Spinning-Frequency-Dependent ^{31}P MAS NMR Spectra of Square-Planar Metal–Phosphine Complexes

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The spinning-frequency dependencies of ^{31}P magic-angle-spinning (MAS) NMR spectra of two square-planar bis(phosphine)metal complexes, $[Ir(PPh_2Me)_2(COD)][PF_6]$ (**1**) and *cis*-$Pt(PEt_3)_2Cl_2$ (**2**), are investigated. Both phosphine ligands of $[Ir(PPh_2Me)_2(COD)][PF_6]$ are found to be crystallographically equivalent, while in the case of *cis*-$Pt(PEt_3)_2Cl_2$, the two phosphine ligands are crystallographically distinct. It is shown that ^{31}P MAS NMR spectra may exhibit similar spinning-frequency-dependent splittings regardless of whether or not the phosphine ligands are crystallographically equivalent. Also, it is demonstrated that carrying out ^{31}P MAS NMR experiments at different applied magnetic fields is an effective method of eliminating the ambiguity associated with determining whether or not two phosphine ligands are crystallographically equivalent.

Introduction

Magic-angle-spinning (MAS), combined with cross-polarization (CP) and high-power proton decoupling, has been routinely utilized to obtain high-resolution NMR spectra of dilute spins such as ^{13}C, ^{15}N, and ^{31}P nuclei in solid materials.[1–4] This combination of techniques has been used to study a large number of metal–phosphine complexes in the solid state.[2,5–20] It is well-known that the analysis of MAS NMR spectra is relatively straightforward if the dilute spin system under investigation can be treated as consisting of "isolated" spins.[21,22] However, in many inorganic systems it is common to have two nuclear spins of the same kind adjacent to one another.[20,23] For example, the two mutually *cis* ^{31}P nuclei in square-planar bis(phosphine)metal complexes form such a homonuclear spin-pair. In a classic paper, Maricq and Waugh[21] first demonstrated that MAS NMR spectra arising from dipolar-coupled spin-pairs may exhibit doublet structures when the two coupled nuclei are crystallographically equivalent but magnetically nonequivalent.[24] They further showed that the combination of homonuclear dipolar coupling and anisotropic chemical shielding is responsible for such doublet features in the MAS NMR spectra of crystallographically equivalent spins. Before proceeding, it is important to emphasize that in the solid state two spins are magnetically equivalent if and only if their positions in space are related by a center of inversion. This element of symmetry ensures that the two nuclei of a spin-pair will have the same chemical shift at all orientations of their internuclear axis in the magnetic field. On the other hand, two nuclei related by a C_2 axis and not a center of inversion will generally have different chemical shifts for a general orientation of their internuclear vector in the applied magnetic field, even though their average or isotropic chemical shifts must be identical. The two nuclei of such a spin-pair will be crystallographically equivalent but magnetically nonequivalent.

Recently, MAS NMR spectra arising from crystallographically equivalent two-spin systems were further investigated.[25–27] For example, Hayashi and Hayamizu[25] and Kubo and McDowell[26] independently studied ^{31}P MAS NMR spectra of $Na_4P_2O_7{\cdot}10H_2O$, where the two ^{31}P nuclei in the pyrophosphate anion are crystallographically equivalent but magnetically nonequivalent. Both groups reported spinning-frequency-dependent ^{31}P NMR line shapes, as predicted by Maricq and Waugh.[21] In particular, the single peak observed at slow or rapid spinning frequencies splits into two peaks at intermediate spinning frequencies. Another interesting solid-state effect occurs when the two crystallographically equivalent but magnetically nonequivalent spins of a spin-pair are also *J*-coupled.[28–33] Under such circumstances it has been shown that the homonuclear *J* interaction can

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be reintroduced in the MAS NMR spectra even though the two nuclei have identical isotropic chemical shifts.[28] That is, for a pair of crystallographically equivalent spins, up to four peaks may be observed in MAS NMR spectra. Moreover, it has been found that the four-line spectra of such spin systems may be unusual compared to well-known AB spectra in solution NMR studies.[31–33] In particular, the *J*-recoupled ^{31}P MAS NMR spectra of some bis(phosphine)metal complexes exhibit spectra in which $^{2}J(^{31}P,^{31}P)$ is given by splittings between alternate peaks in the four-line multiplet as opposed to outer splittings as observed in solution NMR spectra.[31–33]

For spin systems consisting of two crystallographically nonequivalent homonuclear spins, MAS NMR spectra may also be sensitive to the sample spinning frequency.[27,34–36] For example, in the ^{31}P MAS NMR spectra of several rhodium(I)–phosphine complexes, we have noticed some unusual features concerning the relative intensities of the spinning sidebands.[16,37] These features may be attributed to the fact that the ^{31}P nuclei are tightly *J*-coupled. In a more recent study, we derived general theoretical expressions to describe spinning-frequency-dependent MAS NMR spectra arising from second-order (AB) two-spin systems.[38]

The aforementioned anomalous features recently observed in MAS NMR spectra can be attributed to "solid-state effects", since they all originate from the anisotropic nature of the nuclear spin interactions present in solids. Solid-state ^{31}P NMR spectroscopy has often been used to obtain information concerning crystallographic equivalence, which in turn may be compared with results obtained from X-ray diffraction experiments.[20] Therefore, it is important to understand how the appearance of ^{31}P MAS NMR spectra can be related to the crystallographic equivalence of the ^{31}P nuclei.[39–45] In this paper we investigate the spinning-frequency-dependent ^{31}P MAS NMR spectra of two square-planar bis(phosphine)metal complexes, $[Ir(PPh_2Me)_2(COD)][PF_6]$ (**1**) and *cis*-$Pt(PEt_3)_2Cl_2$ (**2**). Our NMR results indicate that the two *cis*-phosphine ligands of compound **1** are crystallographically equivalent but magnetically nonequivalent. In contrast, the phosphine ligands of compound **2** are known to be crystallographically nonequivalent. The importance of carrying out MAS experiments at two different fields is demonstrated.

Experimental Section

Samples of bis(methyldiphenylphosphine)(1,5-cyclooctadiene)iridium(I) hexafluorophosphate, $[Ir(PPh_2Me)_2(COD)][PF_6]$ (**1**), and *cis*-dichlorobis(triethylphosphine)platinum(II), *cis*-$Pt(PEt_3)_2Cl_2$ (**2**), were obtained from Aldrich Chemical Co. and used without further purification.

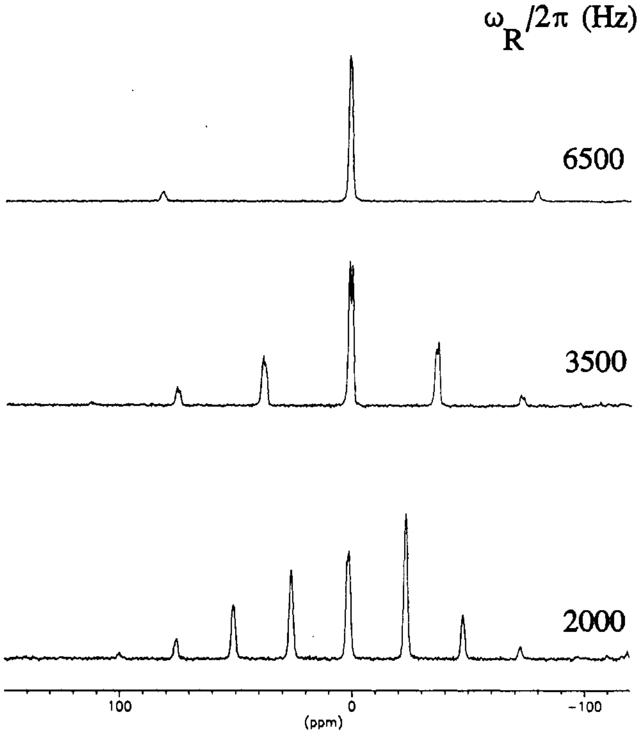

Figure 1. ^{31}P MAS NMR spectra of **1** obtained at 4.70 T with different sample spinning frequencies. The low-frequency septet centered at −143 ppm due to PF_6^- with $^{1}J(^{31}P,^{19}F)$ = 712 Hz is not shown.

All ^{31}P MAS NMR spectra were recorded on Bruker MSL-200 (B_0 = 4.70 T) and Bruker AMX-400 (B_0 = 9.40 T) spectrometers operating at ^{31}P NMR frequencies of 81.0 and 162.0 MHz, respectively. Carbon-13 CP/MAS and dipolar-dephased (nonquarternary carbon suppression) experiments[46] were also performed on the Bruker MSL-200 spectrometer operating at 50.3 MHz. The crystalline samples were packed into zirconium oxide rotors, 7- and 4-mm o.d., for the low- and high-field experiments, respectively. Cross polarization from protons to ^{31}P and ^{13}C nuclei under the Hartmann–Hahn match condition and high-power proton decoupling were employed for the acquisition of all ^{31}P and ^{13}C MAS NMR spectra. Typical ^{1}H 90° pulses were 4.0–5.0 μs for the low-field experiments and 3.5–4.0 μs for the high-field experiments. Contact times of 3–5 ms were used for experiments at both fields. The sample spinning frequency ranged from 1.0 to 6.5 kHz at 4.70 T and from 1.5 to 12.0 kHz at 9.40 T. The sample spinning frequency was controlled using Bruker MAS pneumatic units and was stable within ±2 Hz during all ^{31}P MAS NMR experiments. All ^{31}P NMR spectra were referenced with respect to 85% H_3PO_4(aq) by setting the ^{31}P NMR peak of solid $NH_4H_2PO_4$ to 0.81 ppm. Carbon-13 CP/MAS spectra were referenced with respect to TMS by using solid adamantane as an external secondary reference sample. In the dipolar-dephased ^{13}C experiments, a dephasing delay of 40 μs was used.

Results and Discussion

Phosphorus-31 MAS NMR spectra of $[Ir(PPh_2Me)_2(COD)][PF_6]$ (**1**) obtained at three different sample spinning frequencies are shown in Figure 1. With a sample spinning frequency of 6.5 kHz, the ^{31}P MAS NMR spectrum of **1** obtained at 4.70 T consists of a single strong peak flanked by weak spinning sidebands. This indicates that the sample spinning frequency is comparable to the anisotropic nuclear spin interactions, which in the case of **1** is dominated by the anisotropic ^{31}P chemical shift. Compound **1** is expected to be square-planar with the two phosphine ligands *cis* to one another; observation of a single peak in the ^{31}P MAS NMR spectra obtained at the rapid spinning limit implies that the two mutually *cis* ^{31}P nuclei are crystallographically equivalent with an isotropic chemical shift of 1.03 ppm. We also carried out ^{13}C CP/MAS and dipolar-dephased experiments on **1**. The two methyl groups give rise to a single ^{13}C NMR peak with an

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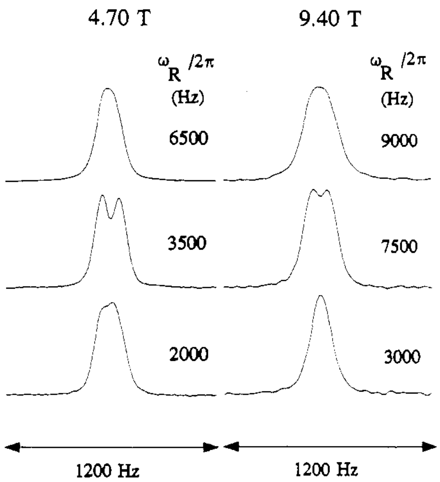

Figure 2. Expansions of the isotropic region of the ^{31}P MAS NMR spectra of **1** obtained at 4.70 and 9.40 T.

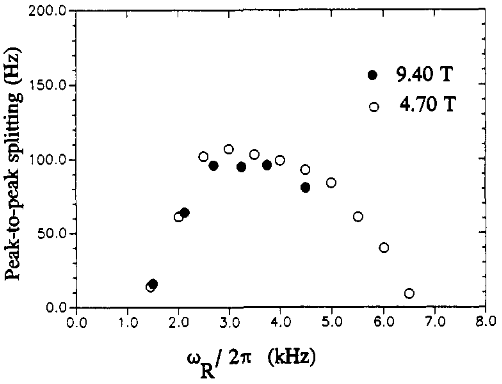

Figure 3. Plots of the peak-to-peak splitting vs the sample spinning frequency in the ^{31}P MAS NMR spectra of **1** at 4.70 and 9.40 T. Note that the spinning frequencies at 9.40 T are scaled by a factor of $^1/_2$.

isotropic carbon chemical shift of 15.5 ppm, providing further evidence for the crystallographic equivalence of the two phosphine ligands. Apparently, the crystal structure of **1** has not been reported in the literature.

Interestingly, the ^{31}P MAS NMR spectrum of **1** obtained with a spinning frequency of 3.5 kHz exhibits a doublet with the peak-to-peak splitting being equal to 103 ± 6 Hz (Figure 1). In fact, doublets are observed in the ^{31}P MAS NMR spectra in the spinning frequency range 2.0–5.5 kHz with the splitting of the doublet being sensitive to the spinning frequency. The peak-to-peak splittings range from 60 to 107 Hz. At very slow spinning frequencies ($\omega_R/2\pi < 1.5$ kHz), the doublet collapses to a single peak. The isotropic portions of the ^{31}P MAS NMR spectra of **1** obtained at two different applied magnetic fields, 4.70 and 9.40 T, are displayed in Figure 2. The ^{31}P MAS NMR spectra obtained at 9.40 T exhibit spinning-frequency-dependent behavior similar to that observed at 4.70 T. At spinning frequencies higher than 9.0 kHz, a single peak is observed. At intermediate spinning frequencies, from 4 to 9 kHz, doublets are observed in the ^{31}P MAS NMR spectra. For example, at a sample spinning frequency of 7.5 kHz, the peak-to-peak splitting of the doublet is 96 ± 6 Hz (see Figure 2). When the sample spinning frequency is decreased below 4 kHz, the doublet collapses to a single peak.

It is convenient to compare MAS NMR spectra obtained at different applied magnetic fields by introducing a scaled sample spinning frequency, ω_R/ω_0, where ω_R is the sample spinning frequency and ω_0 is the Larmor frequency.[32] In Figure 3 the peak-to-peak splittings in the ^{31}P MAS NMR spectra are plotted as a function of the scaled sample spinning frequencies. That is, for the data obtained at 4.70 T, the actual sample spinning frequencies are used whereas, for data obtained at 9.40 T, the sample spinning frequencies are scaled by a factor of $^1/_2$. It is interesting to note that the two curves shown in Figure 3 are approximately coincident. That is, the spinning-frequency dependence of the ^{31}P MAS NMR spectra of **1** is *independent* of the applied magnetic field, provided that scaled spinning frequencies are used (*vide infra*). This observation will be rationalized later in the discussion.

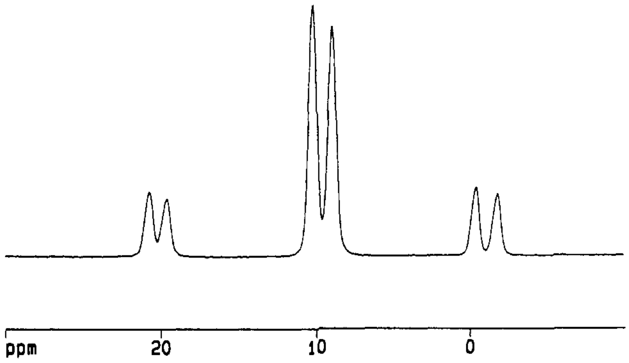

Figure 4. Isotropic region of the ^{31}P MAS NMR spectrum of **2** at 9.40 T. The sample spinning frequency was 9000 Hz.

It is also worth mentioning that multiplets due to $^1J(^{31}P,^{191/193}Ir)$ have not been observed in the ^{31}P MAS NMR spectra of iridium(I)–phosphine complexes,[47–48] even though both naturally occurring isotopes of iridium are magnetically active, ^{191}Ir ($I = {}^3/_2$, NA = 37.3%) and ^{193}Ir ($I = {}^3/_2$, NA = 62.7%). Both of these isotopes have very large quadrupole moments; hence quadrupolar relaxation is expected to be extremely efficient, particularly at elevated temperatures. Rapid quadrupolar relaxation of the iridium nuclei will lead to "self-decoupling". For the same reason, $^{31}P,^{201}Hg$ spin–spin splittings are rarely observed in ^{31}P CP/MAS spectra of mercury–phosphine complexes even though the values of $^1J(^{31}P,^{201}Hg)$ are known to be large.[49]

The isotropic portion of a typical ^{31}P MAS NMR spectrum of *cis*-Pt(PEt$_3$)$_2$Cl$_2$ (**2**) is shown in Figure 4. The spectrum consists of two intense central peaks flanked by satellite peaks which arise from indirect spin–spin coupling with ^{195}Pt ($I = {}^1/_2$, NA = 33.8%). The observation of two intense central peaks in the ^{31}P MAS NMR spectrum of **2** appears to be consistent with the structure derived from X-ray diffraction studies, which indicate that the two phosphorus nuclei are crystallographically nonequivalent.[50] However, it is interesting to note that the peak-to-peak splitting of the doublet is sensitive to the sample spinning frequency.[35] The spinning-frequency dependence of the splitting observed at 4.70 T (see Figure 5) is quite similar to that observed for **1** where the two ^{31}P nuclei are crystallographically equivalent. Therefore, it is dangerous to conclude that the two ^{31}P nuclei of **2** are crystallographically nonequivalent simply because a doublet is observed. To further study the spinning-frequency dependence of the ^{31}P MAS NMR spectra of **2**, we carried out variable-spinning-frequency ^{31}P MAS experiments at a higher magnetic field, 9.40 T. At 9.40 T the ^{31}P MAS NMR spectra of **2** also exhibit spinning-frequency-dependent doublets. However, in contrast to the spectrum of **1**, the peak-to-peak splitting of the doublet increases by a factor of approximately 1.5 at the higher field (see Figure 5). In addition, the sensitivity of the peak-to-peak splitting to the sample spinning frequency is considerably reduced for ^{31}P MAS NMR spectra at the higher field (*vide infra*).

In the discussion which follows, we shall provide qualitative rationalizations of the above observations. In a previous study,[38]

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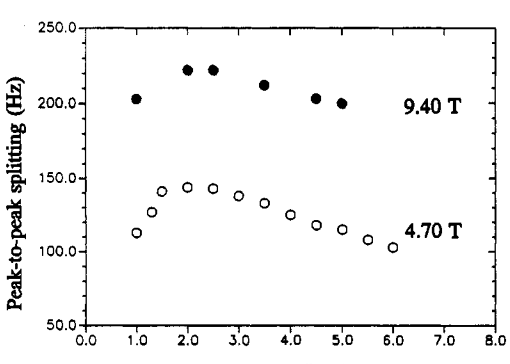

Figure 5. Plots of the peak-to-peak splitting vs the sample spinning frequency in ^{31}P MAS NMR spectra of **2** at 4.70 and 9.40 T. The sample spinning frequencies at 9.40 T are scaled by a factor of $^1/_2$.

we derived general expressions for peak positions and relative intensities of MAS NMR spectra arising from dipolar-coupled homonuclear two-spin systems on the basis of average Hamiltonian theory. It is well-known that, for square-planar bis(phosphine) complexes of iridium(I) and platinum(II) metals, $^2J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{cis}}$ is usually too small to be observed in solid-state one-dimensional (1D) ^{31}P CP/MAS spectra.[16,17,20,51,52] Assuming $^2J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{cis}} = 0$, the four allowed transitions derived for a general "AB" spin-pair reduce to two transitions of equal intensity.[38] The separation of the two peaks, D, can be written in frequency units as

$$D = [(\delta - G)^2 + F^2 + K^2]^{1/2} \qquad (1)$$

where δ is the isotropic chemical shift difference between the two spins in frequency units. The K, F, and G terms are high-order corrections to the average Hamiltonian and they are given by

$$K = \sum_{n=0}^{+\infty} \frac{k_{2n+1}}{\omega_R^{\,2n+1}}, \quad F = \sum_{n=1}^{+\infty} \frac{f_{2n}}{\omega_R^{\,2n}}, \quad G = \sum_{n=1}^{+\infty} \frac{g_{2n}}{\omega_R^{\,2n}} \qquad (2)$$

where k_{2n+1}, f_{2n}, and g_{2n} are $(2n + 1)$ and $2n$th correction coefficients, respectively. They are functions containing the principal components of the chemical shift tensors, the dipolar coupling constant, and the relative orientation of the chemical shift tensors with respect to the dipolar vector. Although exact expressions for these coefficients are complex, it can be shown[32] that the following relationships hold:

$$k_{2n+1} \propto (\Delta\nu)^{2n+1}R, \quad n = 0, 1, 2, \ldots \qquad (3)$$

$$f_{2n} \propto (\Delta\nu)^{2n}R, \quad n = 1, 2, 3, \ldots \qquad (4)$$

$$g_{2n} \propto (\Delta\nu)R^{2n}, \quad n = 1, 2, 3, \ldots \qquad (5)$$

where $\Delta\nu$ represents the instantaneous chemical shift difference of the two spins in frequency units and therefore is proportional to the applied magnetic field; R is the direct dipolar coupling constant between the two spins, $R = (\mu_0/4\pi)(\hbar/2\pi)\gamma_P^{\,2}\langle r_{PP}^{\,-3}\rangle$.

In the fast spinning limit, $\omega_R \rightarrow +\infty$, the high-order terms K, F, and G approach zero and the separation between the two peaks equals the actual isotropic chemical shift difference; i.e., $D = \delta$ (see eq 1). At slower spinning frequencies, i.e., when the sample spinning frequency is smaller than the chemical shift anisotropies, the high-order terms K, F, and G become important and they introduce additional shifts for the two peaks in the MAS spectra. Since the high-order terms are cross terms between the homonuclear dipolar interaction and the anisotropic chemical shift interaction, they are proportional to products of both interactions (see eqs 3–5). Therefore, the influence of small dipolar couplings can be amplified if the coupled nuclei have relatively large chemical shift anisotropies. For example, while ^{31}P–^{31}P homonuclear dipolar coupling constants are on the order of 300–500 Hz for two mutually *cis* phosphorus nuclei in square-planar metal–phosphine complexes, ^{31}P chemical shift anisotropies are usually on the order of 50–100 ppm, corresponding to 4–8 kHz at 4.70 T. Under such circumstances, the separation between the two peaks in MAS spectra differs from the actual isotropic chemical shift difference between the two nuclei. Clearly, since the high-order terms K, F, and G are sensitive to the sample spinning frequency, the resultant additional shifts for the two peaks are also dependent upon the sample spinning frequency, leading to a spinning-frequency-dependent splitting. Only at the rapid spinning limit, i.e., when the spinning frequency is much greater than *all* anisotropic nuclear spin interactions, do MAS NMR spectra correspond to solution NMR spectra. The relative intensities of the spinning sidebands to the isotropic peaks provide an indication of whether or not the rapid spinning limit has been achieved.

For a spin-pair containing two crystallographically equivalent ^{31}P nuclei, the implication of eq 1 is more interesting. In this case, even though the isotropic chemical shift difference between the two ^{31}P nuclei vanishes, i.e., $\delta = 0$, it is still possible to observe two peaks in ^{31}P MAS spectra.[25-27] The peak-to-peak splitting in ^{31}P MAS NMR spectra can be written as

$$D = (G^2 + F^2 + K^2)^{1/2} \qquad (6)$$

Clearly, this splitting results from high-order terms and is sensitive to the sample spinning frequency. When the rapid spinning condition is satisfied, K, F, and G approach zero and a single peak results. Under slow spinning conditions, however, two peaks will be observed in MAS spectra.

As we have noticed from Figures 3 and 5, the peak-to-peak splittings for compounds **1** and **2** behave differently as the applied magnetic field is changed. Since these experiments yield valuable information concerning the crystallographic equivalence of the two coupled nuclei, a more detailed discussion is necessary.

From eqs 3–5 it is clear that if $\Delta\nu$ is much greater than R, the g_{2n} terms are less important than the terms k_{2n+1} and f_{2n}. On the other hand, the term g_{2n} will contribute significantly to D if $\Delta\nu \ll R$. It is important to note that when the scaled spinning frequency is used, k_{2n+1} and f_{2n} are *independent* of the applied magnetic field, whereas g_{2n} is proportional to $(1/\omega_0)^{2n-1}$. Previously observed ^{31}P MAS NMR spectra arising from two crystallographically equivalent spins indicate that the g_{2n} terms are usually negligible.[32] In Figure 3 the observation of two approximately coincident curves implies that the g_{2n} correction terms are indeed negligible for **1**; therefore, in this case, D is independent of the applied magnetic field. It is a general observation that the MAS line widths increase in frequency units (Hz) with the applied magnetic field. This may obscure splittings at high magnetic fields. As expected, for the ^{31}P MAS NMR spectra of **1** at the high field, 9.40 T, the line widths are slightly greater than those at 4.70 T and the two peaks are less well resolved, although the corresponding peak-to-peak splittings are essentially the same for the spectra at both fields.

When two ^{31}P nuclei are crystallographically nonequivalent, as is the case for compound **2**, the presence of the isotropic chemical shift difference term, δ, in eq 1 will introduce a different field dependence for the peak-to-peak splitting in ^{31}P MAS NMR spectra. Since the isotropic chemical shift difference, δ, is doubled

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(51) Pregosin, P. S.; Kunz, R. W. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E.; Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1979; Vol. 16.

(52) Crumbliss, A. L.; Topping, R. J. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers, Inc.: Deerfield Beach, FL, 1987; p 531.

in frequency units by increasing the magnetic field strength from 4.70 to 9.40 T, the splitting of the doublet, *D*, is also increased (see Figure 5). However, since *D* also contains high-order terms *K* and *F*, which are independent of the applied magnetic field, the overall increase in *D* is attenuated compared with the actual field increase. For the case of compound **2**, where the two coupled ^{31}P nuclei are crystallographically nonequivalent, *D* increases approximately by a factor of 1.5 as the applied field strength is doubled. Only at the rapid spinning limit when the splitting approaches the actual isotropic chemical shift difference does the ratio between splittings obtained at different fields correspond to the ratio of the applied fields. It is readily seen from Figure 5 that, at the rapid spinning limit, the peak-to-peak splitting approaches 100 and 200 Hz for the data obtained at 4.70 and 9.40 T, respectively. These values yield the actual isotropic chemical shift difference, $\delta = 1.23$ ppm. Having established that the two phosphine ligands in **2** are crystallographically nonequivalent, it is clear that the values of $^1J(^{31}\text{P},^{195}\text{Pt})$ are 3423 and 3469 Hz for the high- and low-frequency peaks, respectively.

Another interesting feature associated with the field dependence of the peak-to-peak splitting in MAS spectra of compound **2** is the sensitivity of the splitting to the sample spinning frequency. Since the spinning-frequency dependence of MAS NMR spectra results only from high-order correction terms, a large δ will reduce the relative contributions from high-order correction terms and therefore will quench the spinning-frequency dependence of *D* (see eqs 1 and 2). Therefore, the sensitivity of the peak-to-peak splitting to the spinning frequency for ^{31}P MAS NMR spectra of **2** is considerably reduced by carrying out the MAS experiment at a higher field. If even higher fields are used, δ may become large enough to completely quench the spinning-frequency dependence of the MAS NMR spectra.

Conclusions

In summary, we have shown that doublets may be observed in ^{31}P MAS NMR spectra of typical square-planar metal–phosphine complexes regardless of the crystallographic equivalence of the two *cis* phosphine ligands. In either case, the peak-to-peak splitting of the doublet may be sensitive to the sample spinning frequency; hence, care must be exercised in deducing whether or not two ^{31}P nuclei are crystallographically equivalent.

The phenomena reported here are expected to occur frequently in ^{31}P MAS NMR spectra of other metal–phosphine complexes when two ^{31}P nuclei are adjacent to one another. In fact, ^{31}P MAS NMR spectra of several metal–phosphine complexes exhibit two closely separated peaks;[20] it is also a common practice to correlate the number of peaks observed in ^{31}P MAS NMR spectra with the number of phosphorus atoms in the asymmetric unit determined from X-ray crystallography studies. However, in light of the present study, many of the previous ^{31}P MAS NMR spectra may need to be reexamined. If the rapid spinning limit cannot be reached in practice, it is important to study ^{31}P MAS NMR spectra by varying the sample spinning frequency over a large range. In addition, carrying out MAS NMR experiments at different applied magnetic fields proves to be an effective way to eliminate the ambiguity concerning the crystallographic equivalence of the ^{31}P nuclei.

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