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Gold(I) Complexes with Bidentate Tertiary Phosphine Ligands: Formation of Annular vs. Tetrahedral Chelated Complexes

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Titrations of gold(I) complexes [(AuCl)$_2$(P-P)] with ligand (P-P) were studied by ^{31}P NMR for the bidentate tertiary phosphine ligands Ph$_2$P(CH$_2$)$_n$PPh$_2$, where $n = 1$ (dppm), 2 (dppe), 3 (dppp), and 4 (dppb), cis-Ph$_2$PCH=CHPPh$_2$ (dppey), Ph$_2$P(CH$_2$)$_2$PEt$_2$ (eppe), and Et$_2$P(CH$_2$)$_2$PEt$_2$ (depe). Bis-chelated four-coordinate gold(I) phosphine complexes [Au(P-P)$_2$]$^+$ containing either five- or six-membered chelate rings ($n = 2$ or 3) all exhibited exceptionally high thermodynamic and kinetic stabilities in solution. The species containing phenyl-substituted phosphines existed in CDCl$_3$ solutions at Au:P-P ratios of less than 1:1. They were isolated and characterized with Cl$^-$ as the counteranion. [Au(depe)$_2$]$^+$ existed in solution at Au:depe ratios >1:1 and was isolable as a PF$_6$$^-$ or SbF$_6$$^-$ salt. Four-coordinate complexes containing either four- ($n = 1$) or seven-membered ($n = 4$) chelate rings were not observed as stable species in CDCl$_3$ solutions. The solution behavior of species with a 1:1 Au:P-P ratio was also investigated by ^{31}P NMR. In D$_2$O the ^{31}P NMR spectrum of the 1:1 Au:eppe species consisted of two overlapping AA'BB' multiplets corresponding to the two isomers of the annular complex [Au$_2$(eppe)$_2$]$^{2+}$. The isomer containing two Et$_2$P–Au–PPh$_2$ linkages (X) predominated by 2:1 over the other isomer (Y). For the ligands dppe and eppe, the 1:1 Au:P-P complexes were stable in aqueous solution but were involved in dissociative equilibria in CDCl$_3$ with ring-closed species. The analogous complexes of depe, dppm, and dppb appeared to be stable in chloroform. These observations are discussed in terms of a destabilization of the annular [Au$_2$(P-P)$_2$]$^{2+}$ complexes by steric effects.

Introduction

The most commonly observed geometry for Au(I) is linear two-coordination,[1] and chelation is usually considered to be of minor importance in the chemistry of gold(I). Reports of four-coordinate complexes, for example, are rare, and the complexes tend to be unstable.[2-7] We have recently noted the remarkable ability of the bidentate diphosphines R$_2$P(CH$_2$)$_2$PR'$_2$ (R = R' = Ph; R = R' = Et; R = Ph, R' = Et) to stabilize four-coordinate Au(I).[8,9] The species [Au(dppe)$_2$]$^+$, for example, is present in solutions with Au(I):dppe ratios as low as 1:1 at ambient temperature.[8] The geometry of the cation has been confirmed in crystals of SbF$_6$$^-$ and Cl$^-$ salts.[8,10] Bates and Waters[10] obtained their crystals of [Au(dppe)$_2$]Cl from the reaction of [(AuCl)$_2$-(dppe)] with Na$_2$S. These findings suggest that chelation may be more important in Au(I) chemistry than has been assumed hitherto.

The aim of the work described here was to investigate the dependence of the stabilities of chelated bidentate bis(phosphine) complexes on the size of the chelate ring. The formation of complexes [Au(R$_2$P(CH$_2$)$_n$PR'$_2$)$_2$]$^+$, where $n = 1–4$ and R and R' are ethyls or phenyls, was investigated, largely by ^{31}P NMR spectroscopy. Studies on 1:1 Au(I) P-P species with possible monomeric (structure IV) or binuclear (II) structures are also reported.

Experimental Section

Materials. 1,2-bis(diphenylphosphino)ethane (dppe), 1,2-bis(diethylphosphino)ethane (depe), 1,3-bis(diphenylphosphino)propane (dppp), 1,4-bis(diphenylphosphino)butane (dppb), 1-(diethylphosphino)-2-(diphenylphosphino)ethane (eppe), cis-1,2-bis(diphenylphosphino)ethylene (dppey), and bis(diphenylphosphino)methane (dppm) were purchased from Strem Chemicals. Sodium tetrachloroaurate was purchased from Johnson Matthey PLC and thiodiglycol [2,2'-thiobis-(ethanol)] from Sigma.

Experimental Methods. Preparations. [(AuCl)$_2$(eppe)]. Na-[AuCl$_4$]·^{1}/$_2$H$_2$O (0.54 g, 1.44 mmol) was reduced to Au(I) by thiodi-

glycol (0.35 g, 2.88 mmol) in aqueous acetone (2.5:1, 7 mL). eppe (0.22 g, 0.72 mmol) in acetone (2 mL) was added dropwise, giving an immediate white precipitate. After the mixture was stirred for 30 min, this precipitate was filtered off, washed with H$_2$O, and dried in vacuo: yield 0.44 g (80%); mp 84–89 °C. Anal. Calcd for C$_{18}$H$_{24}$P$_2$Au$_2$Cl$_2$: C, 28.18; H, 3.15; P, 8.07; Cl, 9.24. Found: C, 28.56; H, 3.08; P, 8.27; Cl, 9.25.

The complexes of type [(AuCl)$_2$(P-P)], where P-P = dppm, dppe, dppp, dppb, depe, and eppe, were prepared by analogous methods and gave satisfactory elemental analyses.

[(AuCl)$_2$(dppey)]. Na[AuCl$_4$]·^{1}/$_2$H$_2$O (0.5 g, 1.26 mmol) was reduced to Au(I) by thiodyglycol (0.31 g, 2.51 mmol) in aqueous acetone (2.5:1, 7 mL). When the solution became colorless, dppey (0.25 g, 0.63 mmol) in acetone (5 mL) was added dropwise. A precipitate started to form, but this redissolved with further addition of dppey. The solution was stirred for 1 h, and a cream-colored solid was obtained by the addition of H$_2$O (ca. 30 mL). The ^{31}P NMR spectrum revealed that this product consisted of a mixture of [(AuCl)$_2$(dppey)] (12.8 ppm, 72%) and [Au-(dppey)$_2$]Cl (22.4 ppm, 28%). These were separated after the addition of NaBPh$_4$ (0.02 g) to 0.25 g of the solid mixture dissolved in acetone (50 mL). [(AuCl)$_2$(dppey)] crystallized after the solvent was concentrated to 10 mL, by slow evaporation at room temperature, and was recrystallized from CH$_2$Cl$_2$/petroleum ether (40–60 °C) (5:1 v/v). Anal. Calcd for C$_{26}$H$_{22}$Au$_2$Cl$_2$P$_2$: C, 36.26; H, 2.57; P, 7.19; Cl, 8.23. Found: C, 35.99; H, 2.70; P, 7.28; Cl, 8.94.

[Au(dppe)$_2$]Cl. Method a. Na[AuCl$_4$]·^{1}/$_2$H$_2$O (0.5 g, 1.35 mmol) was reduced by thiodiglycol (0.33 g, 2.70 mmol) in aqueous acetone (2.5:1, 7 mL). The solution was cooled to between 0 and 5 °C and was added dropwise to a solution of dppe (1.07 g, 2.70 mmol) in acetone (ca. 30 mL). A clear, colorless solution resulted. After this solution was stirred for 30 min, it was concentrated to 10 mL by evaporation at room temperature. The product was isolated as a white solid by the addition of H$_2$O (10 mL) and was recrystallized from aqueous methanol and dried in vacuo; yield 1.1 g (70%). Anal. Calcd for C$_{52}$H$_{48}$AuClP$_4$·H$_2$O: C, 59.64; H, 4.81; Cl, 3.38; P, 11.83. Found: C, 59.30; H, 4.81; Cl, 3.38; P, 11.85.

Method b. The complex was also prepared in good yield by the addition of solid [(AuCl)$_2$(dppe)] (0.89 g, 1.03 mmol) to a solution of dppe (1.35 g, 3.38 mmol) in acetone (25 mL). White crystals (1.5 g) were obtained by concentrating the solvent to 10 mL by evaporation at room temperature.

[Au(dppey)$_2$]Cl. This was prepared in 88% yield by a route analogous to that for [Au(dppe)$_2$]Cl (method a). Anal. Calcd for C$_{52}$H$_{44}$AuClP$_4$: C, 60.92; H, 4.33; Cl, 3.46; P, 12.08. Found: C, 60.79; H, 4.54; Cl, 3.49; P, 12.25.

[Au(dppp)$_2$]Cl. Solid [(AuCl)$_2$(dppp)] (0.37 g, 0.42 mmol) was added to a stirred solution of dppp (0.57 g, 1.39 mmol) in acetone (5 mL). The solid dissolved and the complex instantaneously crystallized from the solution; yield 0.66 g (75%). Anal. Calcd for C$_{54}$H$_{52}$AuClP$_4$·H$_2$O: C, 60.83; H, 5.07; P, 11.62. Found: C, 60.80; H, 5.00; P, 11.47.

[Au(eppe)$_2$]Cl. Solid [(AuCl)$_2$(eppe)] (0.26 g, 0.34 mmol) was added to a solution of eppe (0.34 g (0.31 mL), 1.12 mmol) in CHCl$_3$ (10 mL), resulting in a clear colorless solution. This was stirred for 30 min and then the solvent was evaporated to dryness, revealing a colorless gum,

(1) Puddephatt, R. J. *The Chemistry of Gold*; Elsevier: Amsterdam, 1978.
(2) Elder, R. C.; Zeiher, E. H. K.; Onady, M.; Whittle, R. R. *J. Chem. Soc., Chem. Commun.* **1981**, 900.
(3) Jones, P. G. *J. Chem. Soc., Chem. Commun.* **1980**, 1031.
(4) Parish, R. V.; Rush, J. D. *Chem. Phys. Lett.* **1979**, *63*, 37.
(5) Mays, M. J.; Vergnano, P. A. *J. Chem. Soc., Dalton Trans.* **1979**, 1112.
(6) Colburn, C. B.; Hill, W. E.; McAuliffe, C. A.; Parish, R. V. *J. Chem. Soc., Chem. Commun.* **1979**, 218.
(7) Parish, R. V.; Parry, O.; McAuliffe, C. A. *J. Chem. Soc., Dalton Trans.* **1981**, 2098.
(8) Berners-Price, S. J.; Mazid, M. A.; Sadler, P. J. *J. Chem. Soc., Dalton Trans.* **1984**, 969.
(9) Berners-Price, S. J.; Brevard, C.; Pagelot, A.; Sadler, P. J. *Inorg. Chem.* **1986**, *25*, 596.
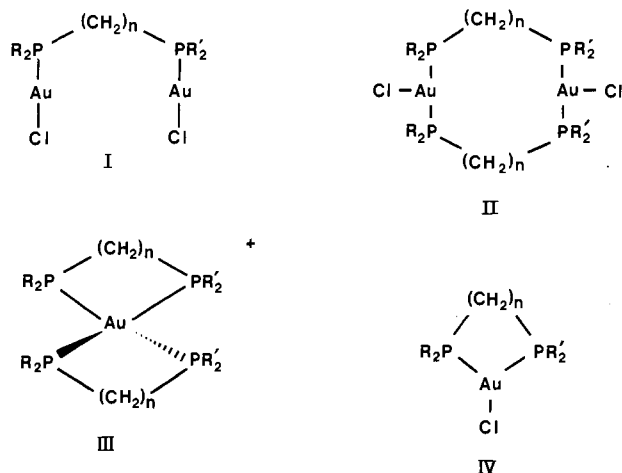(10) Bates, P. A.; Waters, J. M. *Inorg. Chim. Acta* **1984**, *81*, 151.

Figure 1. Structures of some possible bis(tertiary phosphine)gold(I) complexes and abbreviations for the ligands: (a) R = R′ = Ph, n = 1 (dppm); (b) R = R′ = Ph, n = 2 (dppe); (c) R = R′ = Ph, n = 3 (dppp); (d) R = R′ = Ph, n = 4 (dppb); (e) cis-Ph₂PCH=CHPPh₂ (dppey); (f) R = Ph, R′ = Et, n = 2 (eppe); (g) R = R′ = Et, n = 2 (depe).

which was solidified by repeated scratching in ice-cold Et₂O. The yield of white solid was 0.51 g (90%). Anal. Calcd for C₃₆H₄₈AuClP₄: C, 51.65; H, 5.78; P, 14.80; Cl, 4.23. Found: C, 52.18; H, 5.79; P, 15.22; Cl, 4.64.

[Au(depe)₂]PF₆. [(AuCl)₂(depe)] (0.53 g, 0.79 mmol) was suspended in acetone (10 mL), and depe (0.54 g, 2.61 mmol) was added dropwise. After the mixture was stirred for a few minutes, a clear colorless solution was obtained. This was stirred for a further 30 min, and then NaPF₆ (0.27 g, 1.58 mmol) in H₂O (3 mL) was added dropwise. The volume was reduced to 5 mL, and the complex was obtained as a solid by the addition of H₂O (ca. 25 mL) and was recrystallized from ethanol; yield 0.99 g (83%). Anal. Calcd for C₂₀H₄₈AuF₆P₅: C, 31.84; H, 6.41; P, 20.53. Found: C, 31.82; H, 6.17; P, 19.73.

NMR Measurements. ³¹P{¹H} NMR spectra were recorded on JEOL FX60 (24.2 MHz) or Bruker WM250 (101.3 MHz) spectrometers in 10-mm tubes. H₃PO₄/D₂O (85:15 v/v) was used as an external shift reference. ¹H NMR spectra at 199.5 MHz were recorded on a JEOL FX200 spectrometer and were referenced to Me₄Si.

The titrations of the complexes [(AuCl)₂(P-P)] with ligand (P-P) were followed by ³¹P{¹H} NMR. Spectra at 24.2 MHz were recorded for 30–40 mM solutions of [(AuCl)₂(P-P)] in CDCl₃ (1.5 mL), in the presence of between 0 and 12 mol equiv of added phosphine. The solutions were not deoxygenated as phosphine oxidation does not occur very readily for these bis(phosphine) ligands. ³¹P NMR resonances attributable to mono- and bis(phosphine oxides) of dppm were observed in the spectra of solutions containing Au:dppm ratios greater than 1:1, but these products represented less than 5% of the total phosphine in the solutions.

Analysis of the AA′BB′ Spin Systems. The 101.3-MHz ³¹P NMR spectrum of [Au₂(eppe)₂]²⁺ in D₂O consisted of two overlapping AA′BB′ multiplets corresponding to the two isomers (X and Y, Figure 4C,D) of the annular complex. The transitions were assigned letters a–l (Figure 4B) with use of the rules of Hoffmann et al.[11] The values of K, L, M, N, and ν_A − ν_B were then calculated by using the equations

$$\nu_A - \nu_B = (2ab)^{1/2} = [2(ce + df)]^{1/2}$$

$$K = b + g + k - a - h - l = b + i + k - a - j - l$$

$$|L| = [(c - e)^2 - M^2]^{1/2} = [(d - f)^2 - M^2]^{1/2}$$

$$|M| = \frac{ce - df}{\nu_A - \nu_B}$$

$$N = a - b = \pm[c^2 - (\nu_A - \nu_B)^2]^{1/2}$$

where c = a + b = g + j = h + i. The ³¹P–³¹P spin–spin coupling constants were then derived by using the relationships

$$K = J(AA') + J(BB') \qquad L = J(AB) - J(A'B)$$

$$M = J(AA') - J(BB') \qquad N = J(AB') - J(A'B)$$

The relative amounts of the isomers X and Y were calculated from the

(11) Hoffmann, R. A.; Forsen, S.; Gestblom, B. *NMR Basic Princ. Prog.* **1971**, *5*, 110–134.
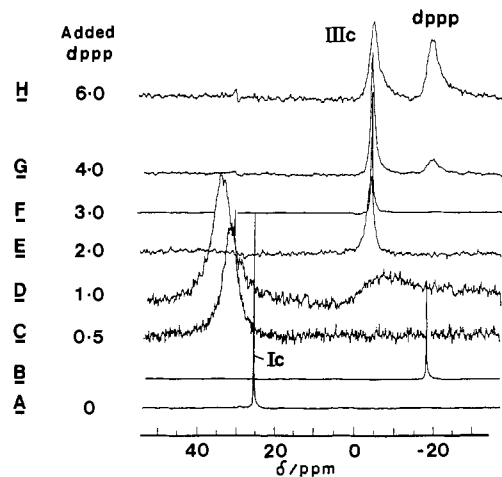

Figure 2. ³¹P{¹H} NMR spectra at 302 K of (A) a 22 mM solution of [(AuCl)₂(dppp)] (Ic) in CDCl₃ and (B) free dppp in CDCl₃. C–H are the spectra of Ic in the presence of 0.5, 1.0, 2.0, 3.0, 4.0, and 6.0 mol equiv of dppp, respectively. Note the appearance of the peak at −2.7 ppm for [Au(dppp)₂]⁺ (IIIc), even at low Au:dppp ratios.

intensities of the peaks corresponding to the k and h′i′ transitions, I(k) and I(h′i′), respectively, by using the relationships

for isomer X

$$I(k) = (3.714/32)[I(x)]$$

I(x) = total intensity of the X multiplet

for isomer Y

$$I(h'i') = (4.0/32)[I(y)]$$

I(y) = total intensity of Y multiplet

Results

Effect of Ring Size on the Formation of Stable Four-Coordinate Au(I) Complexes. The 2:1 Au:P-P complexes [(AuCl)₂(P-P)], where P-P is dppm (structure Ia), dppp (Ic), dppb (Id), cis-dppey (Ie), and eppe (If), were prepared by a method similar to that described previously for [(AuCl)₂(dppe)] (Ib):[8] by the addition of 0.5 mol equiv of the appropriate ligand to a solution of Na[AuCl₄] that had been reduced to Au(I) in situ by reaction of Au(III) with thiodiglycol. The X-ray structures of compounds Ia,[12] Ib,[13] Ic,[14] and Ie[15] have been reported, and in each case the bidentate phosphine ligand bridges two AuCl moieties so that each Au atom is linearly coordinated. It seems likely that the dppb and eppe complexes have a similar structure.

With the aim of investigating the possible formation of the four-coordinate complex [Au(dppp)₂]Cl, the titration of [(AuCl)₂(dppp)] with ligand (dppp) was followed by ³¹P NMR. At 302 K, the ³¹P{¹H} NMR spectrum of [(AuCl)₂(dppp)] in CDCl₃ consisted of a single resonance at 26.4 ppm (Figure 2). With the addition of 1 mol equiv of dppp this peak was replaced by two new broad resonances at ca. 35 and ca. −6 ppm (Δν₁/₂ = 125 Hz). With further addition of dppp, only one broadened resonance with observed at −2.7 ppm. This peak sharpened with each addition until the Au:dppp ratio was greater than 1:2, when a peak for free dppp (−17.8 ppm) appeared. Both peaks were broadened, presumably by exchange at an intermediate rate on the NMR time scale. The peak at −2.7 ppm was assigned to the four-coordinate bis-chelated complex ion [Au(dppp)₂]⁺. This was isolated and characterized with Cl⁻ as the counteranion. The appearance of separate resonances for free and bound dppp in the ³¹P NMR spectrum at 302 K indicates that the rate of ligand exchange must be ≪800 s⁻¹. Therefore, this four-coordinated

(12) Schmidbaur, H.; Wohlleben, A.; Wagner, F.; Orama, O.; Huttner, G. *Chem. Ber.* **1977**, *110*, 1748.
(13) Bates, P. A.; Waters, J. M. *Inorg. Chim. Acta* **1985**, *98*, 125.
(14) Cooper, M. K.; Mitchell, L. E.; Henrick, K.; McPartlin, M.; Scott, A. *Inorg. Chim. Acta* **1984**, *84*, L9.
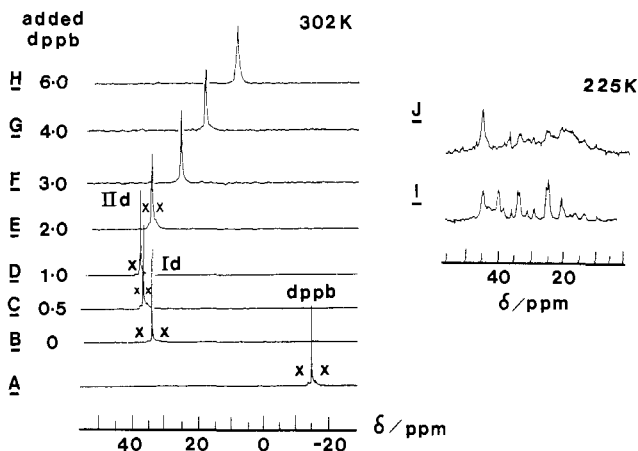(15) Jones, P. G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 2775.

Figure 3. $^{31}P\{^1H\}$ NMR spectra at 302 K of (A) free dppb and (B) a 22 mM solution of [(AuCl)$_2$(dppb)] (Id) in DMF. C–H are the spectra of Id in the presence of 0.5, 1.0, 2.0, 3.0, 4.0, and 6.0 mol equiv, respectively, of added dppb at 302 K. I and J are the spectra with 2.0 and 3.0 mol equiv, respectively, of added dppb at 225 K. The spectra were recorded in an 8-mm tube within a 10-mm tube containing either D$_2$O (at 302 K) or acetone-d_6 (at 225 K) for ^{2}D lock. The peaks labeled X are spinning side bands.

complex containing six-membered chelate rings shows stability comparable to that of [Au(dppe)$_2$]$^+$, and both have much enhanced kinetic stability compared to that of [Au(PR$_3$)$_4$]$^+$ complexes, containing monodentate phosphines.

Similar behavior was observed for the titration of [(AuCl)$_2$(dppey)] (structure Ie) with *cis*-dppey. The $^{31}P\{^1H\}$ NMR spectrum of [(AuCl)$_2$(dppey)] consisted of a sharp resonance at 12.8 ppm. On addition of *cis*-dppey to this solution a second sharp peak appeared at 22.3 ppm. This increased in intensity at the expense of the former resonance, until, at a Au:dppey ratio of 1:2, it was the only resonance observed. Subsequently, a peak for free *cis*-dppey (−23.5 ppm) appeared and both resonances were sharp. The resonance at 22.3 ppm is assigned to [Au(dppey)$_2$]$^+$. This complex was subsequently isolated with Cl$^-$ as the counteranion. It is evident that exchange between free and bound ligand occurs only very slowly on the NMR time scale as resonances for both the tetrahedral complex and excess free ligand are sharp.

The analogous titration of [(AuCl)$_2$(dppb)] (Id) with dppb was carried out with the aim of investigating the possible existence of the seven-membered bis-chelated complex [Au(dppb)$_2$]$^+$ (Figure 3). At Au:dppb ratios greater than 1:1 the products were too insoluble in CDCl$_3$ to obtain ^{31}P NMR spectra, and DMF was chosen as a more suitable solvent for the titration. On addition of dppb to a solution of [(AuCl)$_2$(dppb)] the ^{31}P NMR resonance shifted to high frequency, reaching a maximum deshielding at a Au:dppb ratio of exactly 1:1 (Figure 3D). When this solution was cooled to 225 K, the resonance remained sharp, which suggests that the peak corresponds to a single stable species, i.e. [Au$_2$Cl$_2$(dppb)$_2$] (structure IId). Further addition of dppb at 302 K resulted in a shift of the resonance back to low frequency, and at a Au:dppb ratio of 1:2 a single resonance at 33.5 ppm was observed. However, this peak cannot be assigned to [Au(dppb)$_2$]$^+$ because a second peak for free dppb did not appear at higher Au:dppb ratios. Only an averaged resonance was observed, which shifted closer to the position of free dppb with each addition, indicative of fast exchange between free and bound phosphine on the NMR time scale. When the solutions containing Au:dppb ratios of greater than 1:1 were cooled to 225 K, the single resonance was resolved into a series of peaks between 44 and 6 ppm (Figure 3I,J). In view of the complexity of the spectra it seems likely that oligomeric and polymeric products are formed.

Similar behavior was observed on titration of [(AuCl)$_2$(dppm)] (structure Ia) with dppm. The ^{31}P NMR resonance of Ia shifted to high frequency with the addition of dppm until at a 1:1 Au:dppm ratio a single sharp resonance was observed at 32.6 ppm. This peak remained sharp when the solution was cooled to 228 K and is assigned to the annular complex [Au$_2$Cl$_2$(dppm)$_2$].[16]

With further addition of dppm to this solution the ^{31}P NMR spectrum changed dramatically. The resonance at 32.6 ppm disappeared and was replaced by a very broad peak at 15.4 ppm ($\Delta\nu_{1/2}$ ca. 150 Hz) together with a minor resonance at 70 ppm ($\Delta\nu_{1/2}$ = 40 Hz). Both peaks shifted to low frequency with each subsequent addition of phosphine, and no peak corresponding to free dppm was observed, even at a Au:dppm ratio of 1:6.5. Hence, there was no evidence for a kinetically stable bis-chelated complex, [Au(dppm)$_2$]$^+$. When a solution containing a Au:dppm ratio of 1:2.5 was cooled to 228 K, the spectrum was partially resolved into three peaks at 27.5, 4.0, and −22 ppm, but they were very broad ($\Delta\nu_{1/2}$ > 120 Hz). The last peak is assigned to free dppm. The other two peaks cannot be assigned, although it is possible that the one at 4 ppm is due to [Au(dppm)$_2$]$^+$. However, in view of the line width of the peak this complex is evidently not kinetically stable with respect to exchange reactions, even at this temperature.

Solution Behavior of Complexes with 1:1 Au:P-P Stoichiometry. The titrations of the complexes of type [(AuCl)$_2$(P-P)] with free ligand P-P in CDCl$_3$ showed two different types of behavior. For the ligands dppm, dppb, and depe,[8] the addition of exactly 1 mol equiv of the ligand P-P to a solution containing the corresponding complex [(AuCl)$_2$(P-P)] gave rise to sharp ^{31}P NMR resonance that remained sharp on cooling the solutions to ca. 230 K. For these ligands, the complexes with 1:1 Au:P-P stoichiometry appear to have high thermodynamic stabilities. For the phenylphosphine ligands dppe,[8] eppe, and dppp, on the other hand, the ^{31}P NMR spectra of solutions containing a 1:1 Au:P-P ratio showed that significant amounts of the bis-chelated complexes [Au(P-P)$_2$]$^+$ were present, broadened through exchange with other species at ca. 35 ppm.

The stability of the complexes with a 1:1 Au:P-P ratio depended also on the solvent. The ^{31}P NMR spectrum of a CDCl$_3$ solution containing Au:dppe in a 1:1 ratio consisted of two broad peaks at 34.6 and 20.8 ppm. The solid isolated after evaporation of CDCl$_3$ was redissolved in MeOH:D$_2$O (2:1 v/v). A single sharp resonance was observed at 39.5 ppm.

These results suggested that the 1:1 complex has an annular structure (II) rather than the monomeric structure (IV) (Figure 1) and that in chloroform solution the annular complex is destabilized as a result of steric interactions between adjacent phenyl rings. In order to investigate further the factors influencing the stability of 1:1 Au:P-P complexes the mixed ligand Ph$_2$P-(CH$_2$)$_2$PEt$_2$ was used. Structures II and IV should be distinguishable by ^{31}P NMR giving rise to AB and AA′BB′ spectra, respectively.

Isomers of [Au$_2$(Ph$_2$P(CH$_2$)$_2$PEt$_2$)$_2$]$^{2+}$. In CDCl$_3$ solutions containing a 1:1 Au:eppe ratio, two broad ^{31}P NMR resonances were observed at 36.8 and 19.7 ppm. A 1:1 Au:eppe product was isolated by evaporation of the solvent. This gave rise to a slightly broadened singlet resonance at 41.3 ppm when the product was redissolved in D$_2$O. One small crystal of CuSO$_4$·5H$_2$O was added to the solution. This gave rise to a small amount of a white precipitate, which was filtered off. The spectrum of the solution was resolved into a asymmetrical second-order multiplet pattern (Figure 4A). It seems reasonable to suppose that the ^{31}P NMR resonance was broadened by an exchange reaction involving a trace of excess eppe, which was removed from solution by formation of a copper complex. The spectrum was analyzed as two overlapping AA′BB′ spin systems (see Experimental Section), corresponding to the two isomers of [Au$_2$(Ph$_2$P(CH$_2$)$_2$PEt$_2$)$_2$]$^{2+}$ (Figure 4C,D). For isomer X, which contains two Ph$_2$P–Au–PEt$_2$ linkages, all the transitions were assigned. The derived parameters were used to simulate the X part of the spectrum shown in Figure 4B. For isomer Y (which contains both Ph$_2$P–Au–PPh$_2$ and Et$_2$P–Au–PEt$_2$ linkages), the transitions g and j were too weak to be detected and so the parameter $K = J(AA') + J(BB')$ could not be calculated. The values of the two $^2J(^{31}P-^{31}P)$ couplings (296.5 and 305.5 Hz) were derived via computer simulations and

(16) Schmidbaur, H.; Wohlleben, A.; Schubert, U.; Frank, A.; Huttner, G. *Chem. Ber.* **1977**, *110*, 2751.
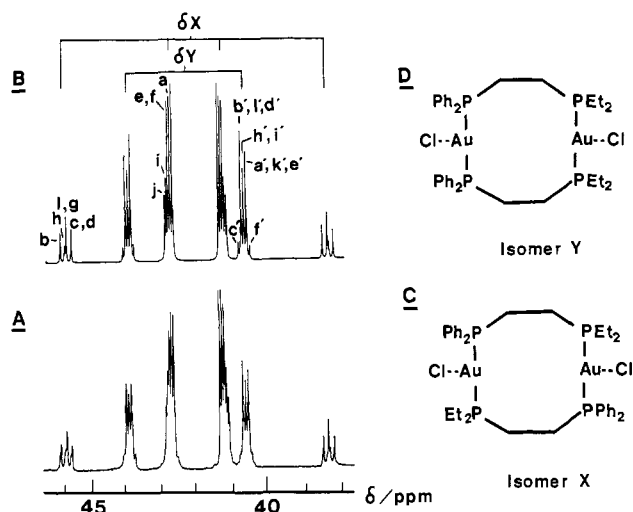
Figure 4. Observed (A) and simulated (B) ^{31}P{^{1}H} NMR spectrum at 101.3 MHz of the two isomers of $[Au_2(Ph_2P(CH_2)_2PEt_2)_2]Cl_2$ in D_2O at 300 K. The spectrum was analyzed as two overlapping AA′BB′ multiplets. Transitions labeled a–l correspond to isomer X (C), and transitions a′–l′ correspond to isomer Y (D). The mirror-image transitions are not labeled for clarity. The relative amounts of the two isomers were calculated from the relative intensities of the k and h′i′ transitions (see text). The derived spectral parameters are as follows: isomer X, δ 41.4, $\delta(^{31}P)_{Ph_2} - \delta(^{31}P)_{Et_2} = 3.35$, $^3J(^{31}P-^{31}P) = 18.8$ Hz, $^2J[^{31}P-(Ph_2)-^{31}P(Et_2)] = 300.9$ Hz, $^5J[^{31}P(Ph_2)-^{31}P(Ph_2)] \approx {}^5J[^{31}P(Et_2)-^{31}P(Et_2)] = -2.8$ Hz; isomer Y, δ 41.7, $\delta(^{31}P)_{Ph_2} - \delta(^{31}P)_{Et_2} = 3.31$ ppm, $^3J(^{31}P-^{31}P) = 18.8$ Hz, $^2J[^{31}P(Ph_2)-^{31}P(Ph_2)] = 296.5$ Hz, $^2J[^{31}P-(Et_2)-^{31}P(Et_2)] = 305.5$ Hz, $^5J[^{31}P(Ph_2)-^{31}P(Et_2)] = -3.5$ Hz.

gave a good fit to the experimental spectrum.

The observation of two AA′BB′ multiplet patterns therefore provides convincing evidence that the complex with a 1:1 Au:eppe stoichiometry has an annular structure in aqueous solution. The three $^2J(^{31}P-^{31}P)$ coupling constants are all large (ca. 300 Hz), which is as expected for linearly coordinated gold(I).[17] The relative amounts of the two isomers X and Y, calculated from the relative intensities of the k and h′i′ transitions (see Experimental Section), was 2.2:1.0.

Preparation and Characterization of the Bis-Chelated Complexes. The complexes [Au(P-P)$_2$]Cl were prepared in high yield for the ligands dppe (IIIb), dppp (IIIc), *cis*-dppey (IIIe), and eppe (IIIf), either by the addition of 3 mol equiv of the bidentate ligand to a solution of [(AuCl)$_2$(P-P)] in acetone or, alternatively, by the addition of 2 mol equiv of the ligand to a solution of Au(I) generated by in situ reduction of AuCl$_4^-$ with thiodiglycol [2,2′-thiobis(ethanol)]. Curiously, [Au(depe)$_2$]$^+$ (IIIg) could not be isolated with Cl$^-$ as the counteranion. The ^{31}P NMR spectrum of [(AuCl)$_2$(depe)] in the presence of 3 mol equiv of depe in CDCl$_3$ showed that [Au(depe)$_2$]Cl (15.8 ppm) was the only species present.[8] However, the complex did not crystallize from solution and a gum was obtained by evaporating the solvent. The ^{31}P NMR spectrum of this product showed that it consisted of at least five species, including [Au(depe)$_2$]Cl. The additional resonances at 31.7 and 52.0 ppm were assigned to [Au$_2$Cl$_2$(depe)$_2$] and Et$_2$P(O)(CH$_2$)$_2$(O)PEt$_2$, but a major resonance at 69.1 ppm could not be assigned. [Au(depe)$_2$]$^+$ was isolated[8] as a single product with either SbF$_6^-$ or PF$_6^-$ as the counteranion.

The complexes IIIb, IIIc, IIIe, and IIIf are all white solids, soluble in a wide range of solvents including CHCl$_3$, acetone, Me$_2$SO, and methanol. [Au(eppe)$_2$]Cl was also highly soluble in water (>24 mM). All four complexes gave the expected ^{31}P NMR resonance when dissolved in CDCl$_3$ (Table I). The ^{31}P NMR spectrum of [Au(eppe)$_2$]Cl consisted of a sharp singlet resonance in CDCl$_3$, D$_2$O, and acetone-d_6 with chemical shifts of 18.8, 21.5, and 24.2 ppm, respectively. This observation was surprising as the four-coordinate complex containing nonequivalent

(17) Pregosin, P. S.; Kunz, R. W. ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes; Springer-Verlag: West Berlin, 1979.

Table I. NMR Data for the Au(I) Bidentate Tertiary Phosphine Complexes

	^{1}H, δ^a				^{31}P, δ^b
complex	CH$_2^c$	CH$_3$	CH=CH	Ph	
[Au(dppe)$_2$]Cl	2.46			7.26	20.8
[Au(dppp)$_2$]Cl	1.24, 2.24			7.21, 7.35	-2.7
[Au(dppey)$_2$]Cl			7.54^d	7.14, 7.36	22.3
[Au(eppe)$_2$]Cl	e	e		e	18.8^f
[Au(depe)$_2$]PF$_6$	1.72^{g,h}	1.07^h			15.6, -145.1^i

^{a}Relative to Me$_4$Si, solvent CDCl$_3$. ^{b}Relative to external 85% H$_3$PO$_4$, solvent CDCl$_3$. ^{c}Broad resonance; ^{31}P–^{1}H spin–spin coupling not resolved. ^{d}Partially concealed by resonances of phenyl protons. ^{e}Full ^{1}H NMR data at different temperatures are tabulated in ref 9. ^{f}AA′BB′ pattern appears as a deceptively simple singlet at 24.2 MHz; see text. ^{g}CH$_2$ bridge and ethyl protons are overlapped. ^{h}Protons occur as second-order multiplet patterns. ^{i}PF$_6^-$ septet; $^1J(^{31}P-^{19}F) = 712$ Hz.

PPh$_2$ and PEt$_2$ groups would be expected to give a second-order AA′BB′ ^{31}P NMR multiplet pattern. To investigate this further, the CDCl$_3$ solution was cooled to 213 K. No broadening of the ^{31}P NMR resonance was observed, which suggests that the apparent magnetic equivalence of the PPh$_2$ and PEt$_2$ groups is not merely the result of averaging the nonequivalent environments by dynamic chemical exchange. The ^{31}P{^{1}H} NMR spectrum at 101.26 MHz (not shown; available as supplementary material) also consisted of a deceptively simple singlet, but with resolution enhancement some fine structure was revealed. The spectrum was not analyzed in detail, but this pattern was consistent with an AA′BB′ spin system in which the values of $\nu_A - \nu_B$, $J(AB)$, and $J(A′B)$ are all very small.

The ^{1}H NMR data for the tetrahedral complexes are tabulated in Table I. The ^{1}H and ^{13}C NMR spectra of [Au(eppe)$_2$]Cl are temperature-dependent, interpretable in terms of inversion at the tetrahedral metal center, and discussed in detail elsewhere.[9] For all the bis-chelated complexes, the –CH$_2$ protons of the phosphine backbone exhibit a small downfield coordination shift with respect to those of the free ligands. These protons would be expected to give rise to highly second-order spectra, and ^{31}P–^{1}H spin–spin coupling was not resolved in the 200-MHz spectra. The CH=CH protons in [Au(dppey)$_2$]Cl were overlapped by the phenyl protons in the 200-MHz spectrum in CDCl$_3$, but in acetone-d_6 the methine protons were deshielded further, so that a distinct second-order multiplet was resolved at 7.88 ppm. The spin system was too complicated to derive the coupling constants by a straightforward analysis. Presumably, it involves spin–spin coupling of each proton with all four phosphorus atoms. The phenyl protons of all the bis-chelated complexes were shielded with respect to those of the free ligands. It is reasonable to assume that the chemical shifts are influenced by ring current effects involving adjacent phenyl rings in the tetrahedral complexes.

Discussion

The stability of tetrahedral complexes of the type [Au(P-P)$_2$]X appears to be influenced by several factors. Within the series [Au(Ph$_2$P(CH$_2$)$_n$PPh$_2$)$_2$]$^+$, where n = 1–4, only the complexes containing either five- or six-membered chelate rings exist as stable species in solution. The bis-chelated structure of [Au(dppe)$_2$]$^+$ has been confirmed in the solid state. In [Au(dppe)$_2$]SbF$_6$·(CH$_3$)$_2$CO^8 the cation contains gold(I) with a flattened-tetrahedral coordination, ideal geometry being prevented by the small bite of the dppe ligand. A similar coordination geometry has been reported for the analogous Cl$^-$ complex,[10] and in both cases all the Au–P bond lengths are approximately equal (2.38–2.41 Å). In solution there was no evidence for the existence of [Au(dppb)$_2$]$^+$, which would require formation of a seven-membered ring, and the complexity of the ^{31}P NMR spectra at Au:dppb ratios greater than 1:1 suggested that the products contained bridging dppb ligands and were polymeric. Similarly, [Au(dppm)$_2$]$^+$ (n = 1) was not observed as a stable species in solution at room

Table II. ^{31}P NMR Parameters for Two-, Three-, and Four-Coordinate Au(I) Phosphine Complexes

| | | $\delta(^{31}\text{P})_{\text{complex}} - \delta(^{31}\text{P})_{\text{ligand}}{}^a$ | | | | | |
ligand	solvent	LAuCl	L$_2$AuCl	[L$_4$Au]Cl	ΔR,^{b} ppm	$\delta_{\text{free}}{}^c$	ref
PPhMe$_2$	CH$_2$Cl$_2$	48.6	62.8	23.2		−45.8	d
PEt$_3$	CH$_2$Cl$_2$	48.1	62.4	13.4		−19.1	e
PPhEt$_2$	CH$_2$Cl$_2$	55.0	64.2	8.0		−18.1	d
PPh$_2$Me	CH$_2$Cl$_2$		54.5	22.8		−38.5	f
PPhPr$_2$	CH$_2$Cl$_2$	54.4	63.3	19.6		−25.4	d
PPhBu$_2$	CH$_2$Cl$_2$	56.8	76.2			−26.2	d
depe	CDCl$_3$	50.4	50.1	34.5	21.1^h	−18.2	g
dppm	CDCl$_3$	46.5	55.5	(26.7)^j	(3.9)^i	−22.8	g
eppe	CDCl$_3$	49.9	k	36.0	22.6,^{h} 13.2^i	−16.7	g
dppe	CDCl$_3$	45.2	k	35.5	12.7^i	−13.0	g
dppey	CDCl$_3$	36.1	k	45.7	22.9^i	−23.5	g
dppp	CDCl$_3$	44.4	k	15.0	−7.8^i	−17.8	g
dppb	CDCl$_3$	45.9	52.1	k		−16.3	g

^{a} Coordination chemical shift (ccs). ^{b} Chelate ring contribution to ccs.^{22} ^{c} Relative to 85% H$_3$PO$_4$. ^{d} Reference 20. ^{e} Reference 5. ^{f} Reference 7. ^{g} This work. ^{h} Nonchelated analogue is [Au(PEt$_3$)$_4$]$^+$. ^{i} Nonchelated analogue is [Au(PPh$_2$Me)$_4$]$^+$. ^{j} Assuming [Au(dppm)$_2$]$^+$ has a chemical shift of 4 ppm at 228 K; see text. ^{k} Not observed as a stable species in this solvent; see text.
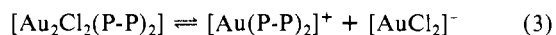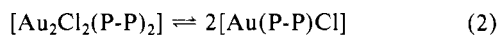
temperature. Presumably, in view of the strain of a four-membered ring, the formation of species in which the ligand is either monodentate or bidentate and bridging is favored. Similar observations have been made for the Hg(II) complex [Hg(dppm)$_2$]$^{2+}$. The ^{199}Hg and ^{31}P NMR data are interpretable in terms of a [Hg(η^1-dppm)$_2$]$^{2+}$ linear two-coordinate structure rather than the alternative bis-chelated structure.^{18}

These ^{31}P NMR studies show that [Au(dppey)$_2$]$^+$ is the most stable bis-chelated complex in the Au(I) series studied here. This might be expected since the geometry of the cis ligand is constrained to favor ring closure. Chelation of this ligand is so favorable that both [Au(dppey)$_2$]Cl and [(AuCl)$_2$(dppey)] were isolated from the reaction of Au(I) with as little as 0.5 mol equiv of dppey.

For the ligands dppe, eppe, and dppp, chelation also appears to be exceptionally favorable since significant amounts of the four-coordinate complexes [Au(P-P)$_2$]$^+$ were detected in chloroform solutions at Au:P-P ratios of less than 1:1. This may be attributable partly to a destabilization of the annular [Au$_2$(P-P)$_2$]$^{2+}$ complexes as a result of steric interactions. The annular complexes of eppe and dppe were observed as stable species in aqueous media (vide infra), suggesting that equilibrium 1 lies to the right in H$_2$O,

$$[\text{Au}_2\text{Cl}_2(\text{P-P})_2] \rightleftharpoons [\text{Au}_2(\text{P-P})_2]^{2+} + 2\text{Cl}^- \quad (1)$$
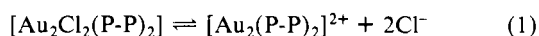
whereas in CDCl$_3$ it is to the left and each gold atom is essentially three-coordinate. From a consideration of molecular models it appeared that steric interactions would not be significant for the annular complexes of dppe, dppp, and eppe, provided that the two gold atoms adopted a linear coordination geometry. However, the addition of a third ligand (Cl$^-$) and distortion toward a trigonal-planar geometry gave rise to severe steric crowding involving the bulky phenyl substituents. This might be expected to destabilize the ring complex, perhaps with respect to the monomeric three-coordinate complex (structure IV, eq 2) or the bis-chelated complex (eq 3). The X-ray structure of the 1:1

$$[\text{Au}_2\text{Cl}_2(\text{P-P})_2] \rightleftharpoons 2[\text{Au}(\text{P-P})\text{Cl}] \quad (2)$$

$$[\text{Au}_2\text{Cl}_2(\text{P-P})_2] \rightleftharpoons [\text{Au}(\text{P-P})_2]^+ + [\text{AuCl}_2]^- \quad (3)$$

AuCl:dppm complex has been determined.^{16} It contains an eight-membered annular structure with a relatively short Au−Au contact and approximately trigonal-planar geometry for the two gold atoms. The complex is only slightly dissociated in polar solvents, and in contrast to the case for the 10-membered macrocycles, steric interactions between the phenyl rings appear to be significantly reduced for trigonally with respect to linearly coordinated gold atoms. Similarly, steric effects do not appear to be important for the 14-membered macrocycle [Au$_2$(dppb)$_2$Cl$_2$], for either linearly or trigonally coordinated gold(I). The ^{31}P NMR spectra of the 1:1 Au:dppm and Au:dppb complexes indicated that

both had high thermodynamic stabilities in chloroform solutions.

The observation of two overlapping ^{31}P AA'BB' multiplets for the two isomers of [Au$_2$(eppe)$_2$]$^{2+}$ provides the first unequivocal evidence for the existence of annular 1:1 Au:P-P complexes *in solution*. Since the ^{31}P NMR spectrum of the 1:1 Au:dppe complex exhibited a similar solvent-dependent change in the position of the equilibrium, it seems likely that it has a similar structure. Ludwig and Meyer^{19} have investigated the structures of 1:1 Au:P-P complexes of 1,2-bis(dimethylphosphino)ethane and 1,2-bis(dimethylphosphino)propane in aqueous solutions. The complexes were assigned 10- and 12-membered annular binuclear structures from conductivity measurements and from the presence of a very strong low-energy band in their absorption spectra.

Analysis of the ^{31}P NMR spectrum of [Au$_2$(eppe)$_2$]$^{2+}$ showed that isomer X, which contains two Ph$_2$P−Au−PEt$_2$ linkages (Figure 4C), predominates over isomer Y (Figure 4D). This may be partly due to both steric and electronic effects. We noted previously that the annular [Au$_2$(depe)$_2$]$^{2+}$ complex (IIg), containing Et substituents, appeared to have a higher stability than the dppe (phenyl) analogue.^{8} Further evidence for the high stability of the ring complex is provided by the observation that [Au(depe)$_2$]$^+$ decomposed unless stabilized by a large counteranion, and [Au$_2$Cl$_2$(depe)$_2$] was one of the products. It would appear that Ph$_2$P−Au−PPh$_2$ linkages in 10- or 12-membered macrocycles are destabilized with respect to either chelated species or Ph$_2$P−Au−PEt$_2$ linkages in mixed systems.

^{31}P NMR has been used previously to investigate the coordination of Au(I) phosphine complexes in solution.^{5,6,7,20} These studies have generally involved monodentate phosphine ligands, but recently some studies of bis(tertiary phosphines) have been carried out.^{8,21} Curiously, for bis(tertiary phosphine)decaborane ligands both three- and four-coordinate species were reported^{21} to be present in CD$_3$COCD$_3$−CH$_2$Cl$_2$ (1:1) solutions at Au:P-P ratios of 1:2, although the geometry of the rigid C$_2$B$_{10}$H$_{10}$ backbone might be expected to favor more strongly the formation of the bis-chelated complex.

^{31}P NMR chemical shifts alone do not appear to be a reliable guide to Au(I) coordination numbers, but some trends in coordination chemical shifts (ccs) have been noted for Au(I) complexes with monodentate phosphine ligands. Generally, the ccs follow the order^{7,20}

$$\text{AuClPR}_3 < \text{Au(PR}_3)_2\text{Cl} > [\text{Au(PR}_3)_3]\text{Cl} > [\text{Au(PR}_3)_4]\text{Cl}$$
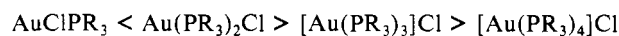
It is apparent from Table II that the ccs for the four-coordinate bis-chelated complexes are generally larger than for [Au(PR$_3$)$_4$]$^+$. This can be attributed to the ring contribution to the chemical shift, ΔR,^{22} which is observed for transition-metal phosphine

(18) Peringer, P.; Lusser, M. *Inorg. Chem.* **1985**, *24*, 109.

(19) Ludwig, W.; Meyer, M. *Helv. Chim. Acta* **1982**, *65*, 934.
(20) Parish, R. V.; Al-Sa'ady, A. K. H.; McAuliffe, C. A.; Moss, K.; Fields, R. *J. Chem. Soc., Dalton Trans.* **1984**, 491.
(21) Al-Baker, S.; Hill, W. E.; McAuliffe, C. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1387.

complexes with chelated bidentate phosphine ligands. The observed large positive Δ*R* values for the complexes with five-membered chelate rings and the negative ring contribution for [Au(dppp)$_2$]$^+$ are fully consistent with the previously reported trends for five- and six-membered chelate rings.[22]

The observation of a deceptively simple singlet in the ^{31}P NMR spectrum of the mixed-ligand complex [Au(eppe)$_2$]$^+$ is interpretable as an AA′BB′ spin system in which the values of *J*(AB) (i.e. $^3J[^{31}$P(Ph$_2$)–^{31}P(Et)]) and ν$_A$ – ν$_B$ are both very small. The $^3J[^{31}$P(Ph$_2$)–^{31}P(Et$_2$)] coupling constants in eppe and [(AuCl)$_2$-(eppe)] are 26 and 53 Hz, respectively. It seems reasonable that this coupling could be very small in the chelated complex in view of previous observations for metal phosphine complexes containing five-membered chelate rings.[23] ^{31}P–^{31}P spin–spin coupling in a chelate ring can be divided into "through the backbone" and "through the metal" contributions. For a five-membered ring these contributions are nearly equal but of opposite sign, resulting in a small overall value for *J*(PP).[23]

Conclusion

Tetrahedral bis(bis(phosphine))gold(I) complexes, [Au(R$_2$P-(CH$_2$)$_n$PR′$_2$)$_2$]$^+$, containing five- and six-membered chelate rings (*n* = 2 or 3), exhibit a remarkably high kinetic and thermodynamic

stability. Those containing phenyl substituents are present even in solutions containing low Au(I):ligand ratios (<1:1). Four- or seven-membered chelate rings were not detected in solution by our ^{31}P NMR studies. These ligands give rise to annular (digold) and polymeric species.

Definitive evidence for the existence in solution of the 10-membered annular complex was obtained from detailed NMR studies of the 1:1 Au(I):eppe complex [Au$_2$(Et$_2$P(CH$_2$)$_2$PPh$_2$)$_2$]$^{2+}$. In D$_2$O, the Et$_2$P–Au–PPh$_2$ isomer predominated (by 2:1) over the Ph$_2$P–Au–PPh$_2$ isomer.

Chelation may be a more important feature of the chemistry of Au(I) than has hitherto been supposed. There appears to be an intriguing interplay between the stabilities of two-, three-, and four-coordinate complexes, influenced by steric and electronic factors, and also solvent effects.

(22) Δ*R* = coordination shift of a chelated phosphine complex minus the ccs of an equivalent phosphorus in a nonchelated analogue: Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.
(23) Grim, S. O.; Barth, R. C.; Mitchell, J. D.; Delgaudio, J. *Inorg. Chem.* **1977**, *16*, 1776.

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Cobalt(II) Bis(1,4,7-trithiacyclononane): A Low-Spin Octahedral Complex

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Cobalt(II) forms a bis complex with 1,4,7-trithiacyclononane (1,4,7-TTCN) with an unprecedentedly large overall formation constant of 8 × 10^{13}. This complex has an effective magnetic susceptibility of 1.71 μ$_B$. Thus, this is a low-spin octahedral Co(II) complex, and such complexes are exceedingly rare. Cyclic voltammetry of Co(1,4,7-TTCN)$_2^{2+}$ shows three diffusion-controlled one-electron steps at 0.573, −0.292, and −0.998 V vs. SHE corresponding to Co(III)/Co(II), Co(II)/Co(I), and Co(I)/Co(0) reductions, respectively. The unique properties of this complex are suggested to be due to ligand conformational control.

Introduction

Thioethers have been widely regarded as rather poor ligands for the coordination of transition metals.[1,2] However, the involvement of thioethers as ligands in cytochromes *c* and certain "blue copper" proteins has inspired more detailed examination of thioether coordination chemistry. A number of macrocyclic polythioether complexes have been examined. These have tended to be tetrathioethers,[3-5] forming four-coordinate complexes or five- and six-coordinate complexes with another ligand. In particular we have focused on medium-sized ring polythioethers (crown thioethers) and their interactions with transition metals. Recently we reported on the preparation and structures of bis 1,4,7-tri-thiacyclonanone (1,4,7-TTCN) complexes of Ni(II), Cu(II), and Co(II).[6] In each complex the metal atom is found in a slightly distorted octahedal environment consisting of two facially coordinated 1,4,7-TTCN ligands. Our previous structural studies of the ligand[7] revealed a conformation in which all three sulfur atoms

are endodentate and are well-positioned for tridentate coordination, suggesting the possibility of forming unusually stable complexes.

Cobalt complexes of thioethers have not been extensively studied. Only one monodentate thioether complex[8] and three bidentate thioether complexes[9-11] have been reported. These are all high-spin Co(II). In studies of mixed-donor Co(II) complexes, it becomes apparent that thioethers allow a high degree of inner-sphere reactivity.[12-15] These complexes are high-spin octahedral Co(II) but seem to be in a close equilibrium with tetrahedral structures, which is not surprising since the energy difference between the two states is less for a d^7 system than for any other first-row transition metal. Low-spin Co(II) complexes are rare and tend to be four- or five-coordinate.[16]

(1) Livingstone, S. E. *Q. Rev., Chem. Soc.* **1965**, *19*, 386.
(2) Murray, S. E.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365.
(3) Pett, V. B.; Diaddorio, L. L.; Dockal, E. R.; Corfield, P.W. R.; Ceccarelli, C.; Glick, M. D.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1983**, *22*, 3661.
(4) Dockal, E. R.; Diaddorio, L. L.; Glick, M. D.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1977**, *99*, 4530.
(5) Baker, E. W.; Norris, G. E. *J. Chem. Soc., Dalton Trans.* **1977**, 877.
(6) Setzer, W. N.; Ogle, C. A.; Wilson, G. S.; Glass, R. S. *Inorg. Chem.* **1983**, *22*, 266.

(7) (a) Glass, R. S.; Wilson, G. S.; Setzer, W. N. *J. Am. Chem. Soc.* **1980**, *102*, 5068. (b) Setzer, W. N.; Coleman, B. R.; Wilson, G. S.; Glass, R. S. *Tetrahedron* **1981**, *37*, 2743.
(8) Anagnostopoulos, A. *J. Inorg. Nucl. Chem.* **1975**, *37*, 268.
(9) Carlin, R. L.; Weissberger, E. *Inorg. Chem.* **1964**, *3*, 611.
(10) Flint, C. D.; Goodgame, M. *J. Chem. Soc. A* **1968**, *68*, 2178.
(11) Hathaway, B. J.; Underhill, A. E. *J. Chem. Soc.* **1961**, *61*, 3091.
(12) Lane, R. H.; Sedor, F. A.; Gilray, M. J.; Eisenhardt, P. F.; Bennett, J. P., Jr.; Ewall, R. X.; Bennett, L. E. *Inorg. Chem.* **1977**, *16*, 93.
(13) Kennard, G. J.; Deutsch, E. *Inorg. Chem.* **1978**, *17*, 2225.
(14) Chia, P. S. K.; Livingstone, S. E. *Aust. J. Chem.* **1968**, *21*, 339.
(15) Chia, P. S. K.; Livingstone, S. E.; Lockyer, T. N. *Aust. J. Chem.* **1967**, *20*, 239.
(16) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 772.