Preparation and Nuclear Magnetic Resonance Spectroscopy of $[Ag_2\{\mu\text{-}CH_2(PPh_2)_2\}_3][O_3SCF_3]_2$, a Disilver(I) Complex with Three Bridging $CH_2(PPh_2)_2$ Ligands

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$[Ag_2(\mu\text{-dppm})_3][O_3SCF_3]_2$ [dppm = bis(diphenylphosphino)methane] has been prepared and characterized by ^{31}P n.m.r. spectroscopy. Variable-temperature n.m.r. studies revealed that the Ag–P bonds are kinetically stable on the n.m.r. time-scale below 233 K. At ambient temperature there is intermolecular ligand exchange whereas at intermediate temperatures intramolecular inter-metal exchange of the phosphorus atoms of the dppm ligands occurs.

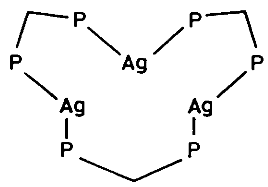
Silver(I)–dppm [dppm = bis(diphenylphosphino)methane] complexes have been reported in the ratios of 3:3, 2:1, and 2:2 correspondiing to the frameworks (I)—(III)[1–3] [the formal charges of the silver(I) compounds are omitted]. Silver(I) is known to co-ordinate up to four unidentate phosphorus-donor ligands. The structures (I)—(III) involve Ag–P ratios of 1:1 or 1:2.

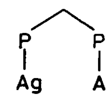
We report here on the preparation and n.m.r. spectroscopy of $[Ag_2(\mu\text{-dppm})_3]^{2+}$, framework (IV), in which two metal centres are bridged by three dppm ligands. Examples of this structural type are rare: $[Pt_2(\mu\text{-dppm})_3]$ has been thoroughly characterized by *X*-ray methods and multinuclear n.m.r. spectroscopy.[4] A compound, $[Pd_2(dppm)_3]$, has been formulated on the basis of elemental analysis and its chemical reactions.[5–7] Very recently the structure of $[Au_2(\mu\text{-dmpm})_3]^{2+}$, involving the methyl analogue of dppm [dmpm = bis(dimethylphosphino)methane] has been determined.[8]

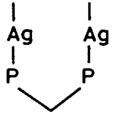
Results and Discussion

The reaction of $Ag[O_3SCF_3]$ and dppm in the ratio of 2:3, *i.e.* a Ag–P ratio of 1:3, afforded the new homobimetallic complex $[Ag_2(\mu\text{-dppm})_3][O_3SCF_3]_2$ (**1**) as a colourless, crystalline, air-stable and light-insensitive solid in quantitative yield. Complex (**1**) is readily soluble in CH_2Cl_2, acetone, Me_2SO and dimethylformamide.

The structure of (**1**) in solution was determined by ^{31}P n.m.r. spectroscopy; the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum (145.8 MHz) recorded at 213 K is shown in Figure 1. The spectrum arises from the superposition of three different spin systems: $([A]_3X)_2$, $([A]_3Y)_2$, and $[A]_3[A^*]_3XY$,† attributable to the isotopomers $[^{107}Ag_2(\mu\text{-dppm})_3]^{2+}$ (abundance 26.9%), $[^{109}Ag_2(\mu\text{-dppm})_3]^{2+}$ (23.2%), and $[^{107}Ag^{109}Ag(\mu\text{-dppm})_3]^{2+}$ (49.9%) respectively. The spectrum is incompletely resolved at this field. Very similar spectra were obtained, however by computer simulation (using the program CYMPLOT)[10] using the parameters $^1J(^{107}AgP) = 308$, $^2J(PCP) = 150$ Hz. Although the simulated spectra are sensitive to the magnitude of $^2J(PAgP)$ only values outside a range of 70—130 Hz give simulations that are recognizably different to the experimental results [Figure 1(*a*)]. The chemical shift of (**1**) is 2.7 p.p.m. The value of $^1J(^{107}AgP)$ falls within the range observed for cationic complexes $[Ag(PR_3)_3]^+$ (R = alkyl or aryl).[11]


(I)


(II)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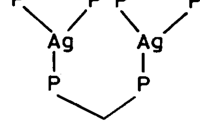
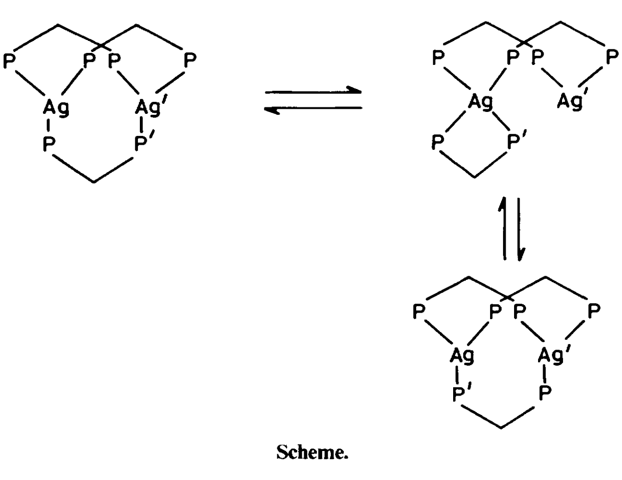

(IV)

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of (**1**) in the temperature range 298—223 K recorded at 32.4 MHz are shown in Figure 2. The structure of (**1**) is kinetically stable on the n.m.r. time-scale at temperatures below 233 K. At ambient temperature one broadened signal indicates intermolecular ligand exchange. At intermediate temperatures there is intramolecular inter-metal exchange of the phosphorus atoms of the μ-dppm ligands. This mechanistic information is obtained from the spectra at 253—293 K (Figure 2): only part of the multiplet collapses with increasing temperature, whereas the other part remains at



Scheme.

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† Nomenclature from ref. 9.

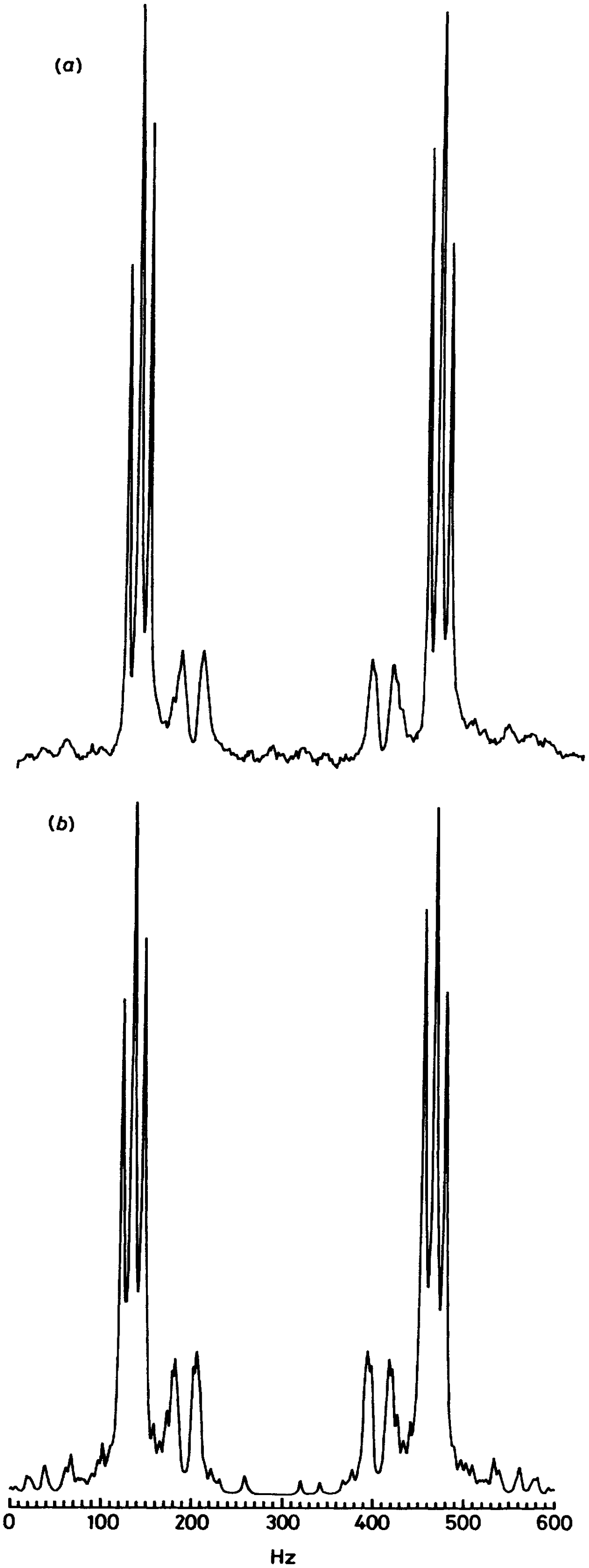

Figure 1. (*a*) Experimental $^{31}P\text{-}\{^{1}H\}$ n.m.r. spectrum (145.8 MHz, 213 K) and (*b*) simulated spectrum of $[Ag_2(\mu\text{-dppm})_3][O_3SCF_3]_2$

constant separation. The presence of the invariant lines is characteristic of a mutual exchange process [12] and they may be assigned to phosphorus transitions involving the silver spin states αα and ββ in (**1**). The collapsing lines are associated with the silver spin states αβ and βα which are permuted by the interchange of the phosphorus atoms. A possible mechanism (indicated in the Scheme) involves $[Ag_2(\mu\text{-dppm})_2(\text{dppm-}PP')]^{2+}$ as the intermediate.

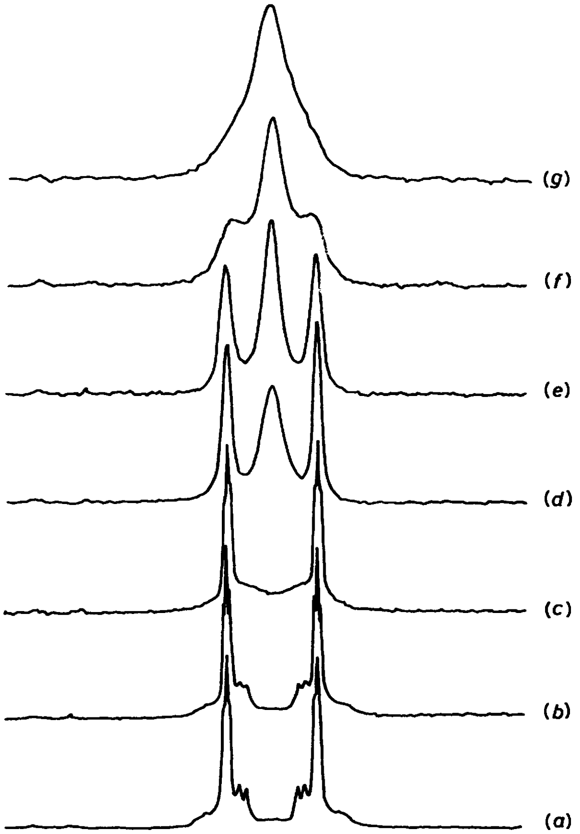

Figure 2. $^{31}P\text{-}\{^{1}H\}$ N.m.r. spectra (32.4 MHz) of $[Ag_2(\mu\text{-dppm})_3][O_3SCF_3]_2$ at (*a*) 223, (*b*) 233, (*c*) 253, (*d*) 273, (*e*) 283, (*f*) 293, and (*g*) 298 K

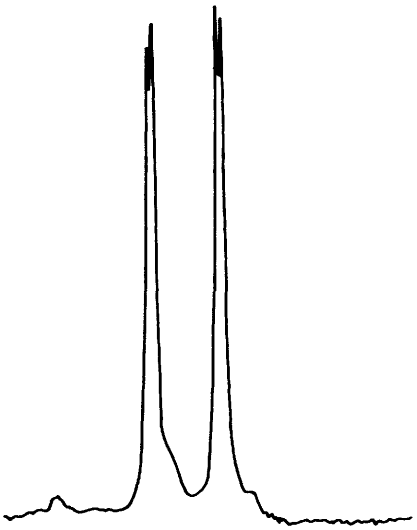

Figure 3. $^{31}P\text{-}\{^{1}H\}$ N.m.r. spectrum (32.4 MHz) of $[Ag(dppm)_3]^+$ at 193 K

A process which interchanges the phosphorus atoms of bridging dppm does not appear to have been described previously. Another intramolecular fluxional process involving bridging dppm is the phosphine exchange at one of the metals of a MM′(μ-dppm)$_2$ ring which has been proposed to result in a single PCH_2P resonance.[13] Fluxionality involving unidentate dppm is more frequently observed: intramolecular 'end-over-end' exchange has ample precedent.[14] Recently, intramolecular exchange of dppm-*PP′* and dppm-*P* at one metal centre has been reported.[15] The structure $[Ag_2(\mu\text{-dppm})_3]^{2+}$ **(IV)** is also present in co-ordinating solvents, *e.g.* dimethylformamide.

A complex of stoicheiometry $[Ag(dppm)_2][O_3SCF_3]$ (corresponding to an Ag–P ratio of 1:4) does not exist: according to ^{31}P n.m.r. studies the disproportionation shown below takes

$$Ag^+ + 2\,dppm \longrightarrow \tfrac{1}{3}\,[Ag_2(dppm)_3]^{2+} + \tfrac{1}{3}\,[Ag(dppm)_3]^+$$

place in solutions of this composition. $[Ag(dppm)_3]^+$ is also produced as the main product in solutions of composition $Ag[O_3SCF_3]$–dppm = 1:3 but it could not be obtained analytically pure. Two structures can be proposed for this species involving either four-co-ordinate silver, [Ag(dppm-*PP′*) (dppm-*P*)$_2$]$^+$ or three-co-ordinate silver, [Ag(dppm-*P*)$_3$]$^+$. The ^{31}P-{^{1}H} n.m.r. spectrum of $[Ag(dppm)_3]^+$ [Figure 3: 193 K, CH_2Cl_2, 32.4 MHz; δ -10.5, $J(^{107}Ag^{31}P)$ 156 Hz] is thought to show the fast-exchange limit of an intramolecular exchange of the co-ordinated and the free phosphorus atoms of dppm. The slow-exchange limit could not be attained.

It is probably ring strain[16] that prevents the formation of a complex [Ag(dppm-*PP′*)$_2$]$^+$: dppm chelate rings exhibit P–M–P angles of 67—74°. This implies a ring strain which should be greater for metals involving a tetrahedral co-ordination geometry (*e.g.* d^{10} Ag^{I}, ideal bonding angle 109°) than for metals involving square-planar or octahedral co-ordination geometry (ideal bonding angle 90°). On the other hand, there is reduced ring strain associated with the bridging bonding mode of dppm in (**1**).

The situation found for d^{10} Ag^{I} largely parallels that reported for d^{10} Pt^0: the compound [Pt(dppm-*PP′*)$_2$] does not exist. The reduction of [Pt(dppm-*PP′*)$_2$]$^{2+}$ leads to [Pt$_2$H(dppm-*P*)(μ-dppm)$_2$]$^+$ which is formally the protonated form of [Pt$_2$(μ-dppm)$_3$].[17] In contrast, d^{10} Hg^{II} forms a complex [Hg(dppm-*PP′*)$_2$]$^{2+}$,[15] but we were unable to obtain $[Hg_2(\mu\text{-dppm})_3]^{2+}$

Experimental

The n.m.r. spectra were recorded using Bruker WP-80 and WM-360 spectrometers. Chemical shifts are defined as positive to high frequency of the reference, 85% H_3PO_4; coupling constants are in Hz. Chemical analyses were performed on a Heraeus EA 415 instrument. All reagents were used as commercially available and experiments were carried out under nitrogen.

Preparation of Tris[μ-*bis*(*diphenylphosphino*)*methane*]-*disilver*(I) *Trifluoromethanesulphonate*, (**1**).—A mixture of $Ag[O_3SCF_3]$ (0.1 mmol, 25.7 mg) and dppm (0.15 mmol, 57.6 mg) in dichloromethane (1 cm^3) was stirred until a clear solution was obtained. Evaporation of the solvent revealed $[Ag_2(\mu\text{-dppm})_3][O_3SCF_3]_2$ as a CH_2Cl_2 solvate. These crystals readily lost CH_2Cl_2 on exposure to the atmosphere. Methanol (1 cm^3) was added and the resulting mixture was stirred for 15 min. The solvent was removed *in vacuo*. Recrystallisation of the solid residue from methanol afforded colourless crystals of non-solvated (**1**), m.p. 260—265 °C, in almost quantitative yield (Found: C, 55.3; H, 4.2. Calc. for $C_{77}H_{66}Ag_2F_6O_6P_6S_2$: C, 55.4; H, 4.0%).

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