *cis*-$Pt(PEt_3)_2Cl_2$ | 76 | −13 | −35 | 100 | 0.33 | 458 | 1356 or 4104 |

[a] Errors in $\delta_{ii}$ ($i = 1{-}3$) are ±1 ppm for the trans complexes and ±4 ppm for the cis complexes; those in $R_{\text{eff}}$ are ±80 Hz (trans) and ±200 Hz (cis) and in $\Delta J$ are ±250 Hz (trans) and ±600 Hz (cis). $\Delta\sigma = \delta_{11} - {}^1/_2(\delta_{22} + \delta_{33})$; $\eta_\sigma = (\delta_{22} - \delta_{33})/(\delta_{11} - \delta_{\text{iso}})$.

dichloromethane solution yielded an identical three-component solid-state spectrum. The crystal structure for this compound,[36] where the compound was isolated from an acetone reaction mixture, showed that the lattice contained a molecule of acetone as solvate for each platinum complex and indicated that only two $^{31}P$ signals should be observed. Recrystallization of this sample from acetone was not possible due to its insolubility in that solvent, so direct comparison of the NMR spectral results to the crystal structure could not be obtained. The differences between the spectra reported in this and an earlier study, with isotropic $^{31}P$ shifts of 12.9 and 8.6 ppm,[24] probably result from an inability to resolve the two high-frequency signals, possibly due to the lower applied field and instabilities in the magic angle in the conventional Andrew–Beams spinner used in the earlier study. The sample used was retrieved from dichloromethane solution. The reason for the discrepancy with respect to more recent studies is less obvious. Allman[35] may not have been able to resolve the two peaks within 2 ppm in the two-dimensional technique that was used. The $^{31}P$ solution NMR data reported by Rahn, Baltusis, and Nelson[27] for *cis*-$Pt(PPh_3)_2Cl_2$ do not correspond to the previous literature data reported for this complex. They did not retrieve their sample from an acetone reaction mixture but from dichloromethane, so correspondence of their NMR spectral results to the crystallographic data is not a possible explanation for the observed differences.

In many cis complexes, two closely-spaced signals have been observed, their shifts differing by only 2–3 ppm.[11] In *cis*-$Pt(PCy_3)_2Cl_2$, no splitting was observed, although the $^{31}P$ MAS isotropic peak was quite broad, with a line width of 170 Hz. Two signals are anticipated on the basis of the crystallographic results.[37] This splitting was apparent in the $^{31}P$ spectrum of *cis*-$Pt(PEt_3)_2Cl_2$ with magic-angle spinning at 2.5 kHz, in agreement with the results of the crystal determination,[38] and the two $^{31}P$ signals were separated by 1.8 ppm (145 Hz). However, the splitting was observed to vary with the spinning speed, a phenomenon that was first explained for $^{31}P$ MAS spectra of $Na_4P_2O_7{\cdot}10H_2O$ by Kubo and McDowell.[39] They attributed this spinning-rate-dependent splitting to a difference in the orientation of the chemical shielding tensors of two otherwise equivalent $^{31}P$ nuclei which are dipolar coupled. The $^{31}P$–$^{31}P$ homonuclear dipolar coupling in that compound was 787 Hz. In *cis*-$Pt(PEt_3)Cl_2$, the peak-to-peak splitting varies from 105 to 145 Hz, the maximum splitting being observed at moderate spinning rates, 2.0–2.5 kHz, as evident in Figure 4. The variation observed in this compound is much less than the rate-dependent splittings that were reported by Kubo and McDowell. This is probably due to a combination of two factors: the smaller $^{31}P$–$^{31}P$ homonuclear dipolar coupling in *cis*-$Pt(PEt_3)_2Cl_2$ (approximately 400 Hz) and a smaller orientation-dependent difference in the $^{31}P$ chemical shielding tensors of the two phosphorus nuclei in the platinum complex. The isotropic values of $\delta(^{31}P)$ and $^1J(^{31}P,^{195}Pt)$ in *cis*-$Pt(PEt_3)_2Cl_2$ were calculated by averaging the appropriate splittings. Similar effects have been noticed in the $^{31}P$ CPMAS NMR spectra of $(OC)_4W$(dppp) (dppp = 1,3-bis(diphenylphosphino)propane) and related complexes.[40]

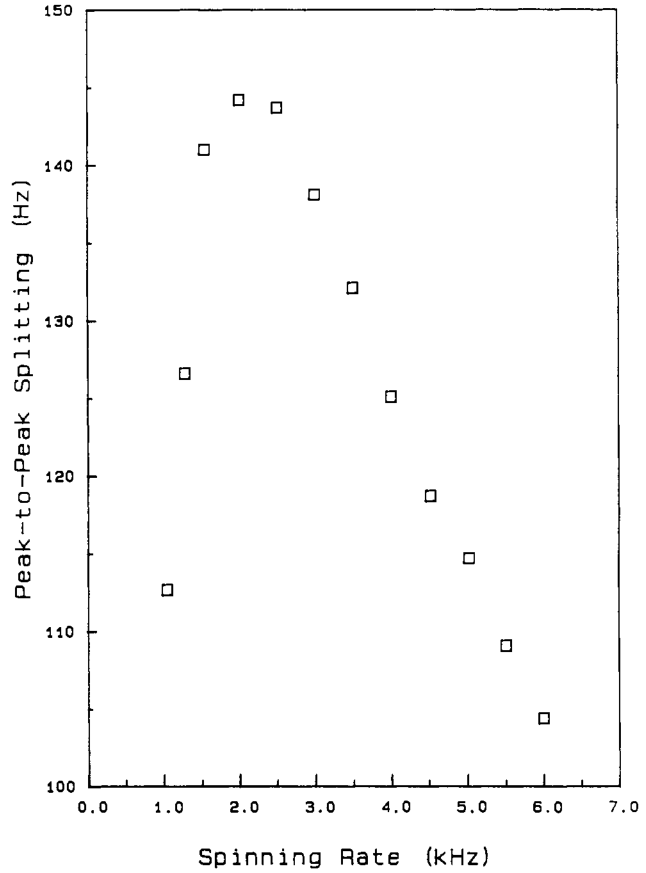

**Figure 4.** Variation of the peak-to-peak splitting with spinning rate of the two isotropic signals of *cis*-$Pt(PEt_3)_2Cl_2$.

An interesting experimental aspect of the $^{31}P$ solid-state NMR spectra of *trans*-$Pt(PEt_3)_2Cl_2$ was the extremely short contact time for cross-polarization. Whereas all other samples were obtained with contact times of 3 ms, comparable sensitivity for this complex could only be realized with a considerably shorter contact time of 300 μs. Polarization transfer is a competing process between an increasing exponential due to the transfer of magnetization from protons to $^{31}P$ nuclei and a decreasing exponential due to the relaxation of the $^1H$ magnetization in the rotating frame.[41] This latter exponential is characterized by $T_{1\rho}(^1H)$, the proton spin–lattice relaxation time in the rotating frame. It is unclear what could be causing the remarkably short $^1H$ $T_{1\rho}$, although it probably indicates that the time scale of methyl rotations in this compound is on the order of the frequency of the proton radiofrequency field ($\omega_1(^1H)/2\pi = 62.5$ kHz).

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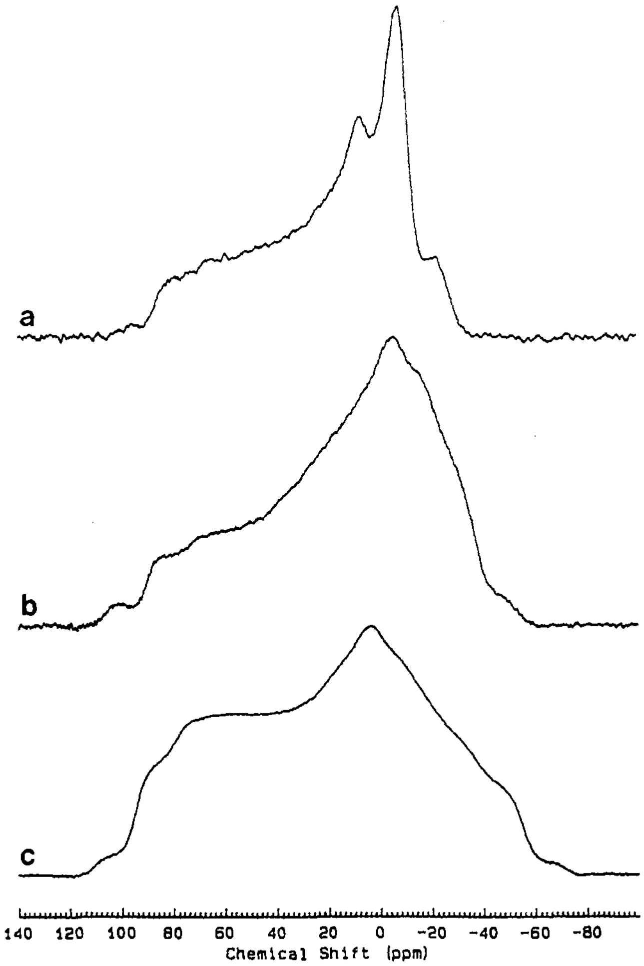

**Figure 5.** Phosphorus-31 static NMR spectra of the trans isomers of (a) $Pt(PPh_3)_2Cl_2$, (b) $Pt(PCy_3)_2Cl_2$, and (c) $Pt(PEt_3)_2Cl_2$.

**B. Static Sample Results.** More detailed information about the NMR parameters that characterize these platinum phosphine complexes can be obtained from the anisotropic information either obtained from static spectra or recovered from slow-spinning MAS spectra using Herzfeld–Berger analysis.[32] The results of such analyses are given in Table II. The chemical shielding anisotropy, $\Delta\sigma$, and the asymmetry in the chemical shielding, $\eta_\sigma$, provide a description of the symmetry about the phosphorus nuclei in these compounds. In all of the platinum phosphine complexes, the chemical shielding anisotropy is roughly equivalent, within 25 ppm of 100 ppm. If one considers the total breadth of the $^{31}$P powder pattern in these compounds ($\delta_{11} - \delta_{33}$), the range of the $^{31}$P chemical shielding in these compounds in much wider, ranging from 95 to 154 ppm. In *trans*-$Pt(PPh_3)_2Cl_2$, the asymmetry in the $^{31}$P chemical shielding of close to zero indicates that there is near-axial symmetry about the phosphorus nuclei. However, the unique component was not the one which was determined to lie along the P–Pt bond (vide infra). This example shows the danger of orienting a chemical shielding tensor on the basis of local symmetry arguments. Although they may be useful in predicting the directions of the principal axes, such arguments are not the proper means to identify which direction corresponds to which element of the chemical shift tensor. Unfortunately, no crystal structure has been reported for *trans*-$Pt(PPh_3)_2Cl_2$ to provide a clear picture of the environment about the phosphorus ligands in this complex. In both *trans*-$Pt(PCy_3)_2Cl_2$ and *trans*-$Pt(PEt_3)_2Cl_2$, there was a large departure from axial symmetry in the $^{31}$P chemical shielding, $\eta_\sigma = 0.45$ and 0.71, respectively. This is in accord with the results from the X-ray diffraction studies for the two compounds,[42,43] which indicate that there is at most $m$ ($C_s$) symmetry at the phosphorus sites. The differences in the three trans complexes were also reflected in the total breadth of the $^{31}$P powder patterns, which were 98 ppm for the triphenylphosphine complex and 130 and 154 ppm for the tricyclohexylphosphine and triethylphosphine complexes, respectively. The static spectra of these compounds are shown in Figure 5.

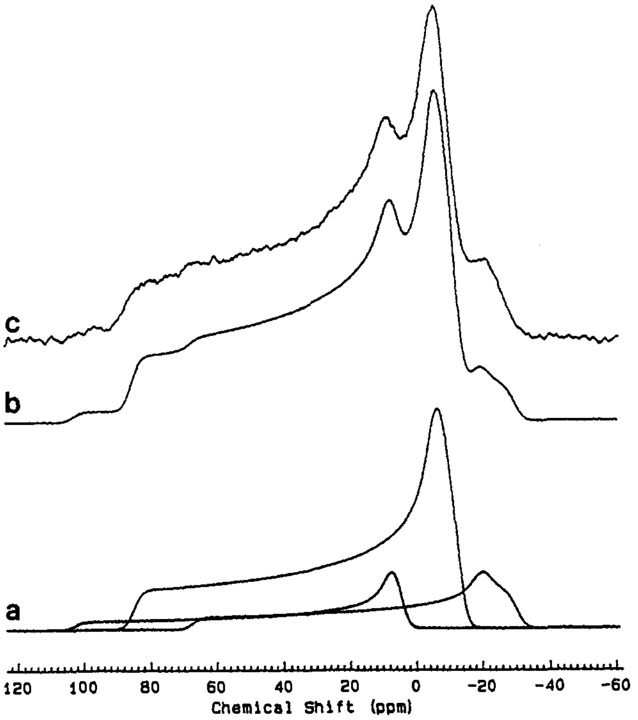

**Figure 6.** Phosphorus-31 powder NMR line shapes for *trans*-$Pt(PPh_3)_2Cl_2$: (a) individual calculated subspectra corresponding to the uncoupled center band and two satellite line shapes; (b) summed calculated line shape; (c) experimental line shape.

In our previous studies of the mercury(II) phosphines[21,22] and phosphonates,[23] the large magnitudes of the isotropic indirect spin–spin coupling constant relative to the direct dipolar coupling and chemical shielding anisotropy simplified analysis of the solid-state NMR line shapes by providing complete or near-complete resolution of the central and satellite line shapes. The smaller values of $J_{iso}(^{31}P,^{195}Pt)$ led to considerable overlap of the central and satellite features of the $^{31}$P line shape for the platinum phosphines. The central uncoupled $^{31}$P line shape, accounting for 66.2% of the $^{31}$P spectral intensity, contained information concerning only the anisotropic phosphorus chemical shielding. From this feature, the three components of the $^{31}$P chemical shift tensor were determined. The two satellite line shapes, comprising 33.8% of the $^{31}$P intensity (or 16.9% each), were sensitive to the combined effects of phosphorus chemical shielding, $^{31}P-^{195}Pt$ direct dipolar and indirect spin–spin couplings, as well as the relative orientations of these tensorial interactions. Using estimates for the magnitudes and orientations of these interactions, each of the three subspectra of the $^{31}$P line shape were calculated separately and then summed with the appropriate relative intensities to yield an overall line shape that could be compared to the experimental spectrum. This procedure is illustrated in Figure 6 for *trans*-$Pt(PPh_3)_2Cl_2$. When the overlap of spectral features prevented a clear distinction of each of the subspectra, slow-spinning MAS spectra were used either to indicate the spectral envelopes of each component or to reconstruct the complete powder spectrum from resolved spinning sideband patterns using the Herzfeld–Berger technique.[32] One interesting aspect of the spectra examined here was the interplay of the effective dipolar coupling and the isotropic $J$ coupling constant. On first examination, it appeared in most cases that the direction of maximum splitting was along the least shielded component, $\delta_{11}$. This was usually the best resolved region of the static spectrum, enhancing this effect. This belief could be strengthened by expectations based on the symmetry of the spectrum and local symmetry arguments, as mentioned previously.

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However, upon careful analysis, the true situation becomes evident. The magnitude of the $J$ coupling between $^{31}P$ and $^{195}Pt$ had to be removed from the magnitudes of the splittings at the different regions of the spectrum before assignment of the orientation of the $^{31}P$ chemical shift tensor could be made. In all cases, it was found that $\delta_{22}$ lies along or near the Pt–P bond. On the basis of the results for cis-chelate ring systems involving platinum and phosphorus ligands,[40] where components with $^{31}P$ chemical shifts close to 0 ppm were oriented along the Pt–P bond, one would expect a similar behavior in the platinum(II) bis(phosphine) complexes.

The most striking feature of the data in Table II is the observation of substantial anisotropies in the indirect spin–spin coupling between $^{31}P$ and $^{195}Pt$. These values were derived under the assumption that the direct dipolar coupling between these two nuclei corresponds to the internuclear separations determined by X-ray crystallography. The reported bond lengths ($r_{PtP}$) and calculated dipolar coupling constants ($R_{DD}$) are as follows: *trans*-$Pt(PCy_3)_2Cl_2$, 2.337 Å,[42] 822 Hz; *trans*-$Pt(PEt_3)_2Cl_2$, 2.298 Å,[43] 865 Hz; *cis*-$Pt(PPh_3)_2Cl_2$, 2.258 Å,[36] 911 Hz; *cis*-$Pt(PCy_3)_2Cl_2$, 2.294 Å,[37] 869 Hz; *cis*-$Pt(PEt_3)_2Cl_2$, 2.259 Å,[38] 910 Hz. As the crystal structure for *trans*-$Pt(PPh_3)_2Cl_2$ has not been reported in the literature, an average value of 2.302 Å (corresponding to $R_{DD} = 860$ Hz) was used. This average value was the reported weighted average of Pt–P bond lengths in 22 trans complexes of platinum(II) phosphines.[44] Direct dipolar coupling and anisotropy in $J$ affect the solid-state NMR line shape in the same fashion, resulting in an "effective" dipolar coupling constant, as described in the theory section. It is sufficient at this point to remark that, as the internuclear separations between P and Pt are quite large (between 2.25 and 2.35 Å), resulting in relatively small $R_{DD}$ values, the estimates of $\Delta J$ were quite robust with respect to any errors in the assumed values of the direct dipolar coupling constant. A change in the Pt–P bond length of ±0.02 Å changes the value of $R_{DD}$ by ±25 Hz; thus the assumption of the bond length from X-ray studies introduces little error to the overall analysis. Librational motion about a cone with a half-angle of 10°, which would be large-amplitude motion for these heavy nuclei in a large molecule, would reduce the observed magnitude of the dipolar coupling constant by only approximately 40 Hz.[45] The values for $R_{eff}$ given in Table II are substantially smaller than the values for $R_{DD}$ anticipated from the X-ray values for the Pt–P separation. For example, if the reduction in the calculated $R_{DD}$ for *trans*-$Pt(PCy_3)_2Cl_2$ to the observed $R_{eff}$ was due only to librational motion, this would indicate that the Pt–P bond was librating through a cone with a half-angle of 41°. Anisotropy in $J$ must be present to account for the enormous reduction of the dipolar coupling in the observed NMR spectra.

The presence of two values for $\Delta J$ for the cis complexes in Table II resulted from a difficulty in assignment of the relative signs of $R_{eff}$ and $J_{iso}$ due to the presence of substantial spectral overlap and line broadening, especially in the case of the cis complexes. In the analysis of the trans complexes, only one value for $\Delta J$ provided a proper simulation of the experimental line shape, as the absolute sign of $J_{iso}(^{31}P,^{195}Pt)$ was determined previously to be positive by McFarlane.[31] The relative signs of $J_{iso}$ and $R_{eff}$ can usually be discerned from the solid-state NMR line shape. The proximity of two $^{31}P$ nuclei in the cis complexes introduced additional line broadening to the $^{31}P$ NMR line shapes of these compounds due to homonuclear $^{31}P$–$^{31}P$ dipolar coupling. On the basis of the separation of the $^{31}P$ nuclei determined by X-ray diffraction, the strength of this $^{31}P$–$^{31}P$ coupling was estimated to be on the order of 400 Hz. While this coupling was probably not strong enough to change the frequencies of the distinct features of the $^{31}P$ line shape, it made analysis of the satellites considerably more difficult, precluding the relative sign determination. The presence of significant $^{31}P$–$^{31}P$ homonuclear dipolar coupling, close to 400 Hz, might be expected to influence the $^{31}P$ NMR line shape; i.e., the $A_2X$ spin system we have analyzed where $A = {}^{31}P$ and $X = {}^{195}Pt$ may have ABX character: $A = B = {}^{31}P$, $X = {}^{195}Pt$. However, such influences will affect the central and satellite regions of the spectrum equally. As our analysis relies on *differences* between the central and satellite regions, our estimates of $R_{eff}$ and $\Delta J$ for the $^{31}P$–$^{195}Pt$ spin pair should still prove quite accurate. However, the values of the principal components of the $^{31}P$ chemical shift tensor for the cis complexes may be less accurate; the larger errors for these parameters in Table II reflect this uncertainty.

## Discussion

The principal components of the $^{31}P$ chemical shift tensor varied little through the six complexes that have been characterized, regardless of ligand or geometry. This indicates that the environments immediately surrounding the phosphorus nuclei are relatively similar, and there are no gross distortions from a regular phosphine structure in any one complex. One component of the $^{31}P$ chemical shift tensor, $\delta_{22}$, lies along the Pt–P bond, and the range of values for this component is less than 25 ppm. This is similar to what was previously observed for the mercury(II) phosphines,[22] although it appeared that the component along the mercury–phosphorus bond in those complexes was about 29 ppm less shielded. The method used to orient the $^{31}P$ chemical shift tensor in this study did not permit the assignment of particular directions to the other two principal components, $\delta_{11}$ and $\delta_{33}$, other than placing them in the plane perpendicular to the Pt–P bond. Their respective values, as well, did not differ greatly in magnitude among the different platinum(II) bis(phosphine) complexes. There is an approximate mirror plane at the phosphorus site in these complexes, containing the Pt–P bond and lying perpendicular to the plane of the complex. This would restrict the orientation of the principal components of the $^{31}P$ chemical shift tensor such that one component would be perpendicular to this mirror plane. In a series of cyclic platinum(II) bis(phosphine) complexes, Lindner et al.[40] have reported shifts between 61 and 111 ppm (mean value of 83 ppm) for the principal component of the $^{31}P$ chemical shift tensor that is oriented in the molecular plane and is perpendicular to the Pt–P bond. This is similar in magnitude to the values of $\delta_{11}$ reported in Table II. On this basis, it appears reasonable to expect $\delta_{11}$ to have a similar orientation in the $Pt(PR_3)_2Cl_2$ complexes. The remaining component, $\delta_{33}$, would be oriented perpendicular to the plane of the molecule. The downfield shift of $\delta_{11}$ upon coordination to the platinum led to an overall deshielding of the $^{31}P$ isotropic shift. It is significant that the entire coordination shift appears limited to one component of the $^{31}P$ chemical shift tensor. Others have reported that a single component of the $^{31}P$ chemical shielding tensor is sensitive to such structural characteristics.[40,46] Further study to unambiguously determine its orientation would clearly be of interest.

Although some ambiguities remain in the possible values of $\Delta J$, it is clear that substantial anisotropies exist in the indirect spin–spin coupling between $^{195}Pt$ and $^{31}P$ in these complexes. Their values are at least 1300 Hz, and could be as large as 4100 Hz, depending on the relative sign of $J_{iso}$ and $R_{eff}$. This observation indicates that mechanisms other than the Fermi contact mechanism contribute to the overall $\mathbf{J}(^{31}P,^{195}Pt)$ tensor. It would appear that $\Delta J$ is at least marginally larger in the cis complexes, parallel with the trend in $J_{iso}$ values. If the greater value for $\Delta J$ was determined to be the proper choice, our results would indicate substantial differences in the coupling mechanisms for the two complexes. However, it is not possible to draw such conclusions from the data presented here. More effort using both experiment and theory will be needed before the full extent of the contributions by the various mechanisms of $\mathbf{J}$ will be known.

Santos et al.[47] have reported an anisotropy of −450 Hz for the coupling between $^{15}N$ and $^{195}Pt$ in a *cis*-platin complex, *cis*-di(ammine-$^{15}N$)bis(thiocyanato-*S*)platinum(II), where the isotropic

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*J* coupling constant is −275 Hz. Although this is much smaller than the isotropic and anisotropic values of the *J* coupling determined in this study, it is not proper to compare them without taking into account the differences in the magnetic moments of $^{31}$P and $^{15}$N. This can be done using reduced coupling parameters, $K_{iso}$ and $\Delta K$. For nuclei A and B

$$K_{A-B} = \frac{4\pi^2 J_{A-B}}{h\gamma_A\gamma_B} \qquad (11)$$

where $K_{A-B}$ is in units of $10^{20}$ kg m$^{-2}$ s$^{-2}$ A$^{-2}$. An equivalent expression can be used to convert $\Delta J$ to $\Delta K$. For the platinum(II) phosphines, the trans complexes have average values for K and $\Delta K$ of 236 and 159 (in the above units), while the values for the cis complexes are 345 and either 170 or 351, respectively. For the *cis*-platin complex, a value for $\Delta K = 171 \times 10^{20}$ kg m$^{-2}$ s$^{-2}$ A$^{-2}$ is derived, remarkably close to the other values for the couplings between $^{195}$Pt and $^{31}$P. The isotropic reduced coupling was smaller in that compound, $K_{iso} = 105 \times 10^{20}$ kg m$^{-2}$ s$^{-2}$ A$^{-2}$.

The values of $\Delta J$ determined for the mercury(II) phosphines, $[HgPR_3X_2]_2$, were much larger than those found in the platinum(II) phosphine complexes, on the order of 5–6 kHz. Conversion to reduced coupling values would only amplify these differences, as $^{199}$Hg has a smaller magnetic moment than $^{195}$Pt. This follows the trend in the isotropic *J* values for couplings between each of these nuclei and $^{31}$P, as both $J_{iso}$ and $\Delta J$ are approximately 5 times larger for $^{199}$Hg–$^{31}$P couplings. This is not surprising, considering the qualitative differences expected on the basis of the different coordination of the metal nuclei. It may be more suitable to compare results for the mercury(II) bis(phosphines), $Hg(PR_3)_2X_2$, to the results reported here.

The results that have been presented here conclusively show that substantial anisotropies are present in the indirect spin–spin coupling between $^{195}$Pt and $^{31}$P. The implication is that mechanisms other than the Fermi contact are making significant contributions to the transmission of spin information between the two nuclei. Such observations should not be surprising, as the anisotropic terms contributing to J($^{31}$P,$^{195}$Pt) ($J^{o}$, $J^{sd}$, and $J^{sd-Fc}$) contain the term $\langle a_0{}^3/r^3\rangle_{nd}$, the radial density of the valence d electrons. The value of this term is very large for Pt.[48]

In light of the results we have presented, it is clear that interpretation of the values of $J_{iso}$ based solely on Fermi contact arguments is tenuous. For example, the values of $\Delta J$ for the trans complexes follow the trend in the values of $J_{iso}$ in these compounds, but this certainly does not indicate that $\Delta J$ is a measure of s character. The observed trends must have a different origin. Although arguments based on the contribution of s orbitals may be a useful tool, it is evident that widespread application of this concept involves a considerable oversimplification.

## Conclusion

A series of *cis*- and *trans*-platinum(II) bis(phosphine) complexes have been investigated using $^{31}$P solid state NMR spectroscopy. One component of the $^{31}$P shift tensor, $\delta_{22}$, was found to lie along the Pt–P bond in all complexes, and its value varies little, between +3 and −18 ppm. The $^{31}$P chemical shift anisotropies are dominated by a high-frequency shift in one component of the $^{31}$P chemical shift tensor. This shift is also the major contributor to the "coordination shift" of the $^{31}$P signal of the phosphine. It was proposed that this component lies in the plane of the complex, perpendicular to the Pt–P bond. Significant anisotropies in J($^{31}$P,$^{195}$Pt) are inferred from the observed dipolar coupling, $R_{eff}$. Using estimates for the direct dipolar coupling constant based on Pt–P bond lengths determined by X-ray diffraction, values of $\Delta J$ in the range from 1500 to 1900 Hz have been unambiguously determined for the trans complexes, while estimates of 1300–2200 or 3300–4100 Hz have been derived for the cis complexes. Although the sign of $R_{eff}$ could not be assigned relative to the sign of $J_{iso}$ for compounds of the latter geometry, it was still possible to show that there are substantial contributions to the overall indirect spin–spin coupling tensor J($^{31}$P,$^{195}$Pt), from mechanisms other than the Fermi contact. This mechanism has been assumed to dominate these couplings in all previous interpretations of the trends in $J_{iso}$ values for complexes of this type. While it was not possible to identify the source of the anisotropy in *J* in these experiments, conclusions based solely on Fermi contact descriptions have been placed in doubt and should undergo reexamination.

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**Registry No.** *cis*-$Pt(PPh_3)_2Cl_2$, 15604-36-1; *trans*-$Pt(PPh_3)_2Cl_2$, 14056-88-3; *cis*-$Pt(PCy_3)_2Cl_2$, 105762-06-9; *trans*-$Pt(PCy_3)_2Cl_2$, 60158-99-8; *cis*-$Pt(PEt_3)_2Cl_2$, 15692-07-6; *trans*-$Pt(PEt_3)_2Cl_2$, 13965-02-1.

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