Studies of [Ag(PPh3)2]NO3, [Ag{P(CH2CH2CN)3}2]NO3 and [Ag{P(C6H4Me-m)3}2]NO3 by X-Ray Diffraction and Solid-state Nuclear Magnetic Resonance†

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Solid-state magic angle spinning (MAS) 31P NMR spectra of [Ag(PPh3)2]NO3 1, [Ag(P(CH2CH2-CN)3)2]NO3 2 and [Ag{P(C6H4Me-m)3}2]NO3 3 have been obtained. In addition, the crystal structures for 2 and 3 have been determined. The results from the high-resolution NMR study are consistent with the known structure of 1 and the structures of 2 and 3. In each case the 31P NMR spectra exhibit resolved splittings arising from 2Ag and 3Ag with V(31P-31P) values of 524, 564 and 517 Hz for 1, 2 and 3, respectively. In 1 the two phosphorus nuclei are crystallographically non-equivalent, thus analysis of the 31P NMR spectrum indicates two chemically shifted phosphorus nuclei, $\delta_1$ 9.50 and $\delta_2$ 7.67, with $V(31P-31P) = 125$ Hz. The two phosphorus nuclei of 2 are crystallographically and magnetically equivalent in the solid state as evident from the cross polarization/MAS 31P NMR spectrum, $\delta = 9.56$. Crystals of 2 are trigonal, space group $R3c\ a = 12.204(2), c = 26.418(5)\ \AA, Z = 6$. The Ag and P atoms are located on a three-fold rotation axis with Ag at the centre of inversion. The Ag--P bond distance is 2.93(1) Å. The conformation of the cyanophosphine ligands in 2 is analogous to that of the ribs of an umbrella in which the silver atom is encapsulated by the six cyanogroups with an Ag...N separation of 3.439(2) Å. The two phosphorus nuclei in 3 are crystallographically equivalent but magnetically non-equivalent since the molecule sits on a two-fold axis but lacks a centre of inversion. As a consequence of this symmetry the two phosphorus nuclei have identical chemical shifts, $\delta = 11.2$; however, $V(31P-31P)$ can be determined from slow MAS experiments. For 3 the space group is orthorhombic $Abca, a = 15.142(1), b = 24.917(2), c = 10.2536(7)\ \AA, Z = 4$. The two phosphorus atoms are related by a crystallographically imposed two-fold axis. The nitrate group is chelated symmetrically to the Ag atom.

Experimental

Preparations.—Bis(triphenylphosphine)silver(nitrate, [Ag(PPh3)2]NO3 1. Compound 1 was synthesized following literature procedures. Single crystals were characterized by X-ray cell constant check and found to be identical to those reported.

Bis[tris(cyanoethylphosphine)silver(nitrate, [Ag{P(CH2CH2-CN)3}2]NO3 2. Silver nitrate (2.5 mmol) dissolved in hot acetonitrile (3 cm3) was added to a warm solution containing 2 equivalents of P(CH2CH2-CN)3 dissolved in warm ethanol (50 cm3). The warm clear solutions were allowed to cool slowly in the dark to give well formed colourless crystals, yield 85%, IR (Nujol mull): ν(CN) 2240s cm−1 (Found: C, 38.35; H, 4.60; N, 17.10. Calc. for C18H17AgN4O4P2: C, 38.85; H, 4.30; N, 17.60%), m. p. 123 °C.

Bis[tris(m-tolylphosphine)silver(nitrate, [Ag{P(C6H4Me-m)3}2]NO3 3. The preparation followed the method used for compound 2 giving colourless crystals in 80% yield (Found: C, 64.55; H, 5.45; N, 1.85. Calc. for C24H42AgNO3P2: C, 64.80; H, 5.40; N, 1.80%), m. p. 130 °C.

**Table 1** Crystallographic data

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<td>( \text{Ab2} )</td>
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<td>( c/\text{Å} )</td>
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<td>( R_1 = 0.0231, wR_2 = 0.0650 )</td>
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* \( \sum (|F_{o}| - |F_{c}|)^2/(M - N) \), where \( M \) is the number of reflections and \( N \) the number of parameters refined.

**Table 2** Atomic coordinates (\( x \times 10^4 \)) for \([\text{Ag(P(CH}_2\text{CH}_2\text{CN)}_2]_2\text{-NO}_3 \)_2]

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**Spectroscopy.** —Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer, and solution \(^{31}\text{P}\)\(^{1}\text{H}\) NMR spectra on a Varian XL-200 spectrometer using an internal deuterium lock. High-resolution solid-state NMR results were obtained on a Bruker MSL-300 spectrometer operated at 121.5 MHz for \(^{31}\text{P}\). The samples were packed into a 7 mm zirconium oxide rotor. A Bruker CP MAS broad-band probe was used. The 90° pulse for \(^{31}\text{P}\) was 5 μs and the cycle time was 60 s. The homogeneity of the static magnetic field was checked by \(^{13}\text{C}\) CP MAS NMR spectroscopy of adamantane. A linewidth of 1.5 Hz at half-maximum height was obtained. The two-dimensional J-resolved \(^{31}\text{P}\) spectrum was obtained using the pulse sequence CP-(\( t_1/2 \)-180°-\( t_1/2 \))-acquisition, with an eight-pulse-phases cycle, and the increment of \( t_1 \) was synchronized with the rotation period of the sample. All phosphorus chemical shifts are referenced to external 85% \( \text{H}_2\text{PO}_4(\text{aq}) \).

**Structure Determinations.** —Colourless crystals of \([\text{Ag}[\text{P(CH}_2\text{CH}_2\text{CN)}_2]]_2\text{-NO}_3 \)_2 and \([\text{Ag}[\text{PC}_{6}\text{H}_{4}\text{Me-m}]]_2\text{-NO}_3 \)_3 suitable for X-ray diffraction analyses were grown from a MeCN solution and a \( \text{CH}_2\text{Cl}_2 \) solution, respectively, at ambient temperatures. Refined cell parameters were determined from the setting angles of 25 reflections with \( 20 < 20 < 30° \) for 2 and 30 < 20 < 35° for 3. For 2, data were obtained at room temperature using Mo-Kα radiation (\( λ = 0.71073 \) Å) and a Nicolet R3/m diffractometer controlled by a Data General Nova 4 minicomputer. For compound 3, data were obtained at Notre Dame on an Enraf-Nonius CAD4 diffractometer equipped with a graphite-crystal, incident-beam monochromator. Friedel pairs were collected.

The data were corrected for absorption, Lorentz and polarization effects. An empirical absorption correction based on a series of \( ψ \) scans was applied.

The Laue symmetry and systematic absences were consistent with the space group \( \text{R3c} \) for compound 2 and \( \text{Ab2} \) for 3. The structure 2 was solved by direct and Fourier methods and refined using the SHELXL 93 crystallographic software package. All non-hydrogen atoms were refined anisotropically. The hydrogen-atom positions were calculated using fixed \( \text{C-H} \) bond lengths of 0.96 Å. The structure of 3 was solved by direct and Fourier methods and refined on a VAX station 3200 computer using SDP/VAX. The hydrogen-atom positions were refined isotropically and fixed for the anisotropic refinement. The isotropic thermal parameters were set to 1.1 times the \( B_{eq} \) of their bonded atoms. Refinement using the opposite chirality for the phasing produced a somewhat higher \( R_1 \) value of 0.030 82. The crystallographic details are given in Table 1. Atomic coordinates for structures 2 and 3 are listed in Tables 2 and 3, selected bond lengths and angles in Tables 4 and 5.

**Results and Discussion**

**Structures.** —The X-ray diffraction study demonstrates that the crystal structure of compound 1, \([\text{Ag[Pt}_{6}\text{H}_{4}]\text{NO}_3 \)_3, which crystallizes in the space group \( \text{P3} \), is identical to that reported previously. Although the two distinct Ag-P bond lengths are essentially identical [2.443(1) and 2.440(1) Å], the solid-state \(^{31}\text{P}\) NMR results (see below) indicate that the two phosphorus nuclei have different isotropic chemical shifts (Table 7) and are thus crystallographically non-equivalent, in agreement with the X-ray results.

A thermal ellipsoid drawing of the structure of compound 2 is shown in Fig. 1. Both the Ag and the P atoms are located on a three-fold rotational axis with the Ag at the inversion centre. The Ag-P distance is 2.3832(9) Å. The conformation of the \( \text{PCH}_2\text{CH}_2\text{CN} \) ligand in structure 2 is like the ribs of an umbrella. The silver atom is encapsulated by the six CN groups with an Ag separation of 3.439(2) Å. There
is no significant Ag-...NC interaction, which is consistent with the IR spectrum wherein the position of the v(CN) band is the same as found for the free phosphine, 2240 cm$^{-1}$. The cation has $S_6$ point-group symmetry. The nitrate ion is disordered with the N atom located on the crystallographically imposed three-fold symmetry axis. The P–Ag–P angle is 180$^\circ$. The torsional angle P–C–C–CN is 71.4(1)$^\circ$. Based on the X-ray data, the cone angle is the most frequently employed measure of the steric size character. It is a better approach than the crystallographically imposed two-fold axis. The Ag–O–Ag’ angle is 50.25(9)$^\circ$. The two phosphorus atoms are related by the crystallographically imposed two-fold axis. The Ag–P distance is 2.4128(8) Å and the P–Ag–P’ angle is 180$^\circ$.

Unlike bis(phosphine)gold(I) complexes which tend to be linear, two-co-ordinate species, the silver analogues are not readily obtained. In general, only very large and bulky tertiary phosphines form linear, two-co-ordinate complexes. Larger, less-bulky tertiary phosphines tend to form non-linear species with stronger anion co-ordination. Compound 2 is only the second example of a structurally characterized, mononuclear bis(phosphine)silver(I) complex having a strictly linear geometry. In the previous example [Ag{P(mes)$_2$}]$_2$PF$_6$ (mes = C$_6$H$_4$Me$_2$-2,4,6) the ligand cone angle is 203$^\circ$.9$^\circ$. The CP MAS spectrum (Fig. 3) shows a second-order $^{31}$P NMR-Although the crystal structure of [Ag(P(CH$_2$CH$_3$)$_2$CN)$_2$]NO$_3$ 3 determined by us is the same as that reported by Healey et al. the variations in chemical shifts of the phosphorus nuclei of sixteen peaks were resolved in our study of this ABX spin system (Fig. 3). The spectrum indicates that the two phosphorus nuclei are non-equivalent, $\delta_P$ 9.50 and $\delta_P$ 7.67, and spin–spin coupled to each other, $J^{(31)P}[^{(13)P}]$ 125 Hz. In addition, each of the four peaks of the AB portion of the spin system is split by spin–spin coupling to $^{109}$Ag (spin 1/2, natural abundance 51.82%) and $^{107}$Ag (spin 3/2, natural abundance 48.18%). Spectral analysis yields: $J^{(109)Ag[^{31}P]} = 467 \pm 6$ and $J^{(107)Ag[^{31}P]} = 524 \pm 7$ Hz. As expected, the ratio $J^{(109)Ag[^{31}P]}:J^{(107)Ag[^{31}P]}$ 1.08:1 is in good agreement with the magnetogyric ratios $\gamma^{(109)Ag}:\gamma^{(107)Ag}$ = 0.870:1. In solution, the two phosphorus nuclei of 1 have the same phosphorus chemical shift (10.75$^\circ$) and are thus chemically equivalent. Owing to rapid intermolecular phosphorus exchange in solution at the probe temperature, it is necessary to acquire spectra at low temperatures in order to resolve splittings due to silver–phosphorus spin–spin coupling. In CDC$_3$ solution at $-60^\circ$C, $J^{(107)Ag[^{31}P]} = 467 \pm 6$ and $J^{(109)Ag[^{31}P]} = 534 \pm 1$ Hz. Note that the ratio is now 0.873:1 and closer to the theoretical value of 0.870:1 because of the smaller errors associated with the solution-state measurement.

Since the $J^{(31)P}$ values (Table 7) are comparable with, but smaller than, the chemical shift difference between the two P atoms, the CP MAS spectrum (Fig. 3) shows a second-order deep ligands in an umbrella shape have been structurally characterized (Table 6). They are isoostructural and both have the metal atom (Au or Ag) encapsulated. No others are linearly two-co-ordinate species.

The structure determination of compound 3 (Fig. 2) confirms the 2:1 stoichiometry of the [Ag{P(C$_6$H$_4$Me$_2$-2,4,6)CN)$_2$]$^+$ fragment, with the nitrate group symmetrically chelating to the silver atom. The nitrate group and the silver atom are in the same plane with an Ag–O distance of 2.516(3) Å. The Ag, N and O(2) atoms lie on a crystallographic two-fold axis. The O–Ag–O’ angle is 50.25(9)$^\circ$. The two phosphorus atoms are related by the crystallographically imposed two-fold axis. The Ag–P distance is 2.4128(8) Å and the P–Ag–P’ angle is 138.1$^\circ$.14

Table 3

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Table 4

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Table 5

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Table 7

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<td>C(1)–P</td>
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<tr>
<td>C(2)–P</td>
</tr>
<tr>
<td>C(3)–P</td>
</tr>
<tr>
<td>P–Ag–O’</td>
</tr>
<tr>
<td>O(1)–O’</td>
</tr>
<tr>
<td>O(2)–N</td>
</tr>
</tbody>
</table>

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Fig. 1 Thermal ellipsoid drawing (50% probability) of [Ag(P-(CH$_2$CH$_2$CN)$_2$)$_2$]NO$_3$

Fig. 2 Thermal ellipsoid drawing (50% probability) of [Ag(P-(C$_6$H$_5$Me)$_3$)$_2$]NO$_3$

effect with irregular intensities for each $^{31}$P doublet. The two $^{31}$P atoms are close to each other, thus there is a dipole-dipole interaction between them. Such interactions can be averaged to zero by fast spinning at the magic angle. The spectral pattern depends on the spinning rate. When the instantaneous difference in the chemical shifts of the two homonuclear dipole-coupled nuclei is comparable to the coupling between them, the system shows an unusual spin-rate dependence. Such behaviour has been extensively studied.$^{5,16-34}$ Fig. 4 shows the CP MAS spectra of the sample at different spinning rates. It can be seen that the position of each peak in the isotropic region does not change with the spin rate but the peak intensities vary dramatically from sideband to sideband. The total MAS spectrum is the summation of the isotropic peaks and all the spinning sidebands (Fig. 5). It can be seen that the anomalous features for individual sidebands disappear and a symmetric spectrum is obtained at all spin rates. It was found in a previous study that the CP MAS $^{31}$P NMR spectra of cis-1,2-bis(diphenylphosphino)ethylene and trans-[Rh(CO)Cl(PPh$_3$)$_2$] have similar features.$^{32}$

The above analysis is confirmed by the $^{31}$P CP MAS

Fig. 3 The CP MAS $^{31}$P NMR spectrum of [Ag(PPh$_3$)$_2$]NO$_3$, at a rotor spinning rate of 4.0 kHz

Fig. 4 The CP MAS $^{31}$P NMR spectra of [Ag(PPh$_3$)$_2$]NO$_3$ at different rotor spinning rates: top, 4.0; middle, 2.5; bottom, 1.6 kHz

homonuclear J-resolved two-dimensional spectrum shown in Fig. 6. In this spectrum the two non-equivalent $^{31}$P atoms with different isotropic chemical shifts are not only spin-spin coupled with the silver nuclei resulting in four peaks in the F2 dimension, but are also spin–spin coupled to each other in the F1 dimension. The $^{1}J(^{107,109}Ag^{31}P)$ and $^{2}J(^{31}P^{31}P)$ data extracted match the results calculated above (Table 7).

Fig. 7 is the static CP $^{31}$P NMR spectrum of [Ag(PPh$_3$)$_2$]NO$_3$. The spectral width is about 7 kHz, which is much larger than the dipole–dipole interaction estimated to be about 212 Hz based on a distance of 4.54 A between P atoms. The difference between the two non-equivalent P atoms can be neglected because the difference between the isotropic chemical shifts of two $^{31}$P atoms is about 200 Hz. It is assumed that the chemical shift tensors of the two $^{31}$P atoms are approximately the same. In solution the two $^{31}$P atoms are equivalent. The three phenyl rings on each P are also equivalent since there is...
Table 6  Metal complexes containing the P(CH₂CH₂CN)₃ (tcep) ligand

<table>
<thead>
<tr>
<th>Compound</th>
<th>Torsional angle°</th>
<th>Conformation of ligand</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ag(tcep)₂]NO₃</td>
<td>71.4</td>
<td>Umbrella</td>
<td>This work</td>
</tr>
<tr>
<td>[Au(tcep)Cl]</td>
<td>71.4</td>
<td>Umbrella</td>
<td>15</td>
</tr>
<tr>
<td>[Ni(NCS)₂(tcep)]²⁻</td>
<td>174.6, 173.2, 78.9</td>
<td>b</td>
<td>16</td>
</tr>
<tr>
<td>[Ni(NCS)₃(tcep)]₆⁺</td>
<td>178.6, 175.8, 37.4</td>
<td>b</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>176.4, 167.5, 88.4</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>b⁺</td>
<td>179.1, 179.0, 67.2</td>
<td>b</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>169.8, 84.4, 60.6</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td></td>
<td>180.0, 171.1, 70.6</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>[HgBr₂(tcep)₂]₂⁺</td>
<td>171.3, 170.2, 74.5</td>
<td>b</td>
<td>18</td>
</tr>
<tr>
<td>[Cr(CO)₆(tcep)]</td>
<td>176.8, 169.3, 72.5</td>
<td>b</td>
<td>19</td>
</tr>
<tr>
<td>[Mo(CO)₆(tcep)]</td>
<td>176.8, 169.3, 72.5</td>
<td>b</td>
<td>19</td>
</tr>
<tr>
<td>[NiBr₂(tcep)₂]</td>
<td>179.8, 172.0, 66.3</td>
<td>b</td>
<td>20</td>
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<tr>
<td>[HgCl₂(tcep)₂]</td>
<td>171.3, 160.8, 49.0</td>
<td>b</td>
<td>21</td>
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<tr>
<td></td>
<td>151.3, 120.8, 49.1</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>[AuCl₂(tcep)]³⁺</td>
<td>178.9, 70.9, 61.6</td>
<td>b</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>176.9, 169.9, 66.8</td>
<td>b</td>
<td>22</td>
</tr>
<tr>
<td>[Ni₂(OCO)₆(tcep)₆⁺]</td>
<td>179.5, 179.5, 179.5</td>
<td>Inverted umbrella</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>175.4, 167.9, 87.2</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>[HgBr₂(tcep)₂]³⁺</td>
<td>176.1, 175.1, 172.6</td>
<td>Inverted umbrella</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>177.2, 174.6, 173.6</td>
<td>Inverted umbrella</td>
<td></td>
</tr>
<tr>
<td>trans-[PtCl₂(tcep)₂]</td>
<td>179.0, 171.0, 166.5</td>
<td>Inverted umbrella</td>
<td>15</td>
</tr>
<tr>
<td>[Au₂(S₂CO)₂(tcep)₂]</td>
<td>177.9, 166.4, 62.2</td>
<td>b</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>177.8, 167.8, 149.7</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>[MoₓCl₄(tcep)₃(NCMe)₃]MeCN</td>
<td>174.7, 173.9, 165.4</td>
<td>Inverted umbrella</td>
<td>25</td>
</tr>
</tbody>
</table>

*a P–C–C–CN. Only the absolute value of the angle was used. Crystallographic errors are generally ±0.1°. b Between the umbrella and inverted umbrella. c Polymorph.

Table 7  Phosphorus-3¹ CP MAS NMR parameters

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ ± 0.05</th>
<th>¹J(¹⁰⁷,¹⁰⁹Ag–³¹P) ± 6 Hz</th>
<th>²J(³¹P–³¹P) ± 6 Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ag(PPh₃)₂]NO₃</td>
<td>9.50, 7.67</td>
<td>467, 524</td>
<td>125</td>
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<tr>
<td>[Ag(P(CH₂CH₂CN)₃)₂]NO₂</td>
<td>-9.56</td>
<td>496, 564</td>
<td></td>
</tr>
<tr>
<td>[Ag(P(CH₂CH₂CN)₃)₂]NO₃</td>
<td>11.2</td>
<td>453, 517</td>
<td></td>
</tr>
</tbody>
</table>

* See ref. 35.

Fig. 5 Total MAS spectra of [Ag(PPh₃)₂]NO₃ at different rotor spinning rates. Details as in Fig. 4

Fig. 6 The ³¹P CP MAS homonuclear J-resolved two-dimensional spectrum of [Ag(PPh₃)₂]NO₃

local C₃ symmetry which goes through the P–Ag axis. In the solid state, tensor fitting shows that δ₁₁ = 34.0 ± 1.0, δ₂₂ = 17.0 ± 1.0 and δ₃₃ = 24.5 ± 1.0. This indicates that the local C₃ symmetry is distorted and the three phenyl rings on each P are not exactly related by a C₃ axis. Based upon the axial shape of the spectrum and previous studies, it is reasonable to assume that δ₃₃ aligns nearly parallel to the P–Ag axis while δ₁₁ and δ₂₂ are perpendicular to this axis. However, we do not have data which provides this information.

Initially we attempted to understand why our ³¹P NMR spectrum of compound I is different from that reported previously by Healy and co-workers.⁵ Their published spectrum appeared inconsistent with the P₅₇ symmetry, Z = 2,
of the crystalline material. Besides signal resolution, it seemed possible to us that a higher symmetry might have been introduced by sample handling. A symmetrical structure is obtained for compound 3 which shows a CP MAS $^{31}$P NMR spectrum similar to that reported by Healy and co-workers. Thus we heated and cooled our sample in a vain attempt to change the NMR spectrum. However, by introducing a line broadening of 100 Hz, the spectrum of ref. 5 can be reproduced. Hence spectral resolution, as suggested by Healy and co-workers is the origin of the differences observed.

Fig. 8 presents the CP MAS $^{31}$P NMR spectrum of $[\text{Ag}(\text{P(CH}_2\text{CH}_2\text{CN})_3])\text{NO}_3$ upon spinning with a rotor speed of 3.5 kHz. The two P atoms, which are related to each other by the inversion centre, are crystallographically and magnetically equivalent with a linear P--Ag--P bonding. Therefore, the dipole-dipole interaction between the two P atoms is small due to their relatively large separation and is averaged to zero by fast sample spinning. Only the effect of the presence of two silver isotopes with the spin-spin coupling between $^{31}$P and $^{109}$Ag is observed. The inner peak pair of the doublet is the spin-spin coupling of $^{197}$Ag = 496 ± 6 Hz and the outer peak pair is the spin-spin coupling of $^{109}$Ag = 564 ± 6 Hz. The isotropic chemical shift of the $^{31}$P is $\delta = 9.56$. The static spectrum of this compound shows an axially symmetric chemical shift tensor pattern with $\delta_1 = 7.2 \pm 1.0$ and $\delta_2 = 14.0 \pm 1.0$ by tensor fitting; $\delta_3$ is perpendicular to the P--Ag--P axis and $\delta_3$ aligns on the P--Ag--P axis.

The two phosphorus atoms of compound 3 are crystallographically equivalent but magnetically non-equivalent. They are related by a two-fold rotation axis in the space group $\text{Ab}2_{1}$. The solid-state $^{31}$P NMR spectra exhibit interesting rotor spinning-frequency-dependent line shapes with details which are reported elsewhere.\textsuperscript{10,15,23}

Acknowledgements

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25. F. A. Cotton and E. Walke, unpublished work.


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