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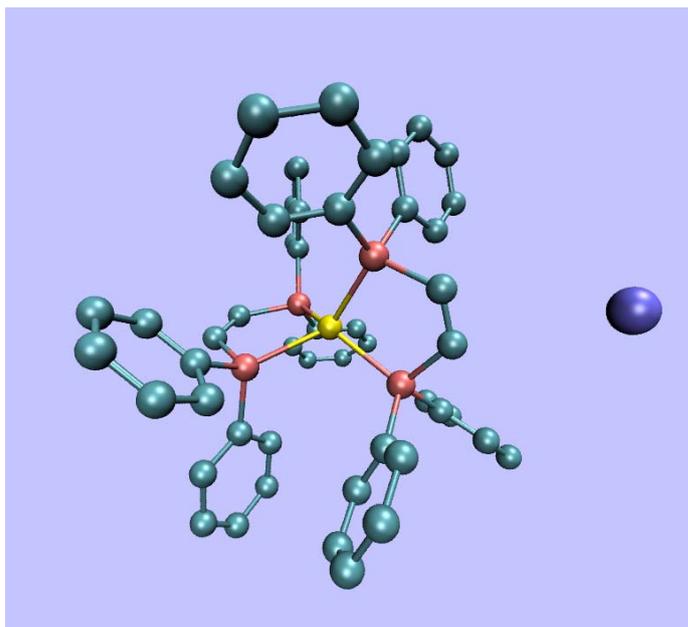
Structural, ^{197}Au Mössbauer and solid state ^{31}P CP/MAS NMR studies on bis (*cis*-bis(diphenylphosphino)ethylene) gold(I) complexes $[\text{Au}(\text{dppey})_2]\text{X}$ for $\text{X} = \text{PF}_6, \text{I}^\dagger$

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Abstract

^{197}Au Mössbauer spectra for the d^{10} gold(I) phosphine complexes, $[\text{Au}(\text{dppey})_2]\text{X}$ ($\text{X} = \text{PF}_6^-$, I^- ; $\text{dppey} = (cis\text{-bis}(\text{diphenylphosphino})\text{ethylene})$), and the single crystal X-ray structure and solid state ^{31}P CPMAS NMR spectrum of $[\text{Au}(\text{dppey})_2]\text{I}$ are reported here. In $[\text{Au}(\text{dppey})_2]\text{I}$ the AuP_4 coordination geometry is distorted from the $\sim D_2$ symmetry observed for the PF_6^- complex with Au-P bond lengths $2.380(2) - 2.426(2)$ Å and inter-ligand P-Au-P angles $110.63(5) - 137.71(8)^\circ$. Quadrupole splitting parameters derived from the Mössbauer spectra are consistent with the increased distortion of the AuP_4 coordination sphere with values of 1.22 and 1.46 mm s^{-1} for the PF_6^- and I^- complexes respectively. In the solid state ^{31}P CPMAS NMR spectrum of $[\text{Au}(\text{dppey})_2]\text{I}$, signals for each of the four crystallographically independent phosphorus nuclei are observed, with the magnitude of the ^{197}Au quadrupole coupling being sufficiently large to produce a collapse of $^1J(\text{Au-P})$ splitting from quartets to doublets. The results highlight the important role played by the counter anion in the determination of the structural and spectroscopic properties of these sterically crowded d^{10} complexes.

Introduction

^{197}Au Mössbauer spectroscopy has been used extensively in studies of the coordination geometry and bonding properties of ligands in gold(I) phosphine and arsine complexes through measurement of the transition from a 77.34 keV level of spin $1/2$ to the ground state of spin $3/2$ transition and the splitting of this transition into two lines of equal intensity as a result of nuclear quadrupole interactions.¹⁻⁸ For two- and three-coordinate complexes these quadrupole splitting parameters are quite large with values in general ranging from $7 - 10$ mm s^{-1} . With mixed ligand four-coordinate complexes, the magnitude of this splitting decreases by approximately 50% with, for example, a value of 4.38 mm s^{-1} observed for $[\text{Au}(\text{PPh}_3)_3\text{Cl}]$.² For four-coordinate complexes with identical ligands and ideal tetrahedral geometry, the quadrupole splitting is expected to be zero, and this is observed in the spectra of all four-coordinate monodentate complexes reported to date:

$[\text{Au}(\text{AsPh}_3)_4]\text{ClO}_4$,¹ $[\text{Au}(\text{PMePh}_2)_4]\text{ClO}_4$,¹ $[\text{Au}(\text{PMePh}_2)_4]\text{BPh}_4$,² $[\text{Au}(\text{PMe}_2\text{Ph})_4]\text{BPh}_4$ ² and $[\text{Au}(\text{PPh}_3)_4]\text{ClO}_4$ ³ (Table 1). Unfortunately, crystal structural information available for compounds incorporating these cations is for compounds with different counter anions. Nevertheless, there is a reasonable correlation between the structural and spectroscopic results. Thus, the structure of $[(\text{AsPh}_3)_4\text{Au}]\text{BF}_4$ ⁹ shows an almost tetrahedral geometry for

the AuAs₄ core with the Au-As bond lengths 2.556(1) - 2.588(1) Å and the As-Au-As bond angles 109.35(2) - 109.59(3)°. For [Au(PMePh₂)₄]PF₆¹⁰ the (symmetrically equivalent) Au-P bond lengths are 2.449(1) Å while the P-Au-P bonds angles are 105.24(4) and 118.32(4)°. Structural results for [Au(PPh₃)₄]BPh₄ are more diverse with results available for three different crystalline modifications which show significant variation in the Au-P bond lengths and P-Au-P angles.¹¹ These, however, do approach tetrahedral geometry at low temperatures (e.g. for [(PPh₃)₄Au]BPh₄.MeCN at 150 K, Au-P = 2.504(6), 2.561(2) Å, P-Au-P = 108.96, 110.65°).

For the four-coordinate bis(bidentate) complex, [(dmpa)₂Au][Au((C₆F₅)₂)], (dmpa = bis(o-phenylenebis(dimethylarsine))), a quadrupole splitting of 1.1 mm s⁻¹ is observed for the cation.⁸ In the crystal structure of this complex¹² the Au-As bond lengths lie in a narrow range from 2.462(2) to 2.478(1) Å while the bidentate chelation of the ligands results in the intra-ligand As-Au-As angles decreasing to 87.5(2) and 86.7(2)°, and inter-ligand angles increasing to 120.8(2) – 123.0(2)° (Table 2). In the structure of the bis(bidentate) phosphine complex, [Au(dppey)₂]PF₆ (dppey = *cis*-bis(diphenylphosphino)ethylene),¹³ the Au-P bond lengths span a narrow range from 2.377(2) – 2.388(2) Å. The intra-ligand P-Au-P angles are 86.87(5) and 86.90(2)° while the inter-ligand P-Au-P angles range from 110.95(5) to 133.21(5)° (Table 2).

In this present work, ¹⁹⁷Au Mössbauer spectra have been measured for [Au(dppey)₂]PF₆ and [Au(dppey)₂]I and the single crystal X-ray structure of the iodide complex determined. These results provide the first opportunity to directly examine both Mössbauer and structural data for a series of different four-coordinate cationic gold(I) complexes with corresponding counter anions. As part of this work, we also recorded the solid state ³¹P CP MAS spectrum of the iodide complex and discuss the unusual results obtained in terms of the structural and Mössbauer parameters for these complexes.

Experimental

Synthesis

cis-bis(diphenylphosphino)ethylene (dppey) was obtained from Strem Chemicals.

[Au(dppey)₂]PF₆ was prepared as previously described.¹³ [Au(dppey)₂]I was prepared by the reaction of [NBu₄][AuI₂]¹⁴ (0.36 g, 0.52 mmol) and dppey (0.40 g, 1.01 mmol) in 5 ml warm dimethylformamide (Equation 1) to give well-formed air stable pale yellow crystals of the complex suitable for X-ray diffraction studies on slow evaporation of the solvent.



Co-crystallized [NBu₄]I was removed by dissolution of the precipitate in acetone and eluting the resultant solution through a short alumina column (Aldrich aluminium oxide, neutral, 150 mesh) with acetone as eluent. Evaporation of solvent yielded analytically pure samples of the complex. M.p. 290–291 °C; NMR: ¹H (d₆DMSO), δ 7.11-7.15 (m, 16H, C₆H₅ *meta*), 7.19-7.24 (m, 16H, C₆H₅ *ortho*), 7.36-7.41 (m, 8H, C₆H₅ *para*) 7.83-7.98 (m, 4H, CH); ESMS (m/z): +ve ion, calcd m/z for [Au(dppey)₂]⁺: 989.81, found: 989.64 (100 %), -ve ion, calcd m/z for I⁻: 126.90, found: 126.41 (100 %); Elemental Analysis, calcd % for C₅₂H₄₄AuP₄I: C 55.93, H 3.97; found: C 55.76, H 4.01.

Spectroscopy

¹⁹⁷Au Mössbauer spectra on the complexes were recorded in a liquid helium bath cryostat at 4.2 K in the Physics Department, Technical University of Munich following previously reported procedures.¹⁵ Isomer shifts are given with respect to the ¹⁹⁷Pt source.

³¹P cross-polarisation (CP), magic-angle-spinning (MAS) NMR data were obtained at ambient temperatures using a Bruker MSL-400 spectrometer operating at the ³¹P frequency of 161.98 MHz. Conventional cross-polarisation and magic angle spinning techniques, coupled with spin temperature alternation to eliminate spectral artefacts, were implemented using a Bruker 4 mm double-air-bearing probe in which MAS frequencies of 10-12 kHz were achieved. A recycle delay of 30 s, a Hartmann-Hahn contact period of 10 ms and an initial ¹H π/2 pulse length of 3 μs were common to all ³¹P spectra. This represents a nominal ¹H decoupling field strength ~80 kHz during data acquisition.. No spectral smoothing was employed prior to Fourier transformation. All ³¹P chemical shifts were externally referenced to 85% H₃PO₄ via solid ammonium dihydrogen phosphate (δ 1.0) which was also used to establish the Hartmann-Hahn match.

Crystallography

Structure Determination. A unique data set for $[\text{Au}(\text{dppey})_2]\text{I}$ was obtained at 295(2) K with $2\theta_{\text{max}} = 50^\circ$ using a Rigaku AFC7R four-circle diffractometer [θ - 2θ scan mode, monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), from a 12kW rotating anode source] yielding N independent reflections, N_o with $I > 2.0\sigma(I)$ being considered 'observed' and used in the expression of the conventional refinement residual R . The structures were solved by direct methods and refined by full-matrix least-squares refinement on F^2 using *SHELXL-97*¹⁶ after semi-empirical absorption corrections based on ψ -scans. Anisotropic thermal parameters were refined for all non-hydrogen atoms while $(x, y, z, U_{\text{iso}})_{\text{H}}$ were included and constrained at estimated values. Neutral atom complex scattering factors were employed while computation used the TeXsan crystallographic software package of Molecular Structure Corporation¹⁷ and ORTEP 3.¹⁸

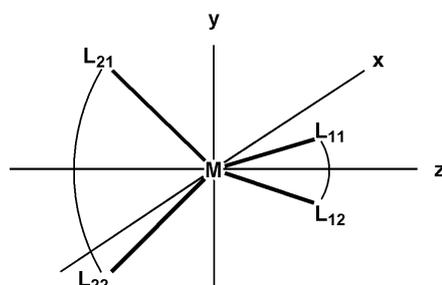
Crystal Data $[\text{Au}(\text{dppey})_2]\text{I}$. $\text{C}_{52}\text{H}_{44}\text{AuP}_4\text{I}$, M 1116.6, monoclinic, space group $P2_1/n$, $a = 18.854(8)$, $b = 19.537(4)$, $c = 12.569(4) \text{ \AA}$, $\beta = 96.79(3)^\circ$, $U = 4597(3) \text{ \AA}^3$, $Z = 4$, $D_c = 1.61 \text{ g cm}^{-3}$, $F(000) = 2192$, $\mu = 40.5 \text{ cm}^{-1}$, $T'_{\text{min/max}} 0.377, 0.498$. Crystal size: 0.30 x 0.30 x 0.20 mm, $N = 8094$ ($R_{\text{int}} = 0.037$), $N_o = 4734$. $R(I > 2\sigma(I)) = 0.044$, $wR2$ (all data) = 0.109.

Results and Discussion

Structures

The single crystal X-ray structure determination of $[\text{Au}(\text{dppey})_2]\text{I}$ shows that the complex crystallizes as discrete $[\text{Au}(\text{dppey})_2]^+$ cations and I^- anions. A view of the structure is shown in Fig. 1 with selected geometric parameters listed in Table 2. In this structure, the iodide anion is located in a general position within the crystal lattice with seven C-H...I contact distances ranging from 3.08 – 3.30 \AA . For comparison, nineteen C-H...F distances are observed in the PF_6^- complex, with distances ranging from 2.48 – 2.46 \AA . These differences in the cation – anion interactions for the two complexes are reflected in changes in the geometry of the AuP_4 core where the range of Au-P bond lengths (2.390(2) to 2.426(2) \AA , average, 2.40(2) \AA) is significantly greater than that of the the PF_6^- complex, while the range of the inter-ligand angles expands to 110.63(8) - 137.71(8) $^\circ$ (Table 2).

Angular distortions of the ML_4 core in four-coordinate bis(bidentate) d^{10} complexes have been parameterized in terms of three angles θ_x , θ_y , and θ_z ¹⁹ which define the orientations of the triangles with vertices L_{21} -M- L_{22} of ligand 2 with respect to the corresponding triangle L_{11} -M- L_{12} of ligand 1 (Scheme 1)



The definition of θ_x , θ_y , and θ_z is as follows. Orthonormal unit vectors \mathbf{x} , \mathbf{y} , \mathbf{z} are chosen so that the triangle L_{11} -M- L_{12} lies in the \mathbf{xz} plane with \mathbf{z} lying along the bisector of L_{11} -M- L_{12} and $\mathbf{y} = \mathbf{z} \times \mathbf{x}$. θ_x and θ_y are the angles between the bisector of L_{21} -M- L_{22} and \mathbf{y} and \mathbf{x} respectively, and represent rocking motions of the two triangles with respect to each other. θ_z is the dihedral angle between the normals to L_{11} -M- L_{12} and L_{21} -M- L_{22} and is a measure of the twist between the two planes. For complexes with D_{2d} symmetry or higher, the two triangles are orthogonal with $\theta_x = \theta_y = \theta_z = 90^\circ$. For complexes with D_2 symmetry the triangles twist but do not rock with respect to each other such that $\theta_x = \theta_y = 90^\circ$ and $\theta_z \neq 90^\circ$. For complexes with no (C_1) symmetry, the triangles both twist and rock and in general $\theta_x \neq \theta_y \neq \theta_z \neq 90^\circ$. Values of θ_x , θ_y , θ_z listed in Table 2 show that the $AuAs_4$ core in $[(dmpa)_2Au][Au((C_6F_5)_2)]$ is very close to D_{2d} symmetry: in $[Au(dppey)_2]PF_6$, the symmetry of the AuP_4 core decreases to D_2 ; while there is no symmetry for the AuP_4 core in $[Au(dppey)_2]I$.

An analysis of the effects of rocking and twisting distortions in the structures of a range of analogous four-coordinate sterically hindered bis(bidentate) copper(I) complexes $[Cu(dmp)_2]^+X^-$ ($dmp = \text{bis}(2,9\text{-dimethyl-}1,10\text{-phenanthroline})$),²⁰ has shown that rocking distortions result in displacement of the copper atom from the plane of the ligand(s) and an increase in one of the Cu-N bond lengths by $\sim 0.02 - 0.05 \text{ \AA}$ with respect to the other three bonds. These effects are observed also in the structure of $[Au(dppey)_2]I$ where the gold atom is displaced by 0.02 and 0.42 \AA from the P1-C=C-P2 and P3-C=C=P4 planes respectively (cf. PF_6^- : 0.01, 0.04 \AA) and the Au-P4 bond length of 2.426(2) \AA is $\sim 0.03 \text{ \AA}$ longer than the other

three Au-P bond lengths. These present results further serve to highlight the importance of the counter anion as a structure determinant in these sterically crowded d^{10} systems.

^{197}Au Mössbauer spectroscopy

The ^{197}Au Mössbauer spectra of $[\text{Au}(\text{dppey})_2]\text{X}$ for $\text{X} = \text{PF}_6^-$ and I^- are shown in Fig. 2. The isomer shift (IS) and quadrupole splitting (QS) parameters are listed in Table 1. It has been noted in the earlier studies of complexes involving monodentate ligands that the isomer shifts increase in the order $\text{L} = \text{PPh}_3 < \text{PMePh}_2 < \text{PMe}_2\text{Ph}$, and this is attributed to the increase in σ -donor capacity as phenyl groups are substituted for the more electron-releasing methyl groups in these ligands.² The isomer shifts for the $[\text{Au}(\text{dppey})_2]\text{X}$ ($\text{X} = \text{PF}_6^-, \text{I}^-$) complexes of 0.93 and 1.21 mm s^{-1} are significantly greater than the values 0.01 and 0.30 mm s^{-1} observed for $[\text{Au}(\text{PMePh}_2)_4]\text{X}$ ($\text{X} = \text{BPh}_4^-, \text{ClO}_4^-$) complexes, consistent with the decrease in the Au-P bond lengths by $\sim 0.05 \text{ \AA}$ in passing from the monodentate to bidentate ligands with the bridging ethylene group resulting in stronger coordination of the phosphine ligands to the central gold atom. The difference of 0.28 mm s^{-1} between the isomer shifts of the PF_6^- and I^- complexes is similar to the difference of 0.29 mm s^{-1} between the values for $[\text{Au}(\text{PMePh}_2)_4]\text{X}$ ($\text{X} = \text{ClO}_4^-, \text{BPh}_4^-$) (Table 1) and is most likely due to differences in the Au-P bond lengths. While this data is not available for the PMePh_2 complexes, for the $[\text{Au}(\text{dppey})_2]\text{X}$ complexes, as noted above, the mean Au-P bond length for the $\text{X} = \text{PF}_6^-$ complex (2.38 Å) is shorter than that for the $\text{X} = \text{I}^-$ complex (2.40 Å). This implies slightly stronger Au-P bonding in the former case, consistent with the greater observed value of the isomer shift.

An approximate indication of the relative degrees of distortion from regular tetrahedral coordination geometry in $[\text{Au}(\text{dppey})_2]\text{X}$ can be obtained from the range of Au-P bond lengths and P-Au-P angles. These are 0.011 Å , 47.3° and 0.041 Å , 52.6° for $\text{X} = \text{PF}_6^-, \text{I}^-$ respectively. As noted above, the angular distortion, while large, is relatively similar for the two complexes, while the bond length distortion is larger for the I^- complex with the range of Au-P nearly four times that of the PF_6^- complex. This suggests that it is the greater degree of radial distortion that is responsible for the higher observed quadrupole splitting for this compound. More quantitative measures of the distortion from tetrahedral coordination about metal atoms in inorganic materials and coordination compounds have been proposed in the past, and these show a good correlation with the nuclear quadrupole coupling of the metal

nucleus in some cases. These parameters are called the longitudinal and shear strain parameters α and χ , defined as follows:

$$\alpha = \sum_{i=1}^4 |\ln(l_i / l_0)| \quad (2)$$

$$\chi = \sum_{i=1}^6 |\tan(\theta_i - 109.48)| \quad (3)$$

where l_i are the M-Y bond lengths, l_0 is the bond length in the undistorted tetrahedron having the same volume as the distorted tetrahedron, and θ_i are the six Y-M-Y angles in the distorted tetrahedron.²¹ In accordance with the discussion above, the values of the shear strain parameter χ are very similar for the Γ and PF_6^- complexes (1.8 and 1.9 respectively). More surprisingly, the values of the longitudinal strain parameter α for these two compounds are also very similar (0.24 in both cases). The reason is that this parameter, as defined in equation (2), is not solely dependent on the Au-P bond lengths, but also depends on the P-Au-P bond angles through the parameter l_0 . If this parameter is replaced by the average bond length l_{av} , the values of the resulting modified longitudinal strain parameter α' for the $X = \text{PF}_6^-$, Γ complexes (0.009 and 0.023 respectively) are quite different, and indicate considerably more longitudinal strain for the $X = \Gamma$ complex, as expected from the greater range of Au-P bond lengths. This is probably the reason for the greater quadrupole splitting observed for this complex. This result highlights the fact that the longitudinal strain parameter as defined in equation (2) includes a contribution from shear strain, and this strongly influences the value of this parameter in complexes such as the present ones, which show a high degree of shear strain.

The strain parameters for $[\text{Au}(\text{dmpa})_2][\text{Au}((\text{C}_6\text{F}_5)_2)]$ are calculated to be $\chi = 1.69$, $\alpha = 0.15$ and $\alpha' = 0.007$. The decrease in the value of α' here is consistent with the smaller quadrupole splitting observed for this complex. By comparison with these bis(bidentate) complexes, $[\text{Au}(\text{PMePh}_2)_4]\text{PF}_6$ containing only monodentate phosphine ligands shows a much less distorted AuP_4 coordination environment in which all of the Au-P bond lengths are symmetrically equivalent and the P-Au-P angles are close to the ideal tetrahedral value.¹⁰ The strain parameters for this complex ($\alpha = 0.024$, $\alpha' = 0$, $\chi = 0.61$) are considerably lower than for the bidentate complexes and, although the anion is different from those in the compounds used in the Mössbauer studies,^{1,2} this is consistent with the zero quadrupole splitting seen in the Mössbauer spectra of $[\text{Au}(\text{PMePh}_2)_4]$ ($X = \text{BPh}_4$, ClO_4) (Table1).

Solid state ^{31}P CPMAS NMR spectroscopy

The solid state ^{31}P CP MAS NMR spectrum of $[\text{Au}(\text{dppey})_2]\text{I}$ is shown in Fig. 3. The spectrum for the PF_6^- complex has been published previously¹³ and is a broad singlet at 21.7 ppm, while that of the iodide is a multiplet containing at least seven resolved or partially resolved lines centred at about 19 ppm. Both complexes contain four inequivalent P atoms; these are clearly not resolved in the PF_6^- complex but the I^- complex contains more than the expected four lines, which may be due to $^1J(\text{AuP})$ coupling. The large nuclear quadrupole moment of ^{197}Au (100% natural abundance, nuclear spin $S = 3/2$) would be expected to give rise to rapid quadrupole relaxation, so that any $^1J(^{31}\text{P}-^{197}\text{Au})$ coupling would normally be averaged to zero, giving rise to singlets in the ^{31}P NMR spectrum for each P environment.^{14, 22-25} However, in a few cases it has been shown that splitting due to $^1J(^{31}\text{P}-^{197}\text{Au})$ coupling can be observed in the MAS ^{31}P NMR spectra of gold(I) complexes containing phosphine ligands.^{13, 26-28} The expected form of the MAS NMR spectrum of a spin $I = 1/2$ nucleus coupled to a quadrupolar ($S > 1/2$) nucleus has been discussed by a number of authors.²⁹⁻³² Menger and Veeman,³² adopted a full Hamiltonian diagonalisation and space-partitioning procedure to demonstrate that the appearance of the spin $I = 1/2$ spectrum depends on the parameters $R = D/J$ (where D is the dipolar coupling constant and J is the indirect or scalar coupling constant) and

$$K = -3C_Q/4I(2I-1)Z \quad (4)$$

where C_Q is the quadrupole coupling constant and Z the Zeeman interaction for the quadrupolar nucleus of spin I . In the case of ^{31}P coupled to ^{197}Au ($S = 3/2$), the parameter R is small, and an equally spaced four-line pattern (spacing = $^1J(^{31}\text{P}-^{197}\text{Au})$) of the ^{31}P spectrum is predicted for small K . This has been observed in the ^{31}P MAS NMR of $[\text{Au}(\text{dppey})_2]\text{Cl}$,¹³ where it is assumed that the ^{197}Au quadrupole coupling constant is close to zero, thus corresponding to $K \approx 0$. For the opposite case of large K a doublet pattern is predicted with a spacing of about 1.65 times the $^1J(^{31}\text{P}-^{197}\text{Au})$ coupling constant,³² and this has been observed in the linear two-coordinate complexes $[\text{Au}(\text{Ph}_3\text{P})\text{X}]$ ($X = \text{Cl}, \text{Br}, \text{I}$),²⁶ $[\text{Au}(\text{Me}_3\text{P})\text{X}]$ ($X = \text{Cl}, \text{I}$)²⁷ and $[\text{Au}(\text{Me}_3\text{P})_2]\text{X}$ ($X = \text{Cl}, \text{Br}$).²⁸ In these cases the linear coordination of the gold atom and the large quadrupole moment of the gold nucleus results in a large ^{197}Au quadrupole coupling constant and hence a large value of K (estimated to be ≈ 34).²⁷ However, this splitting is not observed in all cases where it might be expected and is noticeable absent in the case of $[\text{Au}(\text{tmpp})\text{X}]$ (tmpp = tris(2,4,6-trimethoxyphenyl)phosphine),¹⁴ despite the close similarity between these and the

corresponding PPh₃ complexes. Furthermore, it is not observed in [Au(Me₃P)Br], despite the fact that the doublet splitting is clearly resolved in the corresponding Cl and I systems.²⁷ In [Au(Me₃P)₂]X the doublet splitting is observed for X = Cl, Br but not for X = I.²⁸ There are clearly very subtle structural effects that influence the ¹⁹⁷Au relaxation processes, which determine whether the coupling is observed or not. In the present study, the splitting does not appear to occur (or is not resolved) for [Au(dppey)₂]PF₆, but it may be present in the spectrum of the corresponding iodide. Whether the conditions for observing a quartet or doublet splitting of each ³¹P signal are met can be determined from the magnitude of the ¹⁹⁷Au quadrupole coupling, which can be determined from the quadrupole splitting in the ¹⁹⁷Au Mössbauer spectrum, as explained below.

The ¹⁹⁷Au quadrupole splitting energy ΔE is given by:

$$\Delta E = \frac{1}{2}C_Q(1-\eta^2/3)^{1/2} \quad (5)$$

where C_Q is the nuclear quadrupole coupling constant and η is the electric field gradient asymmetry parameter. This latter parameter ($0 \leq \eta \leq 1$) cannot be determined from the Mössbauer quadrupole splitting, but the assumption $\eta = 0$ yields the lower limit of C_Q (the minimum value of $(1-\eta^2/3)^{1/2}$ in equation (5) is 0.82; the assumption that it is unity involves an 18% error at most). From the Mössbauer quadrupole splittings for [Au(dppey)₂]X (X = I, PF₆), the lower limits of the resulting ¹⁹⁷Au quadrupole coupling constants are thus 2.92 and 2.44 mm s⁻¹ or 182 and 152 MHz respectively (for the ¹⁹⁷Au 77.34 keV γ transition, 1 mm s⁻¹ = 62.37 MHz). The resulting K values for the I⁻ and PF₆⁻ and complexes are 6.6 and 5.5 respectively, which places both well above the quartet splitting region.³² In order for a quartet pattern to be observed, a K value of 0.5 or less is required. For the iodide complex, the K value is apparently sufficiently high to result in splitting of each of the four expected lines in the ³¹P spectrum into doublets, so that a total of eight lines is expected. This agrees well with the observed spectrum if the most intense line is assumed to be the superposition of two lines. The spectrum can thus be interpreted as being four doublets at 13, 15, 21 and 26 ppm with a doublet splitting of approximately 200 Hz. This corresponds to $^1J(\text{Au-P}) \approx 120$ Hz. This is somewhat lower than the values obtained previously for the two-coordinate complexes [Au(Ph₃P)X] (412-521 Hz) and [Au(Me₃P)X] (553-648 Hz),^{26, 27, 33} but is comparable to the value *ca.* 200 Hz estimated from the quartet observed in the ³¹P CPMAS NMR spectrum of [Au(dppey)₂]Cl.¹³ A reduction in the coupling constant of the four-coordinate complexes relative to the two-coordinate complexes is expected because the Au 6s character of the Au-P bonds decreases as the coordination number increases.

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Table 1 ^{197}Au Mössbauer isomer shift (IS) and quadrupole splitting (QS) parameters (mm s^{-1}) for four-coordinate monodentate and bidentate gold(I) cationic complexes with phosphorus and arsenic donor atoms.

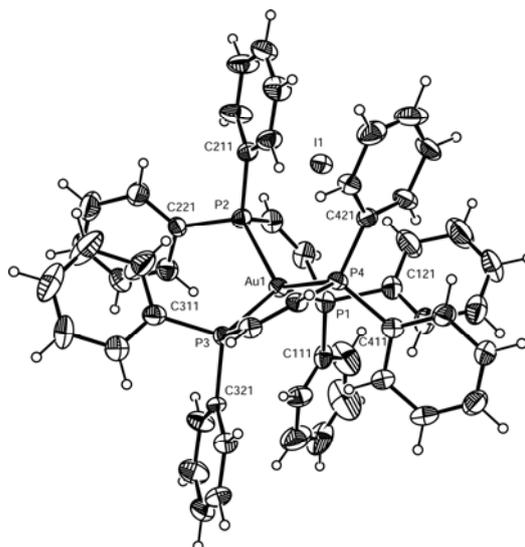
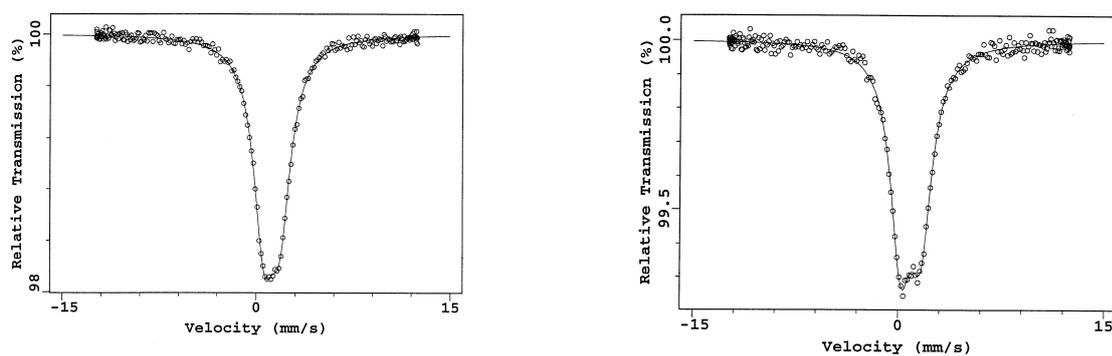
Compound	IS.	QS.	ref.
$[\text{Au}(\text{AsPh}_3)_4]\text{ClO}_4$	-1.57(5)	0.00(5)	1
$[\text{Au}(\text{PPh}_3)_4]\text{ClO}_4$	-1.35(5)	0.00(5)	3
$[\text{Au}(\text{PMePh}_2)_4]\text{BPh}_4$	0.01(5)	0.00(5)	2
$[\text{Au}(\text{PMePh}_2)_4]\text{ClO}_4$	0.30(5)	0.00(5)	1
$[\text{Au}(\text{PMe}_2\text{Ph})_4]\text{BPh}_4$	0.80(5)	0.00(5)	2
$[\text{Au}(\text{pdma})_2][\text{Au}(\text{C}_6\text{F}_5)_2]$	-0.4(1)	1.1(1)	8
$[\text{Au}(\text{dppey})_2]\text{PF}_6$	1.21(2)	1.22(2)	this work
$[\text{Au}(\text{dppey})_2]\text{I}$	0.93(2)	1.46(2)	this work

The isomer shifts listed above are referenced to the Pt-metal source. In order to refer the shifts to metallic gold, 1.18 mm s^{-1} have to be added to these values.⁴

Table 2 Geometric parameters for the AuAs₄ core in [Au(pdma)₂][Au(C₆F₅)₂]¹² and the AuP₄ core in [Au(dppey)₂]X for X = PF₆,¹³ and I.

	[Au(pdma) ₂][Au(C ₆ F ₅) ₂]	[Au(dppey) ₂]PF ₆	[Au(dppey) ₂] I
Au-P1	2.471(2)	2.378(2)	2.391(3)
Au-P2	2.473(2)	2.388(2)	2.404(3)
Au-P3	2.478(2)	2.377(2)	2.380(2)
Au-P4	2.462(2)	2.388(2)	2.426(2)
P1-Au-P2	87.5(2)	86.87(5)	85.60(8)
P1-Au-P3	121.8(2)	134.16(6)	137.71(8)
P1-Au-P4	123.0(2)	110.95(5)	110.63(8)
P2-Au-P3	121.1(2)	111.69(5)	117.37(8)
P2-Au-P4	120.8(2)	133.21(5)	126.09(8)
P3-Au-P4	86.7(2)	86.90(5)	85.04(8)
θ _x	89.6	90.7	98.2
θ _y	91.2	90.0	91.2
θ _z	89.3	110.2	106.0

Equations for the calculation of θ_x, θ_y, and θ_z from the six P-Au-P angles are provided in ref.¹⁹

Fig. 1 Representative view of the molecular structure of $[\text{Au}(\text{dppey})_2]\text{I}$ **Fig. 2** ^{197}Au Mössbauer spectra of (a) $[\text{Au}(\text{dppey})_2]\text{PF}_6$ and (b) $[\text{Au}(\text{dppey})_2]\text{I}$ **Fig. 3** Solid State Phosphorus-31 CP MAS NMR spectra for $[\text{Au}(\text{dppey})_2]\text{I}$ 