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Variable co-ordination numbers in 1:1 adducts of silver(I) tetrakis(pyrazolyl)borates with tertiary phosphines

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

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

Silver(I) derivatives containing tertiary phosphines and anionic tetrakis(pyrazol-1-yl)borates were prepared from AgO_3SCF_3, PR_3 (R = phenyl, benzyl, cyclohexyl, 2,4,6-$Me_3C_6H_2$, *o*-, *m*- or *p*-tolyl) or PPh_2R' (R′ = methyl or ethyl) and K[B(pz)$_4$] or K[B(mpz)$_4$] (Hpz = pyrazole, Hmpz = 3-methylpyrazole) and characterized through analytical and spectral (IR, ^{1}H, ^{13}C and ^{31}P NMR) measurements. These compounds are stable, soluble in chlorinated solvents, and non-electrolytes in CH_2Cl_2 and acetone. Room-temperature single-crystal structural characterizations were made for several of them. The pyrazolyl ligand is potentially maximally tridentate, and the maximally four-co-ordinate array about the silver potentially of threefold symmetry (excepting the fourth pz moiety) where the symmetry of the phosphine permits. The variation in the silver(I) co-ordination number and environment in various combinations of various degrees of steric interaction among the above entities has been explored. The reactivity of [{AgB(pz)$_4$}{P(C$_6$H$_4$Me-*m*)$_3$}] and [{AgB(pz)$_4$}{P(C$_6$H$_4$Me-*o*)$_3$}] towards unidentate N-, S- and P-donors was also investigated.

Since the first report of 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. In most of the previous reports the preparation and the characterization of extensive series of stable complexes of Groups 7–13 have been described[2–12] and it has been shown that nuclearity, geometry, spectroscopic properties and reactivities of metal complexes may be controlled by varying the size and shape of the metal centered cavities generated by the poly(pyrazolyl)borates.[2–5] The poly(pyrazolyl)borates are also extremely versatile ligands because of the ease of modification of steric and electronic properties by variation of the substituents on the pyrazole rings, offering unique opportunities to examine detailed dynamic behavior in solution.[13]

Extensive chemistry has been published concerning tris(pyrazolyl)borate complexes, but comparatively little on tetrakis(pyrazolyl)borate co-ordination chemistry. The latter gives metallic and organometallic derivatives which are generally very stable in solution and in the solid state,[13–29] indicating that the tetrakis(pyrazolyl)borate ligand can impart considerable stability to its complexes. It usually co-ordinates to transition metals in tridentate mode, although some examples are known where it may act as bidentate or bis(bidentate).[13,20–30]

More recently, silver(I) poly(pyrazol-1-yl)borate derivatives have attracted attention, but to date the majority of these studies have involved the use of tris(pyrazolyl)borate ligands.[31–36] In order further to understand the co-ordination chemistry of silver(I) towards the poly(pyrazolyl)borate family we decided to investigate the reactions of K[B(pz)$_4$] and K[B(mpz)$_4$] (Hpz = pyrazole, Hmpz = 3-methylpyrazole) and a number of $Ag^I(PR_3)$ or $Ag^I(PPh_2R')$ acceptors. The spectroscopic data, behavior in solution and reactivity of these compounds have been discussed in terms of electronic (*e.g.* pK_a and χ values[37]) and steric properties (*e.g.* Tolman angle[38]); we have further sought to explore the interaction between tetrakis(pyrazolyl)borates and PR_3 ligands of variable steric profiles about a central silver(I) atom, in particular with respect to consequent variations in co-ordination number and distortions in co-ordination environment. We record hereunder room-temperature single crystal X-ray studies undertaken to provide such steric information for a variety of combinations of [B(pz)$_4$] and [B(mpz)$_4$] ligands with P(CH$_2$Ph)$_3$, PPh$_2$Me, PPh$_2$Et), PR_3 (R = *o*-, *m*- or *p*-tolyl), P(C$_6$H$_2$Me$_3$-2,4,6)$_3$ or P(C$_6$H$_{11}$)$_3$ as tertiary phosphines in complexes of the above type.

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, as necessary, the reactions were protected from light by covering the 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) (*ca.* 13.3 Pa)]. Elemental analyses (C,H,N) were performed in house with a Carlo Erba model 1106 instrument. Infrared 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 NMR 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. Osmometric measurements were carried out at 40 °C over a range of concentrations with a Knauer KNA0280 vapor pressure osmometer calibrated with benzil. The solvent was Baker Analyzed Spectrophotometric grade chloroform. The results were reproducible to ±2%.

Syntheses

The donors K[B(pz)$_4$] and K[B(mpz)$_4$] were prepared in accordance with literature procedures.[39]

[Ag{B(pz)$_4$}(PPh$_3$)] 1. A mixture of $AgNO_3$ (0.17 g, 1 mmol) and PPh_3 (0.26 g, 1 mmol) in methanol (30 ml) was added to K[B(pz)$_4$] (0.32 g, 1 mmol) in methanol (50 ml) at 298 K. After

the addition the solution was stirred overnight at room temperature. After 1 h the solvent was removed with a rotary evaporator. Chloroform (50 ml) was added. The suspension was filtered and the organic layer dried on Na_2SO_4, then filtered and concentrated under reduced pressure. A colorless precipitate was formed which was filtered off, washed with light petroleum (b.p. 40–60 °C)–diethyl ether (1 : 1) and shown to be compound **1**. Recrystallized from benzene–ethyl acetate (1 : 1) (0.52 g, 0.8 mmol, yield 80%). M.p. 204–207 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 6.30 (qnt, 4 H, 4-CH), 7.18 (d, 4 H, 3- or 5-CH), 7.20–7.60 (m, 15 H, CH) and 7.72 (d, 4 H, 3- or 5-CH). ^{31}P-{^{1}H} NMR ($CDCl_3$, 293 K): δ 16.9 (s, br). ^{31}P-{^{1}H} NMR ($CDCl_3$, 223 K): δ 16.8 (dd), $^1J(^{31}P–^{107}Ag) = 622$, $^1J(^{31}P–^{109}Ag) = 719$ Hz. ^{13}C NMR ($CDCl_3$): δ 105.0 (s, C4), 129.1 (d, C_{arom}), 130.9 (s, C_{arom}), 133.8 (d, C_{arom}), 135.4 (s, C5) and 142.1 (C3). IR (Nujol, cm^{-1}): 3131w, 3093w (CH), 1573w, 1496s (C⋯C,C⋯N), 524s, 512s, 487s, 427 (br) (PPh_3), 352m and 257m (Found: C, 55.5; H, 4.2; N, 17.2. Calc. for $C_{30}H_{27}AgBN_8P$: C, 55.6; H, 4.2; N, 17.2%).

[Ag{B(pz)$_4$}{P(C$_6$H$_4$Me-*o*)$_3$}] 2. Compound **2** was prepared similarly to **1**, by using $AgNO_3$ (0.17 g, 1 mmol), P(C$_6$H$_4$Me-*o*)$_3$ (0.30 g, 1 mmol) and K[B(pz)$_4$] (0.32 g, 1 mmol) in methanol (50 ml) at 298 K. It was recrystallized from benzene–ethyl acetate (1 : 1) (yield 72%). M.p. 191–193 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 2.39 (s, 9 H, CH_3), 6.13 (t, 4 H, 4-CH), 6.90 (t, 3 H, CH), 7.10 (d, 4 H, 3- or 5-CH), 7.18–7.45 (m, 9 H, CH) and 7.48 (d, 4 H, 3- or 5-CH). ^{1}H NMR ($CDCl_3$, 193 K): δ 2.4 (s br, 9 H, CH_3), 6.10 (t, 4 H, 4-CH), 6.70 (br, 3 H, CH), 6.90 (br, 3 H, CH), 7.15 (br, 4 H, 3- or 5-CH) and 7.20–7.60 (m, 9 H, CH, 3 or 5-CH). ^{31}P-{^{1}H} NMR ($CDCl_3$, 293 K): δ −14.8 (d br). ^{31}P-{^{1}H} NMR ($CDCl_3$, 253 K): δ −16.2 (dd), $^1J(^{31}P–^{107}Ag) = 611$, $^1J(^{31}P–^{109}Ag) = 701$ Hz. IR (Nujol, cm^{-1}): 3091w, 3056w (CH), 1588w, 1496s (C⋯C,C⋯N), 556m, 517m, 461s (PR_3), 351m and 263w (Found: C, 57.5; H, 5.1; N, 16.3. Calc. for $C_{33}H_{33}AgBN_8P$: C, 57.4; H, 4.8; N, 16.2%).

[Ag{B(pz)$_4$}{P(C$_6$H$_4$Me-*m*)$_3$}] 3. Compound **3** was prepared similarly to **1**, by using $AgNO_3$ (0.17 g, 1 mmol), P(C$_6$H$_4$Me-*o*)$_3$ (0.30 g, 1 mmol) and K[B(pz)$_4$] (0.32 g, 1 mmol) in methanol (50 ml) at 298 K. It was recrystallized from benzene–ethyl acetate (1 : 1) (yield 80%). M.p. 191–194 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 2.35 (s, 9 H, CH_3), 6.20 (t, 4 H, 4-CH), 7.05–7.38 (m, 12 H, CH) 7.17 (d, 4 H, 3- or 5-CH) and 7.64 (d, 4 H, 3- or 5-CH). ^{1}H NMR ($CDCl_3$, 193 K): δ 2.39 (s, 9 H, CH_3), 6.23 (t, 4 H, 4-CH), 6.97–7.25 (m, 12 H, CH), 7.25 (d br, 4 H, 3- or 5-CH) and 7.70 (d br, 4 H, 3- or 5-CH). ^{31}P-{^{1}H} NMR ($CDCl_3$, 293 K): δ 17.1 (s br). ^{31}P-{^{1}H} NMR ($CDCl_3$, 223 K): δ 17.4 (dd), $^1J(^{31}P–^{107}Ag) = 624$, $^1J(^{31}P–^{109}Ag) = 720$ Hz. IR (Nujol, cm^{-1}): 3144w, 3103w (CH), 1590w, 1500s (C⋯C,C⋯N), 558m, 536m, 450s (PR_3), 350m and 243w (Found: C, 57.3; H, 5.0; N, 16.2. Calc. for $C_{33}H_{33}AgBN_8P$: C, 57.4; H, 4.8; N, 16.2%).

[Ag{B(pz)$_4$}{P(C$_6$H$_4$Me-*p*)$_3$}] 4. Compound **4** was prepared similarly to **1**, by using $AgNO_3$ (0.17 g, 1 mmol), P(C$_6$H$_4$Me-*p*)$_3$ (0.30 g, 1 mmol) and K[B(pz)$_4$] (0.32 g, 1 mmol) in methanol (50 ml) at 298 K. It was recrystallized from benzene–ethyl acetate (1 : 1) (yield 79%). M.p. 192–195 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 2.39 (s, 9 H, CH_3), 6.21 (t, 4 H, 4-CH), 7.17 (d, 4 H, 3- or 5-CH), 7.19–7.26 (m, 12 H, CH) and 7.64 (d, 4 H, 3- or 5-CH). ^{31}P-{^{1}H} NMR ($CDCl_3$, 293 K): δ 15.5 (d br). ^{31}P-{^{1}H} NMR ($CDCl_3$, 253 K) δ 15.0 (dd), $^1J(^{31}P–^{107}Ag) = 627$, $^1J(^{31}P–^{109}Ag) = 724$ Hz. IR (Nujol, cm^{-1}): 3144w, 3092w (CH), 1596w, 1498 (sh) (C⋯C,C⋯N), 519m, 405m, 421m (PR_3), 347m and 245w (Found: C, 57.2; H, 4.9; N, 16.1. Calc. for $C_{33}H_{33}AgBN_8P$: C, 57.4; H, 4.8; N, 16.2%).

[Ag{B(pz)$_4$}{P(C$_6$H$_2$Me$_3$-2,4,6)$_3$}] 5. Compound **5** was prepared similarly to **1**, by using $AgNO_3$ (0.17 g, 1 mmol), trimesitylphosphine (0.39 g, 1 mmol) and K[B(pz)$_4$] (0.32 g, 1 mmol) in methanol (50 ml) at 298 K. It was recrystallized from benzene–ethyl acetate (1 : 1) (yield 55%). M.p. 179–182 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 2.07 (s br, 18 H, CH_3), 2.29 (s br, 9 H, CH_3), 6.12 (t, 4 H, 4-CH), 6.82 (br, 6 H, CH); 7.06 (d, 4 H, 3- or 5-CH) and 7.37 (d, 4 H, 3- or 5-CH). ^{31}P-{^{1}H} NMR ($CDCl_3$, 223 K): δ −28.2 (d br). ^{31}P-{^{1}H} NMR ($CDCl_3$, 223 K): δ −29.0 (dd), $^1J(^{31}P–^{107}Ag) = 598$, $^1J(^{31}P–^{109}Ag) = 691$ Hz. IR (Nujol, cm^{-1}): 3144w, 3092w (CH), 1602w, 1500w (br) (C⋯C,C⋯N), 554m, 425m (PR_3), 367w, 349m and 260w (Found: C, 59.5; H, 6.2; N, 14.4. Calc. for $C_{39}H_{45}AgBN_8P$: C, 60.5; H, 5.8; N, 14.5%).

[Ag{B(pz)$_4$}{P(CH$_2$Ph)$_3$}] 6. Compound **6** was prepared similarly to **1**, by using $Ag(CF_3SO_3)$ (0.17 g, 1 mmol), tribenzylphosphine (0.30 g, 1 mmol) and K[B(pz)$_4$] (0.32 g, 1 mmol) in methanol (50 ml) at 298 K. It was crystallized from benzene–ethyl acetate (1 : 1) (yield 81%). M.p. 88 °C (decomp.) ^{1}H NMR ($CDCl_3$, 293 K): δ 2.95 (qnt, 6 H, CH_2), 6.20 (t, 4 H, 4-CH), 7.11 (d, 4 H, 3- or 5-CH), 7.05–7.36 (m, 15 H, CH) and 7.49 (d, 4 H, 3- or 5-CH), ^{31}P-{^{1}H} NMR ($CDCl_3$, 293 K): δ 20.2 (dd), $^1J(^{31}P–^{107}Ag) = 636$, $^1J(^{31}P–^{109}Ag) = 735$ Hz. ^{13}C NMR ($CDCl_3$, 293 K): δ 33.5 (m, CH_2), 104.7 (s, C4), 127.1 (d, C_{arom}), 129.1 (s, C_{arom}), 129.4 (d, C_{arom}), 135.2 (s, C5) and 141.8 (s, C3). IR (Nujol, cm^{-1}): 3149w, 3082w (CH), 1599m, 1501w (br) (C⋯C,C⋯N), 477m (PR_3), 351m, 264w and 252w (Found: C, 57.4; H, 4.7; N, 16.3. Calc. for $C_{33}H_{33}AgBN_8P$: C, 57.4; H, 4.8; N, 16.2%).

[Ag{B(pz)$_4$}(PMePh$_2$)] 7. Compound **7** was prepared similarly to **1**, by using $AgNO_3$ (0.17 g, 1 mmol), $PMePh_2$ (0.19 g, 1 mmol) and K[B(pz)$_4$] (0.32 g, 1 mmol) in methanol (50 ml) at 298 K. It was recrystallized from benzene–ethyl acetate (1 : 1) (yield 70%). M.p. 125–127 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.88 (s) and 1.91 (s) (3 H, CH_3), 6.22 (t, 4 H, 4-CH), 7.17 (d, 4 H, 3- or 5-CH), 7.43–7.51 (m, 10 H, CH) and 7.65 (d, 4 H, 3- or 5-CH). ^{31}P-{^{1}H} NMR ($CDCl_3$, 293 K): δ −3.2 (br). ^{31}P-{^{1}H} NMR ($CDCl_3$, 223 K): δ −3.3 (dd), $^1J(^{31}P–^{107}Ag) = 637$, $^1J(^{31}P–^{109}Ag) = 735$ Hz. IR (Nujol, cm^{-1}): 3140w, 3082w (CH), 1580w, 1499w (br) (C⋯C,C⋯N), 509s, 475m, 442m, 420w ($PMePh_2$), 352m and 252w (Found: C, 51.5; H, 4.5; N, 19.5. Calc. for $C_{25}H_{25}AgBN_8P$: C, 51.2; H, 4.3; N, 19.1%).

[Ag{B(pz)$_4$}(PEtPh$_2$)] 8. Compound **8** was prepared similarly to **1**, by using $AgNO_3$ (0.17 g, 1 mmol), $PEtPh_2$ (0.20 g, 1 mmol, g, 1 mmol) and K[B(pz)$_4$] (0.32 g, 1 mmol) in methanol (50 ml) at 298 K. It was recrystallized from benzene–ethyl acetate (1 : 1) (yield 83%). M.p. 143–146 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.07 and 1.18 (2t, 3 H, CH_3), 2.20 and 2.24 (2q, 2 H, CH_2), 6.23 (t, 4 H, 4-CH), 7.19 (d, 4 H, 3- or 5-CH), 7.29–7.50 (m, 10 H, CH) and 7.66 (d, 4 H, 3- or 5-CH). ^{31}P-{^{1}H} NMR ($CDCl_3$, 293 K): δ 16.0 (br). ^{31}P-{^{1}H} NMR ($CDCl_3$, 223 K): δ 15.8 (dd), $^1J(^{31}P–^{107}Ag) = 627$, $^1J(^{31}P–^{109}Ag) = 723$ Hz. IR (Nujol, cm^{-1}): 3148w, 3132w, 3105w (CH), 1500 (sh) (C⋯C,C⋯N), 513s, 476m, 445m, 431w, 422w ($PEtPh_2$), 355m, 347m, 331m, 255w and 243m (Found: C, 51.8; H, 4.6; N, 18.7. Calc. for $C_{26}H_{27}AgBN_8P$: C, 52.0; H, 4.5; N, 18.7%).

[Ag{B(pz)$_4$}{P(C$_6$H$_{11}$)$_3$}] 9. (i) Compound **9** was prepared similarly to **1**, by using $AgNO_3$ (0.17 g, 1 mmol), P(C$_6$H$_{11}$)$_3$ (0.28 g, 1 mmol) and K[B(pz)$_4$] (0.32 g, 1 mmol) in methanol (50 ml) at 298 K. It was recrystallized from benzene–ethyl acetate (1 : 1) (yield 55%). M.p. 225–227 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.27 (m, 15 H, C_6H_{11}), 1.78 (m, 18 H, C_6H_{11}), 6.21 (t, 4 H, 4-CH), 7.11 (d, 4 H, 3- or 5-CH) and 7.64 (d, 4 H, 3- or 5-CH). ^{31}P-{^{1}H} NMR ($CDCl_3$, 293 K): δ 42.0 (dd), $^1J(^{31}P–^{107}Ag) = 609$, $^1J(^{31}P–^{109}Ag) = 703$ Hz. ^{13}C NMR ($CDCl_3$, 293 K): δ 26.5 (s), 27.7 (d), 31.5 (m), 32.3 (m), (C_6H_{11}), 105.0 (s, C4), 135.7 (s, C5) and 142.0 (s, C3). IR (Nujol, cm^{-1}): 3140w, 3094w (CH), 1540w, 1518m, 1499 (sh) (C⋯C,C⋯N), 514m, 489w, 471m, 457w, 408m, 385m, 351m, 346m, 335 (sh) (PR_3) and 248m (Found: C, 53.8; H, 7.0; N, 16.6. Calc. for $C_{30}H_{45}AgBN_8P$: C, 54.1; H, 6.8; N, 16.8%).

(ii) To a stirred diethyl ether (20 ml) suspension of compound **1**, **2** or **3**, $P(C_6H_{11})_3$ (0.28 g, 1.0 mmol) was added at room temperature. The suspension obtained was then filtered and the residue washed with light petroleum–diethyl ether and filtered to give compound **9**. Recrystallized from benzene–ethyl acetate (yield 80%).

[Ag{B(mpz)$_4$}(PPh$_3$)] 10. A mixture of $AgNO_3$ (0.17 g, 1 mmol) and PPh_3 (0.26 g, 1 mmol) in methanol (30 ml) was added to K[B(mpz)$_4$] (0.37 g, 1 mmol) in methanol (50 ml) at 298 K. After the addition the solution was stirred overnight at room temperature. After 1 h the solvent was removed with a rotary evaporator. Chloroform (50 ml) was added. The suspension was filtered and the organic layer dried over Na_2SO_4, then filtered and concentrated under reduced pressure. A colorless precipitate was formed which was filtered off, washed with light petroleum–diethyl ether (1:1) and shown to be compound **10** (0.56 g, 0.8 mmol, yield 80%). M.p. 220 °C (decomp.) ^{1}H NMR ($CDCl_3$, 293 K): δ 2.12 (s, 12 H, 3-CCH_3), 5.90 (d, 4 H, 4-CH), 7.19 (d, 4 H, 5-CH) and 7.38–7.45 (m, 15 H, CH). ^{1}H NMR ($CDCl_3$, 193 K): δ 2.00 (s, 9 H, 3-CCH_3), 2.40 (s, 9 H, 3-CCH_3), 5.80 (br, 3 H, 4-CH), 6.0 (br, 1 H, 4-CH), 6.70 (br, 1 H, 5-CH) and 7.0–7.8 (m, 18 H, 5-CH, CH). ^{31}P-{^{1}H} NMR ($CDCl_3$, 293 K): δ 15.2 (br). ^{31}P-{^{1}H} NMR ($CDCl_3$, 223 K): δ 16.7 (dd), $^1J(^{31}P–^{107}Ag)$ = 608, $^1J(^{31}P–^{109}Ag)$ = 701 Hz. ^{13}C NMR ($CDCl_3$, 293 K): δ 14.8 (s, 3-CH_3), 104.7 (s, C4), 129.4 (d, C_{arom}), 131.1 (s, C_{arom}), 132.5 (d, C_{arom}), 134.3 (d, C_{arom}), 136.6 (s, C5) and 150.0 (s, C3). IR (Nujol, cm^{-1}): 3152w, 3109w, 3071w (CH), 1585w, 1514s (C⋯C,C⋯N), 524s, 499s, 438m (PPh_3), 406m, 395m, 378m, 333m and 260m (Found: C, 57.9; H, 5.2; N, 15.4. Calc. for $C_{34}H_{35}AgBN_8P$: C, 58.0; H, 5.0; N, 15.9%).

[Ag{B(mpz)$_4$}{P(C$_6$H$_4$Me-*o*)$_3$}] 11. Compound **11** was prepared similarly to **10**, by using $AgNO_3$ (0.17 g, 1 mmol), $P(C_6H_4Me\text{-}o)_3$ (0.30 g, 1 mmol) and K[B(mpz)$_4$] (0.37 g, 1 mmol) in methanol (50 ml) at 298 K. It was recrystallized from benzene–ethyl acetate (1:1) (yield 70%). M.p. 227 °C (decomp.). ^{1}H NMR ($CDCl_3$, 293 K: δ 1.97 (s, 12 H, 3-CCH_3), 2.40 (s, 9 H, CH_3), 5.84 (d, 4 H, 4-CH), 7.10 (d, 4 H, 5-CH) and 6.76–7.50 (m, 12 H, CH). ^{31}P-{^{1}H} NMR ($CDCl_3$, 293 K): δ −14.9 (dd), $^1J(^{31}P–^{107}Ag)$ = 593, $^1J(^{31}P–^{109}Ag)$ = 685 Hz. ^{13}C NMR ($CDCl_3$, 293 K): δ 14.8 (s, 3-CH_3), 104.7 (s, C4), 126.7 (d, C_{arom}), 127.2 (d, C_{arom}), 131.5 (s, C_{arom}), 131.6 (d, C_{arom}), 132.8 (m, C_{arom}), 136.0 (s, C5), 142.7 (d, C_{arom}) and 149.4 (s, C3). IR (Nujol, cm^{-1}): 3149w (CH), 1586w, 1508m (C⋯C,C⋯N), 562m, 522m, 514m, 470m, 461m (PPh_3), 417m, 405m, 394m, 379m, 329m and 260m (Found: C, 59.1; H, 5.9; N, 14.8. Calc. for $C_{37}H_{41}AgBN_8P$: C, 59.5; H, 5.5; N, 15.0%).

[Ag{B(mpz)$_4$}{P(C$_6$H$_4$Me-*m*)$_3$}] 12. Compound **12** was prepared similarly to **1**, by using $AgNO_3$ (0.17 g, 1 mmol), $P(C_6H_4Me\text{-}m)_3$ (0.30 g, 1 mmol) and K[B(mpz)$_4$] (0.37 g, 1 mmol) in methanol (50 ml) at 298 K. It was recrystallized from benzene–ethyl acetate (1:1) (yield 66%). M.p. 120–122 °C. ^{1}H NMR ($CDCl_3$): δ 2.13 (s, 12 H, 3-CCH_3), 2.32 (s, 9 H, CH_3), 5.89 (d, 4 H, 4-CH), 7.15 (d, 4 H, 5-CH) and 7.21–7.38 (m, 12 H, CH). ^{31}P-{^{1}H} NMR ($CDCl_3$, 293 K): δ 17.3 (d br). ^{31}P-{^{1}H} NMR ($CDCl_3$, 223 K): δ 17.1 (dd), $^1J(^{31}P–^{107}Ag)$ = 613, $^1J(^{31}P–^{109}Ag)$ = 707 Hz. ^{13}C NMR ($CDCl_3$, 293 K): δ 14.2 (s, 3-CH_3), 21.4 (s, CH_3), 104.1 (s, C4), 126.7 (d, C_{arom}), 127.2 (d, C_{arom}), 128.7 (d, C_{arom}), 130.8 (d, C_{arom}), 131.3 (s, C_{arom}), 131.5 (s, C_{arom}), 131.6 (d, C_{arom}), 134.4 (d, C_{arom}), 136.1 (d, C5), 138.6 (d, C_{arom}) and 149.5 (s, C3). IR (Nujol, cm^{-1}): 3160w, 3117w (CH), 1592w, 1508m (C⋯C,C⋯N), 555m, 543m, 526w, 465s, 447s (PR_3), 409w, 391m, 323w and 260w (Found: C, 59.0; H, 5.8; N, 14.8. Calc. for $C_{37}H_{41}AgBN_8P$: C, 59.5; H, 5.5; N, 15.0%).

[Ag{B(mpz)$_4$}{P(C$_6$H$_4$Me-*p*)$_3$}] 13. Compound **13** was prepared similarly to **1**, by using $AgNO_3$ (0.17 g, 1 mmol), $P(C_6H_4Me\text{-}p)_3$ (0.30 g, 1 mmol) and K[B(mpz)$_4$] (0.37 g, 1 mmol) in methanol (50 ml) at 298 K. It was recrystallized from benzene–ethyl acetate (1:1) (yield 72%). M.p. 117–118 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 2.13 (s, 12 H, 3-CCH_3), 2.38 (s, 9 H, CH_3), 5.90 (d, 4 H, 4-CH), 7.21 (d, 4 H, 5-CH) and 7.16–7.35 (m, 12 H, CH). ^{31}P-{^{1}H} NMR ($CDCl_3$, 293 K): δ 14.9 (d br). ^{31}P-{^{1}H} NMR ($CDCl_3$, 223 K): δ 14.9 (dd), $^1J(^{31}P–^{107}Ag)$ = 615, $^1J(^{31}P–^{109}Ag)$ = 709 Hz). ^{13}C NMR ($CDCl_3$, 293 K): δ 14.8 (s, 3-CH_3), 21.9 (s, CH_3), 104.7 (s, C4), 128.7 (d, C_{arom}), 129.4 (d, C_{arom}), 130.2 (d, C_{arom}), 130.8 (d, C_{arom}), 131.5 (s, C_{arom}), 131.6 (d, C_{arom}), 134.2 (s, C_{arom}), 136.5 (s, C5), 141.3 (s, C_{arom}) and 150.1 (s, C3). IR (Nujol, cm^{-1}): 3134w (CH), 1597w, 1514m, 1497m (C⋯C,C⋯N), 519 (br), 433w, 416w, 393w, 331w and 258w (Found: C, 59.2; H, 5.8; N, 14.9. Calc. for $C_{37}H_{41}AgBN_8P$: C, 59.5; H, 5.5; N, 15.0%).

[Ag{B(mpz)$_4$}{P(CH$_2$Ph)$_2$}] 14. Compound **14** was prepared similarly to **1**, by using $AgNO_3$ (0.17 g, 1 mmol), $P(CH_2Ph)_3$ (0.30 g, 1 mmol) and K[B(mpz)$_4$] 0.37 g, 1 mmol) in methanol (50 ml) at 298 K. It was recrystallized from benzene–ethyl acetate (1:1) (yield 65%). M.p. 196–198 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.98 (s, 12 H, 3-CCH_3), 2.93 (m, 6 H, CH_2), 5.84 (d, 4 H, 4-CH), 7.11 (d, 4 H, 5-CH), 7.06–7.30 (m, 12 H, CH). ^{1}H NMR ($CDCl_3$, 223 K): δ 1.80 (s, br, 9 H, 3-CCH_3), 2.40 (s br, 9 H, 3-CCH_3), 2.93 (m, 6 H, CH_2), 5.76 (s, 3 H, 4-CH), 6.00 (s, 1 H, 4-CH), 6.80 (s, 3 H, 5-CH), 7.10 (m, 10 H, CH, 5-CH) and 7.30–7.40 (m, 12 H, CH). ^{31}P-{^{1}H} NMR ($CDCl_3$, 293 K): δ 23.3 (dd), $^1J(^{31}P–^{107}Ag)$ = 629, $^1J(^{31}P–^{109}Ag)$ = 727 Hz). IR (Nujol, cm^{-1}): 3110w (CH), 1599w, 1515m, 1494m (C⋯C,C⋯N), 482m, 413m, 394w, 306w, 272w, 259w and 248w (Found: C, 59.4; H, 5.7; N, 15.0. Calc. for $C_{37}H_{41}AgBN_8P$: C, 59.5; H, 5.5; N, 15.0%).

[Ag{B(mpz)$_4$}{(PMePh$_2$)] 15. Compound **15** was prepared similarly to **1**, by using $AgNO_3$ (0.17 g, 1 mmol), $PMePh_2$ (0.20 g, 1 mmol) and K[B(mpz)$_4$] (0.37 g, 1 mmol) in methanol (50 ml) at 298 K. It was recrystallized from benzene–ethyl acetate (1:1) (yield 90%). M.p. 151–154 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.90, 1.93 (2s, 3 H, CH_3), 2.20 (s, 12 H, 3-CCH_3), 5.95 (d, 4 H, 4-CH), 7.10 (d, 4 H, 5-CH) and 7.20–7.58 (m, 10 H, CH). ^{31}P-{^{1}H} NMR ($CDCl_3$, 293 K): δ −4.4 (d br). ^{31}P-{^{1}H} NMR ($CDCl_3$, 273 K): δ −4.4 (dd), $^1J(^{31}P–^{107}Ag)$ = 616, $^1J(^{31}P–^{109}Ag)$ = 710 Hz. ^{13}C NMR ($CDCl_3$, 293 K): δ 14.3 (s, 3-CH_3), 14.3 (d, CH_3), 104.2 (s, C4), 129.0 (d, C_{arom}), 130.5 (s, C_{arom}), 132.4 (d, C_{arom}), 135.8 (d, C_{arom}), 136.1 (s, C5) and 149.6 (s, C3). IR (Nujol, cm^{-1}): 3145w, 3125w, 3102w (CH), 1559w, 1508m (C⋯C,C⋯N), 508m, 476m, 452m, 433w, 418m ($PMePh_2$), 396m, 339 (br), 305w (br) and 246 (br) (Found: C, 54.0; H, 5.4; N, 16.7. Calc. for $C_{29}H_{33}AgBN_8P$: C, 54.2; H, 5.2; N, 17.4%).

[Ag{B(mpz)$_4$}(PEtPh$_2$)] 16. Compound **16** was prepared similarly to **1**, by using $AgNO_3$ (0.17 g, 1 mmol), $PEtPh_2$ (0.20 g, 1 mmol) and K[B(mpz)$_4$] (0.37 g, 1 mmol) in methanol (50 ml) at 298 K. Compound **16** was recrystallized from benzene–ethyl acetate (1:1) (yield 61%). M.p. 132–135 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.15 (m, 3H, CH_3), 2.23 (m, 2 H, CH_2), 2.20 (s, 12 H, 3-CCH_3), 5.95 (d, 4 H, 4-CH), 7.11 (d, 4 H, 5-CH) and 7.35–7.58 (m, 10 H, CH). ^{31}P-{^{1}H} NMR ($CDCl_3$, 293 K): δ 14.1 (d br). ^{31}P-{^{1}H} NMR ($CDCl_3$, 273 K): δ 14.1 (dd), $^1J(^{31}P–^{107}Ag)$ = 612, $^1J(^{31}P–^{109}Ag)$ = 706 Hz. ^{13}C NMR ($CDCl_3$, 293 K): δ 10.0 (d, CH_2), 14.3 (s, 3-CH_3), 21.3 (d, CH_3), 104.2 (s, C4), 129.0 (d, C_{arom}), 130.6 (s, C_{arom}), 132.8 (d, C_{arom}), 135.8 (d, C_{arom}), 136.1 (s, C5) and 149.6 (s, C3). IR (Nujol, cm^{-1}): 3139w, 3126w, 3113w (CH), 1580w, 1510m (C⋯C,C⋯N), 513m, 481m, 452m, 430m, 415m ($PEtPh_2$), 391m, 339 (br) and 247 (br) (Found: C, 54.5; H, 5.7; N, 16.8. Calc. for $C_{30}H_{35}AgBN_8P$: C, 54.9; H, 5.4; N, 17.1%).

[Ag{B(mpz)$_4$}{P(C$_6$H$_{11}$)$_3$}] 17. Compound **17** was prepared similarly to **1**, by using $AgNO_3$ (0.17 g, 1 mmol), $P(C_6H_{11})_3$

(0.28 g, 1 mmol) and K[B(mpz)$_4$] (0.37 g, 1 mmol) in methanol (50 ml) at 298 K. Compound **17** was recrystallized from benzene–ethyl acetate (1 : 1) (yield 85%). M.p. 234–238 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.10–1.90 (m, 33 H, C_6H_{11}), 2.29 (s, 12 H, 3-CCH_3), 5.94 (d, 4 H, 4-CH) and 7.00 (d, 4 H, 5-CH). ^{1}H NMR ($CDCl_3$, 203 K): δ 1.10–1.90 (m, 33 H, C_6H_{11}), 2.25 (s, 9 H, 3-CCH_3), 2.35 (s, 12 H, 3-CCH_3), 5.93 (br, 3 H, 4-CH), 6.15 (br, 1 H, 4-CH), 7.12 (br, 3 H, 5-CH) and 7.52 (br, 1 H, 5-CH). ^{31}P-{^{1}H} NMR ($CDCl_3$, 293 K): δ 38.3 (dd), $^1J(^{31}P–^{107}Ag)$ = 599, $^1J(^{31}P–^{109}Ag)$ = 692 Hz. IR (Nujol, cm^{-1}): 3123m (CH), 1552w, 1514m (C⋯C,C⋯N), 513m, 470m, 410m, 392m, (PR_3), 331w, 273w, 258w and 243w (Found: C, 55.9; H, 7.7; N, 11.3. Calc. for $C_{34}H_{53}AgBN_8P$: C, 56.5; H, 7.4; N, 11.5%).

[Ag{B(pz)$_4$}(Him){P(C$_6$H$_4$Me-*m*)$_3$}] 18. To a diethyl ether suspension of compound **3** (0.69 g, 1.0 mmol), was added imidazole (Him) (0.14 g, 2.0 mmol). After 2 d, the suspension was filtered and the residue obtained washed with *n*-hexane and diethyl ether and shown to be compound **18** (yield 85%). M.p. 193–195 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 2.30 (s, 9 H, CH_3), 6.20 (d, 2 H, 4-CH), 6.25 (d, 2 H, 4-CH), 7.00 (d, 4 H, 5-CH), 7.0 (m, 2 H, CH), 7.20 (d, 2 H, 5-CH), 7.22 (d, 2 H, 5-CH), 7.26 (s, 1 H, H_{imid}), 7.30 (m, 8 H, CH), 7.40 (s, 1 H, H_{imid}), 7.50 (br, 3 H, CH, H_{imid}), 7.62 (d, 2 H, 3-CH) and 7.72 (d, 2 H, 3-CH). ^{31}P-{^{1}H} NMR ($CDCl_3$, 293 K): δ 17.3 (dd) $^1J(^{31}P–^{107}Ag)$ = 621, $^1J(^{31}P–^{109}Ag)$ = 719 Hz and 7.5 (d, br). ^{31}P-{^{1}H} NMR ($CDCl_3$, 223 K): δ 17.2 (dd), $^1J(^{31}P–^{107}Ag)$ = 623, $^1J(^{31}P–^{109}Ag)$ = 718 Hz and 7.2 (dd), $^1J(^{31}P–^{107}Ag)$ = 393, $^1J(^{31}P–^{109}Ag)$ = 454 Hz. IR (Nujol, cm^{-1}): 3120w, 3060w (CH), 1580w, 1500 (sh) (C⋯C,C⋯N), 548m, 537m, 473m, 455m, 450m (PR_3), 352m and 263w (Found: C, 57.1; H, 5.1; N, 18.3. Calc. for $C_{36}H_{37}AgBN_{10}P$: C, 56.9; H, 4.9; N, 18.4%).

Reaction of [Ag{B(pz)$_4$}{P(C$_6$H$_4$Me-*o*)$_3$}] 2 with imidazole

To a benzene solution of compound **2** (0.69, 1.0 mmol) was added Him (0.14 g, 2.0 mmol). After 2 d, the suspension was filtered and the precipitate washed with *n*-hexane and diethyl ether and shown to be the starting derivative **2**.

Reaction of [Ag{B(pz)$_4$}{P(C$_6$H$_4$Me-*m*)$_3$}] 3 with 1-methylimidazoline-2(3*H*)-thione (Hmimt)

To a benzene solution of compound **3** (0.693 g, 1.0 mmol) was added Hmimt (0.21 g, 1.82 mmol). After 2 d the suspension was filtered and the precipitate washed with *n*-hexane and diethyl ether and shown to be the starting derivative **3**.

Crystallography

Unique room-temperature four-circle diffractometer data sets were measured ($2\theta_{max}$ as specified, 2θ–θ scan mode; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å; $T \approx 295$ K) yielding N independent reflections, N_o of these with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after gaussian absorption correction and solution of the structure by vector methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms, (x, y, z, $U_{iso})_H$ being included constrained at estimated values where practicable. Conventional residuals R, R' [statistical weights, derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\ \sigma^4(I_{diff})$] are quoted at convergence. Neutral atom complex scattering factors were employed, the XTAL 3.4 program system being used.[40] Pertinent results are given in Figs. 1 and 2 and Tables 1 and 2. Abnormal features/idiosyncrasies/variations in procedure are discussed as needful for individual complexes. Difference map residues, where substantial and not associated with other features such as high 'thermal motion', as in **14**, were modelled in terms of solvent occupancy; although not a preferred or practical solvent for the syntheses or crystallizations, which were conducted in ambient atmosphere, water was the preferred model on the basis of the crystallographic evidence. All complexes are of the form [AgL(PR$_3$)](·nH$_2$O), L = B(pz)$_4$ or B(mpz)$_4$, R diverse; for unco-ordinated pz groups, nitrogen atom assignment was made on the basis of refinement and difference map evidence.

Crystal/refinement data. [Ag{(pz)$_2$B(pz)$_2$}(PPh$_3$)] **1**. $C_{30}H_{27}AgBN_8P$, $M = 649.3$, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 15.825(6)$, $b = 14.976(8)$, $c = 14.766(8)$ Å, $\alpha = 89.83(5)$, $\beta = 114.05(4)$, $\gamma = 113.45(4)°$, $U = 2878$ Å^3, D_c ($Z = 4$) = 1.49$_8$ g cm^{-3}; $F(000) = 1320$, $\mu_{Mo} = 7.9$ cm^{-1}, specimen 0.10 × 0.66 × 0.45 mm, $A^*_{min,max} = 1.08$, 1.38, $2\theta_{max} = 50°$, $N = 10\ 108$, $N_o = 6534$, $R = 0.062$, $R' = 0.066$, $n_v = 739$; $|\Delta\rho_{max}| = 2.1$ e Å^{-3}.

Two pseudo-symmetrically related molecules comprise the asymmetric unit.

[Ag{(pz)B(pz)$_3$}{P(C$_6$H$_4$Me-*o*)$_3$}]·3H$_2$O **2**. $C_{33}H_{33}AgBN_8P$·3H$_2$O, $M = 745.4$, rhombohedral, space group $R\bar{3}$ (C_{3i}^2, no. 148; hexagonal setting), $a = 14.513(3)$, $c = 30.733(6)$ Å, $U = 5604$ Å^3, D_c ($Z = 6$) = 1.32$_5$ g cm^{-3}, $F(000) = 2304$, $\mu_{Mo} = 6.2$ cm^{-1} specimen 0.38 × 0.50 × 0.48 mm, $A^*_{min,max} = 1.20$, 1.34, $2\theta_{max} = 60°$, $N = 3656$, $N_o = 2329$, $R = 0.051$, $R' = 0.058$, $n_v = 152$, $|\Delta\rho_{max}| = 0.46$ e Å^{-3}.

For merging of an equivalent data set, R_{int} was 0.026. A pair of difference map peaks was modelled as water molecule oxygen atoms, site occupancies set at 0.33, 0.5 after trial refinement; no counterpart residues were found in isomorphous compounds **10** and **11**. The unco-ordinated pz ring is disordered about the crystallographic 3 axis which passes through the molecule; associated non-hydrogen atoms were refined with isotropic thermal parameter forms, as also was that of the water molecule, site occupancy 0.33.

[Ag{(pz)$_2$B(pz)$_2$}{P(C$_6$H$_4$Me-*m*)$_3$}] **3**. $C_{33}H_{33}AgBN_8P$, $M = 691.4$, monoclinic, space group $P2_1/n$ (C_{2h}^5 no. 14; variant), $a = 14.233(5)$, $b = 15.071(2)$, $c = 15.349(7)$ Å, $\beta = 100.29(3)°$, $U = 3239$ Å^3, D_c ($Z = 4$) = 1.41$_7$ g cm^{-3}; $F(000) = 1416$, $\mu_{Mo} = 7.1$ cm^{-1}, specimen 0.50 × 0.26 × 0.55 mm, $A^*_{min,max} = 1.20$, 1.35, $2\theta_{max} = 50°$, $N = 5691$, $N_o = 4481$, $R = 0.037$, $R' = 0.042$, $n_v = 398$, $|\Delta\rho_{max}| = 0.55$ e Å^{-3}.

[Ag{(pz)$_2$B(pz)$_2$}(PMePh$_2$)] **7**. $C_{25}H_{25}AgBN_8P$, $M = 587.2$, monoclinic, space group $P2_1/n$, $a = 12.244(6)$, $b = 17.142(1)$, $c = 13.117(3)$ Å, $\beta = 100.35(3)°$, $U = 2708$ Å^3, D_c ($Z = 4$) = 1.44$_0$ g cm^{-3}, $F(000) = 1192$, $\mu_{Mo} = 8.3$ cm^{-1}, specimen 0.66 × 0.27 × 0.20 mm, $A^*_{min,max} = 1.17$, 1.23, $2\theta_{max} = 50°$, $N = 4755$, $N_o = 3120$, $R = 0.046$, $R' = 0.047$, $n_v = 426$, $|\Delta\rho_{max}| = 0.80$ e Å^{-3}.

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

[Ag{(pz)$_2$B(pz)$_2$}(PEtPh$_2$)] **8**. $C_{26}H_{27}AgBN_8P$, $M = 601.2$, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 8.887(3)$, $b = 20.450(6)$, $c = 16.049(4)$ Å, $\beta = 110.10(2)°$, $U = 2739$ Å^3, D_c ($Z = 4$) = 1.45$_8$ g cm^{-3}, $F(000) = 1224$, $\mu_{Mo} = 8.2$ cm^{-1}, specimen 0.44 × 0.24 × 0.45 mm, $A^*_{min,max} = 1.20$, 1.39, $2\theta_{max} = 50°$, $N = 4818$, $N_o = 3588$; $R = 0.031$, $R' = 0.033$, $n_v = 334$, $|\Delta\rho_{max}| = 0.39$ e Å^{-3}.

The terminal methyl group of the ethyl substituent was modelled as disordered over two sites, site occupancies set at 0.5 after trial refinement.

[Ag{(pz)$_2$B(pz)$_2$}{P(C$_6$H$_{11}$)$_3$}] **9**. $C_{30}H_{45}AgBN_8P$, $M = 667.4$, orthorhombic, space group $Pbca$ (D_{2h}^{15}, no. 61), $a = 25.784(3)$, $b = 13.855(1)$, $c = 18.063(5)$ Å, $U = 6453$ Å^3, D_c ($Z = 8$) = 1.37$_4$ g cm^{-3}, $F(000) = 2784$, $\mu_{Mo} = 7.1$ cm^{-1}, specimen 0.21 × 0.42 × 0.71 mm, $A^*_{min,max} = 1.15$, 1.33, $2\theta_{max} = 50°$, $N = 5666$, $N_o = 4045$, $R = 0.045$, $R' = 0.050$, $n_v = 371$, $|\Delta\rho_{max}| = 0.56$ e Å^{-3}.

[Ag{(mpz)B(mpz)$_3$}(PPh$_3$)] **10**. $C_{34}H_{35}AgBN_8P$, $M = 705.4$, rhombohedral, space group $R\bar{3}$, $a = 13.933(3)$, $c = 30.82(2)$ Å, $U = 5225$ Å^3, D_c ($Z = 6$) = 1.34$_5$ g cm^{-3}, $F(000) = 2172$, $\mu_{Mo} = 6.2$ cm^{-1}, specimen 0.40 × 0.32 × 0.60 mm, $A^*_{min,max} = 1.20$, 1.36, $2\theta_{max} = 56°$, $N = 2802$, $N_o = 2262$, $R = 0.050$, $R' = 0.063$, $n_v = 141$, $|\Delta\rho_{max}| = 0.68$ e Å^{-3}.

The R_{int} for merging of an equivalent data set was 0.062. The structure is isomorphous with compound **2** above and was refined in the same setting, with the same vicissitudes in respect of the unco-ordinated pz ring.

[Ag{(3-mpz)B(mpz)$_3$}{P(C$_6$H$_4$Me-*o*)$_3$}] **11**. $C_{37}H_{41}AgBN_8P$, M = 747.4, rhombohedral, space group $R\bar{3}$ (hexagonal setting), a = 14.223(4), c = 31.221(8), U = 5470 Å^3, D_c (Z = 6) = 1.36$_1$ g cm^{-3} $F(000)$ = 2316, μ_{Mo} = 6.3 cm^{-1}, specimen 0.21 × 0.45 × 0.39 mm, $A^*_{min,max}$ = 1.13, 1.20, $2\theta_{max}$ = 50°, N = 2145, N_o = 1464, R = 0.054, R' = 0.057, n_v = 152, $|\Delta\rho_{max}|$ = 0.66 e Å^{-3}.

The R_{int} for the merging of an equivalent data set was 0.09. The structure is isomorphous with compounds **2** and **10** and was refined similarly in that setting.

[Ag{(mpz)B(mpz)$_3$}{P(C$_6$H$_4$Me-*m*)$_3$}] **12**. $C_{37}H_{41}AgBN_8P$, M = 747.5, monoclinic, space group $P2_1/n$, a = 13.091(3), b = 15.574(4), c = 19.070(4) Å, β = 108.01(2)°, U = 3698 Å^3, D_c (Z = 4) = 1.34$_3$ g cm^{-3}, $F(000)$ = 1544, μ_{Mo} = 6.3 cm^{-1}, specimen 0.36 × 0.42 × 0.60 mm, $A^*_{min,max}$ = 1.24, 1.31, $2\theta_{max}$ = 50°, N = 6490, N_o = 2483, R = 0.056, R' = 0.052, n_v = 433, $|\Delta\rho_{max}|$ = 0.49 e Å^{-3}.

For 2762 additional equivalent data measured, R_{int} was 0.038.

[Ag{(mpz)$_2$B(mpz)$_2$}{P(C$_6$H$_4$Me-*p*)$_3$}] **13**. $C_{37}H_{41}AgBN_8P$, M = 747.5, triclinic, space group $P\bar{1}$, a = 15.174(3), b = 12.079(3), c = 11.813(4) Å, α = 65.23(2), β = 87.82(2), γ = 72.41(2)°, U = 1864 Å^3, D_c (Z = 2) = 1.33$_1$ g cm^{-3}, $F(000)$ = 772, μ_{Mo} = 6.2 cm^{-1}, specimen 0.10 × 0.59 × 0.44 mm, $A^*_{min,max}$ = 1.06, 1.27, $2\theta_{max}$ = 50°, N = 6542, N_o = 4452, R = 0.041, R' = 0.041, n_v = 434, $|\Delta\rho_{max}|$ = 0.56 e Å^{-3}.

[Ag{(mpz)$_2$B(mpz)$_2$}{P(CH$_2$Ph)$_3$}] **14**. $C_{37}H_{41}AgBN_8P\cdot 0.5H_2O$, M = 756.5, monoclinic, space group $P2_1/c$, a = 14.219(5), b = 14.647(4), c = 18.34(1) Å, β = 96.52(4)°, U = 3796 Å^3, D_c (Z = 4) = 1.32$_4$ g cm^{-3}, $F(000)$ = 1564, μ_{Mo} = 6.1 cm^{-1}, specimen 0.25 × 0.31 × 0.44 mm, $A^*_{min,max}$ = 1.15, 1.19, $2\theta_{max}$ = 55°, N = 6659, N_o = 3362, R = 0.050, R' = 0.050, n_v = 442, $|\Delta\rho_{max}|$ = 0.53 e Å^{-3}.

For 4007 additional equivalent data measured R_{int} was 0.035. A difference map residue was assigned as the oxygen of a water molecule, site occupancy set as 0.5 after trial refinement.

[Ag{(mpz)$_2$B(mpz)$_2$}(PMePh$_2$)] **15**. $C_{29}H_{33}AgBN_8P$, M = 643.3, monoclinic, space group $P2_1/n$, a = 12.646(3), b = 19.422(3), c = 12.787(4) Å, β = 97.48(2)°, U = 3114 Å^3, D_c (Z = 4) = 1.37$_2$ g cm^{-3}, $F(000)$ = 1320, μ_{Mo} = 7.3 cm^{-1}, specimen 0.75 × 0.26 × 0.50 mm, $A^*_{min,max}$ = 1.21, 1.40, $2\theta_{max}$ = 50°, N = 5457, N_o = 3545, R = 0.050, R' = 0.057, n_v = 362, $|\Delta\rho_{max}|$ = 0.78 e Å^{-3}.

For the merging of an equivalent data set R_{int} was 0.049.

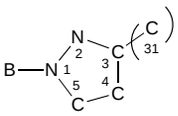
[Ag{(mpz)$_2$B(mpz)$_2$}{P(C$_6$H$_{11}$)$_3$}] **17**. $C_{34}H_{53}AgBN_8P$, M = 723.5, monoclinic, space group $P2_1/c$, a = 12.832(9), b = 15.577(4), c = 19.15(2) Å, β = 107.84(7)°, U = 3644 Å^3, D_c (Z = 4) = 1.31$_8$ g cm^{-3}; $F(000)$ = 1520, μ_{Mo} = 6.3 cm^{-1}, specimen 0.32 × 0.22 × 0.48 mm, $A^*_{min,max}$ = 1.13, 1.20, $2\theta_{max}$ = 50°, N = 6422, N_o = 3585, R = 0.061, R' = 0.062, n_v = 407, $|\Delta\rho_{max}|$ = 1.69 e Å^{-3}.

For 2286 additional equivalent data measured, R_{int} was 0.037.

In the B(mpz)$_4$ ligands, atoms are designated C, N(*lm*), *l* = ring number 1–4 (except for the rhombohedral systems where they are 1, 2) and *m* = 1–5. Rings 1, 1 and 2, or 1, 2, 3 are co-ordinated as appropriate: ring numbers only are shown in the Figures, N(2) having no associated hydrogen. In the PR$_3$ ligands phenyl ring atom numbers are designated C(1*ln*), *l* = ring number, *n* = 1–6; in the Figures ring atom 2 only is identified.

CCDC reference number 186/1043.

See http://www.rsc.org/suppdata/dt/1998/2739/ for crystallographic files in .cif format.



Results and Discussion

Synthesis

From the interaction between a tertiary phosphine PR$_3$ (R = Ph, C$_6$H$_{11}$, CH$_2$Ph, 2,4,6-Me$_3$C$_6$H$_2$, *o*-, *m*- or *p*-tolyl) or PPh$_2$R′ (R′ = Me or Et), silver nitrate and potassium salts of the tetrakis(pyrazol-1-yl)borate [B(pz)$_4$]$^-$ or [B(mpz)$_4$]$^-$, in methanol at room temperature, the complexes **1**–**17** have been obtained in high yield in accordance with equation (1). These

$$K[B(pz)_4] + AgNO_3 + PR_3 \longrightarrow \underset{\mathbf{1–17}}{[Ag\{B(pz)_4\}(PR_3)]} + KNO_3 \quad (1)$$

colorless complexes are very stable to air, soluble in chlorinated solvents, acetone, dmso, ethyl acetate, alcohols and benzene. They are non-electrolytes in CH_2Cl_2 and acetone.

The reaction between 1 equivalent of [Ag{B(pz)$_4$}(PPh$_3$)] **1** or [Ag{B(pz)$_4$}{P(CH$_2$Ph)$_3$}] **6** and 2 equivalents of P(C$_6$H$_{11}$)$_3$ in diethyl ether results in the rapid formation of the compound [Ag{B(pz)$_4$}{P(C$_6$H$_{11}$)$_3$}] **9**, upon displacement of the less basic PPh$_3$ and P(CH$_2$Ph)$_3$.

The reaction between 1 equivalent of compound **3** and ⩾2 equivalents of 1-methylimidazoline-2-(3*H*)-thione was unsuccessful and the starting materials were always recovered. An analogous behavior has been previously found also with some other sterically hindered tris(pyrazol-1-yl)borate silver(I) derivatives.[34,41]

On the other hand reaction of compound **3** with Him in diethyl ether proceeded instantaneously, resulting in the formation of the mixed-ligand complex [Ag{B(pz$_4$)}(Him){P(C$_6$H$_4$Me-*m*)$_3$}] **18**, whereas a different pattern was found when a similar reaction was carried out with **2**, the starting materials always being recovered. This is probably a consequence of the different co-ordination environments found in compounds **2** and **3**, the Him ligand co-ordinating the three-co-ordinate silver(I) center found in **3**, but unable to displace one of the three pyrazol-1-yl groups from four-co-ordinate **2**.

Structure determinations

The crystallisation of diverse combinations of silver(I) salts of the [B(pz)$_4$]$^-$ and [B(mpz$_4$)]$^-$ ligands with 1:1 stoichiometric ratios of various tertiary phosphines from appropriate solvents has resulted, as recorded above, in the production of crystalline air-stable adducts of that stoichiometry as neutral materials, verified in a number of cases by room-temperature single-crystal structure determinations. The results of the latter display a dichotomy in structural type between systems in which the [B(pz)$_4$]$^-$ ligand is chelating two-co-ordinate or tripodal three-co-ordinate in a manner which cuts across the two [B(pz)$_4$]$^-$/[B(mpz)$_4$]$^-$ ligand types; geometrical parameters of the two systems are given in Tables 1 and 2.

We consider first those compounds in which the silver environment is N$_3$AgP, five in total. Both (pz)B(pz)$_3$ and (mpz)B(mpz)$_3$ moieties may co-ordinate as tripodal ligands in which the [B(pz)$_3$]Ag arrays have potential threefold symmetry, to which a symmetrically substituted tertiary phosphine, as found in all of these cases, may conform, so that the totality of the [B(pz)$_3$]Ag(PR$_3$) aggregate may have maximum threefold symmetry. (The symmetry of that array, tridentate co-ordinated, can potentially rise as high as 3*m*; however, this is unlikely to be matched by any of the counterpart tertiary phosphine substituents as encountered here.) In three of the five recorded cases this is realized crystallographically by virtue of the compound crystallizing in the rhombohedral space group $R\bar{3}$ with pairs of molecules disposed on the crystallographic threefold axis of the *R* cell and confronting about an inversion centre to give the familiar EPh$_3$Ph$_3$E motif [*cf.*, *e.g.*, the recent determination of the structure of (β-)SbPh$_3$[42]; one third of the molecule comprises the asymmetric unit of the structure. The

Table 1 Selected geometries (distances in Å, angles in °) of the N_3AgP arrays

		(mpz)B(mpz)$_3$		
	(pz)B(pz)$_3$ P(C$_6$H$_4$Me-*o*)$_3$ **2**	PPh$_3$, **10**	P(C$_6$H$_4$Me-*o*)$_3$, **11**	P(C$_6$H$_4$Me-*m*)$_3$, **12**
Ag–P	2.368(2)	2.328(2)	2.384(2)	2.353(3)
Ag–N(12)	2.358(7)	2.325(3)	2.363(5)	2.297(4)
Ag–N(22)				2.347(9)
Ag–N(32)				2.334(8)
P–Ag–N(12)	131.6(1)	130.77(9)	130.7(1)	129.2(2)
P–Ag–N(22)				123.0(3)
P–Ag–N(32)				140.4(2)
N(12)–Ag–N(22)	80.7(2)	82.0(1)	82.1(2)	81.2(4)
N(12)–Ag–N(32)				80.1(3)
N(22)–Ag–N(32)				82.9(3)
Torsion angles				
Ag–P–C(111)–C(112)	−47.4(3)	−42.4(3)	−49.0(4)	174.3(9)
Ag–P–C(211)–C(212)				−61.8(9)
Ag–P–C(311)–C(312)				161.0(9)
Silver out-of-plane deviations (Å)				
δ [pz(1)]	0.67(1)	0.645(8)	0.52(1)	0.08(2)
δ [pz(2)]				0.81(2)
δ [pz(3)]				0.10(2)

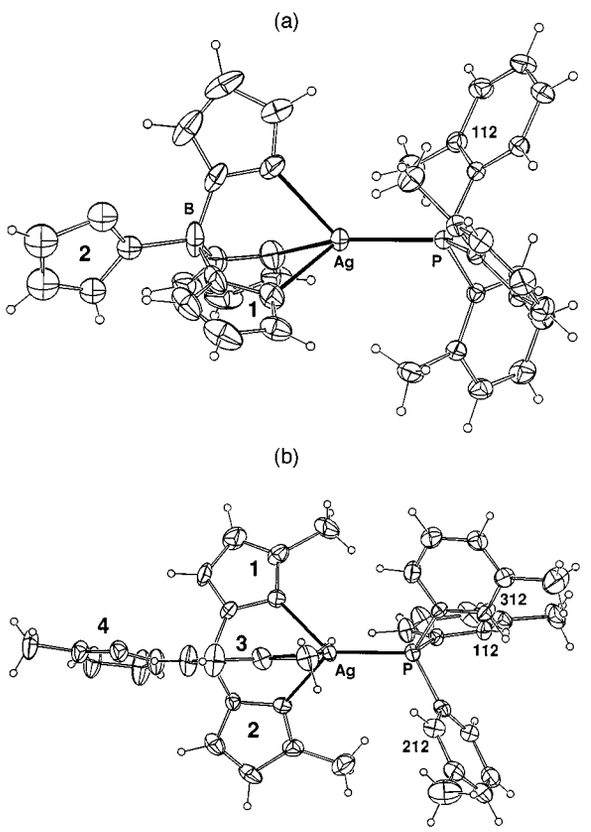


Fig. 1 Molecular projections for (a) [Ag{(pz)B(pz)$_3$}{P(C$_6$H$_4$Me-*o*)$_3$}] **2** and (b) [Ag{(mpz)B(mpz)$_3$}{P(C$_6$H$_4$Me-*m*)$_3$}] **12**. In 2 the array is representative of the more general rhombohedral $R\bar{3}$ family, found also for two of the B(mpz)$_4$ adducts **10** and **11** which are isomorphous; for the fourth unco-ordinated pz ring, which is disordered about the 3 axis which runs through the molecule, one component only is shown. Here and in the other figures 20% thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Schematic labelling is shown, the '2'-carbon atoms of the phenyl rings being identified by number only, and ring numbers for the B(mpz)$_4$ ligands

unco-ordinated pz component cannot conform to the threefold symmetry of the molecule and is modelled as disordered about the threefold axis; interestingly, the axis is not coincident with the centroid of the ring, an observation possibly consequent simply on the intrinsic asymmetry of the ring (even in the absence of the methyl substituent), or possibly on unsymmetrical co-ordination of the tripod, a possibility which seems unlikely, given the generally 'normal' behaviour of [B(pz)$_3$]Ag aggregates in respect of geometry and 'thermal motion'. It is of interest that the three combinations found in the $R\bar{3}$ cell comprise [B(pz)$_4$]$^-$/P(C$_6$H$_4$Me-*o*)$_3$, [B(mpz)$_4$]$^-$/PPh$_3$, P(C$_6$H$_4$Me-*o*)$_3$ combinations, but not [B(pz)$_4$]$^-$/PPh$_3$. In all [B(mpz)$_4$]$^-$ adducts of both types, and in all P(C$_6$H$_4$Me-*o*)$_3$ adducts of both types, the methyl substituents of the three rings are directed inwards towards the other ligand, so as to tend to envelope the silver atom, the [B(mpz)$_4$]$^-$ ligand being the more effective in this respect. The three rhombohedral structures all therefore contain at least one such sterically active ligand, and also the example where both [B(mpz)$_4$]$^-$ and P(C$_6$H$_4$Me-*o*)$_3$ are found in combination. Moreover, in the remaining N_3AgP example, with no imposed crystallographic symmetry, [B(mpz)$_4$]/P(C$_6$H$_4$Me-*m*)$_3$, one of the ligands is also hindered; *i.e.* there is no example in this class in which both ligands are unhindered. The ligand hindrance is not without effect on the N_3AgP geometry (Table 1), the array being clearly 'stretched' in the case of combining hindered ligands of both types, as indeed it is in both arrays containing P(C$_6$H$_4$Me-*o*)$_3$. In the monoclinic [B(mpz)$_4$]$^-$/P(C$_6$H$_4$Me-*m*)$_3$ array, Ag–P is slightly elongated, *cf.* its PPh$_3$ counterpart; the distortion from 3 symmetry is considerable, most notably in the angles which suggest displacement of the Ag–P bond *vis-à-vis* the AgN_3 aggregate as the origin, with some impact on the associated distances.

Taking the [(mpz)B(mpz)$_3$]/P(C$_6$H$_4$Me-*m*)$_3$ compound and its ring numbering as datum, we pass to the second class of compounds in which the silver environment is $PAgN_2$, similar to that of [Ag{Ph$_2$B(pz)$_2$}{P(C$_6$H$_4$Me-*p*)$_3$}].[43] The PAg(pz)$_2$B(pz)$_2$ array here has quasi-*m* symmetry, in consequence of detachment of ring 3 from the co-ordination sphere, and rearrangement of ring 3 by rotation about its B–N bond so that the mirror plane of the quasi-3 array which once described the [B(pz)$_3$]AgP aggregate in which it once lay now bisects it. The other two mirror planes in which the other two co-ordinated rings lay are also lost, *m* being the residual symmetry of the (pz)B(pz)$_3$AgP aggregate and containing the fourth, peripheral, unco-ordinated pz ring. Inspection of the dispositions of the phosphine ligand substituents suggests little, if any, systematic correlation with the disposition of the plane of the quasi-*m*

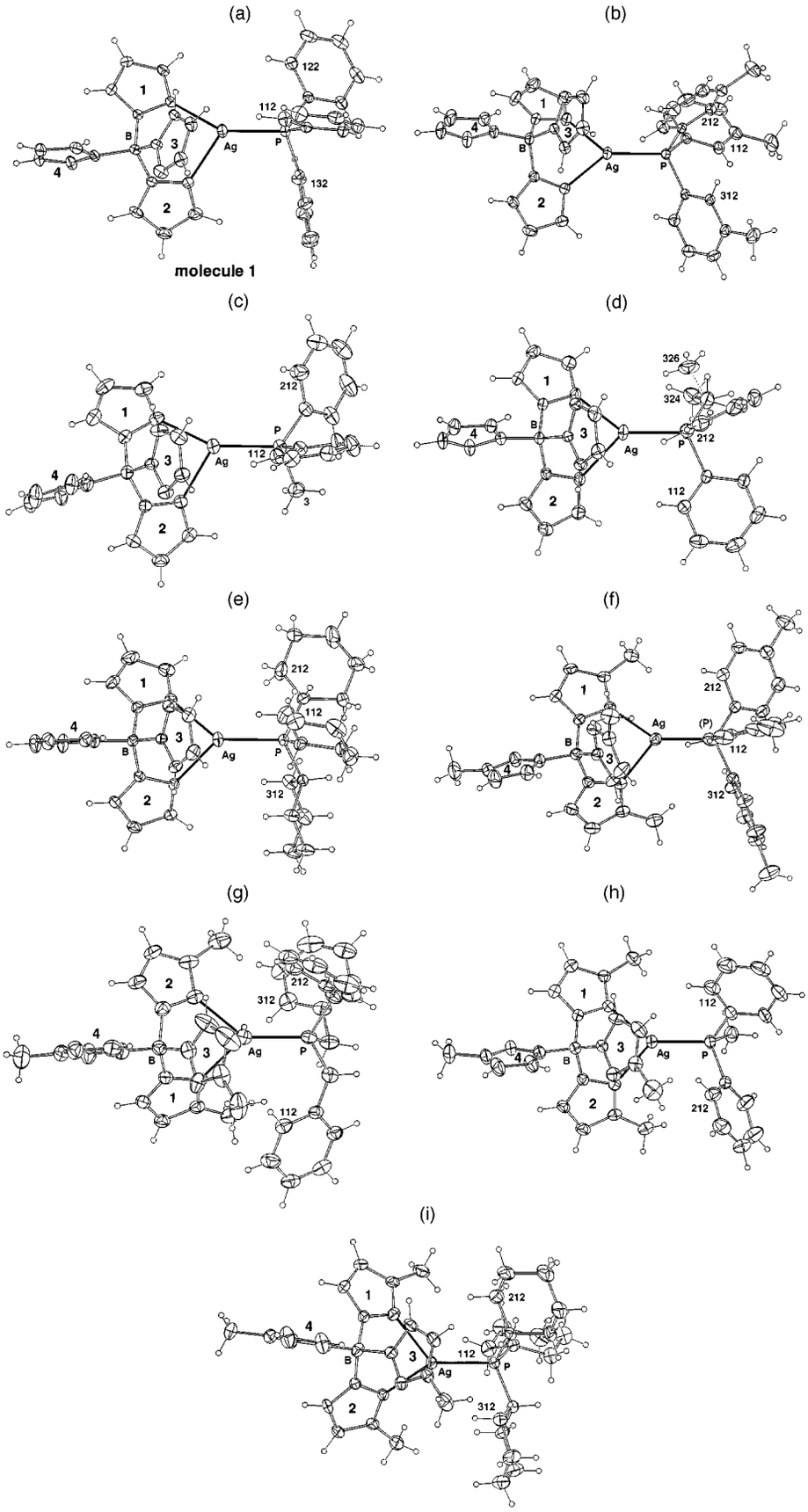


Fig. 2 Molecular projections for the complexes with AgN_2P co-ordination environments: (a) molecule 1 of $[Ag\{(pz_2)B(pz)_2\}(PPh_3)]$ **1**; molecule 2 is of similar aspect; (b) $[Ag\{(pz)_2B(pz)_2\}\{P(C_6H_4Me\text{-}m)_3\}]$ **3**; (c) $[Ag\{(pz)_2B(pz)_2\}(PMePh_2)]$ **7**; (d) $[Ag\{(pz)_2B(pz)_2\}(PEtPh_2)]$ **8**; (e) $[Ag\{(pz)_2B(pz)_2\}\{P(C_6H_{11})_3\}]$ **9**; (f) $[Ag\{(mpz)_2B(mpz)_2\}\{P(C_6H_4Me\text{-}p)_3\}$ **13**; (g) $[Ag\{(mpz)_2B(mpz)_2\}\{P(CH_2Ph)_3\}]$ **14**; (h) $[Ag\{(mpz)_2B(mpz)_2\}(PMePh_2)]$ **15**; and (i) $[Ag\{(mpz)_2B(mpz)_2\}\{P(C_6H_{11})_3\}]$ **17**

$[(pz)_2B(pz)_2]AgP$ array. The angular geometry of the N_2AgP aggregate is such that the sums of the three angles about the silver lie between $358._1$ and $360._0°$ for all cases, a truly planar, if not trigonal array. The bite angle in the N_2Ag component has risen from *ca.* 81° in the N_3AgP species to more nearly 86°. The pairs of P–Ag–N angles vary in the degree of disparity

Table 2 Selected geometries (distances in Å, angles in °) of the N_2AgP arrays

	$(pz)_2B(pz)_2$ complexes					$(mpz)_2B(mpz)_2$ complexes			
	$PMePh_2$ **7**	$PEtPh_2$ **8**	PPh_3(molecules 1,2) **1**	$P(C_6H_4Me\text{-}m)_3$ **3**	$P(C_6H_{11})_3$ **9**	$P(CH_2Ph)_3$ **14**	$PMePh_2$ **15**	$P(C_6H_4Me\text{-}p)_3$ **13**	$P(C_6H_{11})_3$ **17**
Ag–P	2.341(2)	2.347(1)	2.331(2), 2.335(2)	2.352(1)	2.351(1)	2.333(2)	2.328(2)	2.358(1)	2.333(1)
Ag–N(12)	2.217(5)	2.220(3)	2.205(6), 2.217(7)	2.248(3)	2.261(4)	2.276(7)	2.228(4)	2.225(3)	2.206(1)
Ag–N(22)	2.301(4)	2.322(3)	2.296(7), 2.314(7)	2.289(3)	2.297(3)	2.244(6)	2.257(5)	2.281(4)	2.332(7)
P–Ag–N(12)	154.8(1)	141.52(8)	149.1(2), 150.2(2)	137.13(7)	140.3(1)	140.7(2)	141.4(1)	145.7(1)	146.7(2)
P–Ag–N(22)	120.1(1)	132.46(7)	122.8(2), 122.0(2)	137.44(9)	134.45(9)	134.6(2)	130.6(1)	127.91(8)	128.4(2)
N(12)–Ag–N(22)	85.1(2)	85.5(1)	86.6(2), 85.9(3)	85.4(1)	84.9(1)	84.2(2)	88.0(2)	86.4(1)	84.9(3)
Σ	$360._0$	$359._5$	$358._5$, $358._1$	$360._0$	$359._7$	$359._5$	$360._0$	$360._0$	$360._0$
Dihedral angles									
N_2AgP/pz(1)	33.3(3)	41.8(1)	25.3(3), 25.4(3)	32.9(1)	35.6(2)	35.9(3)	29.7(2)	29.6(1)	38.8(2)
pz(2)	29.8(2)	23.4(1)	32.4(4), 32.8(4)	29.7(1)	37.9(2)	38.6(2)	29.1(2)	30.8(1)	40.0(3)
pz(3)	60.1(2)	61.5(1)	57.6(3), 57.8(3)	56.2(1)	57.6(1)	60.7(2)	47.8(2)	85.4(1)	43.0(3)
pz(4)	82.7(3)	59.7(1)	81.7(4), 81.2(4)	88.2(2)	89.3(2)	76.1(3)	70.4(3)	78.1(2)	87.3(4)
pz(1)/pz(2)	52.7(3)	51.3(2)	52.8(4), 52.8(4)	50.2(2)	67.5(2)	65.6(3)	50.0(2)	51.4(2)	57.9(4)
pz(3)/pz(1)	69.2(3)	80.3(2)	66.4(4), 65.8(4)	77.4(2)	79.4(2)	65.4(4)	62.8(3)	69.5(1)	71.7(4)
pz(3)/pz(2)	85.8(3)	81.9(2)	77.6(4), 80.3(4)	76.4(2)	72.2(2)	79.7(3)	69.6(2)	87.3(2)	75.1(3)
pz(4)/pz(3)	80.9(4)	80.3(2)	79.9(4), 76.4(2)	89.3(2)	87.4(2)	85.3(4)	69.6(3)	70.5(2)	89.6(4)
pz(4)/pz(1)	66.7(3)	81.5(1)	76.8(4), 77.5(4)	60.7(2)	58.2(2)	72.8(4)	45.9(3)	55.8(2)	63.9(4)
pz(4)/pz(2)	61.3(3)	47.9(2)	50.5(4), 49.8(5)	69.1(2)	54.6(2)	41.6(3)	84.4(3)	73.5(2)	58.3(4)
Out-of-plane deviations (atom/plane)/Å									
δB/pz(1)	0.05(1)	0.083(6)	0.08(2), 0.09(2)	0.044(7)	0.007(8)	0.01(1)	0.13(1)	0.096(8)	0.08(2)
δB/pz(2)	0.11(1)	0.122(6)	0.10(2), 0.09(2)	0.168(7)	0.067(8)	0.08(1)	0.18(1)	0.062(8)	0.00(2)
δAg/pz(1)	−0.41(1)	−0.063(6)	0.24(1), 0.30(1)	−0.175(7)	0.259(9)	−0.15(2)	−0.28(1)	−0.154(8)	−0.09(2)
δAg/pz(2)	0.01(1)	−0.024(6)	0.68(2), −0.64(2)	−0.055(7)	0.542(8)	−0.38(1)	0.30(1)	−0.291(9)	−0.07(1)

exhibited: in $[Ag\{(pz)_2B(pz)_2\}\{P(C_6H_4Me\text{-}m)_3\}]$ they are almost identical, while in the other adducts disparities of over 30° are found. These excursions do not correlate well with disparities in the Ag–N distances: differences of over 0.1 Å in the latter may be found, the shorter distance usually being associated with the larger angle, so that a tendency toward linear two-co-ordination may be postulated in some instances, but the aggregate of the array is quite varied in this respect.

Spectroscopy

The IR spectra (for which the most significant bands observed in the spectra are reported in the Experimental section) exhibit all the features required by the presence of the tetrakis(pyrazol-1-yl)borate and tertiary phosphine ligand.

In the medium IR region of the spectra of compounds **1**–**17** we always find ν(CH) of the heterocyclic ring above 3100 cm^{-1},[44] ν(CH) of the stretching vibrations due to aryl groups at *ca.* 3080–3040 cm^{-1}, ν(C⋯C) of the phosphorus donor and ν(C⋯N) of $[B(pz)_4]^-$ [41] at *ca.* 1580 and 1530 cm^{-1} respectively and, finally, the B–N stretching vibrations at *ca.* 1400 cm^{-1}.[45]

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}.[46,47] It is worth noting that Whiffen's *y* and *t* vibrations in derivatives **1** and **10**, which contain the same P-donor (PPh_3), and in **3** and **12** which contain the $P(C_6H_4Me\text{-}m)_3$ ligand, are significantly different. Also on the basis of the structure determinations, we suggest that the different pattern of absorptions is most likely due to the different silver co-ordination environments found in both pairs of compounds. No difference has been observed between the spectrum of compound **2** and that of **10**, which have similar silver co-ordination environments.

We are not able to assign the ν(Ag–N) vibrations because they are hidden under some absorptions characteristic of the azole ring system and of phosphines, whereas bands of medium and weak intensity between 200 and 100 cm^{-1}, not present in the spectra of $K[B(pz)_4]$ and of the free P-donor, are likely due to ν(Ag–P) stretching vibrations.[48]

The room-temperature ^1H NMR spectra of $[B(pz)_4]^-$ complexes **1**–**9** exhibited similar signals for their pyrazolyl groups suggesting highly fluxional species with either a rocking motion of the triorganophosphine-silver(I) moieties between the four nitrogen atoms of $[B(pz)_4]^-$ or complete dissociation and reassociation of the pyrazolyl nitrogens which occurs rapidly even at lower temperatures: in fact, on cooling the $CDCl_3$ solutions of **1**–**9** to 193 K, no additional signals due to pyrazole appeared.

The $[B(mpz)_4]^-$ complexes **10**–**17** show a different behaviour: at room temperature only one set of signals is found for the protons of the four pyrazolyl groups, whereas from *ca.* 263 K each resonance type splits into two with 3/1 integrated intensity, indicating that these species are fluxional at room temperature but not at 263 K. At this temperature three of the four pyrazolyl groups appear to be co-ordinated to silver as is likely in a N_3AgP tetrahedral environment.

It is of interest that frequently the disposition of a species in the crystal may be taken as indicative of the form evident in solution at low temperature; the present rather extensive correlation is, in fact, rather random in this respect.

In the ^1H and ^{13}C NMR spectra the chemical shifts of the protons and carbons due to the pyrazole are similar to those observed for corresponding nuclei in their counterpart copper(I) derivatives[26] and in silver(I) (tertiary phosphine)tris(pyrazolyl)borates.[34,35,41] Greater high-field shifts have been found for derivatives containing more sterically hindered triorganophosphines, analogous to those previously observed for tris(pyrazolyl)borate silver(I) derivatives. 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.

The room-temperature $^{31}P\text{-}\{^1H\}$ NMR spectra of compounds **1** and **4** exhibit broad peaks at δ 16.9 and 17.1 respectively. Interestingly, the chemical shift values do not differ significantly from those of the closely related tris(pyrazolyl)borate silver(I) analogues,[34,35,41] moving slowly downfield as the

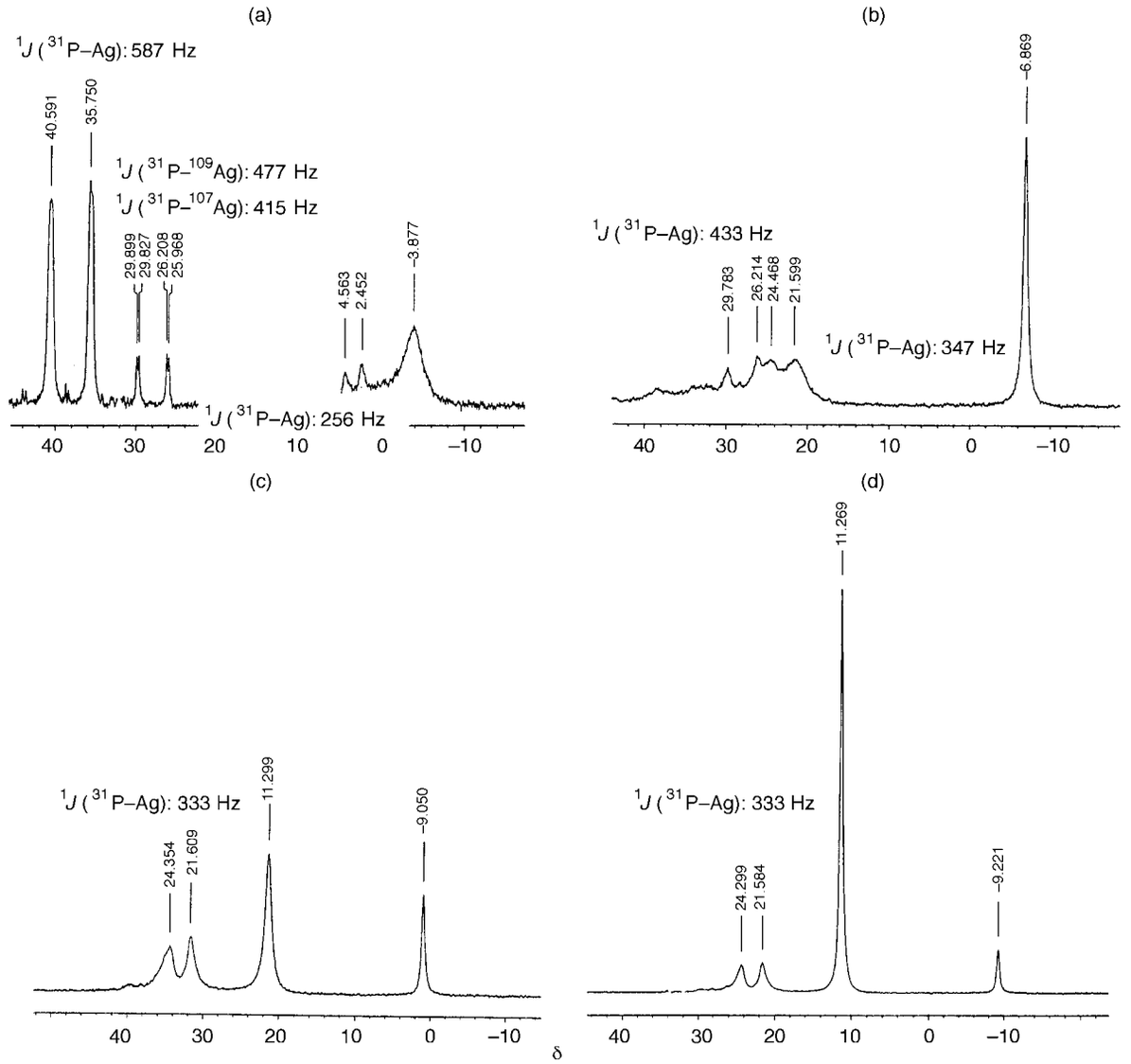


Fig. 3 The ^{31}P NMR spectra of different mixtures of compound **4** and $P(C_6H_{11})_3$: (a) 1 mmol of phosphine and 1 mmol of **4**; (b) 2 mmol of phosphine and 1 mmol of **4**; (c) 5 mmol of phosphine and 1 mmol of **4**; (d) >10 mmol of phosphine and 1 mmol of **4**

temperature was lowered to 223 K: the rapid exchange of the phosphine ligand causes the ^1J(Ag–^{31}P) coupling to be averaged to zero and it is necessary to slow down the ligand exchange by cooling the solution to 223 K in order to observe it. On the other hand the ^{31}P-{^{1}H} NMR spectra of derivatives **2**, **3** and **5**–**17** show coupling to ^{107}Ag and ^{109}Ag. It has been previously observed that the observation of ^1J(Ag–^{31}P) at room temperature is possible in cases where the tertiary phosphine ligand is sterically hindered.[49]

The observed $^1J(^{107}Ag):{}^1J(^{109}Ag)$ ratios of these derivatives are in good agreement with that calculated from the gyromagnetic ratios of the silver nuclei $\gamma(^{107}Ag):\gamma(^{109}Ag)$. The observed Ag–^{31}P coupling constants are rather higher than the values reported for other silver(I) phosphino complexes[50] but are of the same order of magnitude of those found for analogous tris(pyrazolyl)borate complexes[34,35,41] and smaller than those found for fluorinated silver(I) tris(pyrazol-1-yl)borates.[32] Each free phosphine lies upfield with respect to its silver(I) complex; the chemical shift of the complex ranges from *ca.* 6 ppm for **5**, which contains the more sterically hindered triorganophosphine [$P(C_6H_2Me_3$-2,4,6)$_3$, cone angle = 212°],[38] to *ca.* 30–32 ppm for the derivatives **6**, **7** and **9**, which contain the better donor tertiary phosphines.[37] The ^{31}P chemical shift is a function of both cone angle and σ donicity of the phosphorus donor,[37,38] and seems to be also a function of the electronic and steric properties of the tris(pyrazolyl)borate donor: in fact the δ is always greater for derivatives of $[B(pz)_4]^-$ which is less basic and less sterically hindered than $[B(mpz)_4]^-$.

The ^1J(Ag–^{31}P) coupling constants also are dependent on the type of PR_3: the smallest values have been observed for derivatives **2**, **5** and **11** which contain the phosphorus donor with largest cone angles.[38] On the other hand the ^1J(Ag–^{31}P) coupling constant values seem to be not strongly dependent on the nature of the tetrakis(pyrazol-1-yl)borato donors. However the values found in derivatives of $[B(mpz)_4]^-$ are always slightly smaller than those found in $[B(pz)_4]^-$ ones.

The ^{31}P NMR spectrum of derivative **18** indicates that this compound partly dissociates in chloroform solution: in fact two different double doublets at δ 17.3 and 7.5 (relative intensity 1 : 1) have been found at room temperature due to the existence of both derivatives **3** and **18** in accordance with equilibrium (2).

$$\underset{\mathbf{18}}{[Ag\{B(pz)_4\}(Him)\{P(C_6H_4Me\text{-}m)_3\}]} \rightleftharpoons \underset{\mathbf{3}}{[Ag\{B(pz)_4\}\{P(C_6H_4Me\text{-}m)_3\}]} + Him \quad (2)$$

At 223 K the intensity of the signal due to derivative **18** increases, whereas the intensity of signal at δ 17.3 due to derivative **3** decreases, in accordance with a smaller dissociation at low temperature.

In order to obtain information on the existence of the

complexes in solution we also recorded ^{31}P NMR spectra of a known mixture of $[Ag\{B(pz)_4\}\{P(C_6H_4Me\text{-}p)_3\}]$ **4** and $P(C_6H_{11})_3$: addition of 1 mmol of $P(C_6H_{11})_3$ to a 1 mmol dm^{-3} $CDCl_3$ solution of **4** results in the appearance of a broad doublet at δ 38.2 due to $[Ag\{B(pz)_4\}\{P(C_6H_{11})_3\}]$, a broad signal at δ −3.9 due to partly free $P(C_6H_4Me\text{-}p)_3$ and finally two double doublets at δ 27.9 and 3.50, most likely due to bis(triorganophosphino) species $Ag\{P(C_6H_{11})_3\}_2$ and $Ag\{P(C_6H_4Me\text{-}p)_3\}_2$ [Fig. 3(a)], whereas the addition of 2 mmol of $P(C_6H_{11})_3$ results in the complete disappearance of signals due to co-ordinated $P(C_6H_4Me\text{-}p)_3$ and $[Ag\{B(pz)_4\}\{P(C_6H_{11})_3\}]$ and in the appearance of an additional doublet at δ 23.0 likely due to a silver(I) center co-ordinated by three $P(C_6H_{11})_3$ groups [Fig. 3(b)]. The values of the $^1J(Ag–^{31}P)$ (*ca.* 433 and 347 Hz) are of the same order of magnitude of those found in analogous systems.

The addition of 5 mmol of $P(C_6H_{11})_3$ results in the complete disappearance of the signal at δ *ca.* 28.0 due to the 2:1 $Ag\{P(C_6H_{11})_3\}_2$ species and in the appearance of the signal due to free $P(C_6H_{11})_3$ [Fig. 3(c)]. No further changes [Fig. 3(d)] were observed upon addition of a large excess of $P(C_6H_{11})_3$ (>10 mmol), in accordance with the non-existence of the $[Ag\{P(C_6H_{11})_3\}_4$ species, due to the steric hindrance of $P(C_6H_{11})_3$. Lability of the phosphorus ligand in the 2:1 and 3:1 species was evident in the temperature dependence of these ^{31}P NMR spectra.

Conclusion

We have prepared and characterized a series of silver(I)–tertiary phosphine adducts containing anionic tetrakis(pyrazol-1-yl)borates. In the solid state some of them are four-co-ordinate with the donors $[B(pz)_4]^-$ or $[B(mpz)_4]^-$ tridentate, whereas most are three-co-ordinate with the tetrakis(pyrazol-1-yl)borate co-ordinating in the bidentate mode.

At room temperature, in $CDCl_3$ solution, the six-membered AgN_4B rings formed by $[B(pz)_4]^-$ and $[B(mpz)_4]^-$ are fluxional undergoing likely a rapid dissociation–reassociation mechanism (boat–boat flip). At low temperature (*ca.* <263 K) ^1H NMR data indicate, in the case of complexes of $[B(mpz)_4]^-$, the existence of a process which equilibrates only three pyrazole rings whereas the fourth remains un-co-ordinated. On the other hand the complexes of $[B(pz)_4]^-$ are fluxional also at 193 K.

The ^{31}P NMR data show that the structure and stability of the complexes in solution are strongly dependent on the Tolman cone angle and, to a smaller extent, on the σ donicity of the phosphorus donor.

It has also been found that unidentate nitrogen donors such as imidazole can co-ordinate silver(I) tetrakis(pyrazol-1-yl)borate containing unidentate P-donors only if the silver(I) center in the solid state is in a three-co-ordinate environment, but not in a four-co-ordinate one.

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