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Solution and solid-state structural properties of silver(I) dihydrobis(pyrazolyl)borate compounds with tertiary mono(phosphine) ligands†

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New silver(I) derivatives containing triorganophosphines and anionic dihydrobis(pyrazol-1-yl)borates have been prepared from $AgNO_3$ and PR_3 (R = phenyl, benzyl, cyclohexyl, *o*-, *m*- or *p*-tolyl) or PPh_2R' (R′ = methyl or ethyl) and $K[H_2B(pz)_2]$ or $K[H_2B(3,5\text{-}Me_2pz)_2]$ (Hpz = pyrazole); their solid state and solution properties have been investigated through analytical and spectroscopic measurements (IR, ^1H and ^{31}P NMR). The compounds are stable, soluble in chlorinated solvents and non-electrolytes in CH_2Cl_2 and acetone solutions. The structures of $[Ag\{H_2B(pz)_2\}(PPh_3)_2]$, $[Ag\{H_2B(3,5\text{-}Me_2pz)_2\}(PEtPh_2)]$, and $[Ag\{H_2B(3,5\text{-}Me_2pz)_2\}(PCy_3)]$ have been determined by X-ray crystallographic studies. In these compounds the dihydrobis(pyrazol-1-yl)borate ligand is bidentate, with the silver(I) centre adopting a tetrahedral (first) or trigonal geometry (last two).

Introduction

Since the first studies of Trofimenko[1] a number of papers have reported on the synthesis and characterization of poly(pyrazolyl)borate complexes of main group and transition metals. In most of the previous reports extensive series of stable Group 7–13 complexes have been described[2–12] and it has been shown that nuclearity, geometry, spectroscopic properties and reactivity of metal complexes can be controlled by varying the size and shape of the metal centered cavities generated by the poly(pyrazolyl)borates.[2–5]

Structural and solution equilibria and dynamics studies of copper(I) and silver(I) compounds containing phosphine ligands are of importance due to their potential application as potent anti-tumor agents[13] and as free radical scavengers in industrial processes.[14] Whereas extensive chemistry has been published on tris(pyrazolyl)borate metal derivatives,[15–20] comparatively little has been reported concerning bis(pyrazolyl)borate[21] and tetrakis(pyrazolyl)borate co-ordination chemistry. The latter have been also found to give metallic and organometallic derivatives which are generally very stable in solution and in the solid state.[1–12,22–24] They usually co-ordinate to transition metals in a tridentate way, although some examples are known where the ligands act as bidentate or bis-bidentate.[1–12,22–24]

Relatively little information on the structure and dynamics of these complexes in solution has been reported. In a previous study[25] we investigated the co-ordination chemistry of silver(I) towards the tetrakis(pyrazolyl)borate family and obtained 1 : 1 adducts with tertiary phosphines of the type $[Ag\{(pz)B(pz)_3\}(PR_3)]$, containing three- or four-co-ordinate environments (N_2AgP or N_3AgP). In order further to understand the solid state and solution co-ordination chemistry of silver(I) toward the poly(pyrazolyl)borate family we have explored the interaction between $\{H_2B(pz)_2\}^-$ and $\{H_2B(3,5\text{-}Me_2pz)_2\}^-$ ligands and a number of $[Ag(PR_3)_2]^+$ or $[Ag(PPh_2R')]^+$ acceptors. Spectroscopic data, the behaviour in solution and reactivity of these compounds are discussed on the basis of electronic, *e.g.* pK_a values,[26] and steric properties, *e.g.* Tolman angle.[27] Three representative complexes have also been characterized in the solid state by single crystal X-ray studies, providing convenient parallels for comparison with previous analogs using $\{B(pz)_4\}^-$ and $\{B(3\text{-}Mepz)_4\}^-$ ligands.

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. The positive electrospray mass spectrum of compound **12** was obtained with a Series 1100 MSI detector HP spectrometer, using a $CHCl_3$ mobile phase.

Syntheses

Salts of the donors dihydrobis(pyrazol-1-yl)borate, $\{H_2B(pz)_2\}^-$, and bis(3,5-dimethylpyrazol-1-yl)dihydroborate, $\{H_2B(3,5\text{-}Me_2pz)_2\}^-$, were prepared in accordance with the procedure first reported by Trofimenko.[28] $AgNO_3$, PR_3 and PPh_2R' were

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† Electronic supplementary information (ESI) available: $^{31}P\text{-}\{^1H\}$ NMR and selected IR data for compounds **1**–**12**. See http://www.rsc.org/suppdata/dt/b0/b001168l/

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purchased from Aldrich and used without further purification. The compounds studied take the form $[Ag\{H_2B(pz)_2\}(PR_3)_n]$ [$R_3 = Ph_3, n = 2$, **1**; $R_3 = (o\text{-tolyl})_3, n = 1$, **2**; $R_3 = (m\text{-tolyl})_3, n = 2$, **3**; $R_3 = (CH_2Ph)_3$, $n = 2$, **4**; $R_3 = Cy_3$, $n = 2$, **5**] or $[Ag\{H_2B(3,5\text{-}Me_2pz)_2\}(PR_3)_n]$ [$R_3 = Ph_3$, $n = 2$, **6**; $R_3 = (m\text{-tolyl})_3$, $n = 1$, **7**; $R_3 = (p\text{-tolyl})_3$, $n = 2$, **8**; $R_3 = MePh_2$, $n = 2$, **9**; $R_3 = EtPh_2$, $n = 1$, **10**; $R_3 = (CH_2Ph)_3$, $n = 1$, **11**; $R_3 = Cy_3$, $n = 1$, **12**].

Compound 1. To a methanol solution (50 ml) of $AgNO_3$ (0.170 g, 1 mmol) and PPh_3 (0.524 g, 2 mmol) $K[H_2B(pz)_2]$ (0.185 g, 1 mmol) was added at room temperature and the solution stirred for 1 h. The colorless precipitate obtained was filtered off and washed with diethyl ether. Crystallization from CH_2Cl_2–light petroleum (bp 40–60 °C) gave complex **1** as a microcrystalline solid in 70% yield. mp 168 °C decomp. ^1H NMR ($CDCl_3$, 293 K): δ 6.08 (t, 2 H, 4-CH), 7.23 (d, 2 H, 3- or 5-CH), 7.65 (d, 2 H, 3- or 5-CH) and 7.30–7.40 (m, 30 H, CH). Λ_M (acetone) = 1.03 Ω^{-1} cm^2 mol^{-1}. Λ_M (CH_2Cl_2) = 0.23 Ω^{-1} cm^2 mol^{-1}. Found: C, 64.8; H, 4.9; N, 7.2. Calc. for $C_{42}H_{38}AgBN_4P_2$: C, 64.7; H, 4.9; N, 7.1%.

Compound 2. This was prepared similarly to compound **1**, by using $AgNO_3$ (0.170 g, 1 mmol), $P(C_6H_4Me\text{-}o)_3$ (0.608 g, 2 mmol) and $K[H_2B(pz)_2]$ (0.185 g, 1 mmol). Compound **2** was recrystallized from $CHCl_3$–diethyl ether (yield 90%). mp 136 °C decomp. ^1H NMR ($CDCl_3$, 293 K): δ 2.61 (s, 9 H, CH_3), 6.13 (t, 2 H, 4-CH), 6.87–7.37 (m, 12 H, CH), 7.41 (d, 2 H, 3- or 5-CH) and 7.61 (d, 2 H, 3- or 5-CH). Λ_M (acetone) = 2.3 Ω^{-1} cm^2 mol^{-1}. Λ_M (CH_2Cl_2) = 0.7 Ω^{-1} cm^2 mol^{-1}. Found: C, 58.3; H, 5.2; N, 10.0. Calc. for $C_{27}H_{29}AgBN_4P$: C, 58.0; H, 5.2; N, 10.1%.

Compound 3. To a methanol solution (50 ml) of $AgNO_3$ (0.170 g, 1 mmol) and $P(C_6H_4Me\text{-}m)_3$ (0.608 g, 2 mmol), $K[H_2B(pz)_2]$ (0.185 g, 1 mmol) was added at room temperature and the solution stirred for 1 h. The solvent was removed with a rotary evaporator. Chloroform (50 ml) was added, the suspension filtered and the organic layer dried on 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 CH_2Cl_2–light petroleum gave complex **3** as a microcrystalline solid in 89% yield. mp 155 °C decomp. ^1H NMR ($CDCl_3$, 293 K): δ 2.26 (s, 18 H, CH_3), 6.11 (t, 2 H, 4-CH), 7.12–7.24 (m, 24 H, CH), 7.31 (d, 2 H, 3- or 5-CH) and 7.65 (d, 2 H, 3- or 5-CH). Λ_M (acetone) = 2.4 Ω^{-1} cm^2 mol^{-1}. Λ_M (CH_2Cl_2) = 0.9 Ω^{-1} cm^2 mol^{-1}. Found: C, 66.6; H, 5.7; N, 6.5. Calc. for $C_{48}H_{50}AgBN_4P_2$: C, 66.8; H, 5.8; N, 6.4%.

Compound 4. This was prepared similarly to compound **1**, by using $AgNO_3$ (0.170 g, 1 mmol), $P(CH_2Ph)_3$ (0.608 g, 2 mmol) and $K[H_2B(pz)_2]$ (0.185 g, 1 mmol); it was recrystallized from $CHCl_3$–diethyl ether (yield 95%). mp 110 °C decomp. ^1H NMR ($CDCl_3$, 293 K): δ 2.99 (s, 12 H, CH_2), 6.10 (t, 2 H, 4-CH), 7.07–7.29 (m, 32 H, CH and 3- or 5-CH), 7.59 (d, 4 H, 3- or 5-CH). Λ_M (CH_2Cl_2) = 8.5 Ω^{-1} cm^2 mol^{-1}. Found: C, 66.8; H, 5.6; N, 6.7. Calc. for $C_{48}H_{50}AgBN_4P_2$: C, 66.7; H, 5.8; N, 6.5%.

Compound 5. This was prepared similarly to compound **1**, by using $AgNO_3$ (0.170 g, 1 mmol), $P(C_6H_{11})_3$ (0.561 g, 2 mmol) and $K[H_2B(pz)_2]$ (0.185 g, 1 mmol); it was recrystallized from $CHCl_3$–diethyl ether (yield 95%). mp 165 °C decomp. ^1H NMR ($CDCl_3$, 293 K): δ 1.29–1.95 (m, 66 H, C_6H_{11}), 6.14 (t, 2 H, 4-CH), 7.42 (d, 2 H, 3- or 5-CH) and 7.59 (d, 4 H, 3- or 5-CH). Λ_M (acetone) = 0.9 Ω^{-1} cm^2 mol^{-1}. Λ_M (CH_2Cl_2) = 0.6 Ω^{-1} cm^2 mol^{-1}. Found: C, 61.9; H, 9.2; N, 6.9. Calc. for $C_{42}H_{74}AgBN_4P_2$: C, 61.8; H, 9.1; N, 6.9%.

Compound 6. This was prepared similarly to compound **1**, by using $AgNO_3$ (0.170 g, 1 mmol), PPh_3 (0.524 g, 2 mmol) and $K[H_2B(3,5\text{-}Me_2pz)_2]$ (0.242 g, 1 mmol); it was recrystallized from $CHCl_3$–Et_2O (yield 80%). mp 142 °C decomp. ^1H NMR ($CDCl_3$, 293 K): δ 1.98 (s, 6 H, 3- or 5-CCH_3), 2.38 (s, 6 H, 3- or 5-CCH_3), 5.72 (s, 2 H, 4-CH) and 7.37–7.49 (m, 30 H, CH). Λ_M (acetone) = 3.1 Ω^{-1} cm^2 mol^{-1}. Λ_M (CH_2Cl_2) = 1.2 Ω^{-1} cm^2 mol^{-1}. Found: C, 65.83; H, 5.72; N, 6.68. Calc. for $C_{46}H_{46}AgBN_4P_2$: C, 66.13; H, 5.55; N, 6.71%.

Compound 7. This was prepared similarly to compound **3**, by using $AgNO_3$ (0.170 g, 1 mmol), $P(C_6H_4Me\text{-}m)_3$ (0.608 g, 2 mmol) and $K[H_2B(3,5\text{-}Me_2pz)_2]$ (0.242 g, 1 mmol); it was recrystallized from $CHCl_3$–Et_2O (yield 80%). mp 240 °C decomp. ^1H NMR ($CDCl_3$, 293 K): δ 1.82 (s, 6 H, 3- or 5-CCH_3), 2.29 (s, 9 H, CH_3), 2.36 (s, 6 H, 3- or 5-CCH_3), 5.62 (s, 2 H, 4-CH) and 7.21–7.41 (m, 12 H, CH). Λ_M (acetone) = 2.1 Ω^{-1} cm^2 mol^{-1}. Λ_M (CH_2Cl_2) = 0.7 Ω^{-1} cm^2 mol^{-1}. Found: C, 60.6; H, 6.4; N, 5.2. Calc. for $C_{31}H_{37}AgBN_4P$: C, 60.5; H, 6.1; N, 5.0%.

Compound 8. This was prepared similarly to compound **3**, by using $AgNO_3$ (0.170 g, 1 mmol), $P(C_6H_4Me\text{-}p)_3$ (0.608 g, 2 mmol) and $K[H_2B(3,5\text{-}Me_2pz)_2]$ (0.242 g, 1 mmol); it was recrystallized from $CHCl_3$–Et_2O (yield 85%). mp 120–123 °C decomp. ^1H NMR ($CDCl_3$, 293 K): δ 1.91 (s, 6 H, 3- or 5-CCH_3), 2.24 (s, 6 H, 3- or 5-CCH_3), 2.25 (s, 18 H, CH_3), 5.61 (s, 2 H, 4-CH) and 7.03–7.23 (m, 24 H, CH). Λ_M (acetone) = 0.9 Ω^{-1} cm^2 mol^{-1}. Λ_M (CH_2Cl_2) = 0.8 Ω^{-1} cm^2 mol^{-1}. Found: C, 67.85; H, 6.57; N, 6.21. Calc. for $C_{52}H_{58}AgBN_4P_2$: C, 67.98; H, 6.36; N, 6.10%.

Compound 9. This was prepared similarly to compound **3**, by using $AgNO_3$ (0.170 g, 1 mmol), $PMePh_2$ (0.400 g, 2 mmol) and $K[H_2B(3,5\text{-}Me_2pz)_2]$ (0.242 g, 1 mmol); it was recrystallized from $CHCl_3$ and light petroleum (yield 80%). mp 110–113 °C decomp. ^1H NMR ($CDCl_3$, 293 K): δ 1.83 (s, 6 H, 3- or 5-CCH_3), 2.06 (s, 6 H, CH_3), 2.36 (s, 6 H, 3- or 5-CCH_3), 5.72 (s, 2 H, 4-CH) and 7.36–7.54 (m, 20 H, CH). Λ_M (CH_2Cl_2) = 0.6 Ω^{-1} cm^2 mol^{-1}. Found: C, 60.5; H, 6.0; N, 8.1. Calc. for $C_{36}H_{42}AgBN_4P_2$: C, 60.8; H, 5.9; N, 7.9%.

Compound 10. This was prepared similarly to compound **3**, by using $AgNO_3$ (0.170 g, 1 mmol), $PEtPh_2$ (0.428 g, 2 mmol) and $K[H_2B(3,5\text{-}Me_2pz)_2]$ (0.242 g, 1 mmol); it was recrystallized from $CHCl_3$ and Et_2O–n-heptane (yield 49%). mp 119–122 °C decomp. ^1H NMR ($CDCl_3$, 293 K): δ 1.21 and 1.28 (2t, 3 H, CH_3), 2.07 (s, 6 H, 3- or 5-CCH_3), 2.31–2.36 (m, 10 H, 3- or 5-CCH_3 and CH_2), 5.71 (s, 2 H, 4-CH) and 7.40–7.67 (m, 20 H, CH). Λ_M (CH_2Cl_2) = 0.8 Ω^{-1} cm^2 mol^{-1}. Found: C, 55.0; H, 5.9; N, 10.7. Calc. for $C_{24}H_{31}AgBN_4P$: C, 54.9; H, 5.9; N, 10.7%.

Compound 11. This was prepared similarly to compound **1**, by using $AgNO_3$ (0.170 g, 1 mmol), $P(CH_2Ph)_3$ (0.608 g, 2 mmol) and $K[H_2B(3,5\text{-}Me_2pz)_2]$ (0.242 g, 1 mmol); it was recrystallized from $CHCl_3$ and Et_2O (yield 75%). mp 190 °C decomp. ^1H NMR ($CDCl_3$, 293 K): δ 1.72 (s, 6 H, 3- or 5-CCH_3), 2.35 (m, 6 H, 3- or 5-CCH_3), 3.04 (s, 12 H, CH_2), 5.66 (s, 2 H, 4-CH) and 7.22–7.25 (m, 30 H, CH). Λ_M (CH_2Cl_2) = 6.5 Ω^{-1} cm^2 mol^{-1}. Found: C, 60.6; H, 6.2; N, 9.3. Calc. for $C_{31}H_{37}AgBN_4P$: C, 60.5; H, 6.1; N, 9.1%.

Compound 12. This was prepared similarly to compound **1**, by using $AgNO_3$ (0.170 g, 1 mmol), PCy_3 (0.561 g, 2 mmol) and $K[H_2B(3,5\text{-}Me_2pz)_2]$ (0.242 g, 1 mmol); it was recrystallized from $CHCl_3$–diethyl ether (yield 67%). mp 179 °C decomp. ^1H NMR ($CDCl_3$, 293 K): δ 1.25–1.98 (m, 33 H, C_6H_{11}), 2.20 (s, 6 H, 3- or 5-CCH_3), 2.35 (m, 6 H, 3- or 5-CCH_3) and 5.70 (t, 2 H, 4-CH). Positive ES ($CHCl_3$): m/z 205 (78%, as center of an isotopic cluster, $[Ag(Hpz)]^+$), 299 (5%, as center of an isotopic cluster, $[Ag(Hpz)_2]^+$), 445 (100%, as center of an isotopic cluster, $[\{Ag(pz)(H_2O)\}_2 + H]^+$), 592 (3%, as center of an isotopic cluster, $[M + H]^+$) and 669 (5%, as center of an isotopic cluster,

$[\mathrm{Ag(PCy_3)_2}]^+$). Λ_M (acetone) = 1.2 Ω^{-1} cm^2 mol^{-1}. Λ_M (CH_2Cl_2) = 0.6 Ω^{-1} cm^2 mol^{-1}. Found: C, 56.6; H, 8.3; N, 9.6. Calc. for $C_{28}H_{49}AgBN_4P$: C, 56.9; H, 8.3; N, 9.5%.

Structure determinations

For complex **1** a unique room temperature single counter diffractometer data set was measured (gaussian absorption correction); for **10** and **12** full spheres of low-temperature CCD area detector data (Bruker AXS instrument) were measured, $N_{t(otal)}$ reflections merging to N unique (R_{int} quoted) after processing using proprietary software incorporating 'empirical' (multi-scan) absorption correction, N_o being considered 'observed' and used in the full matrix least squares refinement. Monochromatic Mo-Kα radiation (λ = 0.71073 Å) was employed for both structures. Anisotropic thermal parameters were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being refined throughout. Conventional residuals R, R_w are quoted at convergence. Neutral atom complex scattering factors were used within the context of the XTAL 3.4 program system.[29] Pertinent results are given below and in the Figures and Tables.

Crystal/refinement data. 1. $C_{42}H_{38}AgBN_4P_2$, M_r = 779.4, T *ca.* 295 K, monoclinic, space group $P2_1/c$, a = 13.154(2), b = 14.724(2), c = 19.690(3) Å, β = 94.93(2)°, V = 3800 Å^3, D_c (Z = 4) = 1.36_2 g cm^{-3}, μ_{Mo} = 6.5 cm^{-1}, specimen 0.98 × 0.31 × 0.26 mm, $T_{min,max}$ = 0.81, 0.85, $2\theta_{max}$ = 60°, N = 11068, N_o ($I > 3\sigma(I)$) = 7326, R = 0.046, R_w = 0.048, $|\Delta\rho_{max}|$ = 0.89(3) e Å^{-3}.

10. $C_{24}H_{31}AgBN_4P$, M = 525.2, T *ca.* 153 K, triclinic, space group $P\bar{1}$, a = 8.939(1), b = 13.815(2), c = 20.376(2) Å, α = 93.542(2), β = 91.594(2), γ = 96.641(2)°, V = 2493 Å^3, D_c (Z = 4) = 1.39_9 g cm^{-3}, μ_{Mo} = 8.9 cm^{-1}, specimen 0.40 × 0.20 × 0.15 mm, 'T'$_{min,max}$ = 0.79, 0.90, $2\theta_{max}$ = 58°, N_t = 28836, N = 12173 (R_{int} = 0.024), N_o ($F > 4\sigma(F)$) = 10257, R = 0.044, R_w = 0.062, $|\Delta\rho_{max}|$ = 1.09(5) e Å^{-3}.

12. $C_{28}H_{49}AgBN_4P$, M = 591.4, T *ca.* 153 K, orthorhombic, space group $Pbca$, a = 12.712(1), b = 18.682(2), c = 25.410(2) Å, V = 6035 Å^3, D_c (Z = 8) = 1.30_2 g cm^{-3}, μ_{Mo} = 7.4 cm^{-1}, specimen 0.50 × 0.38 × 0.10 mm, 'T'$_{min,max}$ = 0.70, 0.86, $2\theta_{max}$ = 58°, N_t = 58108, N = 7754 (R_{int} = 0.028), N_o ($F > 4\sigma(F)$) = 6604, R = 0.031, R_w = 0.045, $|\Delta\rho_{max}|$ = 0.71(4) e Å^{-3}.

CCDC reference number 186/1972.

See http://www.rsc.org/suppdata/dt/b0/b001168l/ for crystallographic files in .cif format.

Results and discussion

Synthesis

From the interaction between a tertiary mono(phosphine) PR_3 (PPh_3, PCy_3, $P(CH_2Ph)_3$, $P(C_6H_4Me\text{-}o)_3$, $P(C_6H_4Me\text{-}m)_3$, $P(C_6H_4Me\text{-}p)_3$, $PMePh_2$ and $PEtPh_2$), $AgNO_3$ and the potassium salt of the bis(pyrazol-1-yl)borate ligand $[H_2B(pz)_2]^-$ or $[H_2B(3,5\text{-}Me_2pz)_2]^-$ (Hpz = pyrazole), in methanol at room temperature, the complexes **1**–**12** have been obtained in high yield. Compounds **1**, **3**–**6**, **8**, and **9** have been synthesized upon mixing an equimolar ratio of the dihydrobis(pyrazolyl)borate ligand $[H_2B(pz)_2]^-$ and $AgNO_3$ with two moles of phosphine ligands, in accordance with reactions (1) and (2). When $P(C_6H_4Me\text{-}o)_3$ was used as ancillary ligand the 1 : 1 complex $[Ag\{H_2B(pz)_2\}\{P(C_6H_4Me\text{-}o)_3\}]$ **2** was obtained also with a large excess of the phosphorus donor, eqn. (3). Using the same conditions we have obtained the compounds **7**, **10**, **11** and **12**. The excess of phosphine is necessary also in these reactions due to the instability in solution of this class of compounds in the absence of stabilizing P-donor ancillary ligands: in fact deposition of metallic silver occurs when an equimolar ratio of $AgNO_3$ and phosphine ligands was employed.

$$K[H_2B(pz)_2] + AgNO_3 + 2PR_3 \longrightarrow [Ag\{H_2B(pz)_2\}(PR_3)_2] + KNO_3 \quad (1)$$

$$K[H_2B(3,5\text{-}Me_2pz)_2] + AgNO_3 + 2PR_3 \longrightarrow [Ag\{H_2B(3,5\text{-}Me_2pz)_2\}(PR_3)_2] + KNO_3 \quad (2)$$

$$K[H_2B(pz)_2] + AgNO_3 + 2P(C_6H_4Me\text{-}o)_3 \longrightarrow [Ag\{H_2B(pz)_2\}\{P(C_6H_4Me\text{-}o)_3\}] + KNO_3 + P(C_6H_4Me\text{-}o)_3 \quad (3)$$

Silver complexes containing the dihydrobis(pyrazolyl)borate ligands are significantly less stable than the previously described complexes obtained with more highly substituted ligands,[17,25] this property being related to the higher reducing power arising from the presence of the two hydrogens linked to the boron atom.

All the derivatives **1**–**12** show good solubility in most common organic solvents. They are generally sufficiently stable in chloroform, but only in the dark and under anaerobic conditions. With the exception of **4** and **11**, which are partly ionized in CH_2Cl_2, none of the dihydrobis(pyrazol-1-yl)borate derivatives is an electrolyte in CH_2Cl_2 and acetone solution.

Spectroscopy

The IR spectra (the most noteworthy bands are reported in the Experimental section) exhibit all the absorptions required by the presence of the dihydrobis(pyrazolyl)borate and tertiary phosphine ligands.

In the spectra of derivatives **1**–**12** we always found the ν(CH) vibrations of the heterocyclic ring at *ca.* 3100 cm^{-1},[30] the ν(CH) vibrations of the aryl groups at *ca.* 3080–3040 cm^{-1}, the $\nu(C\overset{\cdots}{-}C)$ of the phosphorus donor and the $\nu(C\overset{\cdots}{-}N)$ frequencies of the bis(pyrazolyl)borate heterocyclic ring[21] at *ca.* 1580 and 1530 cm^{-1} respectively, and finally the B–N stretching vibrations at *ca.* 1400 cm^{-1}.[31] We have observed several ν(BH) bands, confirming the presence of the dihydrobis(pyrazolyl)borate ligands. The presence of both ^{10}B and ^{11}B in natural boron results in a multiplicity of bands at 2350–2410 and 2340–2260 cm^{-1} for derivatives of the $[H_2B(pz)_2]^-$ ligand, 2370–2460 and 2250–2320 cm^{-1} for $[H_2B(3,5\text{-}Me_2pz)_2]^-$. These bands are shifted to higher frequency with respect to the same absorptions of free dihydrobis(pyrazolyl)borate ligands.

In the far IR region of the arylphosphino derivatives broad absorptions between 500 and 400 cm^{-1} are due to Whiffen's *y* and *t* vibrations, whereas the *u* and *x* vibrations appear as bands of weak intensity between 280 and 240 cm^{-1}.[32,33] We are not able to assign the ν(Ag–N) vibrations, because they are hidden beneath some absorptions characteristic of the azole ring system and of the phosphines.

The ^{1}H NMR spectra of all complexes in $CDCl_3$ present one set of signals for the pyrazolyl rings of the dihydrobis(pyrazolyl)borate ligand: only one resonance absorption for the 4-CH protons and two for the 3- and 5-CH or 3- or 5-CCH_3 protons. The pattern observed indicates magnetic equivalence of the pyrazolyl rings and of the phosphine ligands coordinated to the metal center. This observation is not consistent with the symmetry of these molecules and suggests that some dynamic process is occurring in solution. This is common in complexes of d and f elements with poly(pyrazolyl)borates,[2–5,7,17,25,34,35] suggesting highly fluxional species with either a rocking motion of the triorganophosphinesilver(I) moieties between the two nitrogen atoms of $[H_2B(pz)_2]$ and $[H_2B(3,5\text{-}Me_2pz)_2]$, or complete dissociation and re-association of the pyrazolyl nitrogens, which occurs rapidly even at lower temperatures: in fact, on cooling the $CDCl_3$ solutions of **1**–**12** to 223 K, no additional signals due to pyrazole appeared. In the ^{1}H NMR spectra the chemical shift of the protons due to the pyrazole is similar to those observed for

Table 1 Solution ^{31}P NMR parameters

No.	Compound	δ	$\delta_{(\text{complex})} - \delta_{(\text{ligand})}$	^1J(P–Ag)(av.)/Hz	T/K
1	$[Ag\{H_2B(pz)_2\}(PPh_3)_2]$	4.8	9.4	387	223
2	$[Ag\{H_2B(pz)_2\}\{P(C_6H_4Me\text{-}o)_3\}]$	−18.3	10.7	637	223
3	$[Ag\{H_2B(pz)_2\}\{P(C_6H_4Me\text{-}m)_3\}_2]$	5.6	10.5	384	223
4	$[Ag\{H_2B(pz)_2\}\{P(CH_2Ph)_3\}_2]$	21.3	33.1	666	223
		14.1	25.9	498	
		5.8	17.6	438	
5	$[Ag\{H_2B(pz)_2\}(PCy_3)_2]$	25.0	13.2	425	223
6	$[Ag\{H_2B(3,5\text{-}Me_2pz)_2\}(PPh_3)_2]$	3.4	8.0	301	223
7	$[Ag\{H_2B(3,5\text{-}Me_2pz)_2\}\{P(C_6H_4Me\text{-}m)_3\}]$	4.8	9.7	580	223
8	$[Ag\{H_2B(3,5\text{-}Me_2pz)_2\}\{P(C_6H_4Me\text{-}p)_3\}_2]$	3.5	11.0	247	223
9	$[Ag\{H_2B(3,5\text{-}Me_2pz)_2\}(PMePh_2)_2]$	−9.3	18.7	458	223
10	$[Ag\{H_2B(3,5\text{-}Me_2pz)_2\}(PEtPh_2)]$	13.4	25.4	615	223
11	$[Ag\{H_2B(3,5\text{-}Me_2pz)_2\}\{P(CH_2Ph)_3\}]$	13.6	25.4	647	223
12	$[Ag\{H_2B(3,5\text{-}Me_2pz)_2\}(PCy_3)]$	37.7	26.9	628	293

corresponding nuclei in complexes of copper(I) and silver(I) of tris- and tetrakis-(pyrazolyl)borates with tertiary phosphine coligands.[17–20,25] Greater high-field shift has been found in derivatives containing more sterically hindered triorganophosphines analogously to that previously observed in tris- and tetrakis-(pyrazolyl)borate silver(I) compounds. This peculiarity can be explained by considering the shielding effect exerted on H3, H4 and H5 protons by protons of the aryl rings linked to phosphorus.

^{31}P NMR. The chemical shift and coupling-constant data, determined from the ^{31}P NMR solution spectra for derivatives **1**–**12**, are reported in Table 1. Each spectrum at room temperature consists of a broad singlet, presumably due to rapid exchange equilibria. However, at lower temperatures, exchange is quenched and, except for compound **1**, only one unresolved doublet, arising from coupling between the phosphorus and silver atom, is observed in the accessible temperature range. In the spectrum of **1**, recorded at 183 K, typical pairs of doublets, due to $^1J(^{31}P–^{107}Ag)$ and $^1J(^{31}P–^{109}Ag)$ coupling, are resolved 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 $\gamma(^{107}Ag):\gamma(^{109}Ag)$.

The signal due to each free phosphine is upfield with respect to that of the corresponding silver(I) complex. The magnitudes of the chemical shifts and coupling constants decrease with the decreasing basicity, also correlating with the steric bulk of the ligands. For example, the chemical shifts of compounds **5** and **12**, which contain the more sterically hindered triorganophosphine (PCy_3, cone angle = 170°) are the most deshielded (δ 25.0 and 37.7, respectively). The ^{31}P chemical shift is a function of both cone angle and σ-donor power of the phosphorus coligand[26,27] and seems not to be strongly dependent on the electronic and steric properties of the poly(pyrazolyl)borate donor: in fact the shifts observed for derivatives of $[H_2B(3,5\text{-}Me_2pz)_2]$ are always slightly smaller than those found in compounds of $[H_2B(pz)_2]$, being less basic and less sterically hindered than $[H_2B(3,5\text{-}Me_2pz)_2]$. The $^1J(Ag–^{31}P)$ coupling constants are also dependent on the type of PR_3, the smallest values being observed for those derivatives which contain the phosphorus donors with the larger cone angles.[27] On the other hand the $^1J(Ag–^{31}P)$ coupling constant values seem not to be strongly dependent on the nature of the poly(pyrazol-1-yl)borato donors. However the values observed for derivatives of $[H_2B(3,5\text{-}Me_2pz)_2]$ are always slightly smaller than those for compounds of $[H_2B(pz)_2]$, with similar type of phosphine.

The $^1J(Ag–^{31}P)$ coupling constants are also strongly dependent on the stoichiometric ratio N : Ag : P (N = poly(pyrazolyl)-borate ligand, P = triorganophosphine). In fact the chemical shifts and $^1J(Ag–^{31}P)$ coupling constants of the compounds **2**, **7**, **10**, **11** and **12**, in which the metal centers are most probably three-co-ordinate (N_2AgP), are of the same order of magnitude as those found for analogous tris- and tetrakis-(pyrazolyl)-borate complexes[17,25] in which the metal center is three- or four-co-ordinate (N_2AgP or N_3AgP), with one phosphine group for each silver atom, as found in the solid state structure. On the other hand the ^{31}P NMR spectra of derivatives **1**, **3**, **5**, **6**, **8** and **9**, four-co-ordinate compounds with two phosphine groups for each silver atom (type N_2AgP_2), show chemical shift values and $^1J(Ag–^{31}P)$ coupling constants which differ significantly from those of the closely related tris- and tetrakis-(pyrazolyl)borate silver(I) analogues (type N_2AgP or N_3AgP).[17,25] The values of $^1J(Ag–^{31}P)$ for compounds **1**, **5**, **6** and **9** are in the range reported for analogous silver(I)–bis(triorganophosphine) species $[Ag(PR_3)_2]^+$.[36,37]

It is worth noting that in the spectrum of compound **4** at 223 K three different doublets were observed. On the basis of the $^1J(Ag–^{31}P)$ values we can assign the signal at δ 21.34 ($^1J(^{109}Ag–^{31}P) = 713$ Hz) to $[Ag\{H_2B(pz)_2\}\{P(CH_2Ph)_3\}]$ species, that at δ 14.07 ($^1J(^{109}Ag–^{31}P) = 533$ Hz) to $[Ag\{H_2B(pz)_2\}P(CH_2Ph)_3\}_2]$ and finally that at δ 5.81 ($^1J(^{109}Ag–^{31}P) = 438$ Hz) to the ionic $[Ag\{P(CH_2Ph)_3\}_3]^+[H_2B(pz)_2]^-$ also in accordance with the conductivity data for this sample which are typical of a partly ionized species.

The coupling constant $^1J(Ag–^{31}P)$, in conjunction with other physical data, provides a useful probe for studying changes in molecular structure in solution. This is conveniently possible by analyzing, as a first approximation, the correlation between ^1J(Ag–P) and θ(P–Ag–P) in terms of the hybridization model,[37–41] based on the equation given by Pople and Santry,[42] which assumes that changes in this constant $^1J(Ag–^{31}P)$ are dominated by changes in the Fermi contact term, *via* eqn. (4)

$$^1J(\text{Ag–P}) = a_M{}^2 a_P{}^2(\Delta E)^{-1}|\Psi_{ns}(0)_M|^2|\Psi_{3s}(0)_P|^2 \quad (4)$$

where $a_M{}^2$ and $a_P{}^2$ are the s characters of the hybrid orbitals used to form the M–P bond, ΔE is the mean triplet excitation energy and $|\Psi_{ns}(0)_M|^2$ and $|\Psi_{3s}(0)_P|^2$ are the valence s-electron densities at the metal and phosphorus nuclei respectively. It is generally accepted that the terms $|\Psi_{ns}(0)|^2$ and ΔE do not change significantly for a related series of molecules, and that $a_P{}^2$ is constant for a given phosphine ligand,[41] the value of the coupling constant being determined by the metal s-orbital character $a_M{}^2$. This parameter is determined by the metal–ligand bond angle *via* symmetry and the orthogonality conditions and is expected to increase as the P–Ag–P angle increases. Such a positive correlation between P–Ag–P angle and solution $^1J(Ag–^{31}P)$ data has been observed previously for the complexes: silver(I) diphosphine,[38,39] four-co-ordinate $[HgX_2(PPh_3)_2]$[40] and $[AgX(PCy_3)_2]$[37] species. 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[40] that decreasing the M–P distance results in only small changes in ^1J(Ag–P), changes in the bond angles affecting ^1J(Ag–P) much more.

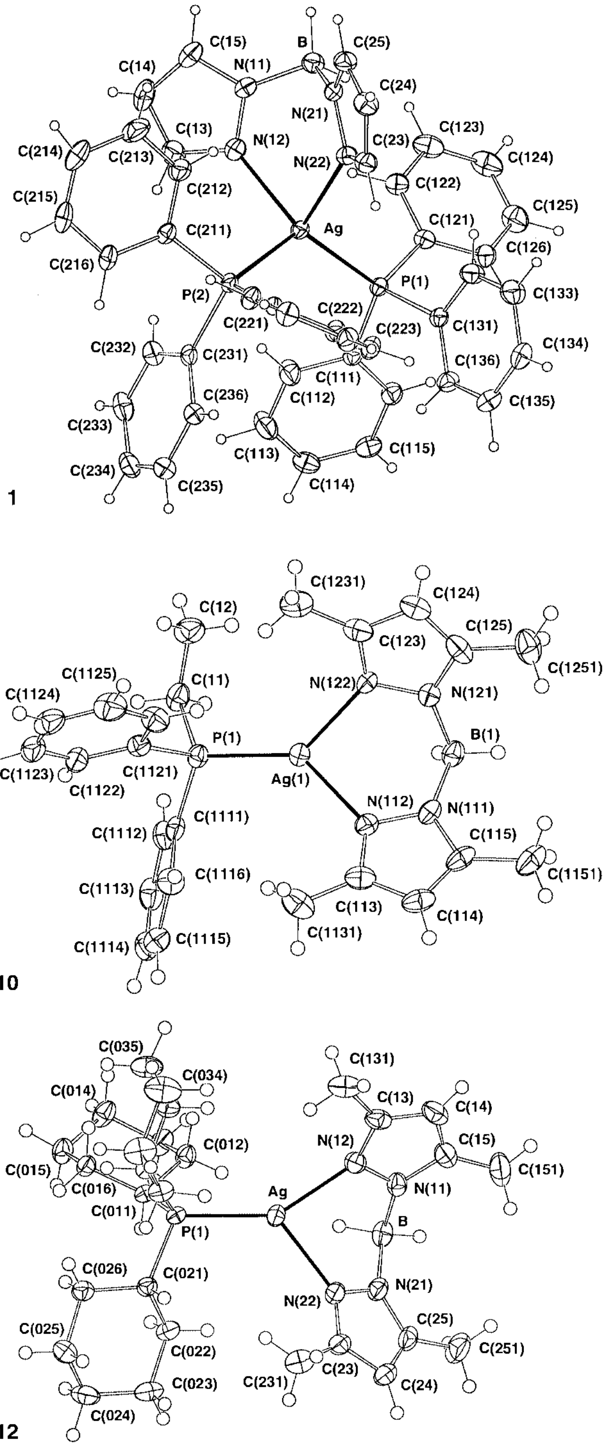
Given the observed dependence of ^1J(Ag–^{31}P) on P–Ag–P angle and by extension of the range of anions in consideration, including the poly(pyrazolyl)borate ligands, the results reported in Table 1 may qualitatively suggest, in solution, an increase in ^1J(Ag–^{31}P) to be consistent with increasing P–Ag–P angle due to ligand–ligand interaction arising from greater steric hindrance of the substituent rings.

Compound **12** was also studied by ESMS. The mass spectrum is dominated by the peak at *m*/*z* 445 which is due to the ion $[\{Ag(pz)(H_2O)\}_2 + H]^+$, but there are also relatively low peaks at *m*/*z* 299, 592, and 669 which are assigned to $[Ag(Hpz)_2]^+$, $[M + H]^+$, and $[Ag(PCy_3)_2]^+$ respectively. The peak at *m*/*z* 205 is most probably due to the $[Ag(Hpz)]^+$ species.

Diffraction studies

The results of the single crystal X-ray structural studies are consistent with the stoichiometries and connectivities as given for compounds **1**, **10**, **12**, above. In **1** and **12** one molecule, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure; in **10** there are two such molecules, stereochemically very similar to each other (Fig. 1). Selected details of the molecular core geometries are given in Tables 2, 3; in **1** (Table 2) the silver atom is four-co-ordinate N_2AgP_2, in **10** and **12** the silver atoms are three-co-ordinate N_2AgP, the borate ligand being bidentate in each case. Values for the latter (**10**, **12**) are also compared with their immediate counterparts in recently described tetrakis(pyrazolyl)borate type adducts in Table 3.

Despite its apparent obviousness and simplicity there are few examples of the mononuclear four-co-ordinate N_2AgP_2 array recorded in the Cambridge Crystallographic Data Base. For (unidentate P-ligand)$_2$Ag(unidentate N-ligand)$_2$ there are none at all, all (unidentate P-ligand)$_2$AgN$_2$ arrays being found with N_2 ligands of bi- or (potentially) higher denticity; of these latter, a number contain the rigid NCCN phenanthroline array, or the similar but less rigid bibenzimidazole or terpyridyl. Systems in which the chelate ring is six-membered are notably absent except for one which parallels the present type, namely Y(XN)$_2$Ag. This is a binuclear complex in which the (XN) array (as in the present) is pyrazolate, a pair of these units being hinged at a central atom, not B (as in the present) but silver itself, in [(PPh$_3$)$_2$Ag(pz-*N*,*N*′)$_2$Ag′(PPh$_3$)], the hinging silver atom (Ag′) being three-co-ordinate, and planar (angle sum 359.$_9$°)[43] rather than (quasi-) tetrahedral (as at the boron). The comparison is of interest. The closeness of the angle sum about the hinging silver (Ag′) in the binuclear complex to 360° suggests a constraint of some rigidity toward coplanarity with its PN$_2$ environment. This is carried through in greater degree to the pyrazolate rings than is the case when Ag′ is supplanted by B as in the present: the PAg′N$_2$ (χ^2 388)/C$_3$N$_2$ (pz1,2) interplanar dihedral angles are 24.4(1), 21.7(1)° with torsion angles in the Ag′–N bonds only −11.3(2), 27.3(2)° *cf.* the ring torsion angles of −72.5(4), 68.4(4)° in the B–N bonds in the present compound. In the binuclear complex this is carried through to the interplanar dihedral angles between the C$_3$N$_2$ pyrazolate planes which are more nearly parallel than in the present. Finally we find that the tetrahedral silver atom lies well out of the (pz)$_2$ array in the binuclear complex with Ag–N ring torsion angles of 58.1(2), −42.7(2)° whereas the present silver atom counterpart has corresponding ring torsion angles of 6.1(3), −8.9(3)°. The overall result is an effectively planar N$_4$ array, with the B hinge atom deviant in the present compound and the silver atom essentially coplanar, while in the binuclear array the roles are reversed, with the planar three-co-ordinate Ag′ hinge atom coplanar and the tetrahedral silver atom out of plane. A useful indicator is that, relative to the N$_4$ 'planes', the silver and boron atoms in both cases are at the prows of 'boat' conformations, δAg,B(12) being 0.201(6), 0.728(6) Å and in the binuclear array δAg,Ag′ 0.963(4), 0.363(4) Å. It is of interest that, with P–Ag–P closely comparable in both complexes, in the present complex about the four-co-ordinate silver, the N–hinge atom (B)–N angle is appreciably greater than for its three-co-ordinate Ag′ counterpart, while N–Ag–P spans a greater range in the present compound (97.50(8)–124.61(8), *i.e. ca.* 27°; *cf.* 99.38(5)–112.03(6), *i.e. ca.* 13°). These may be consequent upon interring steric interaction being more intrusive in the present complex. It is of interest that in both structures, whereas the conformation of one phosphine is the typically relaxed 'three-bladed propeller' (C_3 array), with Ag–P–C–C torsions greater than 35, 23° respectively, we find that in the second such ligand one of the rings has a torsion angle approaching zero (−0.6(4) (present); −12.1(2)° (binuclear array)), with wider divergences,



1

10

12

Fig. 1 Molecular projections showing 20% (**1**), 50% (**10**, **12**) displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Molecule 1 only is shown for compound **10**, molecule 2 being similar.

Table 2 Selected geometries of compound **1**. Also included are counterpart geometries in the complex $[(PPh_3)_2Ag(pz)_2Ag'(PPh_3)]$; italicized values involve Ag′ (rather than B)

(a) Distances (Å) and angles (°)

Ag–N(12)	2.326(3), 2.295(2)	N(12)–Ag–N(22)	89.3(1), 100.67(8)
Ag–N(22)	2.360(3), 2.323(2)	N(12)–Ag–P(1)	124.61(8), 112.03(6)
Ag–P(1)	2.4256(9), 2.461(1)	N(12)–Ag–P(2)	103.26(8), 108.98(6)
Ag–P(1)	2.5049(9), 2.484(1)	N(22)–Ag–P(1)	111.55(9), 99.38(5)
B–N(11)	1.552(6), *2.235(2)*	N(22)–Ag–P(2)	97.50(8), 111.70(6)
B–N(21)	1.539(6), *2.176(2)*	P(1)–Ag–P(2)	122.51(3), 121.73(3)
		N(11)–B–N(21)	110.8(3), *110.4(1)*

The silver atom lies 0.990(8), 0.772(7) Å out of the C_3N_2 pz(1,2) planes; the pz(1)/pz(2) interplanar dihedral angle is 60.1(2)°. In the binuclear complex the corresponding silver atom deviations are 0.500(6), 0.822(5) Å, with the pz(1)/pz(2) dihedral angle 26.8(2)°.

(b) Torsion angles (°)

(i) The $B(Ag')(N_2)_2Ag$ ring		(ii) The phosphine ligands	
N(11)–N(12)–Ag–N(22)	6.1(3), 58.1(2)	Ag–P(1)–C(111)–C(112)	−0.6(4), −57.9(2)
N(21)–N(22)–Ag–N(12)	−8.9(3), −42.7(2)	Ag–P(1)–C(121)–C(122)	−23.9(3), −53.3(2)
Ag–N(12)–N(11)–B	31.1(4), *−31.6(2)*	Ag–P(1)–C(131)–C(132)	−60.2(3), −12.1(2)
Ag–N(22)–N(21)–B	−25.5(4), *5.1(3)*	Ag–P(2)–C(211)–C(212)	−35.1(4), 23.6(2)
N(21)–N(11)–B–N(12)	−72.5(4), *−11.3(2)*	Ag–P(2)–C(221)–C(222)	−39.6(3), 40.3(2)
N(11)–B–N(21)–N(22)	68.4(4)	Ag–P(2)–C(231)–C(232)	−53.1(3)

Table 3 Selected geometries (distances in Å, angles in °) of compounds **10**, **12** and immediate tetrakis(pyrazolyl)borate counterparts. All complexes have PAg(bidentate pz-N)$_2$ environments

	PCy_3 $[H_2B(3,5\text{-}Me_2pz)_2]^-$ This work (**12**)	PCy_3 $[(pz)_2B(pz)_2]^-$ Ref. 43	$PEtPh_2$ $[H_2B(3,5\text{-}Me_2pz)_2]^-$ This work (**10**)[a]	$PMePh_2$ $[(3\text{-}Mepz)_2B(3\text{-}Mepz)_2]^-$ Ref. 43
Ag–P(1)	2.3538(6)	2.351(1)	2.358(1), 2.349(1)	2.328(2)
Ag–N(12)	2.250(1)	2.261(4)	2.251(4), 2.249(4)	2.228(4)
Ag–N(22)	2.299(2)	2.297(3)	2.260(4), 2.245(3)	2.257(5)
P(1)–Ag–N(12)	146.08(5)	140.3(1)	136.16(9), 136.94(9)	141.4(1)
P(1)–Ag–N(22)	127.21(5)	134.45(9)	137.0(1), 135.6(1)	130.6(1)
N(12)–Ag–N(22)	86.71(7)	84.9(1)	86.2(1), 87.1(1)	88.0(2)
Σ	$360._0$	$359._7$	$359._4$, $359._6$	$360._0$
Dihedral angles				
N_2AgP/pz(1)	43.27(9)	35.6(2)	34.4(2), 33.7(1)	29.7(2)
N_2AgP/pz(2)	46.28(9)	37.9(2)	37.3(2), 34.8(2)	29.1(2)
pz(1)/pz(1)	65.7(1)	67.5(2)	63.8(2), 58.2(2)	50.0(2)
Out of plane deviations (δ atom/plane)				
δAg/pz(1)	0.315(4)	0.259(9)	0.169(8), 0.220(7)	0.28(1)
δAg/pz(2)	0.119(4)	0.542(8)	0.391(8), 0.188(7)	0.30(1)
Phosphine ligand torsion angles				
Ag–P(1)–C(11)–C(12)	−24.5(2)	−3.1(6)	−112.2(4), −105.5(4)	−12.5(7)
Ag–P(1)–C(11)–C(16)	−151.9(1)	159.8(4)	65.6(4), 68.9(4)	166.7(5)
Ag–P(1)–C(21)–C(22)	−58.2(2)	−58.5(3)	−164.0(3), −172.6(3)	−53.4(6)
Ag–P(1)–C(21)–C(26)	174.7(2)	64.0(3)	19.5(4), 12.5(4)	121.8(6)
Ag–P(1)–C(31)–C(32)	−64.8(2)	53.6(4)	(−56.4(4), −62.0(4))	—
Ag–P(1)–C(31)–C(36)	56.7(2)	−172.4(3)	(ethyl group)	—

[a] Two molecules.

most notably in Ag–P–C about that phosphorus (108.24(1)–117.4(1) (present), 110.82(6)–123.31(6)° (binuclear complex)), for that ligand, *cf.* the C_3 ligand (111.5(1)–117.1(1) (present), 111.29(6)–116.69(6)° (binuclear complex)).

Within the present complexes containing three-co-ordinate silver (**10**, **12**) and their tetrapyrazolate counterparts (Table 3) the silver environments, although rigorously planar, exhibit various degrees of asymmetry in the co-ordination of the N,N-bidentate ligand, trivial in **10**, considerable in **12**. The silver environment in **10** would seem to comprise the least hindered ligands, Ag–N being closely ranged over the two independent molecules (2.245(3)–2.260(4), <> 2.25_1 Å), as are the angles (135.6(1)–137.0(1), <> $136._4$°). These means provide useful norms for comparison with related species, suggesting that, in the context of three-co-ordinate silver, the environment is relatively unstrained. The considerable deviations observed in $PMePh_2$/(3-Mepz)$_4$ counterparts may reflect the influence of the additional bulk of the methyl substituents (and/) or the influence of extra- rather than intra-molecular forces, perhaps associated with some tendency towards linear two-co-ordination, the asymmetry in P–Ag–N angles being reflected in a corresponding asymmetry in the Ag–N distances with Ag–P also shorter. There is an appreciable difference in the interplanar dihedral angle between the pair of co-ordinated rings in the pyrazolate ligand, which is more likely to be intramolecular in origin and presumably originates in increased crowding about the boron atom in the more highly substituted array. A parallel difference is not observed in the dihedral angles of the less hindered pyrazolate ligands of **12** and its tetrasubstituted counterpart.

In the last two complexes any diminution in strain due to the less hindered pyrazolate ligand is offset by the increased bulk of the (tricyclohexyl)phosphine ligand. Here large asymmetries in the AgN_2 array are found in both compounds, the greater in the presumably less-strained complex **12**, and again suggestive of some influence of an extramolecular origin. Although the difference in the interpyrazolate dihedral angles is again large here, the smaller dihedral angle again in association with the more highly substituted ligand, the greater disparity in Ag–N is found here in association with the less substituted ligand of **12**, rather than the more highly substituted ligand as in **10** and its counterpart.

The dispositions of the substituent rings of the PCy_3 ligands of **12** and its counterpart are of interest, the C(1)–C(6) bonds (or alternatively the 'planes') of two of the rings lying quasi-parallel to Ag–P and that of the third quasi-normal in both cases, as is also the case with the two $[(Cy_3P)AgN_2]$ arrays in compounds **9** and **17** of ref. 25, all three examples being the chiral type 'R' of Scheme 1 of ref. 44. As with the comparisons above, attempts to correlate the disposition of the phosphorus substituents, both here and with related tertiary phosphines, with variations in pyrazolate ligand co-ordination and other steric parameters, particularly across the wider range of closely related compounds described in ref. 25 have been unfruitful. As suggested above, it appears that intermolecular interactions may be involved in many of the variations noted.

Conclusion

We have prepared and characterized a series of silver(I)–tertiary phosphine adducts containing anionic dihydrobis(pyrazol-1-yl)borates. In the solid state they are three- or four-co-ordinate with the donors $[H_2B(pz)_2]$ or $[H_2B(3,5\text{-}Me_2pz)_2]$ bidentate. 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.

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