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Bridged poly(1-imidazolyl)borate silver(I) complexes containing tertiary mono(phosphine) ligands. The first structurally authenticated bis(imidazolyl)borate metal complex †

Effendy,[a,b] Giancarlo Gioia Lobbia,[c] Maura Pellei,[c] Claudio Pettinari,[c] Carlo Santini,*[c] Brian W. Skelton[a] and Allan H. White[a]

[a] *Department of Chemistry, The University of Western Australia, Nedlands, W.A. 6907, Australia*
[b] *Jurusan Kimia, FMIPA Universitas Negeri Malang, Jalan Surabaya 6, Malang, 65145, Indonesia*
[c] *Dipartimento di Scienze Chimiche, Università degli Studi di Camerino, via S. Agostino 1, 62032 Camerino MC, Italy. E-mail: santini@camserv.unicam.it*

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New silver(I) derivatives containing triorganophosphines and the anionic dihydrobis(1-imidazolyl)borate $[H_2B(im)_2]^-$, or the tetrakis(1-imidazolyl)borate ligand, $[B(im)_4]^-$, have been synthesized from reaction of $AgNO_3$ with PR_3 (R = phenyl, cyclohexyl, *o*-, *m*- or *p*-tolyl) or (PPh_2R') (R′ = methyl or ethyl) and $K\{H_2B(im)_2\}\cdot$DMAC [DMAC = dimethylacetamide) or $K[B(im)_4]$. Binuclear $[Ag(PR_3)_2\{(im)BX_2(im)\}]_2$ or polymeric $[Ag(PR_3)\{(im)BX_2(im)\}]_n$ (X = H or imidazolate) complexes have been obtained and fully characterized by elemental analyses and FT-IR in the solid state and by NMR (^1H and ^{31}P) spectroscopy and conductivity measurements in solution. Solution data are consistent with partial dissociation of complexes, occurring through breaking of both Ag–N and Ag–P bonds. The structures of $[Ag\{P(C_6H_4Me\text{-}p)_3\}_2\{(im)BH_2(im)\}]_2\cdot 2CHCl_3$, $[Ag\{P(cy)_3\}\{(im)BH_2(im)\}]_n$ and $[\{P(cy)_3\}Ag\{(im)B(im)_2(im)\}]_2\cdot MeCN$ have been determined by single crystal X-ray studies. The $[Ag\{P(cy)_3\}\{(im)BH_2(im)\}]_n$ adduct is a single-stranded polymer containing three-coordinate silver atoms ($PAgN_2$ core), while in the two other adducts, the silver atoms are four-coordinate (P_2AgN_2 cores). In all structures the two silver atoms are bridged by independent imidazolate donors from a pair of $(im)BX_2(im)$ moieties.

Introduction

Since their introduction by Trofimenko,[1] a number of studies have been reported on the synthesis and characterization of poly(pyrazolyl)borate complexes of main group and transition metals.[2] The anionic $[(pz)_nBH_{4-n}]^-$ donors have widely been adopted as supporting ligands for various inorganic and organometallic compounds, because they can be prepared by simple thermal dehydrogenation and the properties of their metal complexes (hapticity of the ligands, coordination environment and reactivity of metal centers, solubility in organic solvents, facility of crystallization, *etc.*) can be controlled by introducing different substituents into the pyrazolyl rings.[3] Tris(pyrazolyl)borates bind predominantly in a facial, tripodal fashion;[3] examples of well characterized complexes, in which a tris(pyrazolyl)borate presents different modes of coordination, are rare except for: (*i*) 16-electron square planar species, in which one pyrazolyl arm is pendant;[4] (*ii*) dinuclear complexes, mostly Cu^I and Ag^I, in which a tris(pyrazolyl)borate acts as bridging ligand, bidentate and unidentate, to two metal centres;[5] (*iii*) trinuclear complexes, in which the ligand adopts a tris-unidentate bridging coordination mode with each pyrazolyl donor coordinating to a separate silver(I) ion, resulting in capping of a metal triangle.[6] To our knowledge, the unidentate coordination mode is restricted to a series of closely related complexes of Ni[7] and Rh.[8] A remarkable example of multinucleating bridging combining unidentate and bidentate coordination modes has recently been described for the ligand $[MeB(3,5\text{-}Me_2pz)_3]^-$ bridging between two thallium atoms: one thallium atom is coordinated by two pyrazolyl rings, whereas the third pyrazolyl ring binds the adjacent symmetry related thallium center in a unidentate fashion, to lead to a 2_1-helicoidal coordination polymer.[9] Only a few poly(azolyl)borate complexes with azolyl groups other than pyrazolyl have been investigated, for example: poly(1,2,4-triazolyl)borates and poly(1,2,4-tetrazolyl)borates,[10] poly(2-sulfanyl-1-methylimidazolyl)borate[11] and poly(imidazolyl)-type ligands.[12]

As a part of our studies into the structural and spectroscopic properties of mixed phosphine/N-donor derivatives of silver(I)[13] and copper(I)[14] we have been interested to investigate a variety of complexes incorporating poly(azolyl)borate and phosphine ligands with different steric and electronic profiles. The compounds obtained show an interesting, and in some cases unpredictable, structural variety, both in the local coordination environment and in the overall geometry. We were especially interested to explore the factors causing these variations, structural and solution equilibria and dynamics studies of copper(I) and silver(I) compounds containing phosphine ligands being of importance due to their potential application as potent anti-tumor agents[15] and as free radical scavengers in industrial processes.[16]

Poly(1-imidazolyl)borates have been described but their metal complexes never structurally authenticated[17] with the exception of the ionic lithium salt of tetrakis(imidazolyl)borate.[18] Recently, Janiak *et al.*[19] have reported a structural study for the hydrotris(imidazolyl)boratothallium(I) compound, where, as expected, the positions of the nitrogen donor atoms in the imidazolyl rings prevent chelation of this ligand;

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† Electronic supplementary information (ESI) available: IR spectral and conductivity data for compounds **1**–**10**. See http://www.rsc.org/suppdata/dt/b0/b008135n/

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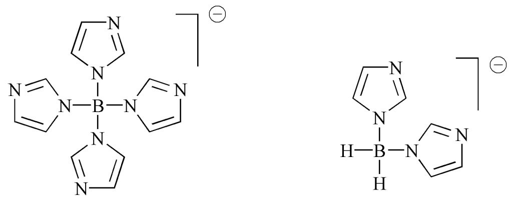

$[B(im)_4]^-$ $[H_2B(im)_2]^-$

Fig. 1 Structure of the donors employed in this work.

in fact each imidazolyl ring coordinates a different thallium ion to form a one-dimensional ladder-like strand. The imidazole nucleus and derivatives thereof are known to play extremely crucial parts in the structures and functioning of a number of biologically important molecules, generally by virtue of their being coordinated to metal ions.[20] The different coordination characteristics of poly(imidazolyl)borate species there offer the opportunity of new and interesting chemistry paralleling that of the pyrazolyl arrays. We report here the synthesis, characterization and reactivity of some new complexes obtained from the interaction of dihydrobis(1-imidazolyl)-borate $[H_2B(im)_2]^-$ and tetrakis(1-imidazolyl)borate $[B(im)_4]^-$ (Fig. 1), with $AgNO_3$ and tertiary mono-phosphines, and the solid state structures of the representative arrays by X-ray diffraction studies, for comparison with their pyrazolyl counterparts.

Experimental

General procedures

All reactions were carried out under an atmosphere of dry oxygen-free dinitrogen, using standard Schlenk techniques and protected from light. All solvents were dried, degassed and distilled prior to use. Elemental analyses (C,H,N,S) were performed with a Fisons Instruments 1108 CHNS-O Elemental analyser. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin-Elmer System 2000 FT-IR instrument, ^1H and ^{31}P NMR spectra on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^1H, and 121.4 MHz for ^{31}P). The electrical resistance of acetone and CH_2Cl_2 solutions was measured with a Crison CDTM 522 conductimeter at room temperature. Selected IR and conductivity data are supplied as ESI.

Syntheses

Potassium or sodium salts of the donor tetrakis(1-imidazolyl)borate, $[B(im)_4]^-$, were prepared in accordance with the procedure first reported by Trofimenko.[1] $AgNO_3$, PR_3 and PPh_2R' were purchased from Aldrich and used without further purification. The compounds studied take the form $K\{H_2B(im)_2\}\cdot DMAC$ **1**, $[Ag(PR_3)_n\{(im)_2BH_2\}]$ ($R_3 = Ph_3$, $n = 2$, **2**; $(C_6H_4Me\text{-}p)_3$, $n = 2$, **3**; or $(cy)_3$, $n = 1$, **4**) or $[Ag(PR_3)_n\{(im)_2B(im)_2\}]$ ($R_3 = Ph_3$, $n = 1$, **5**; $(C_6H_4Me\text{-}m)_3$, $n = 2$, **6**; $(C_6H_4Me\text{-}p)_3$, $n = 2$, **7**; $MePh_2$, $n = 2$, **8**; $EtPh_2$, $n = 2$, **9**; or $(cy)_3$, $n = 2$, **10**).

Compound 1. KBH_4 (3.980 g, 73.7 mmol) and imidazole (10.000 g, 147 mmol) were mixed in anhydrous dimethylacetamide (DMAC) (15 ml), and the mixture was heated slowly under N_2 until reflux began. The refluxing was continued for 6 h, and the volatiles were removed under reduced pressure. The resulting oily residue was dissolved in the minimum amount of acetone and cooled at 0 °C; diethyl ether was added to obtain a colorless and microcrystalline solid in 81% yield. mp 138–140 °C. ^1H NMR ($CDCl_3$, 293 K): δ 2.08 (s, 3H, CH_3), 2.92 (s, 3H, CH_3), 3.06 (s, 3H, CH_3), 6.79 (s, 2H, 4- or 5-CH), 6.84 (s, 2H, 4- or 5-CH) and 7.39 (s, 2H, 2-CH). ^{13}C-$\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 21.61 (s, CH_3), 35.80 (s, CH_3), 38.72 (s, CH_3), 124.38 (s, 4- or 5-CH), 127.62 (s, 4- or 5-CH), 142.25 (s, 2-CH) and 173.68 (s, CO). Calc. for $C_{10}H_{17}BKN_5O$: C, 44.0; H, 6.3; N, 25.6. Found: C, 43.7; H, 6.2; N, 25.3%.

Compound 2. To a methanol solution (50 ml) of $AgNO_3$ (0.170 g, 1 mmol) and Ph_3P (0.524 g, 2 mmol), $K\{H_2B(im)_2\}\cdot DMAC$ (0.273 g, 1 mmol) was added at room temperature. The solution was stirred for 1 h and the solvent removed with a rotary evaporator. Chloroform (50 ml) was added. The suspension was filtered and the organic layer dried over Na_2SO_4, filtered and concentrated under reduced pressure. A colorless precipitate was formed which was filtered off and washed with diethyl ether. Crystallization from diethyl ether gave complex **2** as a microcrystalline solid in 68% yield. mp 222–225 °C. ^1H NMR ($CDCl_3$, 293 K): δ 6.91 (s, 2H, 4- or 5-CH), 7.02 (s, 2H, 4- or 5-CH), 7.30–7.45 (m, 32H, 2-CH and C_6H_5). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 8.3 (s). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, 218 K): δ 9.7 (s br). Calc. for $C_{42}H_{38}AgBN_4P_2$: C, 64.7; H, 4.9; N, 7.2. Found: C, 64.4; H, 5.1; N, 7.2%.

Compound 3. Compound **3** was prepared similarly to **2**, by using $AgNO_3$ (0.170 g, 1 mmol), $P(C_6H_4Me\text{-}p)_3$ (0.608 g, 2 mmol) and $K\{H_2B(im)_2\}\cdot DMAC$ (0.273 g, 1 mmol). It was recrystallized from $CHCl_3$–diethyl ether (yield 45%). X-Ray-quality crystals were grown from MeCN–$CHCl_3$. mp 178 °C (decomp.). ^1H NMR ($CDCl_3$, 293 K): δ 2.35 (s, 18H, CH_3), 6.78 (s, 2H, 4- or 5-CH), 6.95 (s, 2H, 4- or 5-CH), 7.05–7.30 (m, 26H, 2-CH and C_6H_4). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 5.5 (s). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, 218 K): δ 4.9 (s br). Calc. for $C_{48}H_{50}AgBN_4P_2$: C, 66.8; H, 5.8; N, 6.5. Found: C, 66.5; H, 6.0; N, 6.7%.

Compound 4. Compound **4** was prepared similarly to **2**, by using $AgNO_3$ (0.170 g, 1 mmol), $(cy)_3P$ (0.561 g, 2 mmol) and $K\{H_2B(im)_2\}\cdot DMAC$ (0.273 g, 1 mmol). It was recrystallized from $CHCl_3$–diethyl ether (yield 68%). X-Ray-quality crystals were grown from $CHCl_3$–hexane. mp 208 °C (decomp.). ^1H NMR ($CDCl_3$, 293 K): δ 1.20–1.95 (m, 33H, C_6H_{11}), 6.83 (s, 2H, 4- or 5-CH), 7.03 (s, 2H, 4- or 5-CH) and 7.18 (s, 2H, 2-CH). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 40.5 (dd), $^1J(^{31}P,^{107}Ag) = 586$, $^1J(^{31}P,^{109}Ag) = 665$ Hz. Calc. for $C_{24}H_{41}AgBN_4P$: C, 53.8; H, 7.7; N, 10.5. Found: C, 54.1; H, 8.0; N, 10.2%.

Compound 5. Compound **5** was prepared similarly to **2**, by using $AgNO_3$ (0.170 g, 1 mmol), Ph_3P (0.787 g, 3 mmol), and $Na[B(im)_4]$ (0.302 g, 1 mmol). It was recrystallized from $CHCl_3$–diethyl ether (yield 66%). mp 223 °C (decomp.). ^1H NMR ($CDCl_3$, 293 K): δ 6.75 (s, 4H, 4- or 5-CH), 6.84 (s, 4H, 4- or 5-CH), 6.94 (s, 4H, 2-CH), 7.26–7.32 (m, 30H, C_6H_5). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 3.7 (s). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, 218 K): δ 5.05 (s, br). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, 193 K): δ 2.3 (dd), $^1J(^{31}P,^{107}Ag) = 277$, $^1J(^{31}P,^{109}Ag) = 318$; 4.9 (dd), $^1J(^{31}P,^{107}Ag) = 593$, $^1J(^{31}P,^{109}Ag) = 636$ Hz. Calc. for $C_{30}H_{27}AgBN_8P$: C, 55.5; H, 4.2; N, 17.3. Found: C, 55.5; H, 4.3; N, 17.0%.

Compound 6. Compound **6** was prepared similarly to **2**, by using $AgNO_3$ (0.170 g, 1 mmol), $P(C_6H_4Me\text{-}m)_3$ (0.609 g, 2 mmol), and $Na[B(im)_4]$ (0.302 g, 1 mmol). It was recrystallized from $CHCl_3$–diethyl ether (yield 48%). mp 107–110 °C. ^1H NMR ($CDCl_3$, 293 K): δ 2.17 (s, 18H, CH_3), 6.73 (s, 4H, 4- or 5-CH), 6.87 (s, 4H, 4- or 5-CH), 6.96 (s, 4H, 2-CH), 7.12–7.19 (m, 24H, C_6H_4). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 9.27 (s, br). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, 218 K): δ 6.27 (d), $^1J(^{31}P,Ag) = 300$; 7.9 (d), $^1J(^{31}P,Ag) = 406$ Hz. Calc. for $C_{54}H_{54}AgBN_8P_2$: C, 65.1; H, 5.5; N, 11.2. Found: C, 65.3; H, 5.2; N, 11.4%.

Compound 7. Compound **7** was prepared similarly to **2**, by using $AgNO_3$ (0.170 g, 1 mmol), $P(C_6H_4Me\text{-}p)_3$ (0.609 g, 2 mmol), and $Na[B(im)_4]$ (0.302 g, 1 mmol). It was recrystallized from $CHCl_3$–diethyl ether (yield 45%). mp 92–94 °C. ^1H NMR

($CDCl_3$, 293 K): δ 2.33 (s, 18H, CH_3), 6.69 (s, 4H, 4- or 5-CH), 6.89 (s, 4H, 4- or 5-CH), 7.05–7.15 (m, 24H, C_6H_4) and 7.19 (s, 4H, 2-CH). ^{31}P-{^1H} NMR ($CDCl_3$, 293 K): δ 4.55 (s, br). ^{31}P-{^1H} NMR ($CDCl_3$, 218 K): δ 4.54 (d), $^1J(^{31}P,Ag) = 364$ Hz. Calc. for $C_{54}H_{54}AgBN_8P_2$: C, 65.1; H, 5.5; N, 11.2. Found: C, 65.3; H, 5.2; N, 11.4%.

Compound 8. Compound **8** was prepared similarly to **2**, by using $AgNO_3$ (0.170 g, 1 mmol), $MePh_2P$ (0.400 g, 2 mmol), and Na[B(im)$_4$] (0.302 g, 1 mmol). It was recrystallized from diethyl ether (yield 46%). mp 126–129 °C. ^1H NMR ($CDCl_3$, 293 K): δ 1.73 (d, 6H, CH_3), 6.75 (s, 4H, 4- or 5-CH), 6.91 (s, 4H, 4- or 5-CH), 7.03 (s, 4H, 2-CH), 7.20–7.40 (m, 20H, C_6H_5). ^{31}P-{^1H} NMR ($CDCl_3$, 293 K): δ −10.9 (s). ^{31}P-{^1H} NMR ($CDCl_3$, 218 K): δ −10.24 (d), $^1J(^{31}P,Ag) = 355$ Hz. ^{31}P-{^1H} NMR ($CDCl_3$, 193 K): δ −10.37 (d), $^1J(^{31}P,Ag) = 701$; −13.52 (dd), $^1J(^{31}P,^{107}Ag) = 290$, $^1J(^{31}P,^{109}Ag) = 333$ Hz. Calc. for $C_{38}H_{38}AgBN_8P_2$: C, 58.0; H, 4.9; N, 14.2. Found: C, 57.8; H, 5.1; N, 14.0%.

Compound 9. Compound **9** was prepared similarly to **2**, by using $AgNO_3$ (0.170 g, 1 mmol), $EtPh_2P$ (0.428 g, 2 mmol), and Na[B(im)$_4$] (0.302 g, 1 mmol). It was recrystallized from diethyl ether (yield 40%). mp 93–96 °C. ^1H NMR ($CDCl_3$, 293 K): δ 0.96 and 1.05 (2t, 6H, CH_3), 2.05–2.25 (m, 4H, CH_2), 6.74 (s, 4H, 4- or 5-CH), 6.90 (s, 4H, 4- or 5-CH), 7.02 (s, 4H, 2-CH), 7.20–7.42 (m, 20H, C_6H_5). ^{31}P-{^1H} NMR ($CDCl_3$, 293 K): δ 5.1 (s). ^{31}P-{^1H} NMR ($CDCl_3$, 223 K): δ 3.64 (d), $^1J(^{31}P,Ag) = 342$ Hz. ^{31}P-{^1H} NMR ($CDCl_3$, 193 K): δ 3.88 (dd), $^1J(^{31}P,^{107}Ag) = 314$, $^1J(^{31}P,^{109}Ag) = 351$ Hz. Calc. for $C_{40}H_{42}AgBN_8P_2$: C, 58.9; H, 5.2; N, 13.7. Found: C, 59.1; H, 5.4; N, 14.0%.

Compound 10. Compound **10** was prepared similarly to **2**, by using $AgNO_3$ (0.170 g, 1 mmol), (cy)$_3$P (0.561 g, 2 mmol) and Na[B(im)$_4$] (0.302 g, 1 mmol). It was recrystallized from $CHCl_3$–diethyl ether (yield 71%). X-Ray-quality crystals were grown from MeCN–$CHCl_3$. mp 179 °C (decomp.). ^1H NMR ($CDCl_3$, 293 K): δ 1.10–1.40 (m, 24H, C_6H_{11}), 1.70–1.90 (m, 36H, C_6H_{11}), 2.3 (br, 6H, C_6H_{11}), 6.87 (s, 4H, 4- or 5-CH), 7.05 (s, 4H, 4- or 5-CH) and 7.22 (s, 4H, 2-CH). ^{31}P-{^1H} NMR ($CDCl_3$, 293 K): δ 31.62 (d), $^1J(^{31}P,Ag) = 405$ Hz. ^{31}P-{^1H} NMR ($CDCl_3$, 218 K): δ 30.48 (dd), $^1J(^{31}P,^{107}Ag) = 414$, $^1J(^{31}P,^{109}Ag) = 473$ Hz. Calc. for $C_{48}H_{78}AgBN_8P_2$: C, 60.8; H, 8.3; N, 11.8. Found: C, 61.0; H, 8.4; N, 11.6%.

Structure determinations

For [Ag{P(cy)$_3$}$_2${B(im)$_4$}]$_2$·MeCN **10**·MeCN, a unique data set was measured, using a single counter instrument, a gaussian absorption correction being applied; for the other two compounds full spheres of CCD area-detector data were measured ($2\theta_{max} = 58°$; monochromatic Mo-Kα radiation ($\lambda = 0.7107_3$ Å) (all structures)) yielding N_t reflections, these merging to N unique (R_{int} quoted) after 'empirical'/multiscan absorption correction, N_o with $F > 4\sigma(F)$ being considered 'observed' and used in the full matrix least squares refinements (anisotropic thermal parameter forms (non-H atoms), $(x, y, z, U_{iso})_H$ being constrained at estimates). Conventional residuals at convergence R, R_w (weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$) are quoted. Computation used the Xtal 3.4 program system,[22] neutral atom complex scattering factors being employed. Pertinent results are given below and in the Figures and Tables, individual variations in procedure being noted; in the Figures displacement ellipsoids are shown at the 20 (room temperature) or 50% (153 K) probability level, hydrogen atoms having arbitrary radii of 0.1 Å. Carbon atoms are denoted by number only.

Crystal/refinement data. *Compound 4.* $C_{24}H_{41}AgBN_4P$, $M = 535.3$, monoclinic, space group $P2_1/n$ C^5_{2h}, no. 14 (variant)), $a = 10.719(1)$, $b = 17.846(2)$, $c = 13.747(1)$ Å, $\beta = 101.230(2)°$, $V = 2579$ Å^3, D_c ($Z = 4$) = 1.37_8 g cm^{-3}, $\mu_{Mo} = 8.6$ cm^{-1}, specimen 0.20 × 0.14 × 0.10 mm, 'T'$_{min,max} = 0.81$, 0.91, $N_t = 30672$, $N = 6637$ ($R_{int} = 0.047$), $N_o = 4212$, $R = 0.029$, $R_w = 0.033$, $|\Delta\rho_{max}| = 1.09(7)$ e Å^{-3}, T *ca.* 153 K.

All hydrogen atoms were refined in (x, y, z, U_{iso}).

*Compound **10**·MeCN.* $C_{98}H_{159}Ag_2B_2N_{17}P_4$, $M = 1936.7$, triclinic, space group $P\bar{1}$, (C^1_i, no. 2), $a = 18.313(2)$, $b = 13.177(3)$, $c = 12.025(4)$ Å, $\alpha = 112.26(2)$, $\beta = 102.07(1)$, $\gamma = 95.52(1)°$, $V = 2529$ Å^3, D_c ($Z = 1$ (dimeric) f.u.) = 1.27_2 g cm^{-3}, $\mu_{Mo} = 5.0$ cm^{-1}, specimen 0.38 × 0.66 × 0.42 mm, 'T'$_{min,max} = 0.74$, 0.86, $2\theta_{max} = 50°$, $N = 8890$, $N_o = 7060$, $R = 0.044$, $R_w = 0.050$, $|\Delta\rho_{max}| = 0.78(3)$ e Å^{-3}, T *ca.* 295 K.

Difference map residues about one set of crystallographic inversion centres were modelled in terms of acetonitrile of solvation, C at the centre, and the peripheral non-hydrogen atom(s) composite. The N_o ('observed') criterion for data was $I > 3\sigma(I)$. Cyclohexyl ring 21 was modelled as disordered over two sets of conformations, C(212,4,5) being disposed over two sets of sites, occupancies set at 0.5 after trial refinement. Substrate hydrogen atoms were refined in (x, y, z, U_{iso}).

*Compound **3**·2CHCl$_3$.* $C_{98}H_{102}Ag_2B_2Cl_6N_8P_4$, $M = 1965.9$, triclinic, space group $P\bar{1}$, $a = 11.587(1)$, $b = 14.074(1)$, $c = 16.425(1)$ Å, $\alpha = 76.538(1)$, $\beta = 87.005(1)$, $\gamma = 72.383(1)°$, $V = 2482$ Å^3, D_c ($Z = 1$ (dimeric) f.u.) = 1.31_5 g cm^{-3}, $\mu_{Mo} = 6.7$ cm^{-1}, specimen 0.56 × 0.40 × 0.23 mm, 'T'$_{min,max} = 0.74$, 0.89, $N_t = 23998$, $N = 11918$ ($R_{int} = 0.014$), $N_o = 9008$, $R = 0.041$, $R_w = 0.051$, $|\Delta\rho_{max}| = 0.81(2)$ e Å^{-3}, T *ca.* 298 K.

CCDC reference number 186/2315.

See http://www.rsc.org/suppdata/dt/b0/b008135n/ for crystallographic files in .cif format.

Results and discussion

Syntheses

The ligand dihydrobis(imidazolyl)borate, [$H_2B(im)_2$]$^-$, was synthesized by treating KBH_4 with imidazole in dimethylacetamide (DMAC) and isolated as the DMAC adduct[23] which is an air stable colorless solid.

From the interaction of one equivalent of compound **1** with one equivalent of $AgNO_3$ and two equivalents of tertiary mono(phosphine) PPh_3, P(C_6H_4Me-*p*)$_3$ or P(Cy)$_3$ in methanol at room temperature, the complexes **2**–**4** have been respectively obtained in high yield, eqn. (1). They have been obtained also

$$\mathrm{K\{H_2B(im)_2\}{\cdot}DMAC} + \mathrm{AgNO_3} + 2\mathrm{PR_3} \longrightarrow \mathrm{[Ag(PR_3)_n\{(im)_2BH_2\}]} + \mathrm{KNO_3} + \mathrm{DMAC} + (2-n)\mathrm{PR_3} \quad (1)$$

2: R = Ph, $n = 2$
3: R = C_6H_4Me-*p*, $n = 2$
4: R = cy, $n = 1$

when this reaction was conducted with an excess of the phosphorus donor (>4 equivalents), whereas when equimolar quantities of the phosphine and of the N-donor ligand were employed no adduct could be obtained, deposition of metallic silver rapidly occurring; a 1 : 1 phosphine : silver adduct has only been obtained when the sterically hindered (cy)$_3$P has been employed. This same compound **4** can be obtained by interaction of (cy)$_3$P with **2**, with complete displacement of both Ph_3P molecules from the Ag^I. We ascribe the occurrence of this displacement reaction to the greater basicity of (cy)$_3$P with respect to Ph_3P.

When compound **1** was treated with $AgNO_3$ and P(C_6H_4-Me-*o*)$_3$, P(C_6H_4Me-*m*)$_3$, P(CH_2Ph)$_3$, $PMePh_3$ or $PEtPh_2$ under the same reaction conditions rapid decomposition and deposition of metallic silver occurred.

From the interaction of one equivalent of the potassium salt of tetrakis(1-imidazolyl)borate [(im)$_4$B]$^-$, one equivalent of

$AgNO_3$ and two equivalents of Ph_3P, $P(C_6H_4Me\text{-}m)_3$, $P(C_6H_4Me\text{-}p)_3$, $MePh_2P$, $EtPh_2P$ or $(cy)_3P$, in methanol at room temperature, complexes **5**–**10** have been respectively obtained in high yield, eqn. (2). These compounds were obtained also when

$$K[(im)_4B] + AgNO_3 + 2PR_3 \longrightarrow [Ag(PR_3)_n\{(im)_4B\}] + KNO_3 + (2 - n)PR_3 \quad (2)$$

5: R = Ph, $n = 1$
6: R = $C_6H_4Me\text{-}m$, $n = 2$
7: R = $C_6H_4Me\text{-}p$, $n = 2$
8: $R_3 = MePh_2$, $n = 2$
9: $R_3 = EtPh_2$, $n = 2$
10: R = cy, $n = 2$

an excess of the phosphorus donors was employed. This excess appears necessary to avoid formation of polymeric compounds; in fact the polymeric and poorly soluble derivative $[Ag\{(im)_4B\}]_n$ only formed when an equimolar ratio of $AgNO_3$, $[K\{(im)_4B\}]$ and phosphine ligand was employed.[5c] This compound has been obtained also when $P(C_6H_4Me\text{-}o)_3$, $P(C_6H_2Me_3\text{-}2,4,6)_3$ or $P(CH_2Ph)_3$ were employed as phosphorus donors or in the absence of phosphine ligands.

All derivatives **1**–**10** show good solubility in most common organic solvents. They are generally non-electrolytes in CH_2Cl_2 and acetone. Complexes containing the dihydrobis(1-imidazolyl)borate ligands, **2**–**4**, are significantly less stable than the tetrakis(1-imidazolyl)borate ones; in fact after some days decomposition can be detected for derivatives **2**–**4**, silver metal being formed. This property is related to the high reducing power arising from the presence of the two hydrogen atoms linked to the boron atom.

Spectroscopy

The infrared spectra of derivatives **1**–**10** (see ESI) are consistent with the formulations, showing all of the bands required by the presence of the organic nitrogen donor[24,25] and the phosphine ligand,[26,27] the ligand absorptions being only slightly shifted with respect to those of the potassium salts of the same donors. In the spectrum of $K\{H_2B(im)_2\}\cdot DMAC$, **1**, the CO stretching of DMAC appears as a strong and broad peak at *ca.* 1620 cm^{-1}; this value is shifted lower with respect to that observed for free DMAC (*ca.* 1690 cm^{-1}), suggesting coordination of the oxygen atom to the potassium center.[28] In **2**–**4** the BH stretch region exhibits a multiplicity of absorptions, consistent with the presence of both ^{10}B and ^{11}B in natural boron,[29] generally shifted to higher frequency with respect to the same absorptions observed for the "free" ligand.

In the ^1H NMR spectra of complexes **2**–**10** in $CDCl_3$ (see Experimental section) the signals due to the imidazolyl rings are always deshielded with respect to those in the spectra of the free donors, confirming the existence of the complexes in solution. The chemical shifts of the imidazole protons are similar to those observed for analogous rings in complexes of silver(I) with tertiary phosphine coligands.[13d,30] The room-temperature spectra of **2**–**10** exhibit only one set of signals for the protons of the imidazolyl rings of the poly(imidazolyl)borate ligands, resulting from dynamic exchange processes. This is common in complexes of corresponding poly(pyrazolyl)borates,[3] suggesting highly fluxional species with either a rocking motion of the triorganophosphine silver(I) moieties between the two nitrogen atoms of independent $H_2B(im)_2$ and $B(im)_4$, or complete dissociation and re-association of the imidazolyl nitrogens, which occurs rapidly even at lower temperatures. On cooling the $CDCl_3$ solutions of **2**–**10** to 223 K no additional signals due to the imidazole ring appeared.

^{31}P chemical shifts ($CDCl_3$ solution) and ^{31}P–Ag coupling-constants for derivatives **2**–**10** are reported in the Experimental section. The ^{31}P NMR spectra at room temperature of **2** and **3**, containing the dihydrobis(1-imidazolyl)borate, and of **5**–**10**, containing the tetrakis(1-imidazolyl)borate ligand, consist of broad singlets, presumably due to rapid exchange equilibria and are unresolved also in the spectra recorded at 218 K. In the spectrum of **4** typical pairs of doublets, due to $^1J(^{31}P,^{107}Ag)$ and $^1J(^{31}P,^{109}Ag)$ coupling, are resolved also at room temperature and the observed $^1J(^{107}Ag):{}^1J(^{109}Ag)$ ratio is in good agreement with that calculated from the gyromagnetic ratio of the Ag nuclei $\gamma(_{107Ag}):\gamma(^{109}Ag)$. However, for all the derivatives at lower temperature exchange is quenched and one and/or two unresolved doublets or resolved pairs of doublets, arising from coupling between the phosphorus and silver atom, are observed in the accessible temperature range.

The signal due to each free phosphine is upfield with respect to the corresponding silver(I) complex. The magnitude of Δ ($= \delta^{31}P_{complex} - \delta^{31}P_{free\ ligand}$) and of the coupling constants decreases with decreasing basicity, also correlating with the steric bulk of the ligands. For example the chemical shift of **4**, which contains the more sterically hindered triorganophosphine $(cy)_3P$ (cone angle = 170°), is the greatest ($\Delta \sim 29$ ppm). The ^{31}P chemical shift is a function of both cone angle and σ-donor power of the phosphorus coligand[31] and seems not to be strongly dependent on the electronic and steric properties of the poly(imidazolyl)borate donor. The smallest values have been observed for derivatives containing phosphorus donors with larger cone angles.

The chemical shifts and $^1J(Ag,^{31}P)$ coupling constants are strongly dependent on the stoichiometric ratio **N**:Ag:**P** (**N** = poly(pyrazolyl)borate ligand, **P** = triorganophosphine). In fact the ^{31}P NMR spectra of compounds **4** and **5**, in which the metal centers are most probably three-coordinate (N_2AgP), show chemical shift values and $^1J(Ag,^{31}P)$ coupling constants of the same order of magnitude as those found for analogous three-coordinate silver(I) poly(pyrazolyl)borate complexes, whereas the ^{31}P NMR data of derivatives **2**, **3** and **6**–**10** are typical of four-coordinate species with an N_2AgP_2 core.[11a,16] $^1J(Ag,^{31}P)$ for **2**, **3** and **6**–**10** are of the same order of magnitude as those found for analogous silver(I) bis(triorganophosphine) species $[Ag(PR_3)_2]^+$.[32]

In the spectra of complexes **5**, **6** and **8**, at 193 K, a different multiplicity was observed: in particular for **5** and **8** two pairs of doublets were detected; on the basis of the $^1J(Ag,^{31}P)$ values we can assign the signal at δ 2.3 ($^1J(^{107}Ag,^{31}P) = 277$, $^1J(^{109}Ag,^{31}P) = 318$ Hz)) for **5** and that at δ −13.5 ($^1J(^{107}Ag,^{31}P) = 290$, $^1J(^{109}Ag,^{31}P) = 333$ Hz)) for **8** respectively, to the probably four-coordinate species (N_2AgP_2), and the signal at δ 4.9 ($^1J(^{107}Ag,^{31}P) = 593$, $^1J(^{109}Ag,^{31}P) = 636$ Hz)) for **5** and that at δ −10.4 ($^1J(Ag,^{31}P) = 701$ Hz) for **8** respectively to the probably three-coordinate species (N_2AgP). The trends observed in the low-temperature ^{31}P NMR spectra of **5**, **6** and **8** are interpretable as an equilibrium mixture of dimeric (Fig. 2(a,b)) or polymeric (Fig. 2(c)) species, in which the azole ligands coordinate in bridging bidentate mode to Ag^I in the presence of one (N_2AgP core) or two P-donors (N_2AgP_2 core). Only in the spectrum of **9** at 193 K the separate splitting arising from the different ^{107}Ag and ^{109}Ag nuclei is observed at δ 3.8 ($^1J(^{107}Ag,^{31}P) = 314$, $^1J(^{109}Ag,^{31}P) = 351$ Hz)).

For a given phosphine the M–P bond length is expected to increase as the P–M–P angle decreases, but it has been observed[33] that a decrease of the M–P distance results in only small changes in $^1J(Ag,P)$, changes in the bond angles affecting $^1J(Ag,P)$ much more; a positive correlation between P–Ag–P angle and solution $^1J(M,^{31}P)$ data has been observed previously for the complexes $[Ag_2X_2(PP)_2]$ and $[AgX(PP)]$ (PP = chelating diphosphine ligand),[34] four-coordinate $[HgX_2(PPh_3)_2]$[33] and $[AgX\{P(cy)_3\}_2]$.[32b] By extension of the range of anions under consideration, including the poly(imidazolyl)borate ligands, the results reported here may qualitatively suggest that in solution an increase in $^1J(Ag,^{31}P)$ is consistent with increasing P–Ag–P angle consequent on ligand–ligand interactions arising from greater steric hindrance of the phosphine rings.

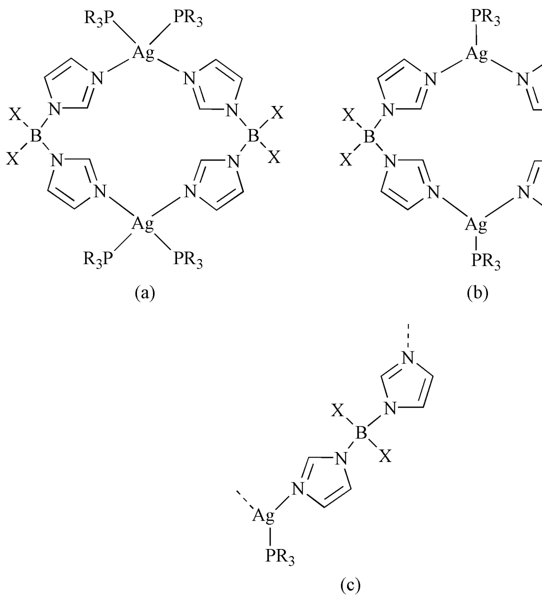

Fig. 2 Dimeric or polymeric structures possible in solution for derivatives **2**–**10**.

Diffraction studies

Single crystal structure determinations were made for three of the above complexes, consistent with their formulation in terms of stoichiometry and connectivity as adducts of the form AgL:R$_3$P (1:x) for $x = 1$ (L = H$_2$B(im)$_2$; R = cy) and $x = 2$ (L, R = B(im)$_4$, cy and H$_2$B(im)$_2$, *p*-tolyl). The $x = 1$ adduct is a single-stranded polymer, while both of the $x = 2$ adducts are centrosymmetric dimers, in which the two silver atoms are bridged by independent im donors of a pair of [(im)BX$_2$(im)] moieties. In all structures one 1:x formula unit comprises the asymmetric unit. The dimeric units are accompanied by one (MeCN) or two (CHCl$_3$) molecules of solvation, the former occupying lattice sites, the latter intimately involved in hydrogen bonding with the BH$_2$ of the anionic ligand. In the $x = 1$ polymer the silver atoms are three-coordinate (PAgN$_2$), but in the $x = 2$ dimers they are four-coordinate (P$_2$AgN$_2$).

In the single-stranded 1:1 AgL:R$_3$P adduct, $[\mathrm{Ag}\{\mathrm{P(cy)_3}\}\{\mathrm{(im)BH_2(im)}\}]_{(\infty|\infty)}$ (Fig. 3), Ag–P is 2.3677(7) Å. That bond is unsymmetrically disposed *vis-à-vis* the two Ag–N(im) bonds, P–Ag–N(13,23′) being 141.43(7), 119.14(6)° and N–Ag–N 99.28(9)°. Ag–N(13,23′) are 2.189(2), 2.349(2) Å, the latter (longer) distance being opposite the larger P–Ag–N angle, as might be expected. The three angles about the silver atom sum to 359.9°, *i.e.* the silver atom environment is essentially planar. Ag lies 0.048(1) Å out of the associated N$_2$P plane. The silver atom lies more nearly coplanar with the more tightly coordinated im ring, as might be expected, deviations δAg from rings 1,2′ being 0.207(5), 0.890(5) Å respectively (Fig. 3(b)). The dihedral angle between the pair of C$_3$N$_2$ ring planes is 86.5(1)°, those between the N$_2$P coordination plane and C$_3$N$_2$ planes 1,2′ being 11.0(1) and 63.8(1)°. The angle between the two coordinated C$_3$N$_2$ planes is 46.2(1)°. Torsion angles N(1′)–B–N(1)–C(2) are −110.5(3), 64.2(4)°.

The polymeric form of the present AgL:P(cy)$_3$ complex may be compared with that of the counterpart array of the adduct found for L = H$_2$B(Me$_2$pz)$_2$, Me$_2$pz = 3,5-dimethylpyrazolate. In the latter a discrete neutral mononuclear [{(cy)$_3$P}AgL] array is found. The pyrazolate ligand chelates through the two available ligand nitrogen atoms, a mode also found for the counterpart adduct with L = [(pz)$_2$B(pz)$_2$].[13c] The extended polymeric form found in the present adduct is presumably a consequence of the inability of the two im nitrogen atoms to chelate to the same metal. Despite this, the silver environments in the two pyrazolate complexes are similar to that of the present. They are planar three-coordinate PAgN$_2$ arrays, in which N–Ag–N are reduced to 86.7(7), 84.9(1)°, with Ag–P 2.3538(6) and 2.351(1) Å. A further significant difference is found, however, in that the symmetry of the PAgN$_2$ array more nearly approaches *C*$_{2v}$/*mm*2, with the pairs of Ag–N distances and P–Ag–N angles more nearly equal (2.250(1), 2.299(1) Å; 146.08(5), 127.21(5)° and 2.261(4), 2.297(3) Å; 140.3(1), 134.45(9)° respectively).

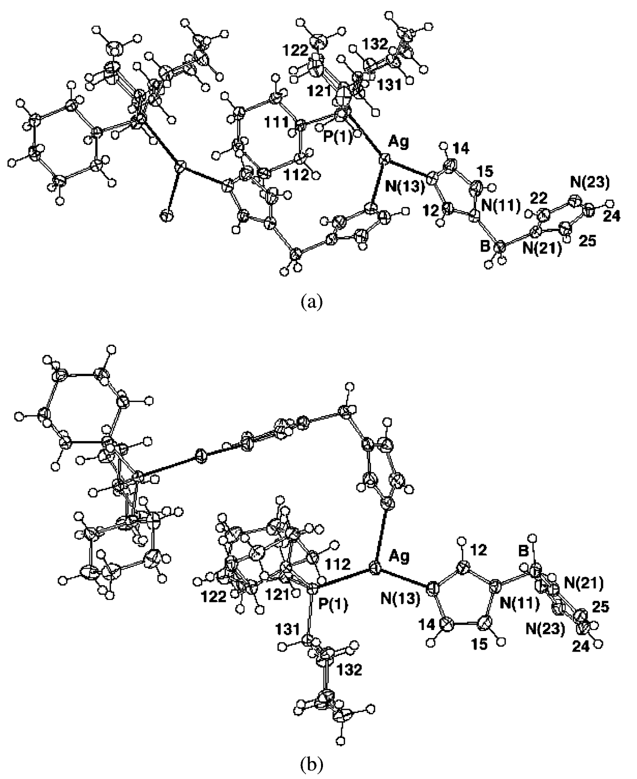

Fig. 3 Two projections of the [Ag{(cy)$_3$P}{(im)BH$_2$(im)}] single-stranded polymer, normal to its axis.

In all three complexes the P(cy)$_3$ conformations are similar (see Table 3 of ref. 13e), Ag–P–C(*n*1)–C(*n*2,6) being −29.1(2), −156.7(2); −172.6(2), −45.2(2); −63.7(2), 57.5(2)° (n = 1;2;3), and similar to those of [Ag{P(cy)$_3$}{(im)B(im)$_2$(im)}]$_2$ (Fig. 4(a)), as documented in Table 1. All (cy)$_3$P arrays are of the common form defined in ref. 35, two rings 'parallel' to the quasi-*3* axis and one 'normal'. This adduct, like the other 1:2 AgL:R$_3$P complex whose structure is reported here, [Ag{P(C$_6$H$_4$Me-*p*)$_3$}$_2${(im)BH$_2$(im}]$_2$ (Fig. 4(b)), is binuclear. The (im)BX$_2$(im) ligand in both cases bridges a pair of silver atoms, as in the 1:1 complexes above, but, unlike the latter, where catenation occurs, a dimer is found in each case. Why a polymer rather than a dimer should be found here is obscure, since the N–Ag–N′ angle at the silver atom is the same for the polymer as it is for the dimer formed with the same ligand, albeit with rather different dihedral angles between the coordinated ligand planes. Insofar as the two dimers are concerned, the conformations of the centrosymmetric AgL$_2$Ag arrays are quite similar with similar Ag···Ag′ distances. Similar interplanar angles are found between the pairs of rings within the ligand, these angles being the same as the dihedral angles between ring pairs coordinated at the same metal (by symmetry). In the ligands the torsions of the im planes about the two B–N bonds are quite (similarly) disparate in both cases, more so than in the ligand of the polymer, where presumably, unconstrained by the dimeric ring, rotation is less restricted, although subject to 'packing forces'. The silver environments of the two dimers (both P$_2$AgN$_2$) are remarkably different. Ag–P bond lengths are similar throughout, 2.479(1)/2.480(1), *cf.* 2.4594(8)/2.4597(9) Å, with P–Ag–P also similar (130.92(4), *cf.* 120.67(2)°), but Ag–N are much longer in the (cy)$_3$P/B(im)$_4$ adduct than in the (*p*-MeC$_6$H$_4$)$_3$P/H$_2$B(im)$_2$ counterpart. N–Ag–N is considerably

Table 1 Selected geometries for AgL : PR_3 (1 : 2). The two values in each entry are for L/R = $B(im)_4$/cy (upper) and *$H_2B(im)_2$/C_6H_4Me-p (lower)*; *r*/Å is the silver–ligand atom distance, the other values being the angles (degrees) subtended by the relevant atoms at the head of the row and column. Primed atoms are centrosymmetrically related

Atom	*r*	P(2)	N(13)	N(23′)
P(1)	2.479(1) *2.4594(8)*	130.92(4) *129.67(2)*	102.56(8) *108.50(7)*	112.28(9) *103.57(8)*
P(2)	2.480(1) *2.4597(9)*		107.9(1) *109.95(8)*	104.79(9) *100.81(7)*
N(13)	2.523(4) *2.327(2)*			91.0(1) *99.48(8)*
N(23′)	2.449(3) *2.380(2)*	Ag · · · Ag′	8.892(1) *8.6054(9)*	

[a] Ag, Ag′ lie 0.897(8), 0.265(8); *0.543(5), 0.501(6)* Å out of the C_3N_2 planes 1,2 of the two complexes. Torsion angles N(21)–B–N(11)–C(12), N(11)–B–N(12)–C(12) are −124.9(4), 16.0(6); *−17.3(5), 116.1(3)*. Within the $P(cy)_3$ ligands, Ag–P–C(*n*1)–C(*n*2,6) are 26.3(4), 154.9(3); 54.4(3), −177.2(3); −60.9(3), 61.1(3) ($n = 1;2;3$) (ligand 1); 11.9(8)/−36.3(7), 160.6(4); 48.0(3), 178.5(2); −59.6(3), 63.5(4)° (ligand 2). Counterpart Ag–P–C–C torsions in the (p-$MeC_6H_4)_3P$ complex are −29.2(3), 34.0(2), −40.3(3); −33.5(3), −41.6(3), −58.9(3)°. The dihedral angles between the coordinated C_3N_2 planes are 65.4(2), *67.8(1)*° (and between the planes within the ligand, the same).

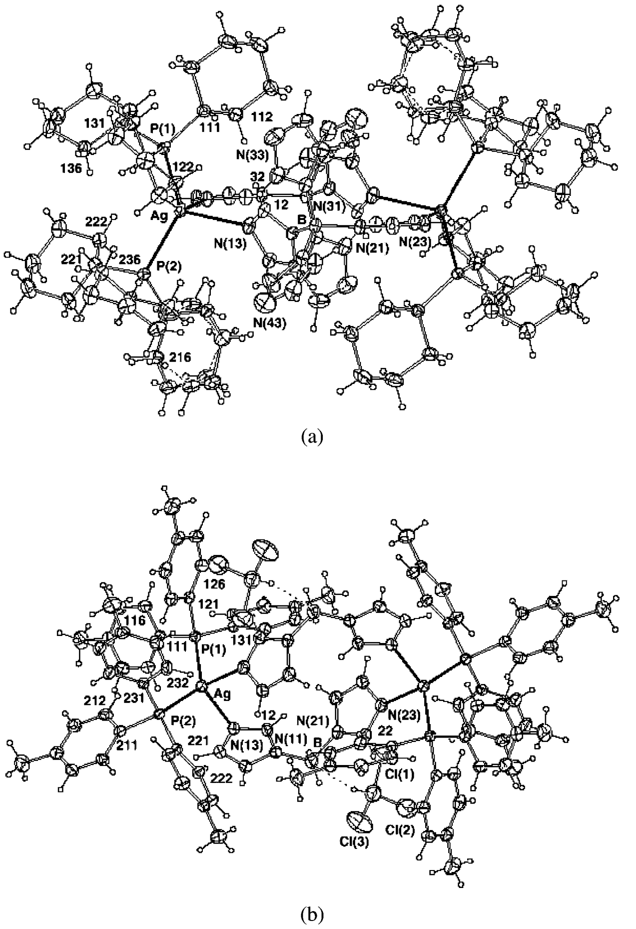

Fig. 4 Projections of the centrosymmetric dimers $[Ag(R_3P)_2\{(im)BX_2(im)\}]_2$: (a) R = cy, X = im; (b) R = *p*-tolyl, X = H, in conjunction with the two molecules of chloroform solvent, which hydrogen bond to the boronic hydrogen atoms.

enlarged in the latter, consistent with the shorter Ag–N distances. Although electronic factors may be relevant, it is tempting to ascribe the difference to the disparity in the relevant steric factors operative through the two complexes, $(cy)_3P$ having a larger cone angle than (p-$MeC_6H_4)_3P$. This is in concert with the enhanced bulk of the additional im substituents on the ligand of that complex, *cf.* their hydrogen counterparts in the other. Interestingly, these are reflected in much closer $PR_3 : X_2B(im)_2$ H · · · H contacts in the former, almost all associated with the disordered substituent of $(cy)_3P$ ligand 2 : H(14) · · · H(212Aa), 2.0_6; H(15) · · · H(113e′), 2.3_6; H(35) · · · H(213A,Be) 2.3_1, 2.3_7 Å (all estimated), *cf.* the (p-$MeC_6H_4)_3P/H_2B(im)_2$ adduct where there are none less than 2.5 Å. Presumably there is a concerted/mutual interaction between the effects of lengthening the Ag–N bonds *and* disordering of the cy substituent group to an energetically less favourable disposition. Interestingly, this does not appear to impact on the central ring conformation to any substantial extent, suggesting that it may be a relatively rigid component of the array.

The (p-$MeC_6H_4)_3P/H_2B(im)_2$ adduct is of particular interest in that, with the foregoing steric impediments diminished and the presence of the H_2B moiety, negatively rather than positively charged, each of the latter units in the dimer interacts *via* some rather unusual H · · · H hydrogen bonding. These are bound to the positively charged hydrogen atoms of chloroform solvent molecules, one per BH_2, H · · · H(2) being 2.2_1 Å, appreciably less than the usual van der Waals estimate of 2.4 Å. The substituents of the phosphine ligands in this complex adopt the common quasi-*3* disposition. Again, the nature of this pair of 1 : 2 complexes may be contrasted with that of the only structurally characterized pyrazolate counterpart AgL : PPh_3 (1 : 2), L = $H_2B(pz)_2$.[13e] This latter is a neutral mononuclear array, also with four-coordinate P_2AgN_2 silver, in which Ag–P are 2.4256(9), 2.5049(9), Ag–N 2.336(3), 2.360(3) Å, with P–Ag–P 122.51(3)°, considerably reduced from both of the present values, with N–Ag–N 89.5(1)°, somewhat reduced also. In that array, N–Ag–P are very diverse, range 97.50(8)–124.61(8)°. This presumably is in consequence of steric stresses imposed by the rather awkward chelate moiety, which reduces the maximum potential local symmetry about the metal to *m*, and associated interactions with the pair of phosphine ligands.

Conclusion

We have synthesized a new dihydrobis(imidazolyl)borate ligand in the form of its dimethylacetamide adduct (**1**) and we have prepared a series of new stable silver(I)–tertiary phosphine complexes containing anionic dihydrobis(imidazolyl)borate (**2**–**4**) and tetrakis(imidazolyl)borate ligands (**5**–**10**). Binuclear $[Ag(PR_3)_2\{(im)BX_2(im)\}]_2$ or polymeric $[Ag(PR_3)\{(im)BX_2(im)\}]_n$ (X = H or imidazolate) complexes have been obtained and fully characterized by analytical and spectroscopic measurements. Solution data are consistent with a partial dissociation of complexes, occurring through breaking of both Ag–N and Ag–P bonds. The ^{31}P NMR data show that the structure and stability of complexes in solution are strongly dependent on stoichiometry and on the Tolman cone angle of the phosphorus donor; besides, the results reported here suggest that in solution an increase in $^1J(Ag,^{31}P)$ is consistent with increasing P–Ag–P angle due to ligand–ligand interaction arising from greater steric hindrance of the phosphine rings.

In the solid state the $[Ag\{P(cy)_3\}\{(im)BH_2(im)\}]_n$ **4** adduct is a single-stranded polymer consisting of three-coordinate silver atoms ($PAgN_2$ core), while in $[Ag\{P(C_6H_4Me\text{-}p)_3\}\{(im)BH_2(im)\}]_2\cdot 2CHCl_3$ **3**·$2CHCl_3$ and $[Ag\{P(cy)_3\}\{(im)B(im)_2(im)\}]_2\cdot MeCN$ **10**·MeCN the silver atoms are four-coordinate with P_2AgN_2 cores. The structures of **3** and **4** are the first ones defined for any dihydrobis(imidazolyl)boratometal complex, **3** exhibiting an unusual H · · · H solvent hydrogen bond.

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