Template synthesis and X-ray crystal structure of a trinuclear complex with four- and five-coordinate silver(I) centres

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Single-crystal X-ray analysis of the trinuclear complex $[Ag_3L_2][CF_3SO_3]_3$ [L = {(*o*-$Ph_2C_6H_4$)CH = NCH_2CH_2}$_3$N], synthesized by interaction of $Ag(CF_3SO_3)$, $N(CH_2CH_2NH_2)_3$ and *o*-$Ph_2PC_6H_4$(CHO) in 3 : 2 : 6 molar ratio in ethanol, shows that the complex has approximate C_2 symmetry and is composed of a four- and two five-coordinate silver(I) centres.

We have been interested in the preparation of diimino-, diamino- and diamido-diphosphine ligands and demonstrated that these ligands do indeed exhibit a very rich coordination chemistry.[1,2] We have extended our study to the preparation of polydentate ligands containing three or more iminophosphino groups. Herein we report the template synthesis of the heptadentate ligand {(*o*-$Ph_2PC_6H_4$)CH=NCH_2CH_2}$_3$N and the structure of its silver(I) complex.

Attempts to synthesize the heptadentate ligand {(*o*-$Ph_2PC_6H_4$)CH=NCH_2CH_2}$_3$N *via* direct condensation of $N(CH_2CH_2NH_2)_3$ with 3 equiv. of *o*-$Ph_2PC_6H_4$(CHO) were unsuccessful. However, when $Ag(CF_3SO_3)$, $N(CH_2CH_2NH_2)_3$ and *o*-$Ph_2PC_6H_4$(CHO) were allowed to react in 3 : 2 : 6 molar ratio in ethanol for 12 h at room temp., work-up gave the trinuclear silver complex $[Ag_3L_2][CF_3SO_3]_3$ **1**,† [L = {(*o*-$Ph_2PC_6H_4$)CH=NCH_2CH_2}$_3$N], as yellow crystals in moderate yield. Crystals of **1**·2EtOH·$2CH_2Cl_2$·H_2O suitable for X-ray diffraction study‡ were grown from dichloromethane-diethyl ether–ethanol. A perspective drawing of the cation $[Ag_3L_2]^{3+}$ of **1** is shown in Fig. 1 with selected bond lengths and bond angles given in the caption. The structure analysis reveals that the trinuclear complex has approximately C_2 symmetry and is composed of a four- and two five-coordinated silver(I) centres. The two five-coordinate silver centres [Ag(1), Ag(3)] adopt a distorted trigonal-bipyramidal geometry with the equatorial positions occupied by two phosphino [P(1), P(2) for Ag(1); P(5), P(6) for Ag(3)] and an amino [N(1) for Ag(1), N(5) for Ag(3)] groups, and the axial positions by two imino [N(2), N(3) for Ag(1); N(7), N(8) for Ag(3)] groups of the heptadentate ligand L. Their equatorial bond angles [114.8(3), 118.8(3), 126.2(1)° summing to *ca.* 360° for Ag(1); 114.8(3), 118.7(3), 126.2(1)° summing to *ca.* 360° for Ag(3)] and axial bond angle [139.5(3)° for Ag(1); 140.2(3)° for Ag(3)] are almost identical. The Ag–P distances [Ag(1)–P(1) 2.430(5), Ag(1)–P(2) 2.429(4), Ag(3)–P(5) 2.429(5), Ag(3)–P(6) 2.440(4) Å] are normal and comparable to those of analogous silver diimino- and diamino-diphosphine complexes.[2] The Ag–amino distances [Ag(1)–N(1) 2.456(9), Ag(3)–N(5) 2.479(8) Å] are comparable to the long Ag–N distance [2.411(4) Å] in [Ag{P(C_6H_4Me-*p*)$_3$}{$BPh_2(pz)_2$}] (pz = pyrazolyl).[3] The Ag–imino distances [Ag(1)–N(2) 2.580(8), Ag(1)–N(3) 2.608(9), Ag(3)–N(7) 2.661(9), Ag(3)–N(8) 2.654(7) Å] are significantly longer and comparable to the Ag–N distance [2.56(1) Å] in [Ag(Binap-P_2N_2)][BF_4] (Binap = binaphthylene).[2] The tetra-coordinated silver atom [Ag(2)] adopts a distorted tetrahedral geometry by coordinating to the two heptadentate ligands *via* pairs of imino [N(4), N(6)] and phosphino [P(3), P(4)] groups. The Ag–P distances [Ag(2)–P(3) 2.370(5); Ag(2)–P(4) 2.366(4) Å] are normal. The Ag–imino distances [Ag(2)–N(4) 2.604(9), Ag(2)–N(6), 2.643(8) Å] are comparable to those of Ag(1). The P(3)–Ag(2)–P(4) and N(4)–Ag(2)–N(6) angles are 164.8(1) and 83.1(3)°, respectively. The observed structural feature shows that the imino groups only interact weakly with the silver centres.

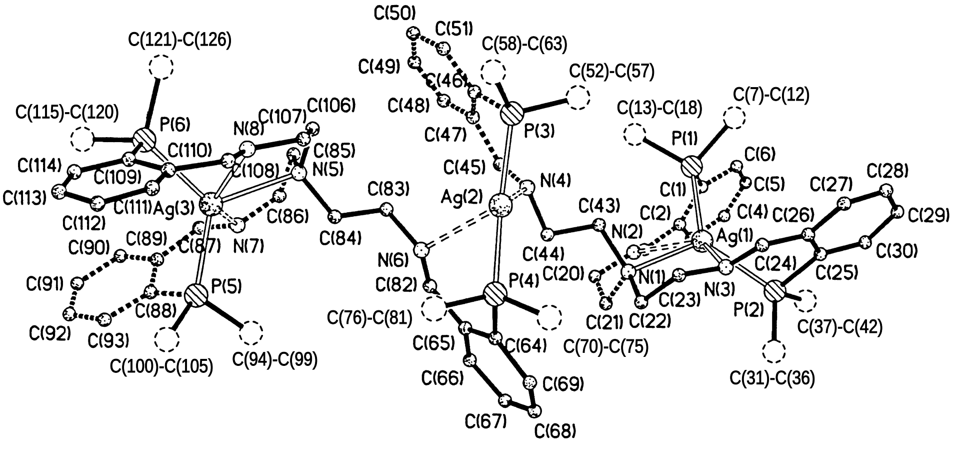
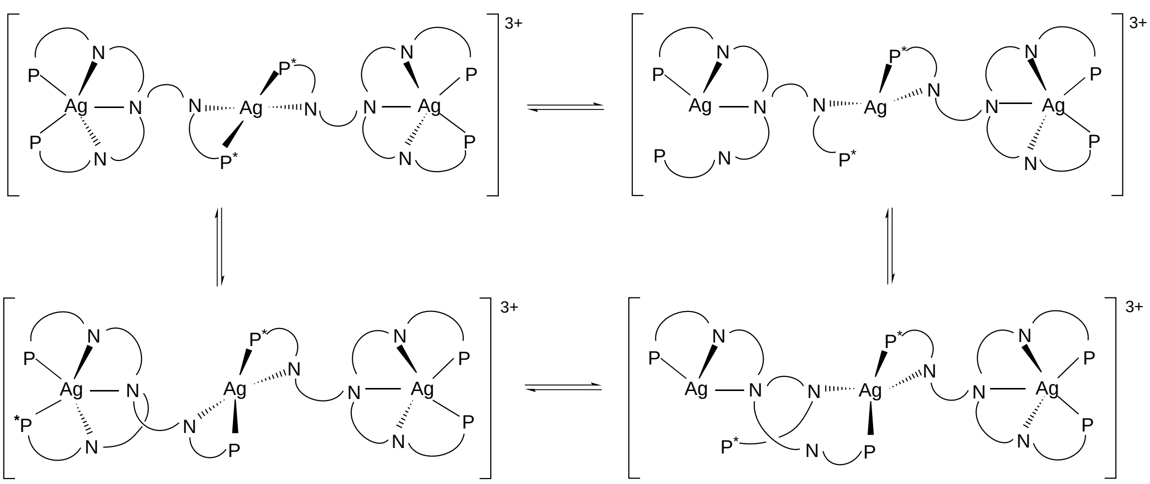


Fig. 1 A perspective drawing of the trinuclear cation $[Ag_3L_2]^{3+}$ of compound **1**. For clarity, the hydrogen atoms are omitted and the phenyl rings of the PPh_2 groups are each represented by a circle with broken outline. Selected bond lengths (Å) and angles (°): Ag(1)–P(1) 2.432(5), Ag(1)–P(2) 2.435(4), Ag(1)–N(1) 2.443(9), Ag(1)–N(2) 2.580(8) , Ag(1)–N(3) 2.608(9), Ag(2)–P(3) 2.370(5), Ag(2)–P(4) 2.366(4), Ag(2)–N(4) 2.604(9), Ag(2)–N(6) 2.643(8), Ag(3)–P(5) 2.429(5), Ag(3)–P(6) 2.440(4), Ag(3)–N(5) 2.479(8), Ag(3)–N(7) 2.661(9), Ag(3)–N(8) 2.654(7), N(2)–C(19) 1.181(14), N(3)–C(24) 1.219(16), N(4)–C(45) 1.221(13), N(6)–C(82) 1.288(17), N(7)–C987) 1.294(11), N(8)–C(108) 1.154(15); P(1)–Ag(1)–P(2) 126.2(1), P(1)–Ag(1)–N(1) 114.8(3), P(2)–Ag(1)–N(1) 118.8(3), N(2)–Ag(1)–N(3) 139.5(3), P(3)–Ag(2)–P(4) 164.8(1), P(3)–Ag(2)–N(4) 73.1(3), P(3)–Ag(2)–N(6) 119.2(3), P(4)–Ag(2)–N(4) 120.1(3), P(4)–Ag(2)–N(6) 72.4(3), N(4)–Ag(2)–N(6) 83.1(3), P(5)–Ag(3)–P(6) 126.2(1), P(5)–Ag(3)–N(5) 114.8(3), P(6)–Ag(3)–N(5) 118.7(3), N(7)–Ag(3)–N(8) 140.2(3).



Scheme 1 Proposed mechanism for the dynamic behaviour of the cation $[Ag_3L]^{3+}$

Complex **1** exhibited temperature-dependent $^{31}P\{^1H\}$ NMR spectra. At room temp. in CD_2Cl_2, two broad peaks centred at δ 6.5 and 10.6 appeared, which at −80 °C broadened into complex multiplets in the range δ 3.0–14.0, indicating non-equivalence of all phosphorus atoms. On the other hand, in $[^2H_7]$DMF at 120 °C the two broad peaks centred at δ 6.9 and 10.4 at 25 °C coalesced into a sharp singlet at δ 7.4, indicating that all the phosphorus atoms were equivalent. The variable-temperature $^{31}P\{^1H\}$ NMR study shows that the phosphino groups undergo facile intramolecular exchange. The observed solution dynamic behaviour can be explained by the proposed mechanism in Scheme 1 which shows that both the imino and the phosphino groups undergo rapid dissociation and association with the metal centres. The free heptadentate ligand $\{(o\text{-}Ph_2PC_6H_4)CH{=}NCH_2CH_2\}_3N$ can be liberated from **1** quantitatively by reacting **1** with an excess of KCN.

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Footnotes and References

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† Crystals of **1** were obtained by the interaction of $Ag(CF_3SO_3)$, $N(CH_2CH_2NH_2)_3$ and $o\text{-}Ph_2PC_6H_4(CHO)$ in 3 : 2 : 6 molar ratio in ethanol for 12 h at room temp. Recrystallization in dichloromethane gave yellow crystals, yield: 0.21 g, 55%, mp 240–242 °C (decomp.) (Found: C, 54.7; H, 4.1; N, 3.9. Calc. for $C_{135}H_{132}Ag_3Cl_4F_9N_8O_{12}P_6S_3$: C, 54.5; H, 4.4; N, 3.8%.) IR (cm^{-1}, in KBr): 3063w, 2841w, 1708w, 1647s, 1560w, 1480w, 1435s, 1263vs, 1223s, 1150s, 1098m, 1086w, 1030vs, 911w, 747s, 696s, 637vs, 575w, 505s. NMR (CD_2Cl_2): $^{31}P\{^1H\}$, δ 8.2 (br, m) and 10.2 (br, m); $^{19}F\{^1H\}$, δ −78.5 (s); ^1H, *H*C=N protons, δ 8.53 (4H, br, s) and 8.60 (2H, br, *s*); phenyl protons, 6.85–7.69 (84H, br, m); NCH_2CH_2N protons, 2.65 (12H, m) and 3.55 (12H, m).

‡ *Crystal data* for $\mathbf{1}\cdot 2C_2H_5OH\cdot 2CH_2Cl_2\cdot H_2O$: $C_{135}H_{132}Ag_3Cl_4F_9N_8O_{12}P_6S_3$, M = 2976.9, triclinic, space group $P\bar{1}$ (no. 2), a = 13.900(2), b = 22.495(2), c = 25.202(2) Å, α = 112.54(2), β = 93.04(2), γ = 94.46(2)°, U = 7226.8(14) Å^3, Z = 2, D_c = 1.368 g cm^{-3}, $F(000)$ = 3044, 294 K, Mo-Kα radiation, λ = 0.71073 Å, μ(Mo-Kα) = 6.56 cm^{-1}, yellow plate 0.10×0.30×0.40 mm, 15731 unique data measured on a MSC/Rigaku RAXIS IIC imaging plate system with a rotating anode (50 kV, 90 mA, 46 3° oscillation frames in the range 0–138°, exposure 10 min per frame),[4] absorption correction using the ABSCOR program,[5] 8731 observed reflections [$F > 6\sigma(F)$]. The structure was solved by direct methods and refined by full matrix least-squares analysis to give R = 0.088, R_w = 0.123. The solvate molecules and the anions exhibit positional disorder and the atoms were each assigned an occupancy factor of 0.5. All non-hydrogen atoms including disordered atoms were refined anisotropically. The total number of refined parameters is 1611. Hydrogen atoms were generated in their idealized positions (C–H bond fixed at 0.96 Å) and allowed to ride on their respective parent carbon atoms. These hydrogen atoms were assigned appropriate isotropic thermal parameters and included in structure-factor calculations but not in the refinement. Computations were performed using the SHELTXL-PLUS (PC version) program package.[6] CCDC 182/496.

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