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Synthesis, spectroscopic characterization, and structural systematics of new triorganophosphinecopper(I) poly(pyrazol-1-yl)-borate complexes †

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Mono- and bis-(trialkyl- and triaryl-phosphine)copper(I) derivatives containing anionic bis-, tris- and tetrakis-(pyrazol-1-yl)borates were prepared from CuCl, [CuBr(Me$_2$S)] or [Cu(C$_6$H$_6$)$_{0.5}$(O$_3$SCF$_3$)]$_2$, R$_3$P (R = phenyl, benzyl, cyclohexyl, *o*-, *m*-, or *p*-tolyl) or R′Ph$_2$P (R′ = methyl or ethyl), and M[H$_n$B(pz)$_{4-n}$] (M = Na or K, *n* = 0, 1 or 2; Hpz = pyrazole in general; in detail, pyrazole (Hpz), 3,5-dimethylpyrazole (Hm$_2$pz), 3-methylpyrazole (Hmpz)) and characterized through analytical and spectral measurements (IR, ^{1}H and ^{31}P NMR). The same complexes can be obtained also from the reaction of [Cu(O$_2$NO)(PR$_3$)$_2$] with M[H$_n$B(pz)$_{4-n}$]. These air-stable compounds are non-electrolytes in CH$_2$Cl$_2$ and in acetone, in which they slowly decompose even with the strict exclusion of oxygen. Low-temperature single crystal structural characterizations were undertaken for several of them. The structurally authenticated arrays fall into three different types: (a) [Cu((pz)$_2$BH$_n$(pz)$_{2-n}$)(PR$_3$)$_2$] with a four-co-ordinate P$_2$Cu(N$_2$) co-ordination sphere, (b) [Cu((pz)$_3$BH)(PR$_3$)] with a four-co-ordinate PCu(N$_3$) co-ordination sphere, (c) [Cu((pz)$_2$BH$_n$(pz)$_{2-n}$)(PR$_3$)] with a three-co-ordinate PCu(N$_2$) co-ordination sphere.

Introduction

The poly(pyrazolyl)borate class of ligands has a widespread and varied chemistry. Complexes containing these ligands are known for almost every transition metal, often showing unusual structural and chemical properties.[1–10] The chemistry of poly(pyrazolyl)borate silver(I) and copper(I) complexes has recently attracted much interest.[11–15] The anionic ligands [HB(3,5-i-Pr$_2$pz)$_3$]$^-$ and [HB(3,5-Ph$_2$pz)$_3$]$^-$ (Hpz = pyrazole) have been employed in clarifying the mode of dioxygen binding at the dicopper site of hemocyanin,[16] whereas the use of [HB-(3,5-t-Bu$_2$pz)$_3$]$^-$ and [HB(3,5-Ph$_2$pz)$_3$]$^-$ has enabled the development of models for nitric oxide adducts of mononuclear copper in nitrite reductase.[17] Furthermore the complexes [Cu(H$_2$B(pz)$_2$)], [Cu(H$_2$B(pz)$_2$)L] (L = (cy)$_3$P or 2,2′-bipyridyl) and [Cu(H$_2$B(pz)$_2$)L′$_2$] (L′ = Ph$_3$P or pyridine) have been shown to catalyse the cyclopropanation of olefin in moderate to high yields in both heterogeneous and homogeneous phases. In the heterogeneous case, this kind of catalyst does not result in undue loss of activity or stereoselectivity and can be used several times.[18,19]

We have recently initiated an investigation into the co-ordination chemistry of poly(pyrazolyl)borates with silver(I) and a variety of tertiary phosphine coligands.[20–23] The complexes obtained display an interesting and in some cases unpredictable structural variety, both in the local co-ordination environment and in their overall geometry. We were especially interested to explore the factors causing these variations, detailed investigation of which suggested that they depend upon the steric demands of the phosphine ligands, and reaction conditions, as well as, primarily, upon the steric demands and electronic properties of the poly(pyrazolyl)borates themselves. We now extend our research to copper(I) and here report full details of the synthesis and spectroscopic characterization of several poly(pyrazol-1-yl)borate–Cu^I–phosphine derivatives, together with the crystal and molecular structures of some representative complexes, and a comparison with structural data reported for analogous silver(I) complexes. All the spectroscopic and structural data are discussed on the basis of electronic and steric arguments.

Experimental

General procedures

All syntheses and handling were carried out under an atmosphere of dry oxygen-free dinitrogen, using standard Schlenk techniques or a glove box. All solvents were dried, degassed and distilled prior to use. Elemental analyses (C,H,N) were performed in house 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, ^{1}H and ^{31}P NMR spectra on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^{1}H, and 121.4 MHz for ^{31}P). The electrical resistance of acetone, DMSO and CH$_2$Cl$_2$ solutions was measured with a Crison CDTM 522 conductimeter at room temperature. Selected IR, NMR and conductivity data are supplied as ESI.

Syntheses

Salts of the donors dihydrobis(pyrazol-1-yl)borate [H$_2$B(pz)$_2$]$^-$, hydrotris(pyrazol-1-yl)borate [HB(pz)$_3$]$^-$, hydrotris(3,5-dimethylpyrazol-1-yl)borate [HB(m$_2$pz)$_3$]$^-$, tetrakis(pyrazol-1-yl)-borate [B(pz)$_4$]$^-$, and tetrakis(3-methylpyrazol-1-yl)borate [B(mpz)$_4$]$^-$, were prepared in accordance with the procedure first reported by Trofimenko.[24] KBH$_4$, NaBH$_4$, R$_3$P, R′Ph$_2$P,

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† Electronic supplementary information (ESI) available: characterization data for compounds **1**–**20**. See http://www.rsc.org/suppdata/dt/b0/b003613g/

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Hpz, Hm_2pz and Hmpz were purchased (Aldrich) and used as received.

The compounds studied may be summarized as follows: (a) bis(trisubstituted phosphine)(bidentate pyrazolate)copper(I), $[Cu((pz)_2BH_2)(PMePh_2)_2]$ **2**, $[Cu((pz)_2B(pz)_2)(PMePh_2)_2]$ **12**, $[Cu((mpz)_2B(mpz)_2)(PR_3)_2]$ ($R_3 = Bn_3$ (Bn = benzyl) **14** or **18**); (b) (trisubstituted phosphine)(tridentate pyrazolate)copper(I), $[Cu((pz)_3BH)(PR_3)]$ ($R_3 = Bn_3$ **3**, (*o*-tolyl)$_3$ **4**, (*m*-tolyl)$_3$ **5** or $MePh_2$ **6**), $[Cu((m_2pz)_3BH)(PR_3)]$ ($R_3 = Bn_3$ **7**, (*o*-tolyl)$_3$ **8** or $MePh_2$ **9**), $[Cu((mpz)_3B(mpz))(PPh_3)]$ **13**, $[Cu((mpz)_3B(mpz))\{P(C_6H_4Me\text{-}p)_3\}]$ **17**; (c) (trisubstituted phosphine)(bidentate pyrazolate)copper(I), $[Cu((pz)_2BH_2)\{P(C_6H_4Me\text{-}o)_3\}]$ **1**, $[Cu((pz)_2B(pz)_2)(PR_3)]$ ($R_3 = Bn_3$ **10** or (*o*-tolyl)$_3$ **11**), $[Cu((mpz)_2B(mpz)_2)(PR_3)]$ (R_3 = (*o*-tolyl)$_3$ **15**, (*m*-tolyl)$_3$ **16**, $EtPh_2$ **19** or (cy)$_3$ **20**).

Compound 1. To a CH_3CN solution (50 ml) of CuCl (0.099 g, 1 mmol) and $P(C_6H_4Me\text{-}o)_3$ (0.304 g, 1 mmol), $K[H_2B(pz)_2]$ (0.185 g, 1 mmol) was added at room temperature. After the addition the solution was stirred for 1 h and the solvent subsequently removed with a rotary evaporator. $CHCl_3$ (50 ml) was added. The suspension was 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. Re-crystallization from CH_2Cl_2–light petroleum (bp 40–60 °C) gave complex **1** as a microcrystalline solid in 61% yield. mp 172–174 °C (decomp.). Calc. for $C_{27}H_{29}BCuN_4P$: C, 62.9; H, 5.7; N, 10.9. Found: C, 63.0; H, 5.5; N, 10.7%.

Compound 2. This was prepared similarly to compound **1** by using CuCl (0.099 g, 1 mmol), $MePh_2P$ (0.400 g, 2 mmol) and $K[H_2B(pz)_2]$ (0.185 g, 1 mmol) in CH_3CN (50 ml) at 298 K. Compound **2** was re-crystallized from CH_2Cl_2–ethyl acetate (1 : 1) (yield 59%). mp 120–124 °C. Calc. for $C_{32}H_{34}BCuN_4P_2$: C, 62.9; H, 5.6; N, 9.2. Found: C, 62.8; H, 5.7; N, 9.1%.

Compound 3. This was prepared similarly to compound **1** by using $Na[HB(pz)_3]$ (0.236 g, 1 mmol), tribenzylphosphine, Bn_3P (0.608 g, 2 mmol), and $[CuBr(Me_2S)]$ (0.205 g, 1 mmol); it was re-crystallized from chloroform–ethyl acetate (1 : 1) (yield 65%). mp 209–211 °C. Calc. for $C_{30}H_{31}BCuN_6P$: C, 62.0; H, 5.4; N, 14.5. Found: C, 62.2; H, 5.5; N, 14.3%.

Compound 4. This was prepared similarly to compound **1** by using CuCl (0.099 g, 1 mmol), $(C_6H_4Me\text{-}o)_3P$ (0.304 g, 1 mmol) and $Na[HB(pz)_3]$ (0.236 g, 1 mmol). Compound **4** was re-crystallized from $CHCl_3$–diethyl ether (yield 90%). mp 178–180 °C. Calc. for $C_{30}H_{31}BCuN_6P$: C, 62.0; H, 5.4; N, 14.5. Found: C, 61.9; H, 5.3; N, 14.4%.

Compound 5. To a methanol solution (50 ml) of CuCl (0.099 g, 1 mmol) and $(C_6H_4Me\text{-}m)_3P$ (0.608 g, 2 mmol), $Na[HB(pz)_3]$ (0.236 g, 1 mmol) was added at room temperature. After the addition the solution was stirred for 3 h. The colorless precipitate obtained was filtered off and washed with diethyl ether. Crystallization from CH_2Cl_2–light petroleum gave complex **5** as a microcrystalline solid in 64% yield. mp 172–175 °C. Calc. for $C_{30}H_{31}BCuN_6P$: C, 62.0; H, 5.4; N, 14.5. Found: C, 62.0; H, 5.5; N, 14.5%.

Compound 6. This was prepared similarly to compound **1** by using CuCl (0.099 g, 1 mmol), $MePh_2P$ (0.400 g, 2 mmol) and $Na[HB(pz)_3]$ (0.236 g, 1 mmol); it was recrystallized from CH_2Cl_2 and light petroleum (yield 80%). mp 166–169 °C. Calc. for $C_{22}H_{23}BCuN_6P$: C, 55.4; H, 4.9; N, 17.6. Found: C, 55.5; H, 5.0; N, 17.4%.

Compound 7. This was prepared similarly to compound **1** by using $K[HB(m_2pz)_3]$ (0.336 g, 1 mmol), Bn_3P (0.608 g, 2 mmol) and $[Cu(C_6H_6)_{0.5}(O_3SCF_3)]_2$ (0.250 g, 0.5 mmol); it was re-crystallized from $CHCl_3$–ethyl acetate (1 : 1) (yield 73%). mp 145–148 °C. Calc. for $C_{36}H_{43}BCuN_6P$: C, 65.0; H, 6.5; N, 12.6. Found: C, 65.3; H, 6.6; N, 12.5%.

Compound 8. This was prepared similarly to compound **1** by using CuCl (0.099 g, 1 mmol), $(C_6H_4Me\text{-}o)_3P$ (0.608 g, 2 mmol) and $K[HB(m_2pz)_3]$ (0.336 g, 1 mmol). Compound **8** was recrystallized from benzene and diethyl ether (yield 53%). mp 233–236 °C. Calc. for $C_{36}H_{43}BCuN_6P$: C, 65.0; H, 6.5; N, 12.6. Found: C, 65.1; H, 6.4; N, 12.5%.

Compound 9. This was prepared similarly to compound **1** by using CuCl (0.099 g, 1 mmol), $MePh_2P$ (0.400 g, 2 mmol) and $K[HB(m_2pz)_3]$ (0.336 g, 1 mmol); it was recrystallized from CH_2Cl_2 and *n*-heptane (yield 86%). mp 206–209 °C. Calc. for $C_{28}H_{35}BCuN_6P$: C, 59.9; H, 6.3; N, 15.0. Found: C, 60.1; H, 6.4; N, 15.1%.

Compound 10. This was prepared similarly to compound **1** by using $K[B(pz)_4]$ (0.318 g, 1 mmol), Bn_3P (0.608 g, 2 mmol) and $[CuBr(Me_2S)]$ (0.205 g, 1 mmol); it was recrystallized from CH_2Cl_2–ethyl acetate (1 : 1) (yield 61%). mp 72–75 °C. Calc. for $C_{54}H_{54}BCuN_8P_2$: C, 68.2; H, 5.7; N, 11.8. Found: C, 68.5; H, 5.5; N, 11.6%.

Compound 11. This was prepared similarly to compound **1** by using $K[B(pz)_4]$ (0.318 g, 1 mmol), $(C_6H_4Me\text{-}o)_3P$ (0.304 g, 2 mmol) and CuCl (0.099 g, 1 mmol); it was recrystallized from CH_2Cl_2–Et_2O (1 : 1) (yield 54%). mp 206–208 °C. Calc. for $C_{33}H_{33}BCuN_8P$: C, 61.3; H, 5.1; N, 17.3. Found: C, 61.5; H, 5.2; N, 17.5%.

Compound 12. This was prepared similarly to compound **1** by using CuCl (0.099 g, 1 mmol), $MePh_2P$ (0.400 g, 2 mmol) and $K[B(pz)_4]$ (0.318 g, 1 mmol) in CH_3CN (50 ml) at 298 K. Compound **12** was recrystallized from $CHCl_3$–ethyl acetate (1 : 1) (yield 74%). mp 154–157 °C. Calc. for $C_{38}H_{38}BCuN_8P_2$: C, 61.4; H; 5.1; N, 15.1. Found: C, 61.5; H, 5.2; N, 15.0%.

Compound 13. This was prepared similarly to compound **5** by using CuCl (0.099 g, 1 mmol), Ph_3P (0.524 g, 2 mmol) and $K[B(mpz)_4]$ (0.374 g, 1 mmol) in CH_3OH (50 ml) at 298 K. Compound **13** was recrystallized from CH_2Cl_2–ethyl acetate (1 : 1) (yield 72%). mp 230–232 °C. Calc. for $C_{34}H_{35}BCuN_8P$: C, 61.8; H, 5.3; N, 16.9. Found: C, 61.5; H, 5.4; N, 17.0%.

Compound 14. This was prepared similarly to compound **1** by using $[CuBr(Me_2S)]$ (0.205 g, 1 mmol), Bn_3P (0.608 g, 2 mmol) and $K[B(mpz)_4]$ (0.374 g, 1 mmol) in CH_3CN (50 ml) at 298 K. Compound **14** was recrystallized from Et_2O (yield 87%). mp 93–95 °C. Calc. for $C_{58}H_{62}BCuN_8P_2$: C, 69.1; H, 6.2; N, 11.1. Found: C, 69.5; H, 6.1; N, 11.0%.

Compound 15. This was prepared similarly to compound **1** by using CuCl (0.099 g, 1 mmol), $(C_6H_4Me\text{-}o)_3P$ (0.608 g, 2 mmol) and $K[B(mpz)_4]$ (0.374 g, 1 mmol) in CH_3OH (50 ml) at 298 K. It was recrystallized from CH_2Cl_2–Et_2O (1 : 1) (yield 62%). mp 175 °C (decomp.). Calc. for $C_{37}H_{41}BCuN_8P$: C, 63.2; H, 5.9; N, 15.9. Found: C, 63.0; H, 6.0; N, 16.0%.

Compound 16. This was prepared similarly to compound **1** by using CuCl (0.099 g, 1 mmol), $(C_6H_4Me\text{-}m)_3P$ (0.608 g, 2 mmol) and $K[B(mpz)_4]$ (0.374 g, 1 mmol) in CH_3OH (50 ml) at 298 K. It was recrystallized from $CHCl_3$–Et_2O (1 : 1) (yield 59%). mp 205–208 °C. Calc. for $C_{37}H_{41}BCuN_8P$: C, 63.2; H, 5.9; N, 15.9. Found: C, 63.4; H, 5.8; N, 16.7%.

Compound 17. This was prepared similarly to compound **1** by using CuCl (0.099 g, 1 mmol), $(C_6H_4Me\text{-}p)_3P$ (0.608 g, 2 mmol) and K[B(mpz)$_4$] (0.374 g, 1 mmol) in CH_3OH (50 ml) at 298 K. It was recrystallized from $CHCl_3$–Et_2O (1 : 1) (yield 59%). mp 238–241 °C. Calc. for $C_{37}H_{41}BCuN_8P$: C, 63.2; H, 5.9; N, 15.9. Found: C, 63.2; H, 6.1; N, 15.6%.

Compound 18. This was prepared similarly to compound **1** by using CuCl (0.099 g, 1 mmol), $MePh_2P$ (0.400g, 2 mmol) and K[B(mpz)$_4$] (0.374 g, 1 mmol) in CH_3CN (50 ml) at 298 K. Compound **18** was recrystallized from $CHCl_3$–heptane (1 : 2) (yield 58%). mp 133–135 °C. Calc. for $C_{42}H_{46}BCuN_8P_2$: C, 63.2; H, 5.8; N, 14.0. Found: C, 63.0; H, 5.6; N, 14.1%.

Compound 19. This was prepared similarly to compound **1** by using CuCl (0.099 g, 1 mmol), $EtPh_2P$ (0.428 g, 2 mmol) and K[B(mpz)$_4$] (0.374 g, 1 mmol) in CH_3CN (50 ml) at 298 K. Compound **19** was recrystallized from $CHCl_3$–heptane (1 : 2) (yield 45%). mp 172–175 °C. Calc. for $C_{30}H_{35}BCuN_8P$: C, 58.8; H, 5.8; N, 18.3. Found: C, 58.9; H, 6.0; N, 18.2%.

Compound 20. *Method (i).* Similarly to compound **1** using CuCl (0.099 g, 1 mmol), (cy)$_3$P (0.280 g, 1 mmol) and K[B(mpz)$_4$] (0.374 g, 1 mmol) in CH_3CN (50 ml) at 298 K. Compound **20** was recrystallized from benzene, Et_2O and heptane (yield 67%). mp 225–228 °C. Calc. for $C_{34}H_{53}BCuN_8P$: C, 60.1; H, 7.9; N, 16.5. Found: C, 60.1; H, 7.8; N, 16.4%.

Method (ii). To a benzene solution of compound **13** (0.660 g, 1 mmol), (cy)$_3$P (0.560 g, 2.0 mmol) was added. After 2 days the solvent was removed with a rotary evaporator. Et_2O (50 ml) was added. The suspension was filtered and the organic layer dried on Na_2SO_4, filtered and concentrated under reduced pressure. A colorless precipitate was filtered off and washed with heptane. Crystallization from CH_2Cl_2–light petroleum gave complex **20** as a microcrystalline solid in 60% yield.

Structure determinations

Full spheres of CCD area-detector diffractometer data were measured at *ca.* 153 K (Bruker AXS instrument, ω scans, $2\theta_{max} = 58°$; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å) yielding $N_{t(otal)}$ reflections, reducing to N unique (R_{int} quoted) after 'empirical'/multiscan absorption correction, N_o with $F > 4\sigma|F|$ being used in the full matrix least squares refinements, refining anisotropic thermal parameter forms for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values. Conventional residuals R, R_w (weights $(\sigma^2(F) + 0.0004(F^2))^{-1}$) are quoted at convergence on $|F|$. Computation used the XTAL 3.4 program system,[25] neutral atom complex scattering factors being employed. Pertinent results are given below and in the Figures and Tables. Individual variations, idiosyncrasies, difficulties are described as 'variata'.

Compound 2. $C_{32}H_{34}BCuN_4P_2$, $M = 611.0$, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 9.882(1)$, $b = 10.560(2)$, $c = 16.301(2)$ Å, $\alpha = 77.826(2)$, $\beta = 79.893(2)$, $\gamma = 66.779(2)°$, $V = 1520._0$ Å^3, D_c $(Z = 2) = 1.33_5$ g cm^{-3}, $\mu_{Mo} = 8.5$ cm^{-1}; specimen, 0.65 × 0.40 × 0.20 mm, 'T'$_{min,max} = 0.74$, 0.90, $N_t = 17049$, $N = 7331$ ($R_{int} = 0.015$), $N_o = 6563$, $R = 0.027$, $R_w = 0.041$, $|\Delta\rho_{max}| = 0.34(4)$ e Å^{-3}.

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

Compound 4. $C_{30}H_{31}BCuN_6P{\cdot}0.5CHCl_3$, $M = 640.6$, trigonal, space group $P\bar{3}c1$ ($D_{3d'}^4$, no. 165), $a = 12.720(1)$, $c = 22.033(2)$ Å, $V = 3087$ Å^3, D_c $(Z = 3) = 1.37_8$ g cm^{-3}, $\mu_{Mo} = 9.2$ cm^{-1}, specimen 0.23 × 0.16 × 0.12 mm, 'T'$_{min,max} = 0.65$, 0.86, $N_t = 36290$, $N = 2738$ ($R_{int} = 0.049$), $N_o = 2065$, $R = 0.062$, $R_w = 0.074$, $|\Delta\rho_{max}| = 1.29(8)$ e Å^{-3}.

Variata. Substantial difference map residues were modelled in terms of chloroform of solvation, disordered about a crystallographic 3 axis; site occupancies for C, Cl(1,2) 0.5, 0.5, 2/3.

Compound 6. $C_{22}H_{23}BCuN_6P$, $M = 476.8$, orthorhombic, space group $Pbca$ (D_{2h}^{15}, no. 61), $a = 11.384(1)$, $b = 19.052(1)$, $c = 20.467(2)$ Å, $V = 4439$ Å^3, D_c $(Z = 8) = 1.42_7$ g cm^{-3}, $\mu_{Mo} = 12.9$ cm^{-1}, specimen 0.42 × 0.22 × 0.20 mm, 'T'$_{min,max}$ = 0.72, 0.86, $N_t = 51559$, $N = 5747$ ($R_{int} = 0.025$), $N_o = 4785$, $R = 0.028$, $R_w = 0.040$, $|\Delta\rho_{max}| = 0.63(7)$ e Å^{-3}.

Compound 9. $C_{28}H_{35}BCuN_6P$, $M = 561.0$, orthorhombic, space group $Pbca$, $a = 14.479(2)$, $b = 18.019(3)$, $c = 21.808(4)$ Å, $V = 5689$ Å^3, D_c $(Z = 8) = 1.31_0$ g cm^{-3}, $\mu_{Mo} = 8.5$ cm^{-1}, specimen 0.70 × 0.40 × 0.07 mm, 'T'$_{min,max} = 0.64$, 0.84, $N_t = 66048$, $N = 7365$ ($R_{int} = 0.051$), $N_o = 5820$, $R = 0.036$, $R_w = 0.046$, $|\Delta\rho_{max}| = 0.50(9)$ e Å^{-3}.

Compound 13. $C_{34}H_{35}BCuN_8P$, $M = 661.0$, triclinic, space group $P\bar{1}$, $a = 12.405(2)$, $b = 12.621(2)$, $c = 12.948(3)$ Å, $\alpha = 66.897(3)$, $\beta = 66.169(3)$, $\gamma = 67.181(3)°$, $V = 1641._1$ Å^3, D_c $(Z = 2) = 1.33_8$ g cm^{-3}, $\mu_{Mo} = 7.5$ cm^{-1}, specimen cuboid, 0.1 mm, 'T'$_{min,max} = 0.81$, 0.93, $N_t = 19220$, $N = 8216$ ($R_{int} = 0.038$), $N_o = 5854$, $R = 0.043$, $R_w = 0.047$, $|\Delta\rho_{max}| = 1.3(2)$ e Å^{-3}.

Compound 17. $C_{37}H_{41}BCuN_8P$, $M = 703.1$, monoclinic, space group $P2_1/n$ (C_{2h}^5, no. 14, variant), $a = 11.2796(8)$, $b = 15.910(1)$, $c = 19.798(2)$ Å, $\beta = 100.523(1)°$, $V = 3493$ Å^3, D_c $(Z = 4) = 1.33_7$ g cm^{-3}, $\mu_{Mo} = 7.0$ cm^{-1}, specimen 0.6 × 0.3 × 0.12 mm, 'T'$_{min,max} = 0.76$, 0.93, $N_t = 40928$, $N = 8831$ ($R_{int} = 0.033$), $N_o = 6649$; $R = 0.041$, $R_w = 0.052$, $|\Delta\rho_{max}| = 0.6(1)$ e Å^{-3}.

Compound 20. $C_{34}H_{53}BCuN_8P$, $M = 679.2$, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 12.736(2)$, $b = 15.229(2)$, $c = 18.834(2)$ Å, $\beta = 105.386(2)$, $V = 3522$ Å^3, D_c $(Z = 4) = 1.28_1$ g cm^{-3}, $\mu_{Mo} = 7.0$ cm^{-1}, specimen 0.3 × 0.2 × 0.15 mm, 'T'$_{min,max} = 0.45$, 0.83, $N_t = 39176$, $N = 8951$ ($R_{int} = 0.065$), $N_o = 6791$, $R = 0.040$, $R_w = 0.046$, $|\Delta\rho_{max}| = 0.8(1)$ e Å^{-3}.

Variata. $(x, y, z, U_{iso})_H$ were refined. The structure is isomorphous with its silver(I) counterpart[21] and was refined in the same cell and co-ordinate setting.

CCDC reference number 186/2099.

See http://www.rsc.org/suppdata/dt/b0/b003613g/ for crystallographic files in .cif format.

Results and discussion

Synthesis

The interaction between a tertiary phosphine R_3P (R = Ph, *o*-, *m*-, or *p*-tolyl, Bn or cy) or RPh_2P (R = Me or Et), copper chloride and potassium (or sodium) salts of bis-, tris- or tetrakis-(pyrazolyl)borate in acetonitrile or in methanol at room temperature readily gives the complexes **1**–**20** in high yield, in accordance with the following general eqn. (1). Only

$$\mathrm{CuCl} + \mathrm{M[H}_n\mathrm{B(pz)}_{4-n}] + x\mathrm{PR}_3 \xrightarrow{\text{Solvent}} \underset{\mathbf{1\text{–}20}}{[\mathrm{Cu(H}_n\mathrm{B(pz)}_{4-n})(\mathrm{PR}_3)_x]} + \mathrm{MCl} \quad (1)$$

1 : 1 adducts are obtained by using sterically hindered $(C_6H_4\text{-}Me\text{-}o)_3P$, even if dihydrobis(pyrazolyl)borate is employed as the anionic N_2-donor ligand, an 'unsaturated' three-co-ordinate copper(I) centre being obtained. Alternatively, with Bn_3P, 2 : 1 adducts (complexes **10** and **14**) are obtained, even when potentially tridentate tetrakis(pyrazolyl)borates are used. It is worth noting that the tribenzylphosphine derivatives **3**, **7**, **10** and **14** can be prepared more efficiently by using as starting materials $[CuBr(Me_2S)]$ or $[Cu(C_6H_6)_{0.5}(O_3SCF_3)]_2$. In fact, it seems that it is only in the presence of a stabilized copper(I) acceptor that Bn_3P is not rapidly oxidized, as already observed.[26] All of the colorless compounds **1**–**20** are soluble in $CHCl_3$, acetone and DMSO in which they are non-electrolytes. However in $CHCl_3$ a non-ionic dissociation equilibrium such as that proposed in eqn. (2) appears likely also on the basis of

$$[\mathrm{Cu(H}_n\mathrm{B(pz)}_{4-n}\mathrm{)(PR}_3)_x] \rightleftharpoons [\mathrm{Cu(H}_n\mathrm{B(pz)}_{4-n}\mathrm{)(PR}_3)_{x-1}] + \mathrm{PR}_3 \quad (2)$$

vaporimetric molecular determination, the ratio between calculated and vaporimetric molecular weight being in the order of 0.60–0.80 at concentrations in the range 0.07–0.10% w/w.[27]

We have observed that $CHCl_3$ solutions of compounds **1**–**20** generally decompose after 36 h giving a blue coloration. From time-dependent NMR studies ($CDCl_3$ solution) the following order of stability emerges: $[B(pz)_4]^- > [HB(pz)_3]^- > [H_2B(pz)_2]^-$; $Ph_3P \approx (p\text{-}MeC_6H_4)_3P > (m\text{-}MeC_6H_4)_3P \approx MePh_2P > EtPh_2P > (o\text{-}MeC_6H_4)_3P > (cy)_3P > Bn_3P$. Further examination of the products formed in solution after 36–48 h suggests that decomposition of these complexes occurs in two stages: first, breaking of the copper(I)–phosphine bond with consequent formation of the well known dinuclear copper(I) complexes,[28] followed by disproportionation of these to copper metal and the known copper(II) complexes (eqns. (3) and (4)).[29] By

$$2\,[\mathrm{Cu(H}_n\mathrm{B(pz)}_{4-n}\mathrm{)(PR}_3)] \rightleftharpoons [\mathrm{Cu(H}_n\mathrm{B(pz)}_{4-n}]_2 + 2\,\mathrm{PR}_3 \quad (3)$$

$$[\mathrm{Cu(H}_n\mathrm{B(pz)}_{4-n})_2] \xrightarrow{\text{Solvent}} [\mathrm{Cu(H}_n\mathrm{B(pz)}_{4-n})_2] + \mathrm{Cu} \quad (4)$$

addition of a large excess of phosphine to the $CHCl_3$ solutions the complexes **1**–**11** are partially recovered, confirming that in solution equilibrium (3) is operating.

As previously observed in the case of analogous silver(I) complexes,[21] tricyclohexylphosphine $(cy)_3P$ interacts with derivative **13** completely displacing the Ph_3P from the copper(I) center and yielding the complex **20**, consistent with the greater basicity of $(cy)_3P$ with respect to Ph_3P, (eqn. (5)). It is interesting

$$[\mathrm{Cu((mpz)_3B(mpz))}] + (\mathrm{cy})_3\mathrm{P} \xrightarrow{\mathrm{Et_2O}} [\mathrm{Cu((mpz)_2B(mpz)_2)(P(cy)_3)}] + \mathrm{Ph_3P} \quad (5)$$

that in this reaction the displacement of Ph_3P is accompanied by a change in the co-ordination mode of the tetrakis(pyrazolyl)borate from κ^3 to κ^2, accounting for this apparent anomaly in stability.

Alternatively compounds **1**–**20** may be also obtained from the reaction of $[Cu(O_2NO)(PR_3)_2]$ with $M[H_nB(pz)_{4\text{-}n}]$ in MeOH. This reaction is not only metathetic, but implies disruption of the chelation of the bidentate O_2NO group and in the case of derivatives **1**, **3**–**9**, **11**–**13**, **15**–**17**, **19** and **20** also the displacement of one phosphine ligand from the copper(I) co-ordination sphere, eqn. (6).

$$[\mathrm{Cu(O_2NO)(PR_3)_2}] + \mathrm{M[H}_n\mathrm{B(pz)}_{4-n}] \xrightarrow{\mathrm{MeOH}} [\mathrm{Cu(H}_n\mathrm{B(pz)}_{4-n}\mathrm{)(PR}_3)_{2-x}] + \mathrm{MNO_3} + x\mathrm{Ph_3P} \quad (6)$$

The attempted reactions between one equivalent of compounds **1**, **3**, **7**, **10** and **13** and two or more equivalents of imidazole, pyrazole or 1,10-phenanthroline were unsuccessful, the starting material always being recovered.

Spectroscopy

The infrared spectra show all of the bands required by the presence of the organic nitrogen donor and the phosphine ligand. For the derivatives of $(m_2pz)_3BH$ and $(pz)_3BH$ **3**–**9** the BH stretch generally appears as a single peak in the regions 2400–2500 and 2400–2500 cm^{-1} respectively. These bands are not significantly shifted upon co-ordination. For the derivatives of $(pz)_2BH_2$ **1** and **2** the BH stretches exhibit a more complex structure, four absorptions being detected. Although only two BH stretching modes would be expected, the presence of both ^{10}B and ^{11}B in natural boron results in a multiplicity of bands at 2419, 2372, 2230 and 2211 cm^{-1} for derivative **1**, and at 2399, 2343, 2294 and 2274 cm^{-1} for **2**. These bands are shifted to higher frequency with respect to the same absorptions observed for free dihydrobis(pyrazolyl)borate ligands. In the far-IR spectra of all derivatives **1**–**20** we assigned, on the basis of a previous report on phosphine copper(I) derivatives,[30] the broad absorptions near 500 cm^{-1} and those at 450–400 cm^{-1} to Whiffen's y and t vibrations, respectively, whereas some bands at *ca.* 350–250 cm^{-1}, similar to those described for some metal(I) azolato derivatives,[31] are tentatively assigned to ν(Cu–N) vibrations.

The room-temperature ^1H NMR spectra of derivatives **1**–**19** exhibit similar signals for the protons of the pyrazolyl groups suggesting highly fluxional species with either a rocking motion of the triorganophosphinecopper(I) moieties between the two, three (or four) nitrogen atoms of the poly(pyrazolyl)borate ligand or complete dissociation and re-association of the pyrazolyl nitrogens which, in the case of **1**–**12**, occurs rapidly, even at low temperature. In fact, on cooling the $CDCl_3$ solutions of **1**–**12** no additional signals appeared.

The $(mpz)_4B^-$ complexes **13**–**19** show a different behaviour: in their ^1H NMR spectra at 223 K each pyrazolyl resonance splits into two with 3:1 integrated intensity, indicating that these species are fluxional at room temperature, but not at 223 K. At this temperature three of the four pyrazolyl groups appear to be co-ordinated to copper as is likely in a $PCu(N_3)$ environment. A different behaviour has been found for derivative **20** which is not fluxional at room temperature. In addition, in the ^1H NMR spectrum of **20** each pyrazolyl resonance splits into two with 2:2 integrated intensity, suggesting that only two of the four pyrazolyl groups are co-ordinated as is likely in a $PCu(N_2)$ environment.

The difference between $B(mpz)_4{}^-$ and $B(pz)_4{}^-$ copper(I) derivatives is presumably steric in origin and arises from the nature of the boron containing ligand. In fact the $(mpz)_4B^-$ group is sterically very demanding, the methyl groups nearest the metal co-ordinating nitrogens presumably interfering with the fourth ligand as in the silver complexes. For this reason the rocking motion of the triorganophosphinecopper(I) moieties between the two, three or four nitrogen atoms of the poly(pyrazolyl)borate ligand and/or the complete rapid dissociation and re-association of the pyrazolyl nitrogens is probably forbidden at room temperature. The two different signals found for the Me protons of $(C_6H_4Me\text{-}o)_3P$ in the ^1H NMR spectrum of **4** suggest inequivalence of the phenyl rings due to restricted rotation of the aryl groups around the P–C bond axis, consistent with the bulkiness of the phosphine moiety.

The metallacycle of compound **2** may be subject to boat inversion as already noted.[32] In principle either the boron-bonded hydrogens or the phosphorus atoms may be used as a probe for fluxionality, since inversion makes them inequivalent and two sets of signals should be observed. The ^{31}P signals, at variance with the BH ones, which are extremely broad (*ca.* 1.0 ppm), may serve this purpose. In the ^{31}P NMR spectrum of **2** only one peak is observed indicating that, unless there is fortuitous synchronicity, boat inversion is operative at room temperature.[32]

The room temperature ^{31}P NMR spectra of complexes **1**–**20** show always a single broad resonance, ascribed to some fluxional behaviour in these complexes. Every free phosphine appears upfield of its corresponding copper(I) complex, $\Delta(\delta^{31}P) = (\delta^{31}P)_{complex} - (\delta^{31}P)_{ligand}$, the difference in shift between each free phosphine and corresponding copper complex being of the order of 0–14.5 ppm. The shifts are always smaller with respect to those observed for the analogous silver(I) complexes,[20,21] consistent with greater instability in solution of **1**–**20** with respect to their analogous silver(I) counterparts,[20,21] and the occurrence of rapid ligand exchange as in eqn. (2). A variable temperature study was performed on selected complexes, lowering the temperature of the sample tube from 293 to 193 K in approximately 10 K decrements: at 250 K the broad resonance generally splits into two or more

Table 1 Selected geometries (distances in Å, angles in °) for $[Cu((pz)_2BH_2)(PMePh_2)_2]$ **2**

Cu–P(1)	2.2480(5)	Cu–P(1′)	2.2730(5)
Cu–N(12)	2.045(1)	Cu–N(22)	2.073(1)
B(1)–N(11)	1.559(2)	B(1)–N(21)	1.551(2)
B(1)–H(1a)	1.13(2)	B(1)–H(1b)	1.11(2)
P(1)–Cu–P(1′)	115.48(2)	N(12)–Cu–N(22)	90.47(5)
P(1)–Cu–N(12)	113.06(3)	P(1′)–Cu–N(12)	113.61(4)
P(1)–Cu–N(22)	109.59(3)	P(1′)–Cu–N(22)	111.94(3)
N(11)–B(1)–N(21)	109.0(1)	H(1a)–B(1)–H(1b)	117(1)
B(1)–N(11)–N(12)	120.6(1)	B(1)–N(21)–N(22)	121.1(1)
B(1)–N(11)–C(15)	129.8(1)	B(1)–N(21)–C(25)	129.6(2)
Cu–N(12)–N(11)	118.65(8)	Cu–N(22)–N(21)	117.64(9)
Cu–N(12)–C(13)	135.0(1)	Cu–N(22)–C(23)	135.9(1)
Torsion angles (carbon atoms denoted by number only)			
Cu–P(1)–111–112	−151.6(2)	Cu–P(1′)–111′–112′	−148.5(1)
Cu–P(1)–121–122	−149.2(1)	Cu–P(1′)–121′–122′	31.5(1)
Out of plane deviations			
δCu[pz(1)]	0.020(2)	δCu[Pz(2)]	0.080(3)
δB[Pz(1)]	0.040(3)	δB[Pz(2)]	0.006(3)

broad resonances, one of these signals often being due to the free triorganophosphine, which rapidly converts into its oxidized form.

As previously observed, the ^{31}P NMR spectra of our complexes showed a shift of the signals to lower field as the number of phosphine ligands increased in accordance with a smaller shielding of this nucleus. This is likely due to reduction in the π contribution to the Cu–P bond as the number of phosphines increases. The ^{31}P chemical shift is a function of both cone angle and σ donicity of the phosphorus donor and seems to be also a function of the steric and electronic properties of the poly(pyrazolyl)borate donor: in fact δ is always greater for derivatives of $EtPh_2P$ and $MePh_2P$, which, for example, are more basic and less sterically hindered than other Ar_3P ligands.

Structure determinations

The structurally authenticated arrays fall into three different types: (a) *bis(unidentate phosphine ligand)(bidentate pyrazolate)copper(I)*, with a four-co-ordinate $P_2Cu(N_2)$ co-ordination sphere, (b) *(unidentate phosphine)(tridentate pyrazolate)-copper(I)*, with a four-co-ordinate $PCu(N_3)$ co-ordination sphere, (c) *(unidentate phosphine)(bidentate pyrazolate)-copper(I)*, with a three-co-ordinate $PCu(N_2)$ co-ordination sphere, all neutral complexes. For type (a) only one example has been characterized, namely $[Cu((pz)_2BH_2)(PMePh_2)_2]$, **2**, for which one molecule comprises the asymmetric unit of the structure, the $P_2Cu((pz)_2BH_2)$ component of the array approximating quite nicely to quasi-*m* symmetry (Fig. 1; Table 1), with the greatest departures being found among the four P–Cu–N angles (range: 109.59(3)–113.61(4)°), presumably in response to minor perturbations arising from lattice forces, and/or the ultimate breaking of that symmetry by the phosphine substituent dispositions, whereby the methyl groups lie to the same side of the putative mirror plane. A variety of other P_2Cu(bidentate N_2) arrays have been characterized, generally involving planar aromatic N_2-donors with associated five-membered chelate rings of much smaller bite than the present, wherein the chelate ring is six-membered and non-planar, being a quasi-boat array with Cu and B at the prows. For comparative purposes, the $[Cu(PPh_3)_4]^+$ array provides a homoleptic P_4 co-ordination environment datum for Cu–P of dubious value, substantial differences therein (2.524(6), 2.605(11) (× 3) (perchlorate);[33] 2.465(2), 2.566(2) (× 3) Å (hexafluorophosphate)[34]) being suggestive of steric crowding,[35] not found in the $[Cu(PMe_3)_4]^+X^-$ arrays[34] where the distances are much shorter and much more tightly ranged (2.254(4)–2.277(3) (X = Cl); 2.266(4)–2.271(7) (X = Br); 2.275(2)–2.282(4) Å (X = I)), and seemingly relaxed in counterpart silver complexes where the range is much closer in isomorphous species (Ag–P 2.650(2), 2.668(5) (× 3) (perchlorate); 2.647(2), 2.67(3) Å (hexafluorophosphate)) and less elevated above the values found for the copper analogues than perhaps might otherwise be expected. The present values certainly lie nearer the $[Cu(PMe_3)_4]^+$ datum, as also do those for $[Cu(bpy)(PPh_3)_2]^+$ and $[Cu(py)_2(PPh_3)_2]^+$ (bpy = 2,2′-bipyridine, py = pyridine) in their perchlorate salts (Cu–P 2.246(3), 2.256(3); 2.271(4), 2.295(3); Cu–N 2.056(8), 2.113(9); 2.102(7), 2.115(8) Å respectively), despite rather different P–Cu–P and N–Cu–N angles (present: 115.48(2); 90.47(5)°; bpy complex: 125.4(1), 79.6(4); $(py)_2$ complex: 115.85(9), 101.5(2)°). The closeness of the co-ordinated copper atom to the pyrazolate planes (Table 1), together with the generally symmetrical $P_2Cu((pz)_2BH_2)$ array, suggests little strain in the present array. The structure is nicely precise, with (X-ray) hydrogens quite well determined even without neutron data, and it is of interest that the H–B–H angle (117(1)°) is seemingly elevated somewhat above the tetrahedral value. At present, there appear to be no counterpart silver arrays of this or similar stoichiometry structurally characterized.

This is not the case for arrays of the form (b) above, $[PM((pz)_3B(X))]$, for which a considerable array of silver(I) complexes has structurally been characterized,[35] and for which we present here a similar volume of determinations for adducts of copper(I): **4**, **6**, **9**, **13**, **17**; despite the use of similar ligands in the two sets of studies, a common stoichiometry and co-ordination environment has been achieved only for $[M((mpz)_3B(mpz))(PPh_3)]$, the two complexes M = Cu (**13**) or Ag not being isomorphous. Common stoichiometries for M = Cu or Ag are also defined thus for $[M(B(mpz)_4)(PR_3)]$, R = *p*-tolyl or cyclohexyl, but in the *p*-tolyl adducts whereas the metal is four-co-ordinate $[PM((mpz)_3B(mpz))]$ in the M = Cu adduct (**17**), it is three-co-ordinate $[PM((mpz)_2B(mpz)_2)]$ in the M = Ag array. For R = cy, both M = Cu (**20**) or Ag adducts take the form $[M((mpz)_2B(mpz)_2)(P(cy)_3)]$, with three-co-ordinate metal, and will be discussed in a separate class below.

Details of the geometries of the present $PCu(N_3)$ arrays are presented in Table 2. They range from the highly symmetrical $[Cu((pz)_3BH)\{P(C_6H_4Me\text{-}o)_3\}]$, in which the molecule lies disposed about a crystallographic 3 axis, with P, Cu, B lying on that axis, and one third of the molecule comprising the asymmetric unit of the structure, to the other complexes where, with one molecule devoid of any crystallographic symmetry comprising the asymmetric unit, any approach to the 3-fold ideal is dependent upon the vagaries of intra- and intermolecular forces present. Superimposed on this may be a tendency to approach a lower co-ordination number, despite the increased size of the metal atom. Despite the limited congruence between these series for these two metals, the present array of copper(I) complexes, like their previously studied silver(I) analogues,[35] encompasses a diversity of ligand types wherein the relative consequences of the presence or otherwise of sterically active substituents may be examined. Thus the steric profile offered by mpz (and m_2pz, which, in the complexes defined here, appears to be little different in all essential respects) species in co-ordinating about a metal will differ from that of the parent pz, as Ph_2MeP, Ph_3P, $(o\text{-}MeC_6H_4)_3P$ also offer a progression in respect of steric bulk, with various ligand combinations possible. Despite this variety, the various changes wrought appear to have little impact on the nature of the species obtained; across the array of complexes of Table 2, Cu–P varies only trivially within the range 2.1472(5)–2.165(1) Å, ⟨Cu–N⟩, subject to more diversity within a given species in the absence of crystallographic constraint being 2.07(2)–2.08(4) Å. These may be compared with counterpart ranges in the analogous silver(I) series (see also Table 3) wherein Ag–P

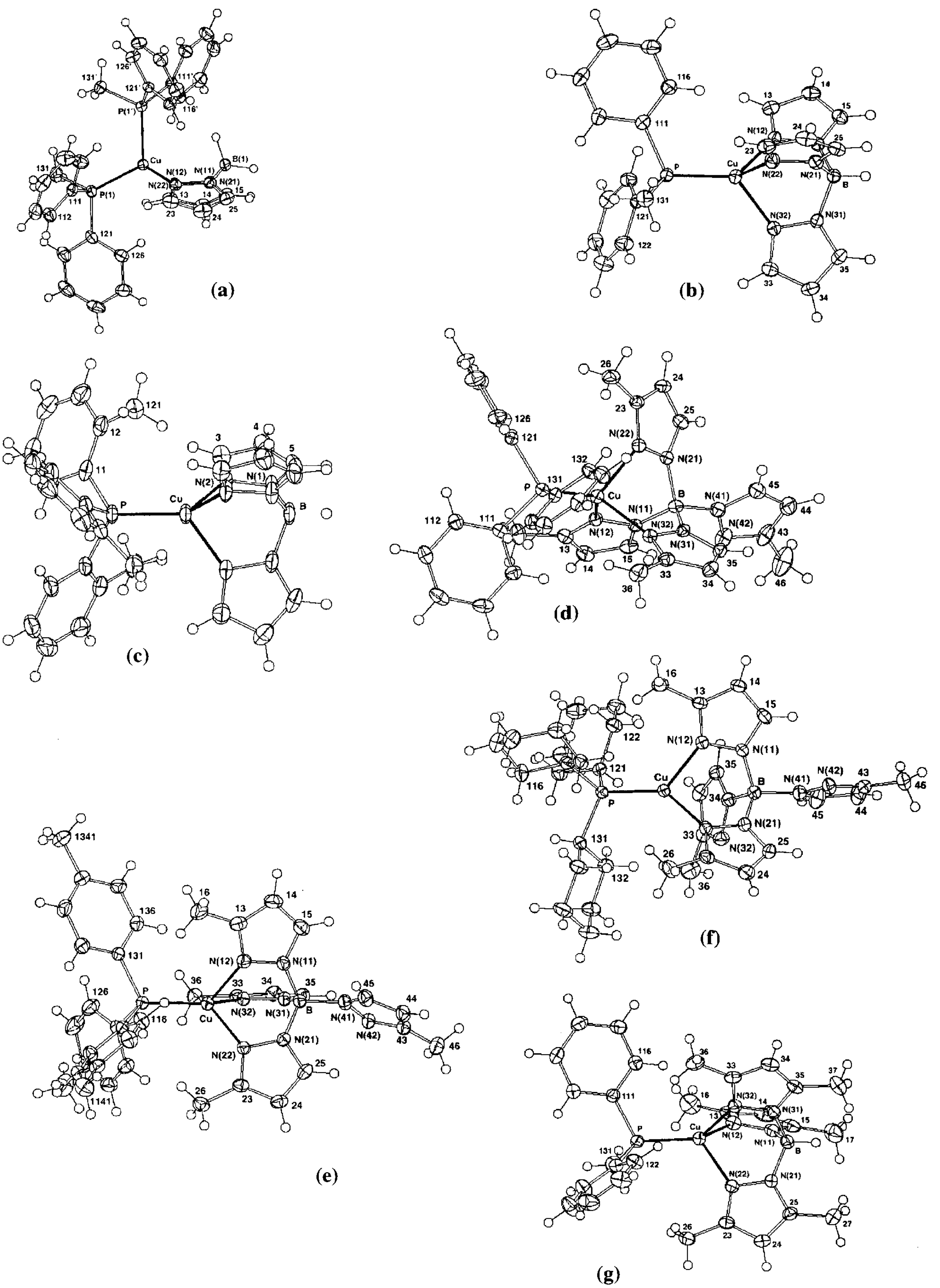

Fig. 1 Individual molecular projections, showing 50% displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. (a) $[Cu((pz)_2BH_2)(PMePh_2)_2]$ **2**, normal to the P_2Cu plane; (b) $[Cu((pz)_3BH)(PMePh_2)]$ **6**; (c) $[Cu((pz)_3BH)\{P(C_6H_4Me\text{-}o)_3\}]$ **4**; (d) $[Cu(mpz)_3B(mpz)(PPh_3)]$ **13**; (e) $[Cu(mpz)_3B(mpz)\{P(C_6H_4Me\text{-}p)_3\}]$ **17**; (f) $[Cu((mpz)_2B(mpz)_2)(P(cy)_3)]$ **20**; (g) $[Cu((m_2pz)_3BH)(PMePh_2)]$.

range between 2.328(2) and 2.368(2) and ⟨Ag–N⟩, 2.325(3)–2.358(7) Å. Notable in this comparison is the change in relativity between M–P and M–N, Cu–P clearly longer than Cu–N, Ag–P and Ag–N very similar. This latter change may be a reflection of relative strengths of interaction as influenced by the diminution in 'bite' of the tridentate consequent on increase

Table 2 $PCuN_3$ core environments (distances in Å, angles in °)

Compound L_p L_N	**6** Ph_2MeP $(pz)_3BH$	**4** $(o\text{-}MeC_6H_4)_3P$ $(pz)_3BH$	**13** Ph_3P $(mpz)_4B$	**17** $(p\text{-}MeC_6H_4)_3P$ $(mpz)_4B$	**9** Ph_2MeP $(m_2pz)_3BH$
Cu–P	2.1472(5)	2.158(1)	2.165(1)	2.1611(7)	2.164(6)
Cu–N(12)	2.065(1)	2.070(3)	2.091(2)	2.134(2)	2.090(2)
Cu–N(22)	2.100(1)		2.099(2)	2.038(2)	2.069(2)
Cu–N(32)	2.051(1)		2.068(2)	2.083(2)	2.093(2)
<Cu–N>	2.07(2)	2.070(3)	2.08(1)	2.08(4)	2.08(1)
B–N(11)	1.547(2)	1.539(4)	1.549(4)	1.551(4)	1.550(3)
B–N(21)	1.546(2)		1.548(4)	1.556(3)	1.546(3)
B–N(31)	1.545(2)		1.561(4)	1.544(3)	1.548(2)
⟨ ⟩	1.546(1)		1.551(8)	1.550(6)	1.548(2)
B–N(41)			1.526(6)	1.524(3)	
P–Cu–N(12)	127.15(4)	125.05(7)	126.60(8)	122.87(6)	124.24(5)
P–Cu–N(22)	119.91(4)		125.01(8)	125.90(5)	120.49(4)
P–Cu–N(32)	127.25(4)		123.86(8)	126.63(6)	128.99(4)
N(12)–Cu–N(22)	89.39(5)	90.3(1)	90.12(9)	89.76(7)	92.94(6)
N(12)–Cu–N(32)	92.01(5)		89.47(9)	90.89(8)	88.81(6)
N(22)–Cu–N(32)	90.02(5)		90.9(1)	89.85(7)	91.22(6)
N(11)–B–N(21)	108.4(1)	109.1(3)	108.1(2)	111.3(2)	109.4(2)
N(11)–B–N(31)	109.6(1)		109.4(2)	106.8(2)	109.0(2)
N(21)–B–N(31)	109.4(1)		109.4(2)	109.2(2)	110.0(1)
Out of (pz)plane deviations, δCu					
δCu[pz(1)]	0.068(3)	0.170(7)	0.314(5)	0.890(4)	0.342(3)
δCu[pz(2)]	0.116(3)		0.729(5)	0.191(4)	0.065(3)
δCu[pz(3)]	0.032(3)		0.399(5)	0.005(4)	0.243(3)
δB[pz(1)]	0.087(3)	0.033(8)	0.073(5)	0.176(4)	0.035(3)
δB[pz(2)]	0.045(3)		0.046(5)	0.230(4)	0.010(3)
δB[pz(3)]	0.005(3)		0.072(5)	0.051(4)	0.057(3)
Torsion angles (carbon atoms denoted by number only)					
Cu–P–111–112	176.8(1)	−47.4(3)	−141.6(2)	−134.7(2)	−177.3(1)
Cu–P–121–122	92.0(1)		−137.1(3)	53.8(2)	33.1(2)
Cu–P–131–132			48.7(3)	−149.0(2)	

Table 3 PMN_3 comparative geometries (distances in Å, angles in °; M = Cu or Ag). Values for M = Ag (ref. 21) are italicized below those for M = Cu

L_p[a] L_N[a]	$(o\text{-}MeC_6H_4)_3P$ $(pz)_3BX$	Ph_3P $(mpz)_3BX$	$(m/p\text{-}MeC_6H_4)_3P$ $(mpz)_3BX$
M–P	2.158(1)	2.165(1)	2.1611(7)
	2.368(2)	*2.328(2)*	*2.353(3)*
⟨M–N⟩	2.070(3)	2.08(1)	2.08(4)
	2.358(7)	*2.325(3)*	*2.33(3)*
⟨P–M–N⟩	125.05(7)	125(1)	125(2)
	131.6(1)	*130.77(9)*	*131(7)*
⟨N–M–N⟩	90.3(1)	90.1(6)	90.2(6)
	80.7(2)	*82.0(1)*	*81(1)*

[a] For the $(o\text{-}MeC_6H_4)_3P$ adducts, X is H for the copper(I) complexes, *pz* for the silver; for the Ph_3P adducts, mpz (both); for X = mpz, adducts have been obtained with $(p\text{-}MeC_6H_4)_3P$ for M = Cu and with $(m\text{-}MeC_6H_4)_3P$ for *M* = *Ag*.

in metal size, and/or more subtle electronic factor(s). The tris(pyrazolyl)boratemetal array for both metals exhibits a remarkable rigidity *vis-à-vis* the other parameters of the metal environment, and it may be that these other, more inherently flexible parameters act as a sponge for absorption of the effects of internal and external species interacting with that array: *e.g.* in Table 2, across the whole spectrum of complexes, parameters such as N–Cu–N, N–B–N, B–N, are remarkably closely ranged, generally at a very acceptable level of precision. Relative to the $(pz)_3$ array, the metal atom may here exhibit considerable deviations from the various pz planes, reflected where these are high, in Cu–N variability, as in $[Cu((mpz)_3B(mpz))\{P(C_6H_4\text{-}Me\text{-}p)_3\}]$ **17**; this latter observation may be pertinent in relation to the silver complexes, whereby, despite substantial adherence to the preceding comments, it is this particular example, common to both metal atoms, among the present where the co-ordination number changes on passing from copper to silver. There appear to be no other cogent steric or electronic reasons why this should occur in this particular case, and it may be that, for silver, the difference in energy between the two types is so delicately poised that the lattice array of the copper(I) complex, inherently distorted, is unsustainable for increased metal atom size (*etc.*) and a change to another form is precipitated.

As indicated here, type (c) *((unidentate phosphine)(bidentate pyrazolate)metal(I))* arrays are accessed more readily and seemingly more haphazardly for silver(I) as metal, being structurally defined for an even greater variety of phosphine/pyrazolate ligand combinations of the above type for that metal than for $PM(N_3)$ type arrays with it; clearly for M = Cu the $PM(N_3)$ form is prevalent, even for the bulkier ligands, and even though it is a smaller metal, whereas for silver $PM(N_2)$ begins to dominate. However, there is one particular phosphine ligand for which this form is found for both metals, in combination with $[B(mpz_4)]^-$ in both cases, in which an overwhelming steric imperative appears to dictate an array of type (c) for both, namely $P(cy)_3$, $[M((mpz)_2B(mpz)_2)(P(cy)_3)]$, the two arrays for M = Cu (**20**) or Ag being isomorphous.

Geometries for the two arrays are compared in Table 4, together with that of $[Ag((pz)_2BH_2)(P(cy)_3)]$, recently reported.[23] Here, again we find the difference in M–P, *cf.* M–N in an effectively planar PMN_2 array, diminished for M = Ag, *cf.* M = Cu; the present complex may further be compared with its silver(I) homologue and two further $[Ag((pz)_2BX_2)(P(cy)_3)]$ type adducts as is done in Table 4. Here we have three different ligand types in association with $(cy)_3P$ about the metal and it is of interest to compare the consequences of their combination

Table 4 Comparative geometries (distances in Å, angles in °) for [M((mpz)$_2$B(mpz)$_2$)(P(cy)$_3$)], M = Cu (**20**) or Ag. Values for the silver(I) complex [Ag(mpz)$_2$B(mpz)$_2$(P(cy)$_3$)] **A** are given following those for the copper(I) counterpart (**20**), followed in turn by the corresponding values for [Ag((m$_2$pz)$_2$BH$_2$)(P(cy)$_3$)] **B** and [Ag((pz)$_2$B(pz)$_2$)(P(cy)$_3$)] **C**

	20	**A**	**B**	**C**
M–P	2.1874(6)	2.333(3)	2.250(2)	2.351(2)
M–N(12)	2.044(2)	2.332(7)	2.250(2)	2.261(4)
M–N(22)	2.005(2)	2.206(7)	2.299(2)	2.297(3)
B–N(11)	1.549(3)	1.56(1)	1.554(4)	1.530(6)
B–N(21)	1.534(3)	1.55(1)	1.549(4)	1.561(6)
B–N(31)	1.538(3)	1.56(1)	—	1.524(6)
B–N(41)	1.526(3)	1.48(1)	—	1.524(6)
P–M–N(12)	126.62(6)	128.4(2)	146.08(5)	140.3(1)
P–M–N(22)	139.83(5)	146.7(2)	127.21(5)	134.45(9)
N(12)–M–N(22)	93.43(7)	84.9(3)	86.71(7)	84.9(1)
$\Sigma\hat{M}$	359.$_8$	360.$_0$	360.$_0$	359.$_7$
Dihedral angles				
N$_2$MP/pz(1)	39.75(2)	38.8(2)	43.27(9)	35.6(2)
N$_2$MP/pz(2)	43.52(5)	40.0(3)	46.28(9)	37.9(2)
pz(1)/pz(2)	57.51(9)	57.9(4)	65.7(1)	67.5(2)
Out of plane deviations				
δM/pz(1)	0.174(3)	0.09(2)	0.119(4)	0.259(0)
δM/pz(2)	0.027(3)	0.07(1)	0.009(4)	0.067(8)
Torsion angles (carbon atoms denoted by number only)				
M–P–111–112	−29(1)	−25.4(7)	−24.5(2)	3.1(6)
M–P–111–116	−157.1(2)	−157.3(6)	−151.9(1)	−159.8(4)
M–P–121–122	−58.9(2)	−58.5(7)	−58.2(2)	53.6(4)
M–P–121–126	172.8(1)	175.0(6)	174.7(2)	172.4(3)
M–P–131–132	−61.9(4)	−59.5(7)	−64.8(2)	−64.0(3)
M–P–131–136	59.8(3)	63.5(7)	56.7(2)	58.5(3)
B–N(11)–N(12)–M	9.9(2)	6.5(9)	10.0(3)	6.8(5)
B–N(21)–N(22)–M	1.6(2)	−2.2(9)	3.3(3)	−12.5(5)
N(21)–B–N(11)–N(21)	−63(2)	−64(1)	−75.3(3)	−64.6(5)
N(11)–B–N(21)–N(22)	56.3(2)	63(1)	64.6(6)	67.8(5)
N(22)–M–N(12)–N(11)	35.8(1)	36.6(6)	39.0(2)	33.0(3)
N(12)–M–N(22)–N(21)	−41.9(1)	−38.3(5)	−46.9(2)	−29.7(3)
N(22)–M–P–131	−9.7(1)	−10.3(4)	131.3(1)	30.2(2)

with the (cy)$_3$P moiety; we note that the present M = Cu adduct and its silver homologue, being isomorphous, might be expected to behave similarly, as indeed they do. The conformational variations of the (cy)$_3$P–M moiety have been described elsewhere.[36] Here, we find the dispositions in all of [Cu,Ag((mpz)$_2$B(mpz)$_2$)(P(cy)$_3$)], and [AgL(P(cy)$_3$)], L = (m$_2$pz)$_2$BH$_2$ or (pz)$_2$B(pz)$_2$, to be very similar, the 'plane' of one of the C$_6$ rings lying 'quasi-normal' to M–P and the other 'quasi-parallel'. Here, in the two examples, [AgL(P(cy)$_3$)], L = (mpz)$_2$B(mpz)$_2$ or (pz)$_2$B(pz)$_2$, the pendant carbon of the 'quasi-normal' ring lies approximately coplanar with N(22)AgP ($\tau_{\text{N-Ag-P-C}}$ −10.3(4), 30.2(2)° respectively). In the former compound, where that cyclohexyl group is confronted by a pyrazolate-methyl substituent, the contained P–Ag–N angle is considerable enlarged (146.7(2), *cf.* 128.4(2)°) with associated Ag–N shortened (2.206(7) (*cf.* 2.332(7) Å), as might be expected; in the latter compound, where the methyl is absent, this angle is now the smaller of the two (134.45(9), *cf.* 140.3(1)°), with associated Ag–N correspondingly enlarged (2.297(3), *cf.* 2.261(4) Å). It might also be noted that in the former compound the orientation of the cyclohexyl group in question correlates with the proximity of the methyl substituent of the pendant (*proto*-co-ordinating) pyrazolyl group. In the remaining compound (L = (m$_2$pz)$_2$BH$_2$), where there is no such pendant group with substituent, although the (cy)$_3$P ligand retains the same conformational array of its rings, it is rotated further about Ag–P so that the 'quasi-normal' ring is more nearly straddled by the pair of methyl substituents on the pyrazolyl groups. P–Ag–N are again seriously unsymmetrical (146.08(5), *cf.* 128.4(2)°) to the same degree as in the (mpz)$_2$B(mpz)$_2$ analogue, despite some presumed relief in steric strain, with concomitant asymmetry in Ag–N; consideration of the torsion angles in the B(N$_2$)$_2$Ag ring suggests the possibility of relaxation here, perhaps consequent on removal of the pendant unco-ordinated pyrazolate groups.

Conclusion

We have prepared and characterized a series of copper(I) phosphine complexes of poly(pyrazolyl)borates, employing X-ray crystallography and NMR spectroscopy to examine how the co-ordination environment is dependent on the cone angle and basicity of the triorganophosphine and on the steric and electronic properties of the poly(pyrazolyl)borate ligand. For example, we have observed 1:1 phosphine:copper(I) adducts always to be obtained when a tris(hydropyrazolyl)borate is employed as anionic ligand, independently of the nature of the phosphine, whereas both 1:1 and 2:1 phosphine:copper(I) adducts are possible with (dihydrobis(pyrazolyl))- and tetrakis(pyrazolyl)-borates. If the phosphine is sterically hindered (C$_6$H$_4$Me-*o*)$_3$P or P(cy)$_3$) a 1:1 adduct is likely, with the copper(I) centre achieving three-co-ordination through bidentate chelation of the ligand (κ^2), whereas phosphines less sterically hindered (such as MePh$_2$P) allow the attainment of 2:1 adducts. With the exception of Bn$_3$P, which, surprisingly, yields 2:1 adducts with copper(I) tetrakis(pyrazolyl)borate fragments, all the other triorganophosphines yield 1:1 adducts, with the copper centre four-co-ordinate through tridentate co-ordination (κ^3) of tris- or tetrakis-(pyrazolyl)borate ligands.

The stability of the complexes in solution is strongly dependent on the nature of both poly(pyrazolyl)borate and phosphine donors.

Finally we have also found that it is possible to displace trialkyl- and triaryl- phosphine from the copper(I) center with a more basic P-donor, but not with a neutral N-donor uni- (imidazole or pyrazole) or bi-dentate (1,10-phenanthroline), even if more basic than R_3P.

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