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Synthesis and structural characterisation of silver(I) compounds with nitrogen ligands

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Some silver(I) complexes of acyclic tri- and tetra-dentate nitrogen-containing ligands have been prepared and structurally characterised. In those complexes containing only the silver ion and the ligand a polymeric structure was observed in the solid state. However, the addition of another co-ordinating ligand, *e.g.* trimethylphosphine, inhibited polymer formation, leading to a dimeric structure.

There is an increasing interest in the use of silver(I) compounds as drugs and diagnostic agents. For example, Sadler and co-workers[1] reported that silver(I) compounds with bidentate phosphine ligands exhibit antimicrobial and anticancer activity. Macrocyclic silver(I) complexes have also been widely studied because such compounds undergo very slow acid-dependent decomplexation and therefore may be useful for ^{111}Ag-based radioimmunotherapy.[2] Most of these macrocyclic compounds and a great number of silver(I) compounds with acyclic multidentate ligands are mono- or di-nuclear complexes. The co-ordination number of silver in these complexes varies from four to six.[3] Polymeric silver(I) complexes with inorganic[4–7] and organic[8–12] ligands have been reported, but the synthesis and characterisation of many of these compounds is incomplete because of their insolubilities.[10,11] Richmond and co-workers have shown that AgO_3SCF_3 with 1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene gives a polymeric derivative,[11] but a reversible polymerisation reaction results when the related phenyl derivatives $XC_6H_4CHNC_2H_4NCHC_6H_4X$ ($X = Cl$ or Br) are added in a 1 : 2 molar ratio.[12]

The study of silver(I) with simple acyclic nitrogen-donor ligands has, however, been relatively neglected. In this paper we describe the synthesis and structural characterisation of some novel silver(I) complexes of diethylenetriamine (dien), tris(2-aminoethyl)amine (tren) and *N*,*N*′-bis(aminoethyl)propane-1,3-diamine (tetraen) as ligands. To our knowledge this work represents the first structural characterisation of silver(I) polymers with simple acyclic aliphatic tri- and tetra-dentate nitrogen ligands.

Results and Discussion

Synthesis and characterisation

Silver hexafluorophosphate dissolved in ethanol reacts at room temperature with dien in a 1 : 1 ratio to give an insoluble compound which could not be fully characterised. However, $AgPF_6$ reacts under similar conditions with dien in a 1 : 2 ratio to yield a compound which remains soluble in ethanol. The resulting solution was stirred for 30 min and the colourless product was precipitated in 85% yield, based on silver, on addition of a large volume of pentane. These and all subsequent reactions of silver(I) salts described in this paper were done in reaction vessels where direct light was excluded. The resulting complex, $[Ag(dien)][PF_6]$ **1** is slightly light-sensitive, but may be stored indefinitely under nitrogen at −30 °C in the dark. It is very soluble in organic solvents such as methanol, ethanol and acetonitrile but not in pentane and toluene. Single crystals suitable for X-ray crystallography were grown by recrystallising the compound from ethanol at room temperature. The compounds $[Ag(tren)][PF_6]$ **2** and $[Ag(tetraen)][PF_6]$ **3** were synthesised in a similar manner, acetonitrile being used as solvent since both these compounds are insoluble in ethanol.

The infrared spectra of **1**–**3** show N—H stretching vibrations in the range 3386–3324 cm^{-1}, δ(NH_2) bending vibrations between 1606–1660 cm^{-1} and ν(Ag–N) bands in the range 559–550 cm^{-1}. The ^{1}H and ^{13}C NMR spectral data for these compounds are summarised in the Experimental section.

Since the crystallographic determinations which are described below have shown that compounds **1** and **2** adopt polymeric structures it was of interest to establish whether the chains could be broken up by the addition of monodentate ligands. Therefore, PMe_3, PPh_3 and Bu^{t}NC were added to silver(I)–dien solutions. Silver hexafluorophosphate reacts with 1 equivalent of PMe_3 and 2 equivalents of dien in ethanol at 23 °C to give $[Ag_2(dien)_2(PMe_3)_2][PF_6]_2$ **4** in 88% yield, based on silver. The complex is slightly light-sensitive, but may be stored under nitrogen at −30 °C in the dark without decomposition. The complex is soluble in organic solvents such as methanol, ethanol and acetonitrile, but not in pentane or toluene.

Single crystals of **4** suitable for X-ray crystallography were grown by crystallising the compound from ethanol and pentane at −25 °C. The compounds $[Ag(dien)(PPh_3)]_n[PF_6]_n$ **5** and $[Ag(dien)(Bu^tNC)]_n[PF_6]_n$ **6** were synthesised in an analogous manner, but acetonitrile was used as solvent since these last two are less soluble in ethanol.

The infrared spectra of **4**–**6** show N—H stretching vibrations in the range 3390–3310 cm^{-1}, δ(NH_2) bending vibrations between 1600 and 1590 cm^{-1} and ν(Ag–N) bands in the range 563–547 cm^{-1}. The ν(NC) band for $[Ag(dien)(Bu^tNC)]_n[PF_6]_n$ appears at 2194 cm^{-1} and the δ(CMe_3) band at 1376 cm^{-1}. The ^{1}H and ^{13}C NMR data of these compounds are summarised in the Experimental section. In the ^{31}P NMR spectra the signals of the phosphines are shifted to low field on complexation, for $[Ag_2(dien)_2(PMe_3)_2][PF_6]_2$ from δ −62.0 (free PMe_3) to −38.0 (complex) and for $[Ag(dien)(PPh_3)]_n[PF_6]_n$ from δ −6.0 (free PPh_3) to 14.3 (complex), the PF_6 resonance is observed at δ −143.9 as a septet for both complexes.

Crystal structures

The crystal data, data collection and refinement parameters for compounds **1**, **2** and **4** are summarised in Table 1 and selected bond lengths and angles are given in Table 2. Unfortunately single crystals of compound **3** suitable for X-ray crystallographic analysis could not be obtained. The X-ray analysis of **1** shows it to have a *catena* structure comprising two crystallographically independent silver atoms and two non-equivalent dien ligands which link adjacent silver centres to form the polymeric chain shown in Fig. 1. The silver co-ordination

Table 1 Details of the crystallographic data collection and refinement for compounds **1**, **2** and **4**[a]

Compound	**1**	**2**	**4**
Empirical formula	$[C_4H_{13}AgN_3{\cdot}PF_6]_n$	$[C_6H_{18}AgN_4{\cdot}PF_6]_n$	$C_{14}H_{44}Ag_2N_6{\cdot}2PF_6$
M	356.02	399.08	864.17
Colour, habit	Colourless, platy needles	Colourless, needles	Colourless, needles
Crystal size/mm	0.27 × 0.20 × 0.07	0.60 × 0.30 × 0.30	0.23 × 0.16 × 0.10
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	$P2_1/n$
a/Å	10.048(1)	10.577(1)	9.998(3)
b/Å	14.776(3)	13.940(1)	9.555(2)
c/Å	14.931(1)	18.088(3)	17.924(2)
β/°	93.59(1)	—	104.66(2)
U/Å^3	2212.5(5)	2667.0(6)	1656.6(6)
Z	8^b	8^b	2^c
D_c/Mg m^{-3}	2.138	1.988	1.732
Radiation (λ/Å)	Cu-Kα (1.541 78)	Mo-Kα (0.710 73)	Cu-Kα (1.541 78)
μ/mm^{-1}	16.616	1.691	12.100
Maximum, minimum transmission	0.1319, 0.0322	0.5341, 0.4891	0.8412, 0.3403
2θ range/°	8–120	3.6–60	9.2–120
F(000)	1392	1584	864
Independent reflections (R_{int})	3274 (0.075)	4331 (0.00)	2462 (0.054)
Observed reflections [$F > 4\sigma(F)$]	2184	3475	1711
No. of parameters refined	356	326	172
Weighting factors a,b^d	0.100, 5.000	0.040, 1.900	0.100, 2.750
Final $R1$, $wR2^e$	0.066, 0.169	0.041, 0.097	0.066, 0.163
Goodness of fit	1.08	1.08	1.04
Largest, mean Δ/σ	0.000, 0.000	−0.003, 0.001	−0.001, 0.000
Largest difference peak, hole/e Å^{-3}	0.734, −1.227	0.786, −0.416	0.691, −0.931
Extinction	0.0016	0.0023	—

[a] Details in common: graphite-monochromated radiation, ω scans, Siemens P4 diffractometer, refinement based on F^2, 293 K, semiempirical absorption corrections from ψ scans. [b] There are two crystallographically independent molecules in the asymmetric unit. [c] The molecule has crystallographic C_i symmetry. [d] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$. [e] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$.

Table 2 Selected bond lengths (Å) and angles (°) for compounds **1**, **2** and **4**

Compound **1**			
Ag(1)–N(16A)	2.17(1)	Ag(9)–N(8)	2.17(1)
Ag(1)–N(2)	2.23(1)	Ag(9)–N(10)	2.22(1)
Ag(1)–N(5)	2.46(1)	Ag(9)–N(13)	2.47(1)
N(16A)–Ag(1)–N(2)	159.0(4)	N(8)–Ag(9)–N(10)	159.7(5)
N(16A)–Ag(1)–N(5)	123.7(4)	N(8)–Ag(9)–N(13)	122.8(4)
N(2)–Ag(1)–N(5)	77.0(4)	N(10)–Ag(9)–N(13)	77.4(4)
Compound **2**			
Ag(1)–N(2)	2.384(6)	Ag(12)–N(1)	2.254(5)
Ag(1)–N(5)	2.478(5)	Ag(12)–N(13)	2.442(6)
Ag(1)–N(8)	2.326(5)	Ag(12)–N(16)	2.545(5)
Ag(1)–N(22A)	2.246(6)	Ag(12)–N(19)	2.285(5)
N(2)–Ag(1)–N(5)	76.0(2)	N(11)–Ag(12)–N(13)	104.7(2)
N(2)–Ag(1)–N(8)	109.7(2)	N(11)–Ag(12)–N(16)	133.6(2)
N(5)–Ag(1)–N(8)	75.3(2)	N(11)–Ag(12)–N(19)	140.8(2)
N(2)–Ag(1)–N(22A)	118.2(2)	N(13)–Ag(12)–N(16)	73.7(2)
N(5)–Ag(1)–N(22A)	126.9(2)	N(13)–Ag(12)–N(19)	109.6(2)
N(8)–Ag(1)–N(22A)	130.5(2)	N(16)–Ag(12)–N(19)	75.3(2)
Compound **4**			
Ag(1)–P(1)	2.372(3)	Ag(1)–N(8)	2.516(9)
Ag(1)–N(5)	2.368(9)	Ag(1)–N(11A)	2.343(8)
P(1)–Ag(1)–N(5)	124.2(3)	N(5)–Ag(1)–N(8)	74.9(3)
P(1)–Ag(1)–N(8)	116.7(2)	N(5)–Ag(1)–N(11A)	94.3(3)
P(2)–Ag(1)–N(11A)	134.9(2)	N(8)–Ag(1)–N(11A)	93.7(3)

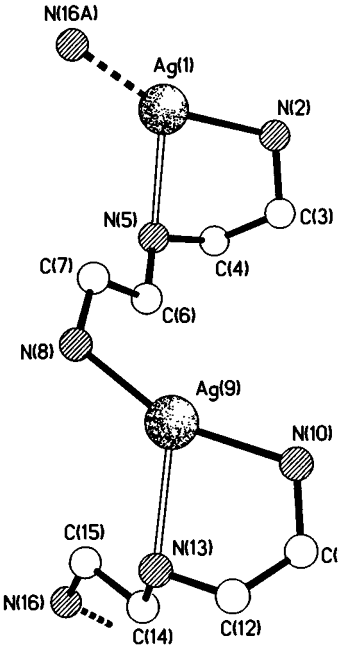

Fig. 1 Structure of the polymeric cation in compound **1**

geometry in the chain is approximately T-shaped. The terminal atoms of the dien ligands generate angles at Ag(1) and Ag(9) of 159.0(4) [N(2)–Ag(1)–N(16A)] and 159.7(5)° [N(10)–Ag(9)– N(8)]. The associated Ag–N distances are 2.23(1) and 2.17(1) Å at Ag(1) for N(2) and N(16A), and 2.22(1) and 2.17(1) Å at Ag(9) for N(10) and N(8) respectively. These silver–nitrogen bond lengths are relatively long compared with those found in polymeric compounds where the silver is two-co-ordinate, *e.g.* $[Ag(XC_6H_4CHNC_2H_4NCHC_6H_4X)]O_3SCF_3$: 2.13(1), 2.16(4) Å;[12] $[Ag(NCS)_2AsF_6]_n$: 2.11(7) Å[5] or $[AgN(CN)_2]$: 2.11(1) Å.[7] The Ag(1)–N(2) and Ag(9)–N(10) bond distances in compound **1** are approximately equal to the average Ag–N bond lengths in compounds with higher co-ordination numbers.[4,8,9] The T-shaped co-ordination geometry in **1** is completed by a secondary weaker 'side-on' interaction to the central nitrogen atom of each dien chain [2.46(1)Å to N(5) and 2.47(1) Å to N(13)], resulting in pairs of five-membered chelate rings. The bond angles 77.0(4)° for N(2)–Ag(1)–N(5) and 77.4(4)° for N(10)–Ag(9)–N(13) are comparable with those reported for other related five-membered chelate rings

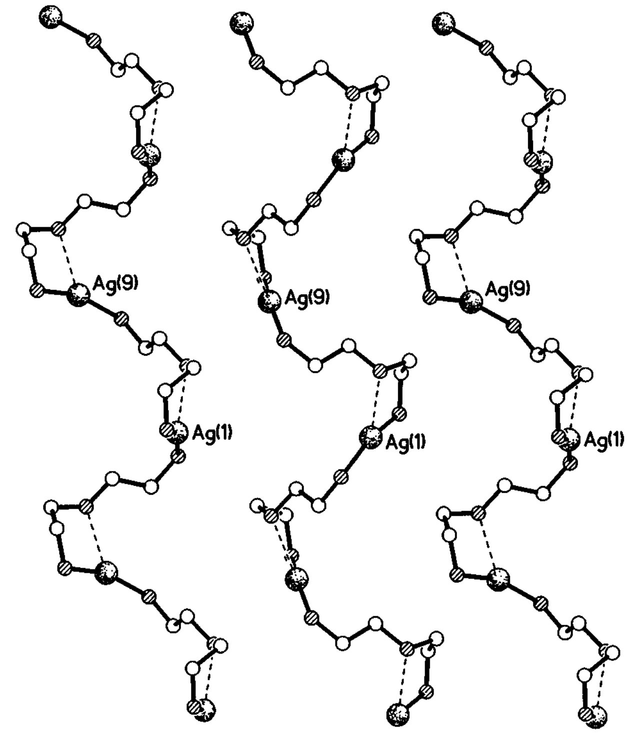

Fig. 2 Packing of the polymeric chains in compound **1**

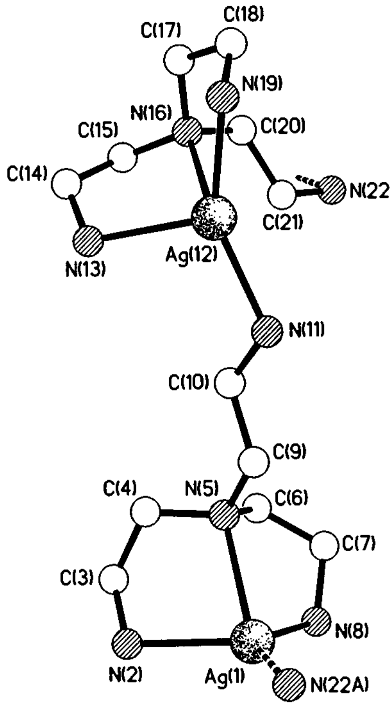

Fig. 3 Structure of the polymeric cation in compound **2**

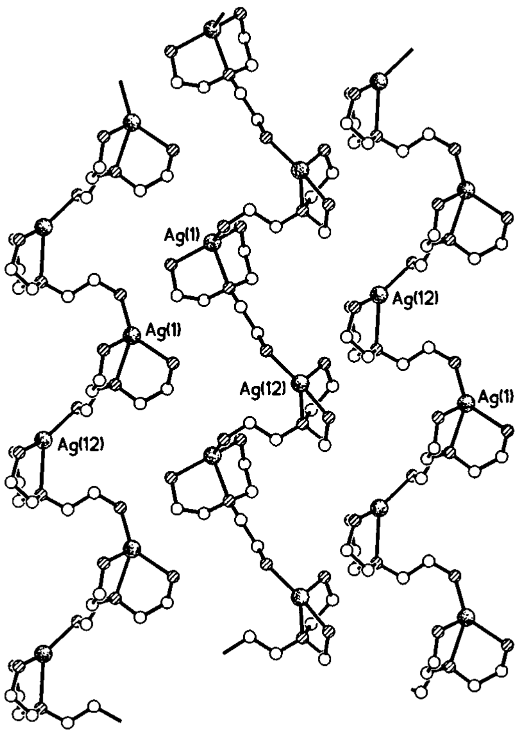

Fig. 4 Packing of the polymeric chains in compound **2**

[73.9(3)°, 76.8(1)° in related silver(I)-nitrogen compounds].[10,13] It is noticeable that the 'in-chain' Ag–N distances within the five-membered chelate rings are slightly longer than those that are outside. Each AgN$_3$ unit is essentially planar, with maximum deviations from planarity of 0.05 Å for Ag(1) and 0.03 Å for Ag(9).

The two ligand conformations are virtually identical; the principal difference being that adjacent ligands within any one chain are enantiomeric giving rise to alternating δ and λ conformations for the five-membered chelate rings. The polymeric chains, which extend in the crystallographic *a* direction, are approximately sinusoidal in nature and pack such that the peaks of one chain lie in the troughs of the next (Fig. 2). There are no short inter-chain contacts. The 'in-chain' Ag···Ag separations of 5.9 and 6.1 Å are shorter than those between Ag atoms in adjacent chains (shortest distance 7.5 Å). The PF$_6$ anions lie in interstices between the polymer chains.

In the analogous gold complex [{Au$_2$(dien)$_2$}$^{2+}$]$_n$ the dien ligand is bidentate and an infinite linear polymer based on weak gold–gold contacts is formed.[14] The only copper(I)–dien complexes with supporting co-ligands which have been structurally characterised are monomeric, *i.e.* [Cu(dien)(CO)]$^+$ [15] and [Cu(dien)R]$^+$ (R = hex-1-ene).[16]

The structure of compound **2** is also based on a polymeric arrangement comprising of two crystallographically independent silver–tris(2-aminoethyl)amine units which are illustrated in Figs. 3 and 4. The amine tren acts as a tetradentate ligand in this complex. The co-ordination geometries at the two silver centres may be described as distorted tetrahedral and exhibit significant differences. The geometry at Ag(1) is less distorted and the trigonal base is formed from N(2), N(8) and N(22A) (the silver atom only lies 0.17 Å out of the plane of the three nitrogen atoms), the 'in-plane' Ag–N distances being 2.384(6), 2.326(5) and 2.246(6) Å to N(2), N(8) and N(22A) respectively. These bond distances are comparable with those reported for other tetrahedral silver(I) complexes with nitrogen ligands.[9–11] There are angled 'apical' approaches of both bridgehead nitrogen atoms N(5), N(16) at slightly longer Ag–N distances of 2.478(5) and 2.545(5) Å respectively, the N(5)–Ag(1) linkage being inclined by 57° to the N(2), N(8), N(22A) plane, the N(16)–Ag(12) vector by 51° to the N(11), N(13), N(19) plane. The N–Ag–N angles [73.7(2)–76.0(2), 109.6(2) and 109.7(2)°] and the longer silver–bridgehead nitrogen bonding are comparable with the values reported for the macrobicyclic hexamine cryptate [Ag$_2${N[(CH$_2$)$_2$N=CH(*p*-C$_6$H$_4$)CH=N(CH$_2$)$_2$]$_3$N}]$^{2+}$.[17] It is interesting that at both silver centres it is the bond from the terminal nitrogen atom which is the shortest.

As in **1** the chains have a sinusoidal nature and pack with the peaks at one chain lying approximately in the troughs of the next. The 'in-chain' Ag···Ag separations are 6.5 and 7.7 Å and the shortest interchain Ag···Ag distance is 6.7 Å. The PF$_6$ anions also lie in the interstices between the polymer chains.

The X-ray structural analysis of compound **4** reveals the formation of a C_i symmetric bimetallic macrocyclic complex

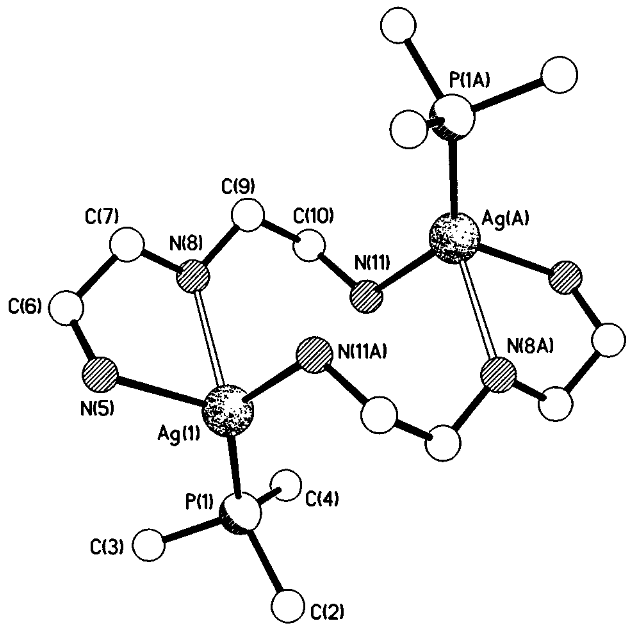

Fig. 5 Structure of the cationic macrocycle in compound **4**

comprising two silver atoms and two bridging diens (Fig. 5). The co-ordination geometries at the silver atoms are probably best described as severely distorted tetrahedral. The atoms N(5), N(11A) and P(1) are at 2.368(9), 2.343(8) and 2.372(3) Å from Ag which lies 0.34 Å out of the plane formed by these three atoms. The Ag–P bond length of 2.372(3) Å is slightly shorter than silver–phosphorus bonds reported in the literature [2.39–2.63 Å].[18] The Ag–N distances with 2.368(9) Å [Ag(1)–N(5)] and 2.343(8) Å [Ag(1)–N(11A)] are in good agreement with the average values of 2.31–2.44 Å found for four-co-ordinated silver.[10,11,13,17] As observed in the 1:1 Ag:dien complex **1** there is a longer approach [2.516(9) Å] of the central nitrogen atom, N(8), to the silver centre, the N(8)–Ag vector being inclined by 66° to the P(1), N(5), N(11A) plane. The transannular Ag···Ag separation is 4.71 Å, and the shortest intermacrocycle Ag···Ag contact is 6.4 Å, there being no notable intercomplex interactions.

The formation of this macrocyclic complex is directly analogous to the cyclic compound formed between $AuBF_4$ and dien[14] which is propagated *via* weak Au···Au interactions to give a polymeric structure. Polymer formation in compound **4**, however, is inhibited by the presence of the co-ordinated trimethylphosphine. Although in both the Au and Ag macrocyclic complexes the dien ligand has consistent *anti* and *gauche* geometries about the C–N and C–C bonds respectively, in the 'chain' polymers a mixture of *anti* and *gauche* geometries is observed for both the C–N and the C–C bonds.

Conclusion

Silver(I) forms an interesting range of polymeric chain compounds with polydentate nitrogen acyclic ligands, two of which have been structurally characterised. The addition of monodentate ligands such as phosphines or isocyanides to these compounds leads to the formation of simpler binuclear species.

Experimental

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques and in vessels from which light was excluded. Organic solvents were of reagent grade and were dried by published procedures and distilled under N_2 and vacuum degassed before use. All chemicals were purchased from Aldrich and used without further purification. The infrared spectra of the compounds were recorded on Nujol mulls using a Perkin-Elmer 1720 Infrared Fourier-transform Spectrometer. The NMR spectra were recorded on a JEOL JNM-EX270 FT-NMR spectrometer; ^{1}H and ^{13}C chemical shifts were referenced to tetramethylsilane and those of ^{31}P to H_3PO_4.

Syntheses

[Ag(dien)][PF$_6$] 1. To $AgPF_6$ (0.2 g, 0.70 mmol) in ethanol (20 cm^3), dien (0.17 cm^3, 1.58 mmol) was added at room temperature. The resulting colourless solution was stirred for 30 min and the product was crystallised by the addition of a large volume of pentane affording colourless microcrystalline [Ag(dien)][PF$_6$]. Yield: 85%, based on silver. IR (Nujol, cm^{-1}): 3386, 3324 (ν N–H), 2922, 2873 (ν C–H), 830 (ν PF$_6$), 559 (ν Ag–N). ^{1}H NMR (CD_3CN): δ 2.84 (4 H, CH$_2$), 2.69 (4 H, CH$_2$), 2.10 (5 H, NH$_2$/NH). ^{13}C NMR (CD_3CN): δ 51.00, 41.70. Fast atom bombardment (FAB) mass spectrum: *m/z* 567 [M]$^{2+}$[PF$_6$], 422 [Ag$_2$(dien)$_2$]$^+$ (Found: C, 13.10; H, 3.60; N, 11.31. $C_4H_{13}AgF_6N_3P$ requires: C, 13.51; H, 3.65; N, 11.80%).

[Ag(tren)][PF$_6$] 2. The amine tren (0.28 cm^3, 1.87 mmol) was added slowly to a solution of $AgPF_6$ (0.22 g, 0.87 mmol) in acetonitrile (30 cm^3) at room temperature. After stirring for 35 min the colourless product was crystallised by the addition of a large volume of ethanol affording colourless, analytically pure [Ag(tren)][PF$_6$]. Yield: 87%, based on silver. IR (Nujol, cm^{-1}): 3386, 3325 (ν N–H), 2920, 2875 (ν C–H), 834 (ν PF$_6$), 558 (ν Ag–N). ^{1}H NMR (CD_3CN): δ 2.81 (6 H, CH$_2$), 2.56 (6 H, CH$_2$), 2.14 (6 H, NH$_2$/NH). ^{13}C NMR (CD_3CN): δ 55.79, 40.57. FAB mass spectrum: *m/z* 413 [Ag(tren)(NH$_2$)]$^{2+}$[PF$_6$], 397 [Ag(tren)]$^{2+}$[PF$_6$] (Found: C, 18.25; H, 4.17; N, 13.79. $C_6H_{18}AgF_6N_4P$ requires: C, 18.05; H, 4.51; N, 14.00%).

[Ag(tetraen)][PF$_6$] 3. The complex was synthesised as described for [Ag(tren)][PF$_6$]. Yield: 79%, based on silver. IR (Nujol, cm^{-1}): 3386 (ν N–H), 2923, 2858 (ν C–H), 820 (ν PF$_6$), 559 (ν Ag–N). ^{1}H NMR (CD_3CN): δ 2.74–2.58 (12 H, CH$_2$), 1.63 (2 H, CH$_2$), 2.12 (6 H, NH$_2$/NH). ^{13}C NMR (CD_3CN): δ 51.53, 48.80, 41.11, 29.47. FAB mass spectrum: *m/z* 267 [Ag(tetraen)]$^+$, 167 [Ag(H$_2$NC$_2$H$_4$NH)]$^+$ (Found: C, 20.96; H, 4.56; N, 13.39. $C_7H_{20}AgF_6N_4P$ requires: C, 20.84; H, 4.34; N, 13.56%).

[Ag$_2$(dien)$_2$(PMe$_3$)$_2$][PF$_6$]$_2$ 4. The phosphine PMe_3 [0.87 cm^3 of 1.0 mol dm^{-3} solution in tetrahydrofuran (thf), 0.87 mmol] was added dropwise to a solution of $AgPF_6$ (0.22 g, 0.87 mmol) in ethanol (25 cm^3) at room temperature. After stirring for 10 min dien (0.18 cm^3, 1.74 mmol) was added. The colourless solution was stirred for 30 min and the product was crystallised by the addition of pentane to give colourless, analytically pure [Ag$_2$(dien)$_2$(PMe$_3$)$_2$][PF$_6$]. Yield: 88% based on silver. IR (Nujol, cm^{-1}): 3390 (ν N–H), 2923, 2857 (ν C–H), 835 (ν PF$_6$), 547 (ν Ag–N). ^{1}H NMR (CD_3CN): δ 2.71 (8 H, CH$_2$), 2.60 (8 H, CH$_2$), 1.97 (10 H, NH$_2$/NH), 1.29, 1.27 (18 H, PCH$_3$). ^{13}C NMR (CD_3CN): δ 49.41, 40.81 (CH$_2$), 15.97, 15.67 (PCH$_3$). ^{31}P NMR (CD_3CN): δ −38. (FAB) mass spectrum *m/z*: 285 [Ag(dien)(PMe) − 2H]$^+$, 260 [M − C$_2$H$_4$]$^+$, 210 [Ag(dien)]$^+$. (Found: C, 19.58; H, 4.22; N, 9.81. $C_{14}H_{44}Ag_2F_{12}N_6P_4$ requires: C, 19.44; H, 5.32; N, 9.72%).

[Ag(dien)(PPh$_3$)]$_n$[PF$_6$]$_n$ 5. To $AgPF_6$ (0.25 g, 0.98 mmol) in acetonitrile (40 cm^3) the phosphine PPh_3 (0.26 g, 0.98 mmol) was added at room temperature. The solution was stirred for 15 min and dien (0.22 cm^3, 1.97 mmol) was added. After stirring for 40 min the product was crystallised by the addition of pentane to give colourless microcrystalline [Ag(dien)(PPh$_3$)]$_n$[PF$_6$]$_n$. Yield: 82%, based on silver. IR (Nujol, cm^{-1}): 3379, 3323 (ν N–H), 2923, 2856 (ν C–H), 823 (ν PF$_6$), 557 (ν Ag–N). ^{1}H

NMR (CD_3CN): δ 7.42 (15 H, Ph_3), 2.70 (4 H, CH_2), 2.66 (4 H, CH_2), 1.90 (5 H, NH_2/NH). ^{13}C NMR (CD_3CN): δ 133.60–128.89 (Ph_3), 48.23, 40.11 (CH_2). ^{31}P NMR (CD_3CN): δ 14.30. FAB mass spectrum: *m*/*z* 472 $[Ag(dien)(PPh_3)]^+$, 369 $[Ag(PPh_3)]^+$, 210 $[Ag(dien)]^+$ (Found: C, 42.76; H, 4.31; N, 6.74. $C_{22}H_{28}AgF_6N_3P$ requires: C, 42.77; H, 4.53; N,6.80%).

$[Ag(dien)(Bu^tNC)]_n[PF_6]_n$ 6. The complex was synthesised as described for $[Ag(dien)(PPh_3)]_n[PF_6]_n$. Yield: 78%, based on silver. IR (Nujol, cm^{-1}): 3384, 3310 [ν N−H], 2915, 2852 [ν C−H], 2194 [ν NC], 838 [ν PF_6], 563 [ν Ag–N]. ^{1}H NMR (CD_3CN): δ 2.73 (4 H, CH_2), 2.62 (4 H, CH_2), 1.99 (5 H, NH_2/NH), 1.58 (9 H, Bu^t). ^{13}C NMR (CD_3CN): 151.43 (NC), 57.03, 29.00 (Bu^t), 48.26, 39.94 (CH_2). FAB mass spectrum: *m*/*z* 293 $[Ag(dien)(Bu^tNC)]^+$, 210 $[Ag(dien)]^+$ (Found: C, 24.44; H, 4.48; N, 11.87. $C_9H_{22}AgF_6N_4P$ requires: C, 24.64; H, 5.02; N, 11.77%).

Crystallography

Compound **1** was solved using the heavy-atom method, **2** and **4** by direct methods. All three structures were refined by full-matrix least-squares based on F^2. The non-hydrogen atoms were refined anisotropically. In **2**, there was disorder in both of the PF_6 anions, which was resolved into alternate partial occupancy orientations, the major occupancies of which were refined anisotropically. For all three structures the N−H hydrogen atoms were located from a difference map and idealised, the C−H hydrogen atom positions were calculated. All hydrogen atoms were assigned isotropic thermal parameters $U(H) = 1.2\ U_{eq}$ (C/N) and allowed to ride on their parent atoms. The absolute structure for **2** was determined by both an *R*-factor test and a Flack parameter test. Computations were carried out using the SHELXTL PC program system 6.[19]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/512.

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