A phosphorus-31 NMR study of solid carbonylhydridotris(triphenylphosphine)rhodium(I). Unusual MAS sideband intensities in second-order NMR spin systems

GANG WU, RODERICK E. WASYLISHEN, and RONALD D. CURTIS

Department of Chemistry, Dalhousie University, Halifax, N.S., Canada B3H 4J3

Received July 25, 1991

The CP/MAS $^{31}$P NMR spectrum of carbonylhydridotris(triphenylphosphine)rhodium(I), RhH(CO)(PPh)$_3$, (1), can be described as a tightly coupled ABMX spin system ($X = 103$Rh). In contrast to the solution $^{31}$P NMR spectrum, the three equatorial phosphorus nuclei are nonequivalent in the solid state and this structural feature allows us to measure the two-bond spin–spin couplings, $J(^{31}P_{P-P})$. A new method is proposed for extracting the principal components of the chemical shift tensor from slow MAS NMR spectra in a tightly $J$-coupled two-spin system. For compound 1, the principal components of the $^{31}$P chemical shift tensors calculated using this method are in good agreement with those obtained from NMR spectra of a static sample. The principal components of the $^{31}$P chemical shift tensors determined for 1 are compared with those reported previously for Wilkinson’s catalyst, RhCl(PPh)$_3$. The $\delta_{xy}$ component of the $^{31}$P chemical shift tensors in 1 shows the largest variation with structure. This is ascribed to differences in the orientation of the P–C$_{eq}$ bond about the equatorial plane of the trigonal bipyramidal structure.

Key words: rhodium–phosphine compounds, AB spin system, $^{31}$P chemical shift tensor, magic-angle spinning, molecular structure.

Introduction

Carbonylhydridotris(triphenylphosphine)rhodium(I), RhH(CO)(PPh)$_3$, (1), is one of the most important commercial homogeneous catalysts (1–3). In solution, $^{31}$P NMR studies indicate that 1 is capable of undergoing dissociation to generate RhH(CO)(PPh)$_2$ as indicated in eq. [1].

$$\text{[1]} \quad \text{RhH(CO)(PPh$_3$) + PPh$_3$} \xrightarrow{\text{+ PPh$_3$}} \text{RhH(CO)(PPh$_2$)}$$

The latter species is an active catalyst for alkene hydrogeration and hydroformylation (4). The dissociation of a triphenylphosphine ligand from 1 is apparent from $^{31}$P NMR ligand exchange studies in toluene solution (5). For example, when a large excess of triphenylphosphine is added to a toluene solution of 1, the doublet at $\delta(^{31}P) = 39.8$ ppm ($J(^{103}Rh, ^{31}P) = 155$ Hz) arising from RhH(CO)(PPh)$_3$ broadens and shifts to a lower frequency ($\delta(^{31}P) = -7.2$ ppm for free triphenylphosphine ligands). Typical exchange rates for dissociation are on the order of 50 s$^{-1}$ at 25°C for a solution containing a 6:1 excess of PPh$_3$. The observation of a simple doublet in the $^{31}$P NMR spectrum of 1 in toluene solution suggests that all three PPh$_3$ groups are chemically equivalent and that they occupy the equatorial sites of a trigonal bipyramid as deduced from X-ray diffraction studies (6).

The yellow crystals of RhH(CO)(PPh)$_3$ are monoclinic and belong to the space group $P2_1/n$ ($C_{2h}$). Examination of the X-ray diffraction results indicates that each of the three PPh$_3$ ligands is nonequivalent due to slight variations in structure (see Fig. 1). One of the primary objectives of the present study is to demonstrate that the $^{31}$P cross-polarization (CP) magic-angle spinning (MAS) NMR spectrum of 1 is sensitive to these subtle structural differences. As well, we describe a general procedure for analyzing the AB portion of a slow MAS NMR spectrum to obtain average principal components of the A and B spin chemical shift tensors. The CP/MAS $^{31}$P NMR spectrum of 1 is analyzed as the ABM portion of a general ABMX spectrum where X = 103Rh ($I = \frac{3}{2}$). The NMR parameters obtained from our solid-state study are compared with corresponding solution NMR studies (5) and with related solid-state NMR studies on Wilkinson’s catalyst, RhCl(PPh)$_3$ (7).

Theory

For an isolated or uncoupled spin-1/2 nucleus, it is well-known that the analysis of slow MAS NMR spectra is ca-

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1 Author to whom correspondence may be addressed.
pable of yielding the principal components of the chemical shift (CS) tensor and, hence, the chemical shift anisotropy (8–14). Such techniques are particularly attractive in cases where the MAS spectrum consists of several isotropic peaks, making the analysis of the corresponding static powder NMR spectrum very difficult. The most widely used procedure for analyzing slow MAS NMR spectra is the well-known Herzfeld–Berger technique (9). In cases where the spin under observation is coupled to a heteronuclear spin through direct dipole–dipole and indirect spin–spin (J) interactions, the relative intensity of the peaks in the J-coupled multiplet in each spinning sideband is modulated by the dipolar and J interactions as well as the chemical shift anisotropy (10, 15).

If the dipolar coupling and the anisotropy in J (AJ) are negligible, then the heteronuclear J-coupled multiplet observed with MAS NMR will show regular fine structure similar to that observed in solution NMR spectra. However, this is not generally true if two nuclei are strongly J-coupled, i.e., an AB spin pair. In such a case, even if the dipolar coupling and ΔJ are zero, it is still possible to have AB multiplets with different relative intensity in each spinning sideband because the mixing between the |eβ⟩ and ||α⟩ states becomes orientation dependent in an AB spin system.

Consider a strongly J-coupled spin pair, A and B, each with anisotropic chemical shift and isotropic J coupling (the dipolar interaction between the two spins is assumed to be negligible). The resulting four transitions, νi, and their relative intensities, Pi, are given by eq. [2]:

\[ P_i = \frac{1}{4} (v_1 + v_2 + v_3 + v_4) = \frac{1}{2} (v_A + v_B) \]

The transition ν0 is not observable, but can be easily constructed in a slow MAS NMR spectrum. Its calculated position appears at the centre of a J-coupled AB multiplet and its intensity is the average of all four peaks. It should be noted, however, that the intensity distribution of such constructed spinning sidebands still cannot be characterized by a single chemical shift tensor, since each constructed sideband equals the average of sidebands due to the two different CS tensors of spin A and B. Only when the magnitudes of the principal components of the two CS tensors are approximately the same (not necessarily in their orientations) can one analyze the constructed sidebands with the usual methods (9, 11, 12) and recover the elements of the chemical shift tensor.

Theoretical justification of the above procedure can be made by applying the Floquet Hamiltonian theory to a homonuclear spin-1/2 pair in rotating solids (16). Assuming that the sample spinning rate is much greater than the isotropic J coupling between the two nuclei of an AB spin pair, one can rewrite eq. 17 in ref. 16 and obtain the intensities of the four transitions in the i th order spinning sideband, P′i, as follows (dipolar interactions and ΔJ are ignored):

\[ P'_i = Y_{i}I'_A + Y_{i}I'_B \]

where D = [(νA − νB)2 + ΔJ2]1/2. If (θA, φA) and (θB, φB) are used to define the orientation of the applied magnetic field B0 in the principal axis system of the two chemical shielding tensors, A and B, respectively, then νA and νB are

\[ \nu_A = \nu_0[1 - (\sigma_{11}^A \sin^2 \theta_A \cos^2 \phi_A + \sigma_{22}^A \sin^2 \theta_A \sin^2 \phi_A + \sigma_{33}^A \cos^2 \theta_A)] \]

\[ \nu_B = \nu_0[1 - (\sigma_{11}^B \sin^2 \theta_B \cos^2 \phi_B + \sigma_{22}^B \sin^2 \theta_B \sin^2 \phi_B + \sigma_{33}^B \cos^2 \theta_B)] \]

It is clear from eqs. [2] and [3] that because of the term D each transition characterizes a more complicated powder line shape than that of an isolated nucleus with anisotropic chemical shift. Therefore, the previous method of analyzing spinning sidebands in a slow MAS NMR spectrum (9) is not directly applicable to a tightly J-coupled AB spin pair, since in this case the envelope of spinning sidebands associated with each transition cannot be characterized by three distinct principal components of a chemical shift tensor.

Fortunately, if we take the average of the four transitions in eq. [2], the term D can be removed and the expressions of both transition frequency and intensity become very simple:

\[ P_0 = \frac{1}{4} (P_1 + P_2 + P_3 + P_4) = \frac{1}{2} (v_A + v_B) \]
Y_1 = \frac{1}{2} (1 - \cos \Psi - \sin \Psi)

Y_2 = \frac{1}{2} (1 + \cos \Psi + \sin \Psi)

Y_3 = \frac{1}{2} (1 - \cos \Psi + \sin \Psi)

Y_4 = \frac{1}{2} (1 + \cos \Psi - \sin \Psi)

\text{and } \sin \Psi = J/D. I_A' \text{ and } I_B' \text{ are the intensities of the } i\text{'th order spinning sideband due to the chemical shift tensors of spin A and spin B, respectively, in the absence of any spin–spin interaction. From eq. [5], it is easy to show that the average intensity of the } J\text{-coupled multiplet in the i' th order spinning sideband becomes independent of the } J \text{ interaction, i.e.,}

[6] \quad \frac{1}{4} (P_{1i} + P_{2i} + P_{3i} + P_{4i}) = \frac{1}{2} (I_A' + I_B')

\text{Furthermore, it is interesting to note in eq. [5] that the relative intensity of peaks in the } J\text{-coupled multiplet deviates from that obtained in solution NMR studies. For example, the relative intensity of } P_{1i} \text{ and } P_{2i} \text{ is given as}

[7] \quad P_{1i} = \frac{(1 - \sin \Psi) (I_A' + I_B') - \cos \Psi (I_A' - I_B')}{(1 + \sin \Psi)(I_A' + I_B') - \cos \Psi (I_A' - I_B')}

P_{2i} = \frac{(1 + \sin \Psi)(I_A' + I_B') - \cos \Psi (I_A' - I_B')}{(1 - \sin \Psi)(I_A' + I_B') - \cos \Psi (I_A' - I_B')}

\text{Obviously, if } I_A' \neq I_B', \text{ this ratio is different from } (1 - \sin \Psi)/(1 + \sin \Psi), \text{ which is the ratio expected for an AB spin pair in the solution NMR spectrum.}

\text{Inspection of eqs. [5] and [7] reveals the following general features regarding the MAS NMR spectrum of two tightly } J\text{-coupled spins: (1) the relative intensities of the four peaks in an } AB \text{ multiplet vary depending on the order of the spinning sidebands, (2) the relative intensities of the } AB \text{ multiplets become distorted in comparison with those obtained in solution NMR studies, and (3) only in the case where the spinning rate is so high that all spinning sidebands are of negligible intensity (i.e., } I_A = I_B = 1 \text{ for the isotropic peaks) do the MAS spectra restore the normal } AB \text{ patterns observed in solution.}

\textbf{Experimental}

\text{Carbonylhydridotris(triphenylphosphine)rhodium(I), } \text{I, was purchased from Aldrich Chemical Company and was used for the present NMR study without further purification. The yellow crystals of } I \text{ were ground and packed into a zirconium oxide rotor (7 mm o.d.). Phosphorus-31 CP/MAS NMR spectra were obtained on a Bruker MSL-200 NMR spectrometer ( } B_0 = 4.70 \text{ T) operating at 81.033 MHz. All spectra were acquired at 20°C with high-power proton decoupling during data acquisition. Cross polarization was accomplished under the Hartmann–Hahn match condition using 90° pulses of 4 μs. Typical values of the contact time were 2–5 ms and the recycle time was 10 s. Sample spinning rates ranged from 2 to 4 kHz. The magic angle was adjusted by examining the } ^{31}\text{Br NMR signal of KBr [17]. All } ^{31}\text{P spectra were referenced to } 85\% \text{ H}_3\text{PO}_4(\text{aq}) \text{ by using solid NH}_4\text{H}_2\text{PO}_4 \text{ as a secondary reference. The latter compound has a chemical shift of } +0.81 \text{ ppm with respect to } 85\% \text{ H}_3\text{PO}_4(\text{aq}). \text{ The acquisition time was 106 ms and the 8 K FID was zero-filled to 16 K prior to Fourier transformation. The line widths at half-height in the MAS NMR spectra were approximately 25 Hz. No improvement in the line width was observed by using longer acquisition times.}

\text{The static } ^{31}\text{P NMR spectrum of a powdered sample of } I \text{ was obtained on a Varian Unity-400 NMR spectrometer ( } B_0 = 9.40 \text{ T) using a slightly modified Varian } 7\text{-mm MAS probehead. Proton and phosphorus } 90° \text{ pulse lengths for cross polarization were } 5 \mu s \text{ with a decoupling field strength in excess of 90 kHz. The contact time was 2.5 ms with an acquisition time of 35 ms and a recycle time of 20 s. The audiofrequency filters were opened to their maximum values, 100 kHz, in order to observe the } ^{31}\text{P NMR signal approximately } 12 \mu s \text{ after the cross-polarization period. This was found to help alleviate spectral distortions associated with a loss of information in the first few data points. A sensitivity enhancement corresponding to } 50 \text{ Hz of line broadening was applied to the FID prior to Fourier transformation.}

\text{The phosphorus-31 NMR spectrum of a toluene solution of } I \text{ (50 mg in } 2.0 \text{ mL) was obtained at } 146.12 \text{ MHz on a Nicolet 360 NB NMR spectrometer with broadband proton decoupling. The solution sample was prepared under a nitrogen environment and sealed in a } 10\text{-mm NMR tube. The NMR spectrum was recorded at room temperature (20°C) and was referenced to external } 85\% \text{ H}_3\text{PO}_4(\text{aq}).

\text{Simulation of the isotropic portion of the MAS NMR spectra was accomplished by the LAME8 program [18]. All the spinning sideband analyses were performed using a Simplex program based on the Herzfeld–Berger method [9]. The static powder line shape was calculated by simply overlapping three independent CS powder patterns.}

\textbf{Results and discussion}

\text{The } ^{31}\text{P CP/MAS NMR spectra of } I \text{ is shown in Fig. 2. The presence of intense first and second-order spinning sidebands indicates that the } ^{31}\text{P chemical shift anisotropies are large compared with the sample spinning frequency, } 4.0 \text{ kHz. The isotropic portion of the } ^{31}\text{P CP/MAS spectrum of } I \text{ is shown in Fig. 3a. Since the three } ^{31}\text{P nuclei are nonequivalent in the solid state, all the possible } J \text{ couplings between } ^{31}\text{P–}^{31}\text{P and } ^{31}\text{P–}^{103}\text{Rh are readily resolved in the high-resolution, solid-state NMR spectrum. The calculated spectrum is also shown in Fig. 3b and best-fit parameters are summarized in Table 1. The resultant pattern suggests an ABM spin system in } I \text{ (A, B, and M represent the three } ^{31}\text{P nuclei; } X = ^{103}\text{Rh}). \text{ The three isotropic chemical shifts were determined to be 45.35, 34.34, and 33.84 ppm compared to the single chemical shift (41.15 ppm) obtained from a solution NMR spectrum. The assignment of three phosphorus chemical shifts to } P_1, P_2, \text{ and } P_3 \text{ shown in Fig. 1 is based on arguments regarding the relative magnitudes of the principal components of the chemical shift tensors (vide infra). It is readily seen from Fig. 3 that, although all the observed line positions are well reproduced (rms deviation } < 0.8 \text{ Hz), the intensities of the outer peaks of the } AB \text{ portion in the simulated spectrum are significantly smaller than the observed intensities. As discussed in the theory section, this is due to the strong } J \text{ coupling and the orientation-dependent chemical shifts in the solid state, so that the } AB \text{ pattern in the MAS spectrum of } I \text{ differs from that expected in solution.}

\text{The one-bond } ^{103}\text{Rh–}^{31}\text{P coupling constants, } J^{(103}\text{Rh,}^{31}\text{P)} \text{, in } I \text{ fall in the normal range reported for related rhodium(I) compounds (19, 20) and agree well with the value observed for the same compound in toluene solution. The three essentially equal } J^{(103}\text{Rh,}^{31}\text{P)} \text{ values confirm that the three phosphorus atoms are at equatorial sites, since } J^{(103}\text{Rh,}^{31}\text{P}_{eq} \text{ has been found to be smaller than } J^{(103}\text{Rh,}^{31}\text{P}_{eq} \text{ (19). Following previous solution NMR investiga-}
Fig. 2. The CP/MAS $^{31}$P NMR spectrum of 1. Sample spinning frequency was 4.0 kHz. The orders of the spinning sidebands are numbered by the usual convention, i.e., positive signs refer to the low-frequency sidebands relative to the isotropic peaks. A small impurity peak is indicated by *.

In Table 2, the principal components of phosphorus CS tensors in 1, obtained from analysis of the MAS NMR spectrum, are given. To confirm the accuracy of these values, a static powder spectrum was obtained at a high magnetic field ($B_0 = 9.40$ T). Analysis of the static powder spectrum (shown in Fig. 5a) permits the determination of the principal components for all three $^{31}$P chemical shift tensors in 1. Since the dipolar couplings and $J$ couplings (ca. 150 Hz) are much

Unusual AB patterns also appear in the different order spinning sidebands as observed in the isotropic part of the slow MAS NMR spectrum. In Fig. 4 several spinning sidebands are shown for easy comparison. It is clear that the relative intensities of peaks within the high-frequency multiplet (M spin) remain essentially unchanged in the different order spinning sidebands, while the relative intensities of peaks within the AB part vary dramatically.

In fact, the relative intensities of peaks within the M-spin multiplet do change very slightly, presumably due to the small deviation from first-order $J$ coupling between the M spin and the other two spins, or due to the residual homonuclear dipolar interactions among the $^{31}$P nuclei in 1.
smaller than the chemical shift anisotropies in Hz (Δν = ν₁₁ − ν₃₃ ≈ 24 kHz at B₀ = 9.40 T), it is reasonable to analyze the static powder line shape by simple overlapping of the three independent chemical shift powder patterns. The calculated ³¹P NMR static powder line shape is also shown in Fig. 5b. It is evident that all of the main shoulders of the experimental line shape are reproduced in the calculated spectrum. The anomalous features at the low-frequency end of the static line shape were also observed at B₀ = 4.70 T.

These features may be attributed to the second-order J coupling effect between P₁ and P₃, or to the homonuclear dipolar coupling between the three ³¹P nuclei. Nonetheless, the effect is small and does not influence the determination of the principal components in the present case. The results obtained from analysis of the static powder line shape (also shown in Table 2) clearly indicate that analysis of the MAS NMR spectrum gives reasonable estimates of the principal components for P₂ (M spin), while for P₁ and P₃ (A and B spins) it yields the averaged values of the corresponding principal components. Also, it is clear that the principal components of the CS tensors for P₁ and P₃ differ by less than 15 ppm.

In Table 2 the values of the chemical shift anisotropy (Δδ = δ₁₁ − δ₃₃) observed for the three ³¹P nuclei of 1 are comparable to those reported previously (7) for the mutually trans phosphorus nuclei in the approximately square planar RhCl(PPh₃)₃. Wilkinson’s catalyst, the only rhodium–phosphorus complex for which complete ³¹P shielding data are available (24). It is interesting to note that the variation of the δ₁₁ components of the three ³¹P chemical shift tensors in 1 is relatively small: furthermore, the three δ₁₁ components in 1 are similar to the corresponding components at the mutually trans ³¹P nuclei in RhCl(PPh₃)₃. Since the orientation of δ₁₁ has been determined to be almost parallel to the Rh–P bond in RhCl(PPh₃)₃ (7), it is reasonable to expect that δ₁₁ of the ³¹P chemical shift tensor also lies along the Rh–P bond for each ³¹P nucleus in 1. Thus, the chemical shieldings along the Rh–P bond in compound 1 are probably similar to those at the two mutually trans phosphorus nuclei in RhCl(PPh₃)₃. Also, the three δ₁₁ components in 1 have approximately the same values as those of the mutually trans ³¹P nuclei in RhCl(PPh₃)₃.

In contrast to δ₁₁ and δ₁₂, the δ₁₃ component of the ³¹P CS tensors in 1 shows large variations and all three δ₁₃ components deviate from the corresponding values in RhCl(PPh₃)₃. From Table 2 it is readily seen that the unique high-frequency isotropic chemical shift at P₂ in 1 is mainly due to the significant deshielding of the δ₁₃ component. From a solution ³¹P NMR study, significantly different isotropic chemical shifts have been found in different conformers associated with rotation of the phenyl groups about the Rh–P bond in trans-[RhX(CO)L₃] complexes (X = halogen; L = tertiary phosphine) (25). Therefore, two distinct isotropic shifts (ca. 45 and 34 ppm) observed in 1 may also reflect the local orientation of the phenyl groups with respect to the trigonal bipyramidal structure in the solid state. Since the unique

### Table 1. Best-fit parameters from the ³¹P CP/MAS NMR spectrum of RhH(CO)(PPh₃)₃

<table>
<thead>
<tr>
<th>ISOTROPIC CHEMICAL SHIFT</th>
<th>³¹P CP/MAS NMR SPECTRUM OF RHX(CO)(PPh₃)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ(P1)</td>
<td>34.34</td>
</tr>
<tr>
<td>δ(P2)</td>
<td>45.35</td>
</tr>
<tr>
<td>δ(P3)</td>
<td>33.84</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>COUPLING CONSTANT</th>
<th>J (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J(¹⁰⁰Rh,³¹P₁)</td>
<td>−156</td>
</tr>
<tr>
<td>J(¹⁰⁰Rh,³¹P₂)</td>
<td>−154</td>
</tr>
<tr>
<td>J(¹⁰⁰Rh,³¹P₃)</td>
<td>−156</td>
</tr>
<tr>
<td>J(³¹P₁,³¹P₂)</td>
<td>+109</td>
</tr>
<tr>
<td>J(³¹P₁,³¹P₃)</td>
<td>+113</td>
</tr>
<tr>
<td>J(³¹P₂,³¹P₃)</td>
<td>+111</td>
</tr>
</tbody>
</table>

The ³¹P[¹H] NMR spectrum of 1 in toluene solution at room temperature consists of a doublet arising from the coupling of three ³¹P nuclei with ¹⁰⁰Rh nucleus (δ = 41.15 ppm, J(¹⁰⁰Rh,³¹P) = 154 Hz).

The estimated error in the chemical shifts is ±0.12 ppm.

The estimated error in the spin–spin coupling constants is ±5 Hz.
isotropic shift at 45.15 ppm results from deshielding of the \( \delta_{23} \) component that is perpendicular to the Rh—P bond, it is reasonable to associate the variations in \( \delta_{23} \) with the different orientations of the P—C\(_{iso}\) bonds at each of the three phosphorus sites. This argument is supported by the X-ray crystal structure of 1 where the dihedral angles of (OC)—Rh—P—C\(_{iso}\) for the three phosphorus sites are P1(−64, +55, +176), P2(+7, +129, −112), and P3(−177, −54, +64) (6). The relative orientation of the phenyl groups is unique at P2. Since the principal components of the \(^{31}\)P CS tensors at P1 and P3 are similar, the assignment of P1 and P3 remains ambiguous.

It is worth noting that in a recent \(^{31}\)P NMR study of a series of solid cyclic and acyclic phosphorus–metal complexes, \( \delta_{23} \) was reported to be much more sensitive to the local geometry at the phosphorus atoms than \( \delta_{11} \) and \( \delta_{33} \) (26). Similarly, we have found evidence that the \( \delta_{22} \) component of the \(^{31}\)P chemical shift tensors in 1 is sensitive to the local orientation of the phenyl groups. However, work on \(^{31}\)P chemical shielding in phosphine–metal complexes is just

**TABLE 2. Principal components of the \(^{31}\)P chemical shift tensors in RhH(CO)(PPh\(_3\)) and RhCl(PPh\(_3\))**

<table>
<thead>
<tr>
<th>RhH(CO)(PPh(_3))</th>
<th>RhCl(PPh(_3))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MAS</strong></td>
<td><strong>Static</strong></td>
</tr>
<tr>
<td>P1, P3, P2</td>
<td>P1, P3, P2</td>
</tr>
<tr>
<td>( \delta_{11} )</td>
<td>107 109</td>
</tr>
<tr>
<td>( \delta_{22} )</td>
<td>52 89</td>
</tr>
<tr>
<td>( \delta_{33} )</td>
<td>−57 −62</td>
</tr>
<tr>
<td>( \Delta \delta )</td>
<td>164 171</td>
</tr>
</tbody>
</table>

\(^a\) All principal components are in ppm and estimated errors are less than ±5 ppm.
\(^b\) All principal components are in ppm and estimated errors are ±2 ppm.
\(^c\) From ref. 7.
beginning and details of how the principal components of chemical shift tensors correlate with the structural parameters are still not fully understood. Therefore, our assignment must be regarded as tentative. Further investigations of phosphorus shift tensors in metal phosphine compounds are in progress in our laboratory.

Summary

We have shown that the relative intensities of the NMR transitions observed for tightly coupled spin systems in the high-resolution MAS NMR spectra of solids do not correspond to those calculated using the conventional high-resolution Hamiltonian applicable to second-order spectra in isotropic solutions. The Herzfeld–Berger method cannot be used directly to recover the principal components of a chemical shift tensor when one of the spins is a part of an AB spin system. Here, we have proposed and successfully applied a simple procedure to recover the average $^{31}$P chemical shift tensors for the AB spin pair in RhH(CO)(PPh$_3$)$_2$. The $\delta_{11}$ and $\delta_{12}$ components are similar to those obtained for the two mutually trans $^{31}$P nuclei in the square planar complex, RhCl(PPh$_3$)$_2$. The intermediate components of the $^{31}$P chemical shift tensors in RhH(CO)(PPh$_3$)$_2$, RhCl(PPh$_3$)$_2$, and related compounds (26) show the largest variation with molecular structure and it is this component that is mainly responsible for variations of $\delta_{120}$ in these compounds.

Acknowledgements

We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support. We thank Mr. Bill Kenny of Varian for making it possible for us to obtain $^{31}$P NMR spectra of 1 at 9.40 T, and Dr. F. Morin, McGill University, for obtaining $^{31}$P NMR spectra at 7.05 T. Finally, we thank Professors T. S. Cameron and O. Knop for helpful discussions concerning the reported X-ray results of compound 1.