Observation of ^{31}P−^{31}P Indirect Spin−Spin Coupling in Copper−Bis(phosphine) Complexes by Two-Dimensional Solid-State NMR

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The first observations of ^{31}P−^{31}P indirect spin−spin (J) coupling in copper(I) phosphine complexes are reported for solid Cu(PPh$_3$)$_2$X (X = NO$_3^-$, BH$_4^-$). Values of $^2J(^{31}P,^{31}P)$, 157 ± 5 and 140 ± 5 Hz for Cu(PPh$_3$)$_2$NO$_3$ and Cu(PPh$_3$)$_2$BH$_4$, respectively, have been obtained from two-dimensional (2D) J-resolved ^{31}P NMR spectra obtained under slow magic-angle spinning (MAS) conditions. In both complexes, the two phosphine ligands are crystallographically equivalent; thus, the two ^{31}P nuclei have identical isotropic chemical shifts. Under rapid sample spinning conditions, the ^{31}P MAS NMR spectra exhibit relatively sharp overlapping asymmetric quartets arising from $^1J(^{63/65}Cu,^{31}P)$ and residual $^{63/65}$Cu−^{31}P dipolar interactions. No evidence of $^2J(^{31}P,^{31}P)$ is apparent from the spectra obtained with rapid MAS; however, under slow MAS conditions there is evidence of homonuclear J-recoupling. Peak broadening due to heteronuclear dipolar interactions precludes measurement of $^2J(^{31}P,^{31}P)$ from standard 1D ^{31}P MAS NMR spectra. It is shown that this source of broadening can be effectively eliminated by employing the 2D J-resolved experiment. For the two copper(I) phosphine complexes investigated in this study, the peak widths in the f_1 dimension of the 2D J-resolved ^{31}P MAS NMR spectra are about three times narrower than those found in the corresponding 1D ^{31}P MAS NMR spectra.

Introduction

Phosphorus-31 NMR spectroscopy is a standard technique used by chemists to study phosphorus-containing organic compounds and metal complexes.[1−4] In solution, many of the transition-metal phosphine complexes are kinetically labile; thus, low-temperature NMR experiments are often required to properly characterize these complexes. In such cases, it is advantageous to obtain NMR spectra in the solid state. The combination of cross polarization (CP) and magic-angle spinning (MAS) has made high-resolution solid-state ^{31}P NMR spectroscopy an extremely versatile tool for studying phosphorus-containing metal complexes.[5] An increasing number of publications dealing with ^{31}P CP/MAS NMR studies of metal phosphine complexes have appeared in the recent literature.[6] Very recently, some new spectral features have been observed in ^{31}P CP/MAS NMR spectra of metal phosphine complexes which contain a pair of crystallographically equivalent ^{31}P nuclei.[7−13]

Copper(I) phosphine complexes were among the first metal phosphine complexes studied by researchers using high-resolution solid-state ^{31}P NMR spectroscopy.[14,15] Since then, solid-state ^{31}P NMR spectroscopy has been routinely used for the characterization of a great variety of copper(I) phosphine complexes.[16−28] Despite the diversity of the copper(I) complexes that have been studied, the ^{31}P CP/MAS NMR spectra of these complexes exhibit similar features. The spectra

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generally consist of two overlapping asymmetric quartets arising from indirect spin−spin (*J*) and residual dipolar couplings of the ^{31}P nuclei to the two magnetically active copper isotopes, ^{63}Cu ($I = {}^3/_2$, natural abundance = 69.09%) and ^{65}Cu ($I = {}^3/_2$, 30.91%). In solution NMR studies, however, the indirect spin−spin coupling, $^1J(^{63/65}\mathrm{Cu},^{31}\mathrm{P})$, has been observed only in very symmetric species, e.g., $[\mathrm{Cu}((\mathrm{P(OCH_3)_3})_4]^+$,[29] where the electric field gradient at the copper nucleus is very small.

Although values of $^1J(^{63/65}\mathrm{Cu},^{31}\mathrm{P})$ are potentially available from ^{31}P CP/MAS NMR spectra of copper(I) phosphine complexes, to the best of our knowledge, values of $^2J(^{31}\mathrm{P},^{31}\mathrm{P})$ have never been reported for any copper phosphine complex. This is somewhat surprising considering the fact that values of $^2J(^{31}\mathrm{P}-\mathrm{M}-^{31}\mathrm{P})$, M = metal, have been reported for numerous transition-metal phosphine complexes involving almost all transition metals including the two other members of group 11, silver and gold. Here we wish to report the first observation of $^2J(^{31}\mathrm{P},^{31}\mathrm{P})$ for two copper(I) phosphine complexes, $\mathrm{Cu(PPh_3)_2X}$ ($\mathrm{X} = \mathrm{NO_3}^-, \mathrm{BH_4}^-$), using two-dimensional (2D) *J*-resolved ^{31}P CP/MAS NMR spectroscopy. One of the primary objectives of this paper is to demonstrate the power of 2D *J*-resolved ^{31}P CP/MAS NMR spectroscopy in achieving spectral resolution far superior to that of corresponding 1D spectra.

Experimental Section

$\mathrm{Cu(PPh_3)_2X}$ ($\mathrm{X} = \mathrm{NO_3}^-, \mathrm{BH_4}^-$) were prepared according to literature procedures.[30,31] Solid-state ^{31}P NMR spectra were obtained using a Bruker MSL-200 spectrometer operating at 81.03 MHz for phosphorus. The spectra were obtained using a Bruker double-air-bearing MAS probe and zirconium dioxide rotors (7 mm o.d.). The sample spinning frequency was stable to within ±5 Hz. Cross polarization under the Hartmann−Hahn match condition and high-power proton decoupling were used to acquire all solid-state ^{31}P NMR spectra. The 90° pulse width, contact time, and recycle time were 3.9 μs, 5 ms, and 30 s, respectively. Typically, 16 transients were recorded for each of the 1D ^{31}P CP/MAS NMR spectra. For 2D *J*-resolved ^{31}P CP/MAS NMR spectra, the standard sequence with an eight-step phase cycling scheme was used.[32] The t_1 increment was synchronized with the sample rotation period. For each t_1 increment, a total of 32 transients were collected. A total of 40 t_1 increments were recorded and zero-filled to 128 prior to the 2D Fourier transformation. The digital resolution in the f_1 dimension of the 2D *J*-resolved ^{31}P CP/MAS NMR spectra was 5 Hz/point. Phosphorus chemical shifts were referenced with respect to 85% $\mathrm{H_3PO_4(aq)}$. Finally, ^{31}P CP/MAS NMR spectra were also obtained under rapid MAS conditions at 162 MHz using a Bruker AMX-400. These spectra were used to obtain values of $^1J(^{63/65}\mathrm{Cu},^{31}\mathrm{P})$ (*vide infra*).

Results and Discussion

The ^{31}P CP/MAS NMR spectra of $\mathrm{Cu(PPh_3)_2NO_3}$ obtained at 4.7 T with three different sample spinning frequencies are shown in Figure 1. The spectrum obtained at the highest sample spinning frequency, $\omega_R/2\pi = 4.800$ kHz, is typical of ^{31}P CP/MAS NMR spectra for copper(I) phosphine complexes.[14−28] The observed overlapping asymmetric quartets arise from *J* and residual dipolar couplings of the ^{31}P nuclei to the only two naturally occurring copper isotopes, ^{63}Cu and ^{65}Cu. Since these two isotopes have similar magnetogyric ratios, $\gamma(^{65}\mathrm{Cu})/\gamma(^{63}\mathrm{Cu}) = 1.071$, only the outer peaks of the quartets are resolved. The quartets are somewhat distorted, particularly at low applied magnetic field strengths, because the axis of quantization for the quadrupolar copper isotopes is not exactly coincident with the direction of the applied magnetic field, $\boldsymbol{B}_0$. Under these conditions MAS is not effective in completely averaging the $^{63/65}\mathrm{Cu}-^{31}\mathrm{P}$ dipolar interaction. As a result, the splittings between adjacent peaks in each quartet are not exactly equal to *J*. The analysis of such spectra has been described in detail in the previous literature, first by Menger and Veeman[15] and more recently by Olivieri.[25] Here, it is sufficient to indicate that from measurements at two relatively high applied magnetic fields, it is possible to obtain the phosphorus chemical shift and values of $J(^{63/65}\mathrm{Cu},^{31}\mathrm{P})$. From ^{31}P CP/MAS NMR spectra of $\mathrm{Cu(PPh_3)_2NO_3}$ obtained at 4.7 and 9.4 T, $\delta_{\mathrm{iso}} = 0.3 \pm 0.2$ ppm, $^1J(^{63}\mathrm{Cu},^{31}\mathrm{P}) = 1460 \pm 10$ Hz, and $^1J(^{65}\mathrm{Cu},^{31}\mathrm{P}) = 1565 \pm 10$ Hz. The value obtained here for $^1J(^{63}\mathrm{Cu},^{31}\mathrm{P})$ is in excellent agreement with that previously estimated by Menger and Veeman, 1450 Hz.[15] The observation of a single phosphorus site for $\mathrm{Cu(PPh_3)_2NO_3}$ (*i.e.*, one chemical shift for the two phosphine ligands) is consistent with the known crystal structure of this complex which indicates that the two phosphine ligands are related by a C_2 axis of symmetry which bisects the P−Cu−P angle.[33] Thus, the two ^{31}P nuclei are crystallographically equivalent and are expected to have identical isotropic chemical shifts, as observed. However, the two phosphorus nuclei of $\mathrm{Cu(PPh_3)_2NO_3}$ are not related by an inversion center; thus, they are magnetically nonequivalent. For example, consider a particular molecule in the bulk sample for which the applied magnetic field lies along one of the Cu−P internuclear vectors. Clearly the neighboring phosphorus nucleus will experience a slightly different applied magnetic field since the phosphorus magnetic shielding interaction is orientation-dependent in this system. For $\mathrm{Cu(PPh_3)_2NO_3}$, the two phosphorus shielding tensors of the two phosphine ligands have the same principal components, but their orientations are not coincident. Previously, it has been shown that ^{31}P MAS NMR spectra of such spin systems contain information about $^2J(^{31}\mathrm{P},^{31}\mathrm{P})$ providing that the spectra are acquired under *slow* sample spinning

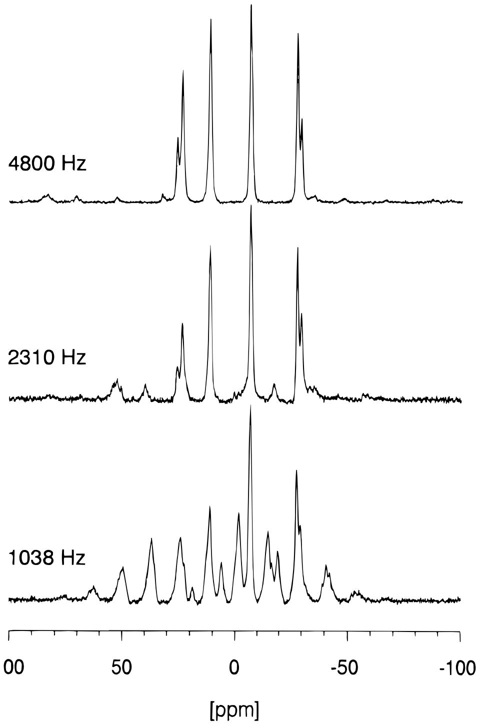

Figure 1. One-dimensional ^{31}P CP/MAS NMR spectra of $\mathrm{Cu(PPh_3)_2NO_3}$ obtained at 81.03 MHz (4.7 T) as a function of the sample spinning frequency, $\omega_R/2\pi$.

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conditions.[7−13,34] For example, under slow spinning conditions, we recently observed triplet patterns in ^{31}P CP/MAS NMR spectra of Ag(P(*m*-tolyl)$_3$)$_2$NO$_3$, where the two phosphine ligands are also crystallographically equivalent but magnetically nonequivalent.[13] Analysis of spectra obtained at several sample spinning frequencies indicates that $^2J(^{31}P,^{31}P) = 140 \pm 10$ Hz in the latter complex. Measurement of homonuclear spin−spin coupling constants between an isolated spin pair is impossible in solution NMR if the nuclei have identical isotropic chemical shifts!

Close inspection of the ^{31}P CP/MAS spectrum of Cu(PPh$_3$)$_2$NO$_3$ obtained with $\omega_R/2\pi = 1.038$ kHz (see Figure 1) indicates that several of the peaks, including the spinning sidebands, are broadened. On the basis of the above discussion,[7−11,13] the observed broadening suggests the presence of unresolved splittings arising from $^2J(^{31}P,^{31}P)$. Unfortunately, it is impossible to determine $^2J(^{31}P,^{31}P)$ from the spectra shown in Figure 1 because of the extent of the line broadening. Examination of the spectra also reveals that the line widths of the peaks increase as the sample spinning frequency decreases. For example, when the sample is spun at 4.800 kHz, the line widths of the peaks are approximately 80 Hz; with $\omega_R/2\pi = 1.038$ kHz, the line widths of the peaks are as large as 400 Hz. It is also interesting to note that the four peaks within the asymmetric quartet exhibit different line widths. The two high-frequency peaks are always broader than their low-frequency counterparts. In addition, the spinning sidebands associated with the two high-frequency isotropic peaks in the asymmetric quartet are more intense than those arising from the two low-frequency isotropic peaks.

The severe line broadening observed in the slow ^{31}P CP/MAS NMR spectra of Cu(PPh$_3$)$_2$NO$_3$ may arise from two major sources. First, the large nuclear quadrupolar interactions experienced by the copper nuclei in these systems (nuclear quadrupolar coupling constants are typically on the order of 50 MHz)[25] lead to a break-down of the high-field approximation, which as already mentioned, means that the heteronuclear dipolar interactions between ^{31}P and $^{63/65}$Cu nuclei are not averaged by MAS. In the case of Cu(PPh$_3$)$_2$NO$_3$, the direct ^{63}Cu−^{31}P dipolar coupling constant is approximately 1.12 kHz. The residual $^{63/65}$Cu,^{31}P dipolar interactions are orientation dependent and give rise to line broadening. Second, the line broadening may arise from multiplet structure due to nonzero values of $^2J(^{31}P,^{31}P)$. Fortunately, the residual $^{63/65}$Cu,^{31}P dipolar interactions are *inhomogeneous* in the sense defined by Maricq and Waugh;[35] hence, they can be refocused by applying a 180° pulse to the ^{31}P nuclei. This immediately suggests the use of various spin-echo NMR techniques such as homonuclear *J*-resolved spectroscopy. The utility of the 2D *J*-resolved ^{31}P CP/MAS experiment for studying several other metal−phosphine complexes in the solid state has been previously demonstrated.[32,36,37]

The 2D *J*-resolved ^{31}P CP/MAS NMR spectrum of Cu(PPh$_3$)$_2$NO$_3$ obtained with $\omega_R/2\pi = 1.11$ kHz is shown in Figure 2, together with the corresponding 1D ^{31}P CP/MAS spectrum. Although the line widths of the peaks in the 1D spectrum range from 120 to 400 Hz, the peaks in the 2D *J*-resolved spectrum are significantly narrower in the f_1 dimension, ca. 40 Hz. This line width is approximately a factor of 2 smaller than that of the 1D CP/MAS spectra obtained at rapid sample spinning frequencies. Therefore, peaks arising from *J*-recoupling between the two crystallographically equivalent ^{31}P nuclei in Cu(PPh$_3$)$_2$NO$_3$ can be clearly resolved. Thus, directly from the 2D spectrum, $|^2J(^{31}P,^{31}P)|$ was determined to be 157 ± 5 Hz. The absolute sign of $^2J(^{31}P,^{31}P)$ is expected to be positive, analogous to $^2J(^{31}P,^{31}P)$ in [Au(PMe$_3$)$_2$]$^+$,[38] which is the only system where the sign of ^2J(P,P) in metal phosphine complexes involving the group 11 metals has been determined. In the 2D spectrum shown in Figure 2, the strong peaks appearing at $f_1 = 0$ arise from the well-known strong-coupling effect.[39] Similar strong-coupling peaks have also been observed in the 2D *J*-resolved ^{31}P CP/MAS spectra of other metal phosphine complexes.[13,32] From the 2D spectrum shown in Figure 2, it is also clear that each of the peaks in the 1D ^{31}P CP/MAS spectrum is composed of three peaks. However, the peaks in the 1D spectrum are so broad that the three individual peaks are unresolved. As mentioned earlier, this type of triplet structure was also observed in ^{31}P CP/MAS NMR spectra of Ag(P(*m*-tolyl)$_3$)$_2$NO$_3$ obtained with slow spinning.[13]

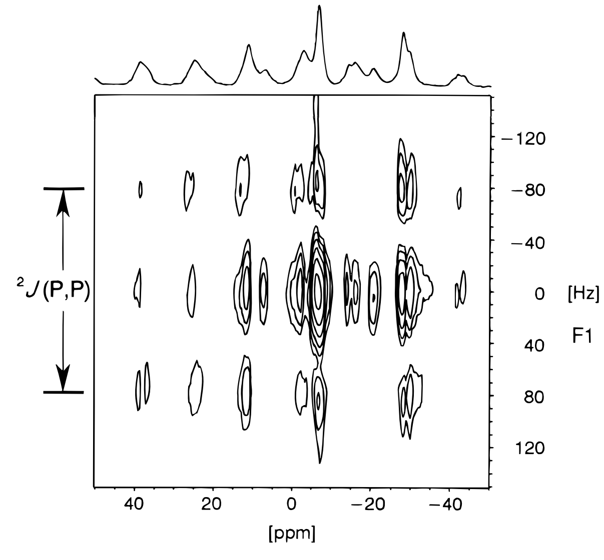

Figure 2. One- and two-dimensional *J*-resolved ^{31}P CP/MAS NMR spectra of Cu(PPh$_3$)$_2$NO$_3$ obtained at 4.7 T with $\omega_R/2\pi = 1.11$ kHz.

The ^{31}P CP/MAS NMR spectra of Cu(PPh$_3$)$_2$BH$_4$ exhibit features very similar to those described for the ^{31}P CP/MAS spectra of Cu(PPh$_3$)$_2$NO$_3$. The crystal structure of Cu(PPh$_3$)$_2$BH$_4$ indicates that the two phosphine groups are also related by a C_2 axis of symmetry.[40] From 1D ^{31}P CP/MAS NMR spectra of Cu(PPh$_3$)$_2$BH$_4$ obtained at 4.7 and 9.4 T, the following parameters were obtained: $\delta_{iso} = -0.7 \pm 0.2$ ppm and $^1J(^{63}Cu,^{31}P) = 1163 \pm 10$ Hz. It is noted that the value of $^1J(^{63}Cu,^{31}P)$ for Cu(PPh$_3$)$_2$BH$_4$ is smaller than that for Cu(PPh$_3$)$_2$NO$_3$. The 2D *J*-resolved ^{31}P CP/MAS NMR spectrum of Cu(PPh$_3$)$_2$BH$_4$ obtained with $\omega_R/2\pi = 1.317$ kHz is shown in Figure 3, together with the corresponding 1D ^{31}P CP/MAS spectrum. Similar to the 2D spectrum of the nitrate analog, the line widths of the peaks in the 2D *J*-resolved spectrum of Cu(PPh$_3$)$_2$BH$_4$ are approximately 40 Hz along the f_1 dimension. This allows for the direct determination of $^2J(^{31}P,^{31}P)$ from the 2D spectrum, 140 ± 5 Hz.

On the basis of the two compounds investigated in this study, it is probably meaningless to speculate about the structural features that might influence $^1J(^{63}Cu,^{31}P)$ and $^2J(^{31}P,^{31}P)$.

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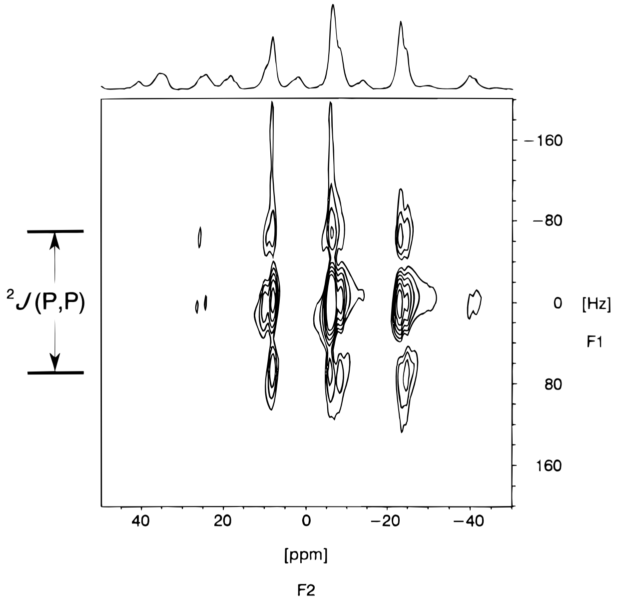

Figure 3. One- and two-dimensional *J*-resolved ^{31}P CP/MAS NMR spectra of $Cu(PPh_3)_2BH_4$ obtained at 4.7 T with $\omega_R/2\pi = 1.317$ kHz.

However, we note that r_{Cu-P} is slightly shorter in the nitrate complex (2.256 *vs* 2.276 Å).[33,40] As well, X-ray crystallography indicates that the P−Cu−P angle in the nitrate is larger than that in the borohydride (131.2 *vs* 123.26°). Both sets of spin−spin coupling data exhibit trends previously noted by Verkade,[41] Pregosin,[42] and Jameson.[43] Finally, we note that the values of $^2J(^{31}P,^{31}P)$ in the two copper(I) complexes studied here are comparable to those found in silver phosphine complexes.[13,44]

Traditionally, $^1J(M,^{31}P)$ values have been interpreted assuming that the Fermi contact mechanism completely dominates. However, recent single-crystal ^{31}P NMR data for $Hg(PPh_3)_2(NO_3)_2$ have established that the ^{199}Hg−^{31}P **J** tensor is anisotropic with $J_{\parallel} = 8.2$ kHz and $J_{\perp} = 4.2$ kHz.[45] Clearly, other mechanisms are required in order to understand the metal−phosphorus spin−spin coupling tensor in this molecule which is closely related to those considered in this study, $Cu(PPh_3)_2X$.

Conclusions

In general, it is desirable to obtain ^{31}P CP/MAS NMR spectra of solids with rapid sample spinning, so that the resulting spectra are directly analogous to solution NMR spectra. However, it is our opinion that ^{31}P CP/MAS NMR studies carried out under slow spinning conditions should receive more attention. First, MAS NMR spectra obtained with slow sample spinning contain valuable information about anisotropic nuclear spin interactions such as chemical shift tensors and dipolar couplings. From slow MAS NMR spectra, it is also possible to obtain indirect spin−spin couplings between crystallographically equivalent spins. Second, because of the large ^{31}P chemical shift anisotropy in many metal phosphine complexes, it is simply impractical to achieve sample spinning frequencies that satisfy the rapid spinning condition. This is particularly true if one wishes to acquire spectra at high applied magnetic fields. Thus, it is important to understand the spectral properties of MAS NMR spectra obtained with slow spinning.

Interestingly, $Cu(PPh_3)_2NO_3$ was one of the first metal−phosphine complexes that was studied using solid-state ^{31}P CP/MAS NMR. In all previous ^{31}P CP/MAS NMR studies of copper phosphine complexes, the possibility of detecting ^2J(P,P) was overlooked, either because the ^{31}P nuclei involved are crystallographically equivalent or because the spectra exhibited broad peaks. It has been shown in this study how 2D *J*-resolved ^{31}P CP/MAS NMR can be used in obtaining *J* between crystallographically equivalent nuclei even when the corresponding 1D ^{31}P CP/MAS spectra consist of broad peaks. The two copper(I) phosphine compounds studied here are representative of a large number of metal−bis(phosphine) complexes where the two phosphine groups are crystallographically equivalent but magnetically nonequivalent, thus 2D *J*-resolved techniques demonstrated here should be applicable. Although the *J*-recoupling phenomenon in these types of systems was predicted some time ago,[35] it has not been observed until recently.[7−13,34] We hope this work will encourage others to investigate indirect spin−spin coupling constants between crystallographically equivalent but magnetically nonequivalent nuclei in the solid-state. Further research in our laboratory is in progress.

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