DALTON
FULL PAPER

Synthesis and structural systematics of mixed triphenylphosphine/imidazole base adducts of silver(I) oxyanion salts†

Augusto Cingolani,[a] Effendy,[b,c] Fabio Marchetti,[a] Claudio Pettinari,*[a] Brian W. Skelton[b] and Allan H. White[b]

[a] *Dipartimento di Scienze Chimiche, via S. Agostino 1, Università degli Studi, 62032 Camerino (MC), Italy*
[b] *Department of Chemistry, University of Western Australia, Nedlands, WA, 6907, Australia*
[c] *Jurusan Pendidikan Kimia, FPMIPA IKIP Malang, Jalan Surabaya 6, Malang 65145, Indonesia*

Received 16th August 1999, Accepted 28th September 1999

From the interaction between imidazole-type ligands B and $[Ag(PPh_3)_4]X$ (X = NO_3, BF_4, ClO_4 or CF_3CO_2), $[Ag(PCy_3)_2(NO_3)]$ and $[Ag(PPh_3)X)]$ (X = NO_2 or CH_3SO_3), new ionic mononuclear $[Ag(PR_3)_{4-n}(B)_n]^+[X]^-$ (R = Ph or Cy) and neutral mono- ($[Ag(PR_3)_{3-n}(B)_n(X)]$) and di-nuclear ($[\{Ag(PPh_3)(B)(\mu\text{-}X)\}_2]$) complexes have been obtained which have been characterized through elemental analysis, IR and far-IR, conductivity, ^1H NMR and in some cases also by vaporimetric molecular weight measurements and ^{31}P NMR. Stoichiometries and molecular structures are dependent on the nature of the azole (steric hindrance and basicity), of the counter ion, and on the number of the *P*-donor ligands in the starting reactants. Solution data are consistent with a partial dissociation of complexes, occurring through breaking of both Ag–N and Ag–P bonds. The majority of the possible Ph_3P/imidazole base combinations have been characterized structurally by room-temperature single crystal X-ray studies, thus: $[Ag(PPh_3)_3(4\text{-Ph-im})]NO_3$ (4-Ph-im = 4-phenylimidazole), $[Ag(PPh_3)_2B_2]NO_3$ for B = imidazole (Him) or 2-methylimidazole (2-Me-im), $[Ag(PPh_3)(2\text{-Me-im})_3][CF_3CO_2]$, $[Ag(PPh_3)_2(2\text{-Me-im})(O_2NO)]$, $[\{Ag(PPh_3)(1\text{-Me-im})(\mu\text{-}OSOCH_3O)\}_2]$ and $[\{Ag(PPh_3)(Him)(\mu\text{-}ONO)\}_2]$; the latter is a mixture of isomers in which one or both oxygen atoms of the anions interact with silver atoms. In the methanesulfonate complex the interactions of the anions with the silver may be regarded as a perturbation on a proto-linear P–Ag–N array (Ag–P,N 2.3662(6), 2.189(1) Å; P–Ag–N 144.28(6)°).

During our studies of the co-ordination chemistry of pyrazole, imidazole and their derivatives, several zinc,[1] cadmium,[1] mercury,[2] tin(IV),[3–5] and organotin(IV)[3–5] complexes were synthesized and characterized. It has been found that these compounds display a diversity of stable structural types in which the azole ring can be N- or C-bonded depending on the relationship between the steric and electronic preferences of the metal ions and the co-ordinating properties of the ligand. In fact, the Group 12 and 14 metal ions, having no stereoelectronic geometric preferences associated with partially filled d shells, permit more extensive examination of the possible co-ordination modes of a ligand in the absence of metal-directed requirements. In particular, from 1980, several papers have appeared reporting the synthesis and characterization of a number of copper complexes relevant for their structural features,[6] useful in organic synthesis and in catalysis[7] and for investigation of the role of copper centres at the active sites of a number of proteins.[8]

Despite the large number of known copper(I)–azole complexes,[9] only a few papers have been published dealing with analogous silver(I) systems,[10] although the first silver(I) azolides were obtained as early as 1983[11] with interest in this class of compounds continuing thereafter, with potential applications in photography or silver plating by electrochemical processes.[12] Furthermore, it has been reported that these silver(I) complexes exhibit antimicrobial and anticancer activity,[13] while macrocyclic silver(I) compounds have widely been investigated because they undergo very slow acid-dependent decomplexation and therefore may be useful for ^{111}Ag-based radioimmunotherapy.[14]

As a part of our studies into the structural and spectroscopic properties of mixed phosphine/*N*-donor derivatives of silver(I)[15] we were interested in extending the available literature data to include complexes incorporating azole and phosphine ligands with different steric and electronic profile. To this end we have synthesized some new silver(I) complexes containing azole-type ligands (Him = imidazole, 1-Me-im = 1-methylimidazole, 2-Me-im = 2-methylimidazole, 4-Me-im = 4-methylimidazole, 2-Et-im = 2-ethylimidazole, 4-Ph-im = 4-phenylimidazole, Bz-im = benzoimidazole), characterizing a representative array by X-ray diffraction studies and spectroscopic and analytical measurements.

Results and discussion

Syntheses

By the interaction of $[Ag(PPh_3)_4]NO_3$ with an excess of 4-Ph-im in diethyl ether the ionic compound $[Ag(PPh_3)_3(4\text{-Ph-im})]NO_3$ **1** has been obtained upon displacement of one Ph_3P ligand from the co-ordination centre. The donors Him, 2-Me-im, 4-Me-im and 2-Et-im react immediately with $[Ag(PPh_3)_4]NO_3$ displacing two molecules of Ph_3P and yielding the ionic 1:2:2 complexes $[Ag(PPh_3)_2B_2]NO_3{\cdot}xH_2O$ (B = Him, $x = 0$ **2**; B = 2-Me-im, $x = 0$ **3**; B = 4-Me-im, $x = 1$ **4**; B = 2-Et-im, $x = 0$ **5**). Different $Ag(NO_3)/PPh_3$/imidazole base combinations may be obtained depending on the imidazole substituents: 1-Me-im forms the

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4047/. *Also available*: synthesis and characterisation data. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/4047/, otherwise available from BLDSC (No. SUP 57652, 9 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

1:1:3 derivative $[Ag(PPh_3)(1\text{-}Me\text{-}im)_3]NO_3$ **6** whereas Bz-im gives 1:1:2 $[Ag(PPh_3)(Bz\text{-}im)_2(ONO_2)]\cdot 2H_2O$ **7**, always with the displacement of three Ph_3P groups. The donor 2-Me-im also forms the 1:2:1 adduct $[Ag(PPh_3)_2(2\text{-}Me\text{-}im)(ONO_2)]$ **8** when its reaction with $[Ag(PPh_3)_4]NO_3$ is carried out in a strictly equimolar ratio.

Variation of the type of *P*-donor ligand in the starting reactants has been found to change the reactivity and also the stoichiometry of the species: no product has been obtained from the reaction of $[Ag(PCy_3)_2(O_2NO)]$ with Him, 1-Me-im, 4-Me-im or 4-Ph-im, whereas 2-Me-im and Bz-im form the derivatives $[Ag(PCy_3)(2\text{-}Me\text{-}im)_2(ONO_2)]$ **9** and $[Ag(PCy_3)_2(Bz\text{-}im)_2]NO_3\cdot H_2O$ **10** respectively. Only the donors 2-Me-im, 4-Me-im and Bz-im were found to interact with $[Ag(PPh_3)_4][CF_3CO_2]$, yielding the ionic derivatives $[Ag(PPh_3)(2\text{-}Me\text{-}im)_3][CF_3CO_2]$ **11**, $[Ag(PPh_3)_2(4\text{-}Me\text{-}im)_2][CF_3CO_2]$ **12**, and $[Ag(PPh_3)_2(Bz\text{-}im)_2][CF_3CO_2]$ **13** upon displacement of 3 or 2 Ph_3P ligands respectively. The reaction between $[Ag(PPh_3)_4]ClO_4$ and $[Ag(PPh_3)_4]BF_4$ is often very difficult to interpret, intractable material being in most cases recovered. Upon continued crystallization of the reagent mixture, the derivatives $[Ag(PPh_3)_2(1\text{-}Me\text{-}im)_2]ClO_4$ **14**, $[Ag(PPh_3)_2(Bz\text{-}im)_2]ClO_4\cdot Bz\text{-}im$ **15**, $[Ag(PPh_3)_3(2\text{-}Me\text{-}im)]BF_4\cdot 2(2\text{-}Me\text{-}im)$ **16**, $[Ag(PPh_3)_3(1\text{-}Me\text{-}im)]BF_4$ **17**, $[Ag(PPh_3)_3(Bz\text{-}im)]BF_4$ **18**, and $[Ag(PPh_3)_3(4\text{-}Ph\text{-}im)]BF_4$ **19** have been obtained. In the case of derivatives **15** and **16** for which silver:phosphine:imidazole base ratios 1:2:3 and 1:3:3 have been found respectively, the presence of ligand molecules clathrated or hydrogen bonded to ClO_4 and BF_4 groups is likely, as has been previously observed in other Group 11–azole derivatives.[16] Finally, when the mono triphenylphosphine complexes $[Ag(PPh_3)(O_3SCH_3)]$ and $[Ag(PPh_3)(O_2N)]$ interact with our imidazole bases B, the dinuclear complexes $[\{Ag(PPh_3)(1\text{-}Me\text{-}im)(OSOCH_3O)\}_2]$ **20**, $[\{Ag(PPh_3)(Him)(ONO)\}_2]$ **21**, $[\{Ag(PPh_3)(1\text{-}Me\text{-}im)(ONO)\}_2]$ **22**, $[\{Ag(PPh_3)(4\text{-}Ph\text{-}im)(ONO)\}_2]$ **23** and $[\{Ag(PPh_3)(Bz\text{-}im)(ONO)\}_2]$ **24** have been obtained. Although derivatives **1**–**24** generally absorb water from atmospheric moisture, they are generally very stable when stored, at room temperature, in a desiccator under reduced pressure. They are soluble in chlorinated solvents, acetonitrile, acetone and DMSO, but insoluble in Et_2O, alcohols, and aromatic and aliphatic hydrocarbons.

The conductance values of dichloromethane solutions of derivatives **2**, **3**, **5**, **6**, **10**, **15** and **23** have been found to fall in the range 14–24 Ω^{-1} cm^2 mol^{-1}, typical of 1:1 electrolytes or of complexes partially ionized in solution. The remainder of the compounds are apparently un-ionized, having Λ_M values lower than 11 Ω^{-1} cm^2 mol^{-1}. This behaviour, however, may be due to the formation in solution of solvated ion pairs or, alternatively, to dissociation of *P*- or *N*-donor ligands from silver with concomitant re-association of the counter ion.

The vaporimetric molecular weight measurements strongly suggest that mixed triphenylphosphine/imidazole base adducts of silver(I) oxyanion salts may be partially dissociated in chloroform solution, the dissociation being generally dependent on the concentration. For example the ratio of experimental M to formula weight for derivative **1**, which is not an electrolyte in solution, is 0.62:1 at $c = 1 \times 10^{-2}$ m and 0.53 at $c = 0.7 \times 10^{-2}$ m.

Spectroscopy

In the spectra of derivatives **1**–**6** and **10** the ν_2, ν_3 and ν_4 modes of vibration of ionic NO_3^- groups (D_{3h} symmetry) and a unique $\nu_1 + \nu_4$ combination band in the overtones region 1700–1800 cm^{-1} have been detected throughout in accordance with their ionic structure.[17] In the spectra of complexes **7** and **8** the separation between ν_1 and ν_4 is *ca.* 60 cm^{-1}, in accordance with a bidentate nitrato group.[17] However, in the spectrum of **9** three combination $\nu_1 + \nu_4$ bands with a separation of *ca.* 20 cm^{-1} were found, in accordance with a unidentate nitrato ligand.[17] The weak interactions between the silver(I) cation and the nitrate group in **8** are reflected in the small magnitude of the splitting of the asymmetric N–O stretching modes.[17]

In the IR spectra of derivatives **11**–**13** the difference Δ between $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ falls in the range 230–260 cm^{-1}, consistent with the presence of ionic trifluoroacetato groups.[18] Although derivatives **14**–**19** also are ionic in the solid state, the ν_3 modes of BF_4 and ClO_4 always show a splitting into three and two components respectively, typical of a lowering in symmetry from T_d to C_{3v}, consistent with the involvement of BF_4 and ClO_4 in a hydrogen-bonding network with N–H of azoles,[19] ν(N–H) also being considerably broadened.

In the far-IR spectra of methanesulfonate (**20**) and nitrito (**21**–**24**) derivatives some absorptions typical of Ag–O stretching are consistently found in the 300–400 cm^{-1} region. The presence of co-ordinated nitrite and methanesulfonate groups has been confirmed also by the presence in the 1500–1000 and 1100–1000 cm^{-1} regions of bands typical of bridging bidentate ONO[20] and $O\cdot SOCH_3\cdot O$ groups.[21] In particular, for the nitrito complexes **21**–**24**, an examination of the literature data[20] suggests that two absorptions peaking at *ca.* 1400 and 1060 cm^{-1} may be attributed to the stretching frequencies of the NO_2^- group: these values are consistent with a μ-1,1 bridging mode.

The ^1H and ^{31}P NMR spectra have been measured in $CDCl_3$, in which these derivatives show good solubility. The solutions are generally stable enough, and only after some days decomposition can be detected, silver metal being formed. In the ^1H NMR spectra of **1**–**24** the signals due to azoles are always deshielded with respect to those in the spectra of the free donors: the higher the Δ ($\Delta = \delta_{adduct} - \delta_{azole}$), the higher is the donation of electron density from the donor to the metal, and the stronger the corresponding Ag–N interaction. The Δ values further confirm the existence, at least partial, of complexation in solution.

The solution ^{31}P NMR spectrum for each triphenylphosphine complex (**1**–**8**, **11**–**24**) at room temperature consists of a broad singlet, presumed to be consequent on the presence of rapid exchange equilibria. A unique absorption is generally detected, always at lower fields than that of the free phosphine. The chemical shift values move upfield towards the values of free Ph_3P with increasing co-ordination number, with very little difference being generally observed between the tris(triphenylphosphine)silver(I) derivatives **1** and **16**–**19** and the starting tetrakis(triphenylphosphine)silver(I) reagent. The Δ ($\Delta = \delta_{adduct} - \delta_{phosphine}$) values vary from 7 to 18 ppm and for analogous complexes are not strongly dependent on the particular imidazole base employed. Lability of the phosphorus ligands was evident in the temperature dependence of the ^{31}P NMR spectra of some derivatives: for example for **1** δ 9.55 at room temperature and 6.16 at 223 K. The ^{31}P NMR chemical shifts of **1**–**10** may be compared with those of the analogous copper(I) compounds,[9] the substitution of silver for copper producing a small but significantly deshielding effect on the ^{31}P nuclei. The trifluoroacetate derivatives **11**–**13** show extensive disproportionation, even at very low temperature: for example, in the ^{31}P NMR spectrum (203 K) of **11**, three signals, presumably corresponding to $[Ag(PPh_3)]X$ (δ 11.6), $[Ag(PPh_3)_2]X$ (4.4), and $[Ag(PPh_3)_3]X$ (2.8) species, have been observed.

The spectra at 218 K of most of these complexes normally show splittings due to $^1J(Ag\text{–}^{31}P)$, but the separate splitting arising from the different ^{107}Ag and ^{109}Ag nuclei is usually observed only at 208 K. The phosphorus ligand exchange rates are sensibly lower in the tricyclohexylphosphine complexes **9** and **10** where the splitting due to ^{107}Ag and ^{109}Ag nuclei is also observed at room temperature. The observation of $^1J(^{107,109}Ag\text{–}^{31}P)$ at room temperature has been reported previously for complexes containing chelating or strongly sterically hindered phosphine ligands, as is also the case in this work.[22] The $^1J(^{107,109}Ag\text{–}^{31}P)$ coupling constants for **9** and **10** are significantly greater than those for analogous Ph_3P

compounds, presumably in consequence of the high base strength of Cy_3P.

The $^1J(^{107,109}Ag–^{31}P)$ coupling constant values observed in this study generally correlate well with the relationship between this parameter and the molecular structure (Ag–P distances), as has previously been found for other silver/phosphine systems.[23,24] They provide a useful guide to the hybridization of the silver atom and hence to its solution co-ordination number: for example the $^1J(Ag–^{31}P)$ coupling constant value of **6** is 642 Hz correspond to sp silver hybridization in association with a co-ordination number of 2, whereas $^1J(Ag–^{31}P)$ of **1** is 297 Hz, corresponding to sp^2 hybridization and co-ordination number 3.

Surprisingly, two different signals have been found in the low temperature ^{31}P NMR spectrum of complex **20**, suggesting disproportionation or the existence of two isomers. The last hypothesis is consistent with the results of the crystallographic studies (see below).

Crystallographic studies

The present array of single crystal structure determinations defines the nature of a variety of complexes encompassing the majority of accessible stoichiometries of mixed triphenylphosphine/imidazole base arrays about a silver(I) central atom, the oxyanion counter ions being less competitive in respect of co-ordinating capacity *vis-à-vis* the unidentate pnictide bases. In the present work, no attempt has been made to introduce control of stoichiometry or stereochemistry by systematic variation of pnictide base steric or electronic parameters beyond that of the parent base, such substituents as are found in the present imidazole bases being introduced for the purpose of accessing a spectrum of complexes readily amenable to congenial crystallization, within the desired range of types. We note at the outset for the purposes of comparison that the prevailing co-ordination number of the silver atoms throughout the present array is (at least) four; the baseline $[Ag(PPh_3)_4]^+$ array is well defined[25] and of putative *32* (*T*) symmetry, perhaps perturbed by distortions suggestive of overcrowding among the phenyl rings, Ag–P being 3 × 2.668(2) Å *plus* 2.650(2) Å in, *e.g.*, the perchlorate, the mean value (2.66 Å), perhaps slightly excessively long *vis-à-vis* that expected for an unstrained system, but with the difference here in the silver complex greatly diminished relative to that in the isomorphous copper(I) counterpart (2.524(6), 2.605(11) Å)[26] suggesting that associated residual strain in the former may not be large. We now discuss the compounds individually, the silver atom environments and other significant/relevant geometries being recorded in Table 1.

$[Ag(PPh_3)_3(4\text{-Ph-im})]NO_3$ 1. This complex crystallizes with one formula unit devoid of crystallographic symmetry comprising the asymmetric unit of the structure. ⟨Ag–P⟩, 2.54 Å, is diminished relative to the value found in $[Ag(PPh_3)_4]^+$ (see above) but comparable with numerous values established in other $[Ag(PPh_3)_3X]$ arrays,[27] as also is the array of angles about the silver atom. There appear to be no other [Ag-$(PPh_3)_3$(unidentate *N*-base)] arrays structurally characterized which might offer counterpart comparators in that dimension. The silver atom lies well out of the imidazole plane, with an associated asymmetry in the two Ag–N–C angles, possibly electronic in origin, because of the persistence of such asymmetry throughout most of the present array of structures, also suggestive of the possibility of steric crowding or lattice forces, in particular here the hydrogen contact H(3a)···O(1) (1.8_7 Å). The major component of the disordered phenyl ring is quasi-coplanar with the parent imidazole ring (dihedral angle 9.5(3)°).

$[Ag(PPh_3)_2(Him)_2]NO_3$ 2. This complex crystallizes with one formula unit as the asymmetric unit of the structure. Despite being devoid of crystallographic symmetry, the cation approximates closely to *2* symmetry. This determination is of modest precision and a study of its 2-Me-im counterpart, which offered better quality material, was undertaken.

$[Ag(PPh_3)_2(2\text{-Me-im})_2]NO_3$ 3. One half of the formula unit now comprises the asymmetric unit, achieved *via* the disposition of the silver atom on a crystallographic *2* axis which relates pairs of each of the ligands, and the nitrate as disordered about an inversion centre. Perhaps because of packing constraints introduced with the imidazole methyl substituents, the geometries of the cations of **2** and **3** differ appreciably, in a manner clearly perceptible in Fig. 1 and Table 1. While the P–Ag–P and N–Ag–N angles differ little between the two complexes, considerable disparities are found in N–Ag–P, range 104.3(4)–115.1(4)° in **2**, 98.15(5) and 119.33(5)° in **3**, reflecting a twist in the relative disposition of the AgN_2 and AgP_2 planes about the (putative) *2* axis, these being almost normal in **2**, and considerably skewed in **3**; remarkably, *both* ((⟨)Ag–P(⟩)) and ((⟨)Ag–N(⟩)) are longer in **3**. Again, close imidazole H(3)···O (anion) interactions are evident, in **2** for ligand a only (O(1)···H(3a) ($1 - x, 1 - y, 1 - z$) 1.8_6 Å) and in **3** bifurcating (H(3)···O(1) ($1 - x, y, \frac{1}{2} - z$), O(3) ($x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$) 1.9_5, 1.8_9 Å). All co-ordinated bond distances are shorter here than in **1**, Ag–P very appreciably (with concomitant enlargement of P–Ag–P), and Ag–N marginally so. The other possible Ag/P/N stoichiometry within the bound of a four-co-ordinate metal environment, $PAgN_3$, is represented by complex **11**.

$[Ag(PPh_3)(2\text{-Me-im})_3][CF_3CO_2]$ 11. One formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. Here, relative to $[Ag(PPh_3)_4]^+$, **1**, **2** and **3**, Ag–P is further shortened, almost linearly, with ⟨Ag–N⟩ little changed; indeed ⟨N–Ag–N⟩ also is little changed down the array. The molecule, in projection down its axis, exhibits quasi-3 symmetry broken primarily by the dispositions of the methyl substituents, two of which might be considered '*endo*' and one '*exo*', *vis-à-vis* the silver, the variation seemingly having little effect on other molecular parameters, and suggesting that, at least in this array, their steric effect, if any, is of little consequence. The bonding parameters may be compared with those in $[(py)_3Ag(Ph_2P(CH_2)_2PPh_2)Ag(py)_3][ClO_4]_2$,[28] wherein Ag–P 2.375(1) Å is closely comparable with the present, Ag–N (range 2.304(3)–2.444(4), average 2.38 Å) being rather longer, and more variable, as are the 'equivalent' P–Ag–N angles (110.6(1)–134.46(9)°), perhaps in response to the asymmetry in the substitution about the phosphorus.

In the above, the role of the oxyanion counter ion is co-ordinatively passive. With reduction in the metal: total unidentate Group 15 base stoichiometry, (implicitly four-) co-ordination saturation is maintained by entry of the oxyanion into the co-ordination sphere. For total metal: base stoichiometry of 1 : 3, two arrays P_2NAg and PN_2Ag (oxyanion) are available. The first of these has been found structurally accessible in complex **8**.

$[Ag(PPh_3)_2(2\text{-Me-im})(O_2NO)]$ 8. Unlike the above, which are all ionic, in this complex a neutral molecular array, one molecule devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. The nitrate interacts with the silver as an essentially symmetrical chelate of small 'bite', essentially coplanar with the silver despite Ag–O being long. Despite the latter, the oxygen interactions clearly impact on the silver environment, the P_2AgN array being well removed from planarity, although the quasi-right angles among the O–Ag–P,N angles strongly suggest the approach to constitute a perturbation on a proto-planar P_2AgN array. Ag–N (im) is now the shortest such distance observed, while Ag–P are lengthened to values comparable to those found in the other AgP_2 arrays above, with a correspondingly large P–Ag–P angle.

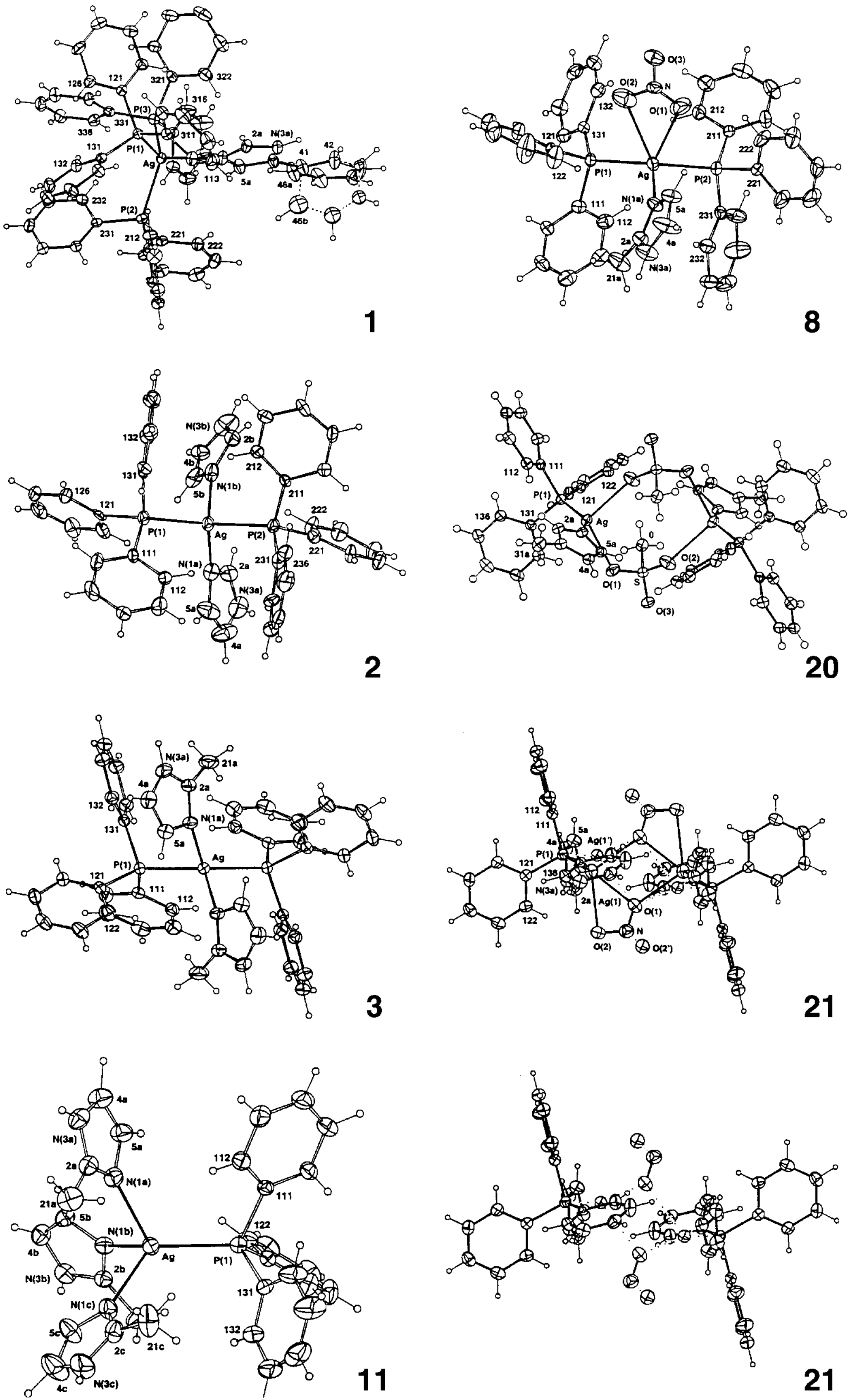


Fig. 1 Molecular projections of the structurally characterized species; 20% thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. For **21** the upper figure shows major solid and minor core components superimposed; in the lower figure the minor component has been isolated.

As yet we do not have a structurally characterized representative of Ag (oxyanion):P:N_2 stoichiometry. Further reduction in metal salt:base stoichiometry leads to 1:1:1 Ag oxyanion:PPh_3:im-base arrays, with an implication of more intimate oxyanion involvement with the silver atom if co-ordination saturation is to be maintained, achievable by increase in anion denticity or by bridging. The two examples structurally characterized are binuclear, involving centrosymmetric arrays with diversely bridging oxyanions; one *O*,*O′* bridging, entailing eight-membered central ring formation, **20**,

Table 1 Silver atom environments. *r*/Å is the silver–ligand atom distance, the other entries in the matrices being the angles (°) subtended at the silver by the relevant atoms at the head of the row and end column

(a) [Ag(PPh_3)$_3$(4-Ph-im)]NO_3 **1**

Atom	*r*	P(2)	P(3)	N(1a)
P(1)	2.521(1)	112.11(5)	113.78(5)	111.2(1)
P(2)	2.554(1)		114.96(4)	106.9(1)
P(3)	2.555(2)			96.6(1)
N(1a)	2.369(4)			

In the anion, N–O (1–3) are 1.231(6), 1.222(7), 1.222(7) Å, with opposite angles of 123.4(5), 116.8(5), 119.8(5)°. Ag–N(1a)–C(2,5a) are 135.6(3), 119.0(3), Ag–P–C range from 110.9(1) to 117.5(2), with C–P–C 101.6(2)–104.7(2)°. The silver atom lies 0.301(9) Å out of the C_3N_2 plane of the Him ligand, H(3a) contacting O(1) of the anion at 1.87 Å.

(b) [Ag(PPh_3)$_2$$B_2$]$NO_3$ (B = Him **2** or 2-Me-im); values for the 2-Me-im adduct are given *italicized* below those for the Him counterpart

Atom	*r*	P(2)	N(1a)	N(1b)
P(1)	2.428(4)	125.1(1)	115.1(4)	106.7(3)
	2.4704(6)	*125.96(3)*	*98.15(5)*	*(119.33(5))*
P(2)	2.458(5)		104.3(4)	106.7(4)
	(2.4704(6))		*119.33(5)*	*(98.15(5))*
N(1a)	2.26(2)			94.4(6)
	2.348(2)			*91.94(7)*
N(1b)	2.34(2)			
	(2.348(2))			

Anion geometries are relatively imprecise/disordered. Ag–N(1a,b)–C(2a,b) are 132(1), 137(1)° with Ag–N(1a,b)–C(5a,b) 123(1), 118(2)° for complex **2**, Ag–N(1a)–C(2,5a) being 129.2(2), 119.2(2)° for **3**; Ag lies 0.70(4), 0.33(4) Å out of the C_3N_2 planes in **2** and 0.875(4) Å in that of **3**. In the phosphine ligands of **2**, Ag–P–C range between 108.1(5) and 116.3(6)° and C–P–C between 102.9(8) and 107.6(7)°; in **3** the counterpart ranges are 111.60(7)–116.49(8) and 103.4(1)–104.6(1)°.

(c) [Ag(PPh_3)$_2$(2-Me-im)(O_2NO)] **8**

Atom	*r*	P(2)	N(1a)	O(1)	O(2)
P(1)	2.447(3)	129.48(9)	113.6(3)	122.2(3)	80.8(3)
P(2)	2.461(3)		105.6(3)	88.9(3)	125.4(3)
N(1a)	2.311(7)			87.8(4)	96.7(3)
O(1)	2.75(1)				42.4(4)
O(2)	2.86(1)				

N–O(1,2,3) are 1.14(2), 1.22(2), 1.23(1) Å with opposite angles 116(1), 126(1), 119(1)°, Ag lying 0.13(2) Å out of the NO_3 plane, 0.04(2) Å out of the ligand plane, with Ag–N(1a)–C(2,5a) being 128.1(8), 124.8(7)°. Ag–P–C range between 109.2(4) and 119.0(4), C–P–C between 101.9(5) and 105.9(5)°.

(d) [Ag(PPh_3)(2-Me-im)$_3$][CF_3CO_2] **11**

Atom	*r*	N(1a)	N(1b)	N(1c)
P(1)	2.376(2)	115.9(2)	123.5(1)	120.6(2)
N(1a)	2.330(9)		92.7(2)	105.0(2)
N(1b)	2.321(5)			93.9(2)
N(1c)	2.336(5)			

Anion geometries are imprecise in consequence of high "thermal motion". Ag–N(1a–c)–C(2a–c) are 136.6(5), 126.2(5), 131.1(6)° and Ag–N(1a–c)–C(5a–c) 119.4(6), 127.4(5), 122.3(5)°, with Ag 0.14(2), 0.49(1), 0.09(2) Å out of the C_3N_2 planes of the three ligands. Ag–P–C range between 113.2(2) and 116.3(2)° and C–P–C 103.5(4)–104.1(3)°.

(e) [{Ag(PPh_3)(1-Me-im)($OSOCH_3O$)}$_2$] **20**; * denotes a centrosymmetrically related atom here and for **21** in (f)

Atom	*r*	N(1a)	O(1)	O(2*)
P(1)	2.3362(6)	144.28(6)	118.55(4)	96.08(4)
N(1a)	2.189(1)		85.88(6)	103.28(5)
O(1)	2.480(2)			103.50(6)
O(2*)	2.666(2)			

S–O(1,2,3),C are 1.463(2), 1.457(2), 1.448(1), 1.762(2) Å; C–S–O(1–3) are 105.6(1), 106.16(9), 107.49(9)°, O–S–O ranging from 111.62(9) to 113.1(1)°. Ag–O(1,2*)–S(*) are 121.48(8), 131.71(9)°. Ag–N(1a)–C(2,5a) are 127.5(1), 125.6(1)°. Ag–P(1)–C(111–113) are 110.14(5), 121.89(7), 112.36(6)°, with C–P–C 103.24(9)–103.8(1)°. The silver atom lies 0.370(3) Å out of the imidazole plane.

(f) [{Ag(PPh_3)(Him)(O_2N)}$_2$] **21**; values for [{Ag(PPh_3)(Him)(ONO)}$_2$] are given *italicized* below those of the major component

Atom	*r*	N(1a)	O(1)	O(1*)	O(2)
P(1)	2.369(1)	129.41(9)	124.0(1)	106.8(1)	113.39(9)
	2.369(4)	*122.6(3)*	*111.3(2)*	*128.8(3)*	—
N(1a)	2.223(3)		105.7(1)	94.9(1)	93.6(1)
	2.365(7)		*92.6(2)*	*107.1(2)*	—
O(1)	2.412(4)			73.2(1)	46.0(1)
	2.739(6)			*75.6(2)*	—
O(1*)	2.571(5)				118.5(1)
	2.082(8)				—
O(2)	2.692(3)	Ag···Ag′ is 0.733(6)			

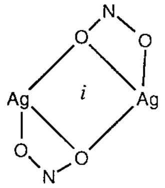
Ag(1) lies 0.02(2) Å out of the NO_2 (as chelate) plane; that plane has a dihedral angle of 48.1(2)° to the central (obligate) $Ag_2O(1)_2$ plane. Ag(1,1′) lie 0.169(7)–0.08(1) Å out of the C_3N_2 ligand plane. Ag,Ag′–N(1a)–C(2a) are 124.6(3), 113.3(3)°; Ag,Ag′–P–C range between 108.8(1) and 116.2(1), 100.2(2) and 123.5(2)°, C–P–C between 104.8(2) and 105.2(1)°.

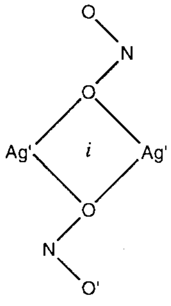
and the other *O* bridging, entailing a four-membered obligate planar system, **21**.

[{Ag(PPh_3)(1-Me-im)($OSOCH_3O$)}$_2$] 20. One half of the binuclear array (= one AgX : PPh_3 : im base (1 : 1 : 1) formula unit) comprises the asymmetric unit of the structure, the dimer being disposed about a crystallographic inversion centre, the central eight-membered ring presumably associated with a lower degree of strain than that of the four-membered Ag(μ-O)$_2$Ag array described below for **21**, with O–Ag–O being 103.50(6)°, a considerably larger effective 'bite' than that of the compact bidentate ligand imposed by that four-membered ring or the four-membered ring in **8** above; Ag–O are shorter than the values found in the monomer **8**, but not the dimer **21**, with which they are comparable. With two Group 15 base donors only now in the co-ordination sphere, these being stronger bases than the oxyanions, a pronounced tendency toward two-co-ordination is observed, Ag–N,P both short and subtending a large P–N–Ag angle; indeed the interactions of the sulfonate ligands may be regarded as perturbations on the novel linear P–Ag–N archetype.

[{Ag(PPh_3)(Him)(ONO)}$_2$] 21. One half of the dimeric array, also a 1 : 1 : 1 formula unit, comprises the asymmetric unit of the structure. Disorder is observed, deconvolutable into major and minor binuclear isomeric components in approximately 10 : 1 ratio. In both isomers O(1) of the nitrate group bridges the two silver atoms; in the major isomer, O(2) together with O(1) of the same anion chelates the silver atom, the NO_2/Ag(μ-O)$_2$Ag interplanar-dihedral angle being 48.1(2)°. The other, minor, dimeric isomer is obtained in association with resolvable disordered components of Ag and O(2), Ag′ and O(2′), constrained to the same site occupancy after trial refinement, wherein the nitrite has swivelled about O(1)–N so that O(2′)

now lies away from the previously chelated silver. (Presumably other components of the structure also move in concert with this change, but to a smaller extent, so that their components are not resolvable.) The two isomers are thus presumed to be of the form below with, possibly, a third in which mixtures of the two nitrite types are incorporated in the one dimer. The geometries of the two centrosymmetric forms are given in Table 1; O(2′) appears to be unfavourably situated to act as a chelating component to the alternative centrosymmetrically related Ag′ component, O(2′)···Ag (1 − *x*, 1 − *y*, 1 − *z*) being 2.98(3) Å.





Experimental

General procedures

All reactions were carried out under an atmosphere of dry oxygen-free dinitrogen, using standard Schlenk techniques. Solvents were freshly distilled over an appropriate drying agent and further degassed before use where necessary. In some cases the reactions were protected from light by covering reaction vessels with aluminium foil. Concentration was always carried out *in vacuo* (water aspirator). The samples for microanalysis were dried *in vacuo* to constant weight (20 °C, *ca.* 0.1 Torr). Elemental analyses (C,H,N) were performed in house with a Carlo-Erba model 1106 instrument. The IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin-Elmer System 2000 FT-IR instrument, ^{1}H, ^{13}C and ^{31}P spectra on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^{1}H, 75 MHz for ^{13}C and 121.4 MHz for ^{31}P). The electrical resistance of acetone solutions was measured with a Crison CDTM 522 conductimeter at room temperature. The osmometric measurements were carried out at 40 °C over a range of concentrations with a Knauer KNA0280 vapour pressure osmometer calibrated with benzil. The solvent was Baker Analyzed Spectrophotometric grade chloroform. The results were reproducible to ±2%.

Synthesis of complexes

[Ag(PPh$_3$)$_4$]NO$_3$. This compound, well described in the literature,[24] can be prepared also by the following procedure: silver(I) nitrate (1.698 g, 10 mmol) was added to a warm ethanol solution (100 ml) of Ph$_3$P (10.492 g, 40 mmol). After 2 h the warm clear solution was allowed to cool slowly in the dark to give well formed crystals of [Ag(PPh$_3$)$_4$]NO$_3$ (10.12 g, 83% yield), mp 218–220 °C. ^{1}H NMR (CDCl$_3$, 293 K): δ 7.20–7.5 (m br, 60 H, C$_6$H$_5$). ^{31}P NMR (CDCl$_3$): (293 K) δ 4.0s (br), (223 K) δ 5.7 d (^1J(Ag,^{31}P) = 238 Hz). IR (Nujol, cm^{-1}): 3046w (CH), 1970m, 1891m, 1814m, 1774m, 1340 (sh), 830m (NO$_3$), 512s, 499s, 437m, 428w (Ph). Calc. for C$_{72}$H$_{60}$AgNO$_3$P$_4$: C, 70.9; H, 5.0; N, 1.1. Found: C, 70.4; H, 5.1; N, 1.1%.

[Ag(PCy$_3$)$_2$(O$_2$NO)]. This compound, previously described,[29] was obtained similarly to [Ag(PPh$_3$)$_4$]NO$_3$ by using Cy$_3$P (5.0 g, 17.8 mmol) and AgNO$_3$ (0.76 g, 4.6 mmol) (93% yield), mp 234–235 °C. ^{1}H NMR (CDCl$_3$, 293 K): δ 1.2–1.8 (m br, 66 H, C$_6$H$_{11}$). ^{31}P NMR (CDCl$_3$, 293 K): δ 32.4 (dd) (^1J(^{109}Ag,^{31}P) = 527, ^1J(^{107}Ag,^{31}P) = 456 Hz). IR (Nujol, cm^{-1}): 1749w, 1738w, 1734w, 1294s (br), 752m, 734m, 704w (NO$_3$), 512 (br), 467m (Cy). Calc. for C$_{36}$H$_{99}$AgNO$_3$P$_2$: C, 59.2; H, 9.1; N, 1.9. Found: C, 59.6; H, 9.5; N, 2.1%.

[Ag(PPh$_3$)$_4$][CF$_3$CO$_2$]·H$_2$O. This compound was obtained similarly to [Ag(PPh$_3$)$_4$]NO$_3$ by using Ph$_3$P (10.492 g, 40 mmol) and AgCF$_3$CO$_2$ (2.2 g, 10 mmol) (88% yield), mp 214–217 °C. ^{1}H NMR (CDCl$_3$, 293 K): δ 7.3 (m br, 60 H, C$_6$H$_5$). ^{31}P NMR (CDCl$_3$): (293 K) δ 3.4 (br), (223 K) δ 5.6 (d) (^1J(Ag,^{31}P) = 239 Hz). IR (Nujol, cm^{-1}): 3300 (br) (H$_2$O), 1645m (H$_2$O), 1684s, 1435m (CF$_3$COO), 511s, 495s (br), 432m (Ph). Calc. for C$_{74}$H$_{62}$AgF$_3$O$_3$P$_4$: C, 69.0; H, 4.9. Found: C, 68.9; H, 5.2%.

[Ag(PPh$_3$)$_4$]ClO$_4$. This compound, previously described,[27,30] was obtained similarly to [Ag(PPh$_3$)$_4$]NO$_3$ by using Ph$_3$P (5.246 g, 20 mmol) and AgClO$_4$ (1.035 g, 5 mmol) (84% yield), mp 266–270 °C. ^{1}H NMR (CDCl$_3$, 293 K): δ 7.3 (m br, 60 H, C$_6$H$_5$). ^{31}P NMR (CDCl$_3$): (293 K) δ 4.0s (br), (223 K) δ 5.7 (d) (^1J(Ag,^{31}P) = 238 Hz). IR (Nujol, cm^{-1}): 1088s (br), 1024m, 998m (ClO$_4$), 514s, 498s, 437m, 427m (Ph). Calc. for C$_{72}$H$_{60}$AgClO$_4$P$_4$: C, 68.8; H, 4.8. Found: C, 68.4; H, 5.1%.

[Ag(PPh$_3$)$_4$]BF$_4$. This compound was obtained similarly to [Ag(PPh$_3$)$_4$]NO$_3$ by using PPh$_3$ (10.48 g, 40 mmol) and AgBF$_4$ (1.94 g, 10 mmol) (92% yield), mp 294–297 °C. ^{1}H NMR (CDCl$_3$, 293 K): δ 7.3–7.5 (m br, 60 H, C$_6$H$_5$). ^{31}P NMR (CDCl$_3$): (293 K) δ 7.3 (br), (223 K) δ 5.6 (dd) (^1J(Ag,^{31}P) = 238 Hz). IR (Nujol, cm^{-1}): 1053s, 541m (BF$_4$), 512s, 499s, 437m, 426m (Ph). Calc. for C$_{72}$H$_{60}$AgBF$_4$P$_4$: C, 69.5; H, 4.9. Found: C, 69.2; H, 5.2%.

[Ag(PPh$_3$)(O$_2$N)]. Silver(I) nitrite (1.54 g, 10 mmol) was added to a warm ethanol solution (100 ml) of Ph$_3$P (2.62 g, 10 mmol). After 24 h the warm clear solution was allowed to cool slowly in the dark to give well formed crystals of [Ag(PPh$_3$)(O$_2$N)] (2.08 g, 50% yield), mp 156–157 °C. ^{1}H NMR (CDCl$_3$, 293 K): δ 7.26–7.50 (m br, 15 H, C$_6$H$_5$). ^{31}P NMR (CDCl$_3$): (293 K) δ 12.2s (br), (203 K) δ 15.8 (dd) (^1J(^{109}Ag,^{31}P) = 768, ^1J(^{107}Ag,^{31}P) = 666 Hz). IR (Nujol, cm^{-1}): 3060w (CH), 1308m, 1204m, 838m (NO$_3$), 522s, 500s, 488s, 436m (Ph). Calc. for C$_{18}$H$_{15}$AgNO$_2$P: C, 51.9; H, 3.6; N, 3.4. Found: C, 52.0; H, 3.8; N, 3.4%.

[Ag(PPh$_3$)(SO$_3$CH$_3$)]·H$_2$O. Silver(I) methanesulfonate (2.02 g, 10 mmol) was added to a warm ethanol solution (100 ml) of Ph$_3$P (2.62 g, 10 mmol). After 24 h the warm clear solution was allowed to cool slowly in the dark to give well formed crystals of [Ag(PPh$_3$)(OS$_3$CH$_3$)]·H$_2$O (4.35 g, 90% yield), mp 199–203 °C. ^{1}H NMR (CDCl$_3$, 293 K): δ 1.3 (br, 2 H, H$_2$O), 2.87 (s, 3 H, CH$_3$), 7.25–7.55 (m br, 15 H, C$_6$H$_5$). ^{31}P NMR (CDCl$_3$): (293 K) δ 14.9 (br), (218 K) δ 15.3 (dd, br) (^1J(Ag,^{31}P) = 718 Hz). IR (Nujol, cm^{-1}): 3155w, 3125w (CH), 2650–2350 (br) (OH), 1198m, 1168m, 1149m (SO$_3$), 515s, 501s, 440 (sh), 432m, 436m (Ph). Calc. for C$_{19}$H$_{20}$AgO$_4$PS: C, 47.2; H, 4.2; S, 6.6. Found: C, 47.3; H, 4.4; N, 6.8%.

[Ag(PPh$_3$)$_3$(4-Ph-im)]NO$_3$ 1. 4-Phenylimidazole (0.144 g, 1.0 mmol) was added to a diethyl ether suspension (100 ml) of [Ag(PPh$_3$)$_4$]NO$_3$ (1.219 g, 1.0 mmol). After 72 h stirring, the solid was filtered off and washed with diethyl ether, affording compound **1**, which was recrystallized from CHCl$_3$–Et$_2$O (3 : 1) (50% yield), mp 170–173 °C (decomp.) ^{1}H NMR (CDCl$_3$, 293 K): δ 3.5 (br, 1 H, NH), 7.2–7.5 (m br, 49 H, C$_6$H$_5$ and 5-CH), 7.7 (d, 2 H, C$_6$H$_5$) and 7.8 (s, 1 H, 2-CH). ^{31}P NMR (CDCl$_3$): (293 K) δ 6.12, (223 K) δ 6.16 (^1J(Ag,^{31}P) = 297 Hz). IR (Nujol, cm^{-1}): 3400–3100 (br) (NH), 1960 (br), 1900 (br), 1830 (br), 1740w, 1434s, 833s, 694s (NO$_3$), 1585w, 1560m ($C\overset{\cdots}{-}C$ and $C\overset{\cdots}{-}N$), 515s, 503s, 491s, 441m, 429m, 419m (Ph). Calc. for C$_{63}$H$_{53}$AgN$_3$O$_3$P$_3$: C, 68.7; H, 4.8; N, 3.8. Found: C, 68.2; H, 5.0; N, 3.6%. Λ_m (CH$_2$Cl$_2$, c = 0.9 M) 0.2 Ω^{-1} mol^2 cm^{-1}. M (CHCl$_3$) ($c = 1 \times 10^{-2}$ m) 682, ($c = 0.7 \times 10^{-2}$ m) 583.

$[Ag(PPh_3)_2(Him)_2]NO_3$ 2. Imidazole (Him) (0.0136 g, 2.0 mmol) was added to a diethyl ether suspension (100 ml) of $[Ag(PPh_3)_4]NO_3$ (1.219 g, 1 mmol). After 48 h stirring the solid was filtered off and washed with diethyl ether, affording compound **2** (0.774 g, 93% yield), which was recrystallized from $CHCl_3$–Et_2O (4 : 1), mp 178–182 °C. ^1H NMR ($CDCl_3$, 293 K): δ 4.4 (br, 2 H, NH), 6.90 (br, 4 H, 4- and 5-CH), 7.3–7.5 (m br, 32 H, C_6H_5 and 2-CH). ^{31}P NMR ($CDCl_3$): (293 K) δ 9.55, (223 K) δ 6.03 (dd) ($^1J(Ag,^{31}P) = 339$ Hz). IR (Nujol, cm^{-1}): 3455 (br) (NH), 1774w, 1437m, 841m, 694s (NO_3), 1580 (br), 1550w ($C\overset{\cdots}{-}C$ and $C\overset{\cdots}{-}N$), 515m, 505m, 492s, 442m, 421m (Ph), 280w, 247w, 226w and 205w. Calc. for $C_{42}H_{38}AgN_5O_3P_2$: C, 60.7; H, 4.6; N, 8.4%. Found: C, 60.9; H, 5.0; N, 8.2%. Λ_m (CH_2Cl_2, $c = 1.2$ M) 14.8 Ω^{-1} mol^2 cm^{-1}. M ($CHCl_3$) ($c = 1 \times 10^{-2}$ m) 471, ($c = 0.7 \times 10^{-2}$ m) 383.

$[Ag(PPh_3)_2(2\text{-}Me\text{-}im)_2]NO_3$ 3. Derivative **3** was obtained similarly to **2** and recrystallized from $CHCl_3$–Et_2O (2 : 1) (90% yield), mp 167–174 °C (decomp.). ^1H NMR ($CDCl_3$, 293 K): δ 2.35 (s, 6 H, 2-CH_3), 4.5 (br, 2 H, NH), 6.92 (br, 4 H, 4- and 5-CH), 7.3–7.5 (m br, 30 H, C_6H_5). ^{31}P NMR ($CDCl_3$, 293 K): δ 9.83. IR (Nujol, cm^{-1}): 3160 (br) (NH), 1962 (br), 1890 (br), 1831 (br), 1812w, 1770w, 1433 (sh), 848m, 692s (NO_3), 1585w, 1565m ($C\overset{\cdots}{-}C$ and $C\overset{\cdots}{-}N$), 512 (sh), 508s, 490s, 428m, 419m (Ph). Calc. for $C_{44}H_{42}AgN_5O_3P_2$: C, 61.6; H, 4.9; N, 8.2. Found: C, 61.4; H, 5.0; N, 7.8%. Λ_m (CH_2Cl_2, $c = 1.1$ M) 15.0 Ω^{-1} mol^2 cm^{-1}. M ($CHCl_3$) ($c = 1.1 \times 10^{-2}$ m) 511, ($c = 0.7 \times 10^{-2}$ m) 480.

$[Ag(PPh_3)(1\text{-}Me\text{-}im)_3]NO_3$ 6. Derivative **6** was obtained similarly to **2** and recrystallized from $CHCl_3$–Et_2O (3 : 1) (89% yield), mp 88–90 °C (decomp.). ^1H NMR ($CDCl_3$, 293 K): δ 3.74 (s, 9 H, 1-CH_3), 6.94 (s, 3 H, 4- or 5-CH), 7.08 (s, 3 H, 4- or 5-CH), 7.3–7.5 (m br, 15 H, C_6H_5) and 7.74 (s, 3 H, 2-CH). ^{31}P NMR ($CDCl_3$): (293 K) δ 13.2, (218 K) δ 12.6 (d br) ($^1J(Ag,^{31}P) = 642$ Hz). IR (Nujol, cm^{-1}): 3117w (CH), 1870 (br), 1836 (br), 1812w, 1770w, 1744w 1436m, 828m, 697s (NO_3), 1521m, 1510w ($C\overset{\cdots}{-}C$ and $C\overset{\cdots}{-}N$), 511m, 504m, 442m, 431m (Ph). Calc. for $C_{30}H_{31}AgN_7O_3P$: C, 53.3; H, 4.6; N, 14.5. Found: C, 53.6; H, 4.8; N, 14.3%. Λ_m (CH_2Cl_2, $c = 1.0$ M) 16.1 Ω^{-1} mol^2 cm^{-1}.

$[Ag(PPh_3)_2(2\text{-}Me\text{-}im)(ONO_2)]$ 8. Derivative **8** was obtained similarly to **3** by using 1 mol of $[Ag(PPh_3)_4]NO_3$ (1.219 g) and 1 mol of 2-Me-im. After 36 h stirring the solid was filtered off and washed with diethyl ether, affording compound **8**, which was recrystallized from $CHCl_3$–Et_2O (2 : 1) (85% yield), mp >200 °C (decomp.). ^1H NMR ($CDCl_3$, 293 K): δ 2.15 (s, 3 H, 2-CH_3), 6.77 (s, 4 H, 4- and 5-CH), 7.1–7.4 (m br, 30 H, C_6H_5). ^{31}P NMR ($CDCl_3$): (293 K) δ 7.98, (218 K) δ 6.51 (d, br) ($^1J(Ag,^{31}P) = 361$ Hz) and 6.69 s (br). IR (Nujol, cm^{-1}): 3000–2700 (br) (NH), 1433 (sh), 1340s, 1278s, 850m, 825s, 692s (NO_3), 1584w, 1565m ($C\overset{\cdots}{-}C$ and $C\overset{\cdots}{-}N$), 512 (sh), 505s, 490s, 436m, 428m, 419m (Ph), 367m, 277m. Calc. for $C_{40}H_{36}AgN_3O_3P_2$: C, 61.9; H, 4.7; N, 5.4. Found: C, 62.1; H, 4.7; N, 5.2%. Λ_m (CH_2Cl_2, $c = 1.0$ M) 0.6 Ω^{-1} mol^2 cm^{-1}.

$[Ag(PPh_3)(2\text{-}Me\text{-}im)_3][CF_3CO_2]$ 11. Derivative **11** was obtained similarly to **2** by treating 1 mmol of $[Ag(PPh_3)_4][CF_3CO_2]$ with 2 mmol of 2-Me-im, and recrystallized from $CHCl_3$–Et_2O (2 : 1) (88% yield), mp 145–148 °C. ^1H NMR ($CDCl_3$, 293 K): δ 2.31 (s, 9 H, 2-CH_3), 6.86 (s, 6 H, 4- and 5-CH), 7.3–7.5 (m br, 15 H, C_6H_5) and 10.0 (br, 3 H, NH). ^{31}P NMR ($CDCl_3$): (293 K) δ 11.3 (br), (203 K) δ 4.4 (dd) ($^1J(^{109}Ag,^{31}P) = 391$, $^1J(^{107}Ag,^{31}P) = 342$) and 11.6 (dd) ($^1J(^{109}Ag,^{31}P) = 629$, $^1J(^{107}Ag,^{31}P) = 545$ Hz). IR (Nujol, cm^{-1}): 3300–3150 (br) (NH), 1679s, 1440s (CF_3CO_2), 520s, 502s, 494s, 434m, 422m (Ph), 272m, 180m and 172m. Calc. for $C_{32}H_{33}AgF_3N_6O_2P$: C, 52.7; H, 4.6; N, 11.5. Found: C, 52.6; H, 4.2; N, 10.9%. Λ_m (CH_2Cl_2, $c = 1.2$ M) 5.3 Ω^{-1} mol^2 cm^{-1}.

$[\{Ag(PPh_3)(1\text{-}Me\text{-}im)(O_2SOCH_3)\}_2]$ 20. Derivative **20** was obtained similarly to **1** by using 1 mmol of $[Ag(PPh_3)(O_2SOCH_3)]$ and 1 mmol of 1-Me-im, and recrystallized from $CHCl_3$–Et_2O (3 : 2) (73% yield), mp 121–124 °C (decomp.). ^1H NMR ($CDCl_3$, 293 K): δ 2.62 (s, 3 H, SO_3CH_3), 3.74 (s, 3 H, 1-CH_3), 6.92, 7.07 (2s, 2 H, 4- and 5-CH), 7.41 (s, 1 H, 2-CH), 7.4–7.6 (m, 15 H, C_6H_5). ^{31}P NMR ($CDCl_3$): (293 K) δ 12.1 (br), (223 K) δ 14.05 (dd) ($^1J(^{109}Ag,^{31}P) = 740$, $^1J(^{107}Ag,^{31}P) = 641$ Hz). IR (Nujol, cm^{-1}): 3120w (CH), 1188s, 1170s (SO_3), 520s, 498s, 437w (Ph). Calc. for $C_{23}H_{24}AgN_2O_3PS$: C, 48.9; H, 4.6; N, 5.0; S, 5.7. Found: C, 48.9; H, 4.5; N, 5.3; S, 5.9%. Λ_m (CH_2Cl_2, $c = 1.0$ M) 3.4 Ω^{-1} mol^2 cm^{-1}.

$[\{Ag(PPh_3)(Him)(\mu\text{-}O_2N)\}_2]$ 21. Derivative **21** was obtained similarly to **1** by using 1 mmol of $[\{Ag(PPh_3)(O_2N)\}_2]$ and 1 mmol of Him, and recrystallized from $CHCl_3$–Et_2O (3 : 2) (75% yield), mp 138–141 °C (decomp.). ^1H NMR ($CDCl_3$, 293 K): δ 6.99 (s, 1 H, 4- and 5-CH), 7.62 (s, 2 H, 2-CH), 9.0 (s br, 1 H, NH), 7.3–7.5 (m, 15 H, C_6H_5), ^{31}P NMR ($CDCl_3$): (293 K) δ 12.9 (br), (201 K) δ 9.0 (dd) ($^1J(^{109}Ag,^{31}P) = 480$, $^1J(^{107}Ag,^{31}P) = 416$) and 12.6 (dd) ($^1J(^{109}Ag,^{31}P) = 692$, $^1J(^{107}Ag,^{31}P) = 599$ Hz). IR (Nujol, cm^{-1}): 3100 (br) (NH), 1331m, 1305m, 1199w, 823m (NO_2), 516s, 494s, 433s (Ph). Calc. for $C_{21}H_{19}AgN_3O_2P$: C, 51.8; H, 4.1; N, 9.0. Found: C, 52.1; H, 3.9; N, 8.7%. Λ_m (CH_2Cl_2, $c = 1.0$ M) 0.2 Ω^{-1} mol^2 cm^{-1}.

The synthesis and spectroscopic characterization of compounds **4–7**, **9**, **10**, **12–19**, and **22–24** are available as SUP 57652.

Structure determinations (general procedure, with individual variations noted)

Unique room-temperature four-circle/single counter diffractometer data sets were measured (2θ–θ scan mode, $2\theta_{max}$ as specified; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å; T *ca.* 295 K) on fibre mounted specimens, yielding N independent reflections, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full matrix least squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values; the unco-ordinated nitrogen atoms of the unsubstituted imidazole ligands were assigned from refinement behaviour and geometrical considerations. Conventional R, R'(statistical weights) at convergence are quoted. Neutral atom complex scattering factors were used, within the XTAL 3.4 program system.[31]

Crystal/refinement data. $[Ag(PPh_3)_3(4\text{-}Ph\text{-}im)]NO_3$ **1**. $C_{63}H_{53}AgN_3O_3P_3$, $M = 1101.0$, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 15.805(4)$, $b = 13.353(3)$, $c = 13.251(2)$ Å, $\alpha = 83.32(2)$, $\beta = 83.92(2)$, $\gamma = 87.91(2)°$, $V = 2761$ Å^3, D_c $(Z = 2) = 1.32_4$ g cm^{-3}, $F(000) = 1136$, $\mu_{Mo} = 5.0$ cm^{-1}, specimen 0.12 × 0.42 × 0.34 mm, $A^*_{min,max} = 1.06$, 1.18, $2\theta_{max} = 50°$, $N = 9673$, $N_o = 6504$, $R = 0.048$, $R' = 0.046$, $n_v = 676$, $|\Delta\rho_{max}| = 0.53$ e Å^{-3}.

The imidazole phenyl substituent was modelled as disordered over two sets of sites, for which occupancies were set at 0.75, 0.25 after trial refinement (see Fig. 1).

$[Ag(PPh_3)_2(Him)_2]NO_3$ 2. $C_{42}H_{38}AgN_5O_3P_2$, $M = 830.6$, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 12.947(7)$, $b = 15.034(2)$, $c = 20.551(2)$ Å, $\beta = 99.43(3)°$, $V = 3946$ Å^3, D_c $(Z = 4) = 1.39_8$ g cm^{-3}, $F(000) = 1704$, $\mu_{Mo} = 6.4$ cm^{-1}, specimen 0.31 × 0.20 × 0.18 mm, $A^*_{min,max} = 1.11$, 1.13, $2\theta_{max} = 46°$, $N = 5482$, $N_o = 2281$, $R = 0.069$, $R' = 0.068$, $n_v = 478$, $|\Delta\rho_{max}| = 0.95$ e Å^{-3}.

$[Ag(PPh_3)_2(2\text{-}Me\text{-}im)_2]NO_3$ 3. $C_{44}H_{42}AgN_5O_3P_2$, $M = 858.7$, monoclinic, space group $C2/c$ (C_{2h}^6, no. 15), $a = 21.888(4)$, $b = 9.895(3)$, $c = 19.241(4)$ Å, $\beta = 92.09(1)°$, $V = 4146$ Å^3, D_c $(Z = 4) = 1.36_9$ g cm^{-3}, $F(000) = 1768$, $\mu_{Mo} = 6.1$ cm^{-1}, specimen 0.40 × 0.50 × 0.68 mm, $A^*_{min,max} = 1.21$, 1.28, $2\theta_{max} = 60°$,

$N = 5932$, $N_o = 4981$, $R = 0.041$, $R' = 0.043$, $n_v = 266$, $|\Delta\rho_{max}| = 0.72$ e Å^{-3}.

The criterion for N_o was $I > 2\sigma(I)$. The nitrate ion was modelled as disposed with the nitrogen located on a crystallographic inversion centre with an O_3 array, occupancy 0.5, disordered about it.

[Ag(PPh$_3$)$_2$(2-Me-im)(ONO$_2$)] 8. $C_{40}H_{36}AgN_3O_3P_2$, $M = 776.6$, monoclinic, space group $P2_1/c$, $a = 13.684(1)$, $b = 12.965(2)$, $c = 23.464(3)$ Å, $\beta = 116.461(8)°$, $V = 3727$ Å^3, D_c $(Z = 4) = 1.38_4$ g cm^{-3}, $F(000) = 1592$, $\mu_{Mo} = 6.7$ cm^{-1}, specimen $0.04 \times 0.52 \times 0.34$ mm, $A^*_{min,max} = 1.03, 1.28$, $2\theta_{max} = 50°$, $N = 6309$, $N_o = 2695$, $R = 0.052$, $R' = 0.048$; $n_v = 443$, $|\Delta\rho_{max}| = 0.52$ e Å^{-3}.

[Ag(PPh$_3$)(2-Me-im)$_3$][CF$_3$CO$_2$] 11. $C_{32}H_{33}AgF_3N_6O_2P$, $M = 729.5$, triclinic, space group $P\bar{1}$, $a = 14.516(5)$, $b = 14.219(5)$, $c = 10.022(4)$ Å, $\alpha = 89.71(3)$, $\beta = 71.83(3)$, $\gamma = 62.54(3)°$, $V = 1720$ Å^3, D_c $(Z = 2) = 1.40_8$ g cm^{-3}, $F(000) = 744$, $\mu_{Mo} = 6.9$ cm^{-1}, specimen $0.20 \times 0.24 \times 0.38$ mm, $A^*_{min,max} = 1.11, 1.21$, $2\theta_{max} = 50°$, $N = 6076$, $N_o = 3537$, $R = 0.047$, $R' = 0.043$, $n_v = 539$, $|\Delta\rho_{max}| = 0.53$ e Å^{-3}.

$(x, y, z, U_{iso})_H$ were refined.

[{Ag(PPh$_3$)(1-Me-im)(OSOCH$_3$O)}$_2$] 20. $C_{46}H_{48}Ag_2N_4O_6P_2S_2$, $M = 1094.7$, monoclinic, space group $C2/c$, $a = 29.421(3)$, $b = 9.270(1)$, $c = 19.122(2)$ Å, $\beta = 117.888(1)°$, $V = 4609$ Å^3, D_c $(Z = 4$ dimers$) = 1.57_7$ g cm^{-3}, $F(000) = 2224$, μ_{Mo} 10.6 cm^{-1}, specimen $0.35 \times 0.25 \times 0.08$ mm, $T_{min,max} = 0.77, 0.93$, $2\theta_{max} = 58°$, $N = 5800$, $N_o = 5800$, $n_v = 377$, $|\Delta\rho_{max}| = 0.66$ e Å^{-3}.

A full sphere of area-detector data was measured at *ca.* 153 K using a Bruker CCD instrument. 26676 Total reflections were merged after 'empirical' absorption correction (proprietary software: SAINT, SADABS, *etc.*) to 5209 independent ($R_{int} = 0.020$). The 'observed' refinement criterion was $F > 4\sigma(F)$; $(x, y, z, U_{iso})_H$ were refined.

[{Ag(PPh$_3$)(Him)(O$_2$N)}$_2$] 21. $C_{42}H_{38}Ag_2N_6O_4P_2$, $M = 968.5$, monoclinic, space group $P2_1/c$, $a = 11.972(5)$, $b = 10.496(6)$, $c = 17.98(2)$ Å, $\beta = 111.24(6)°$, $V = 2105$ Å^3, D_c $(Z = 4) = 1.52_7$ g cm^{-3}, $F(000) = 976$, $\mu_{Mo} = 10.5$ cm^{-1}, specimen $0.85 \times 0.60 \times 1.10$ mm, $A^*_{min,max} = 1.78, 2.41$, $2\theta_{max} = 50°$, $N = 3700$, $N_o = 3105$; $R = 0.037$, $R' = 0.054$, $n_v = 263$, $|\Delta\rho_{max}| = 0.78$ e Å^{-3}.

The criterion for N_o was $I > 2\sigma(I)$. A sphere of data was measured (10291 reflections; $R_{int} = 0.058$). Disorder was evident, most notably and clearly resolved in one nitrite oxygen and the silver atoms, the former bonding in two modes, with O(2) disordered over two sites, seemingly concerted with Ag occupancies constrained to equivalence and refining to 0.911(2) and complement, after independent trial refinement to eliminate the possibility of admixture of any small nitrate component.

CCDC reference number 186/1666.

See http://www.rsc.org/suppdata/dt/1999/4047/ for crystallographic files in .cif format.

Acknowledgements

We gratefully acknowledge support of this work by University of Camerino and by grants from the Australian Research Council and Fondazione "CARIMA".

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Paper 9/06624A