DALTON
FULL PAPER

Copper(I) coordination polymers and mononuclear copper(I) complexes built from poly(1,2,4-triazolyl)borate ligands and tri-organophosphines †

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

[a] *Dipartimento di Scienze Chimiche, Università degli Studi di Camerino, via S. Agostino 1, 62032 Camerino MC, Italy. E-mail: carlo.santini@unicam.it*
[b] *Department of Chemistry, The University of Western Australia, Crawley, W. A. 6009, Australia*

Received 4th January 2002, Accepted 6th March 2002
First published as an Advance Article on the web 24th April 2002

New copper(I) triorganophosphine derivatives $[Cu(R_3P)_n\{(tz)_2BH_2\}]$ and $[Cu(R_3P)_n\{(tz)_3BH\}]$ (n = 1 or 2) have been synthesised from the reaction of CuCl with PR_3 (R = phenyl, cyclohexyl, benzyl, *o*-, *m*-, or *p*-tolyl) or $PMePh_2$ and potassium dihydrobis(1,2,4-triazolyl)borate, $K[H_2B(tz)_2]$, or potassium hydrotris(1,2,4-triazolyl)borate, $K[HB(tz)_3]$. The complexes obtained have been characterized by elemental analyses and FT-IR in the solid state, and by NMR (^1H and $^{31}P\{^1H\}$) spectroscopy and conductivity measurements in solution. The solution data are consistent with partial dissociation of the sterically hindered complexes by way of breaking of Cu–P and Cu–N bonds. Single crystal structural characterizations were undertaken for several of them. The structurally authenticated arrays fall into four different types: (a) discrete mononuclear $[Cu(R_3P)_2\{(tz)_2BH_2\}]$ with a four-coordinate $CuP_2(N_2)$ coordination sphere, (b) one-dimensional polynuclear $[Cu(R_3P)\{(tz)BH_2(tz)\}]_{(\infty/\infty)}$ with a four-coordinate $CuP(N_3)$ coordination sphere due to coordination by way of both N(2) and N(4) in one of the heterocyclic rings, (c) discrete mononuclear $[Cu(R_3P)\{(tz)_3BH\}]$ with a $CuP(N_3)$ coordination sphere, (d) one-dimensional polynuclear $[Cu(R_3P)_2\{(tz)BH(tz)(tz)\}]_{(\infty/\infty)}$ with a four-coordinate $CuP_2(N_2)$ coordination sphere in which one of the ligand tz rings is uncoordinated and the other two bridge through N(4) to successive copper atoms.

Introduction

In recent years the use of scorpionate N_3-donor hydrotris(pyrazolyl)borate ligands has yielded indispensable precursors for more elaborate coordination and organometallic species,[1–3] this family of ligands having found important applications in all fields of bioinorganic, inorganic and organometallic chemistry.[4] By contrast, only a few poly(azolyl)borate complexes with azolyl groups other than pyrazole have been investigated, although it has been shown that the chemistry of poly(azolyl)-borate complexes may be critically dependent upon the pattern of ring substitution.[5] This aspect has induced several researchers to investigate the behavior of metal complexes of analogous ligand systems with modified steric and/or electronic properties, such as poly(tetrazolyl)borate,[6] poly(1,2,3-benzo-triazolyl)borate,[7] poly(2-sulfanyl-1-methylimidazolyl)borate[8] and poly(imidazolyl)borate ligands.[9]

Although a cobalt complex of hydrotris(1,2,4-triazolyl)-borate was reported by Trofimenko in 1967,[10] the chemistry of triazolylborate ligands has remained undeveloped. Two features of triazole-based ligands make them attractive candidates for further examination: *i*) they should be electron-withdrawing relative to their pyrazole-based counterparts and the properties of metal complexes should differ accordingly;[11] *ii*) the *exo* ring-nitrogen atoms of triazole-based ligands may bridge between metal centers, thereby creating coordination polymers with interesting solid-state structures and optical properties, as recently shown by Janiak.[12] Moreover, the exocyclic nitrogen atoms might take part in hydrogen-bond interactions assisting the formation of two-dimensional water-intercalation or water-layer clathrates,[13] thus leading to water soluble species.[14]

We have recently initiated an investigation into the structural and spectroscopic properties of mixed phosphine/N-donor derivatives of copper(I), silver(I) and gold(I).[8a,15] As a part of this study we have been interested in exploring complexes incorporating poly(azolyl)borate and phosphine ligands with different steric and electronic profiles. The different coordination characteristics of poly(triazolyl)borate species offer the prospect of new and interesting chemistry, paralleling that of pyrazolyl, benzotriazolyl and imidazolyl arrays.[16] We report here the synthesis, characterization and reactivity of some new metal complexes obtained from the interaction of dihydrobis(1,2,4-triazolyl)borate $[H_2B(tz)_2]^-$ and tris(1,2,4-triazolyl)borate $[HB(tz)_3]^-$ (Fig. 1) with CuCl and tertiary mono-phosphines, together with the crystal and molecular structures of some representative arrays by X-ray diffraction studies, and a comparison with structural data previously reported for analogous poly(pyrazol-1-yl)borate derivatives.

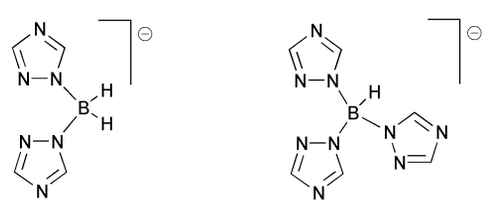

Fig. 1 Structure of the ligands employed in this work.

† Electronic supplementary information available: conductivity data for compounds **1**–**14**. See http://www.rsc.org/suppdata/dt/b2/b200200k/

Experimental

General procedures

All reactions were carried out under an atmosphere of dry oxygen-free dinitrogen, using standard Schlenk techniques and protected from light. All solvents were dried, degassed and distilled prior to use. Elemental analyses (C,H,N) were performed with a Fisons Instruments 1108 CHNS-O Elemental analyser. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin-Elmer System 2000 FT-IR instrument. ^1H and ^{31}P NMR spectra were recorded using a VXR-300 Varian spectrometer (300 MHz for ^1H, and 121.4 MHz for ^{31}P). The molecular weight measurements ($CHCl_3$) were performed at 40 °C with a Knauer KNA0280 vapor pressure osmometer calibrated with benzil. The electrical resistances of acetone or CH_2Cl_2 solutions, measured with a Crison CDTM 522 conductimeter, are supplied as ESI †.

Syntheses

Potassium or sodium salts of the donor hydrotris(1,2,4-triazolyl)borate, $[HB(tz)_3]^-$, and dihydrobis(1,2,4-triazolyl)-borate, $[H_2B(tz)_2]^-$, were prepared in accordance with the procedure first reported by Trofimenko.[1] KBH_4, CuCl, R_3P (R = Ph, Bn, *o*-tolyl, *m*-tolyl, *p*-tolyl and cy), $MePh_2P$ and 1,2,4-triazole were purchased from Aldrich and used without further purification. The compounds studied take the form $[Cu(R_3P)_n\{(tz)_2BH_2\}]$ (R_3 = Ph_3, n = 2, **1**; R_3 = Bn_3, n = 2, **2**; R_3 = *o*-$tolyl_3$, n = 1, **3**; R_3 = *m*-$tolyl_3$, n = 2, **4**; R_3 = *p*-$tolyl_3$, n = 2, **5**; R_3 = $MePh_2$, n = 2, **6**; R_3 = cy_3, n = 1, **7**), $[Cu(R_3P)_n\{(tz)_3BH\}]$ (R_3 = Ph_3, n = 1, **8**; R_3 = Bn_3, n = 1, **9**; R_3 = *o*-$tolyl_3$, n = 1, **10**; R_3 = *m*-$tolyl_3$, n = 2, **11**; R_3 = *p*-$tolyl_3$, n = 1, **12**; R_3 = $MePh_2$, n = 1, **13**; R_3 = cy_3, n = 1, **14**).

Compound 1. $K[H_2B(tz)_2]$ (0.188 g, 1.0 mmol) was added at room temperature to a methanol solution (50 ml) of CuCl (0.099 g, 1.0 mmol) and Ph_3P (0.525 g, 2 mmol). After the addition, the solution was stirred for 2 h. The colourless precipitate obtained was filtered off and washed with diethyl ether. Re-crystallisation from $CHCl_3$–petroleum ether (1 : 3, petroleum ether bp 35–60 °C) gave complex **1** as a micro-crystalline solid in 72% yield. mp 203–207 °C. ^1H NMR ($CDCl_3$, 293 K): δ 7.09 (s, 2H, 3- or 5-C*H*), 7.14–7.40 (m, 30H, C*H*), 8.10 (s, 2H, 3- or 5-C*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ −0.9 (s); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 218 K): δ −0.1 (s). IR (Nujol, cm^{-1}): 3080w (CH), 2404m (BH), 1580m (C=C + C=N), 524m, 511s, 505sh, 496s (Ar_3P), 444w, 434w, 420w, 400vw, 307vw, 280vw, 255vw. Anal. Found: C, 64.93; H, 5.21; N, 11.33. Calc. for $C_{40}H_{36}BCuN_6P_2$; C, 65.18; H; 4.92; N, 11.40%.

Compound 2. $K[H_2B(tz)_2]$ (0.188 g, 1.0 mmol) was added at room temperature to a methanol solution (50 ml) of CuCl (0.099 g, 1.0 mmol) and tribenzylphosphine Bn_3P (0.609 g, 2 mmol). After the addition, the solution was stirred for 2 h and subsequently the solvent was removed with a rotary evaporator. Chloroform (50 ml) was added. The suspension was filtered and the organic layer was 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-crystallisation from $CHCl_3$–diethyl ether–methanol (1 : 3 : 1) gave complex **2·2MeOH** as a microcrystalline solid in 60% yield. mp 163–168 °C. ^1H NMR ($CDCl_3$, 293 K): δ 2.87 (d, 12H, CH_2), 6.96 (s, 2H, 3- or 5-C*H*), 7.00–7.20 (m, 30H, C*H*), 8.03 (s, 2H, 3- or 5-C*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ −8.5 (sbr); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 218 K): δ −16.2 (sbr), −9.8 (s), −8.6 (sbr), −2.5 (s). IR (Nujol, cm^{-1}): 2401w (BH), 1597w, 1492m (C=C + C=N), 476m, 463m (Ar_3P), 420w, 320w, 304w, 278w, 266w, 213w. Anal. Found: C, 66.29; H, 6.12; N, 10.01. Calc. for $C_{47}H_{52}BCuN_6OP_2$; C, 66.16; H; 6.14; N, 9.85%.

Compound 3. Compound **3** was prepared similarly to compound **1**, by using CuCl (0.099 g, 1.0 mmol), *o*-$tolyl_3P$ (0.304 g, 1 mmol) and $K[H_2B(tz)_2]$ (0.188 g, 1.0 mmol) in CH_3CN–methanol (1 : 2) solution. Re-crystallisation from $CHCl_3$ gave complex **3** as a micro-crystalline solid in 55% yield. mp 243 °C dec. ^1H NMR ($CDCl_3$, 293 K): δ 2.49 (s, 9H, CH_3), 6.87–7.84 (mc, 14H, C*H* and 3- or 5-C*H*), 8.10 (sbr, 2H, 3- or 5-C*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ −17.7 (sbr); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 218 K): δ −19.2 (s), −29.1 (s). IR (Nujol, cm^{-1}): 3060w (CH), 2430w (BH), 1495w (C=C + C=N), 564s, 522m, 464s (Ar_3P), 443w, 417w, 352w, 325w, 280w, 268w. Anal. Found: C, 57.81; H, 5.46; N, 15.92. Calc. for $C_{25}H_{27}BCuN_6P$; C, 58.10; H; 5.27; N, 16.26%.

Compound 4. Compound **4** was prepared similarly to compound **2**, by using CuCl (0.099 g, 1.0 mmol), *m*-$tolyl_3P$ (0.609 g, 2 mmol) and $K[H_2B(trz)_2]$ (0.188 g, 1.0 mmol) in CH_3CN–methanol (1 : 3) solution. Re-crystallisation from $CHCl_3$–diethyl ether (1 : 3) gave complex **4** as a micro-crystalline solid in 44% yield. mp 105–109 °C. ^1H NMR ($CDCl_3$, 293 K): δ 2.08 (s, 18H, CH_3), 6.92–7.12 (mc, 24H, C*H*), 7.22 (sbr, 2H, 3- or 5-C*H*), 8.08 (s, 2H, 3- or 5-C*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ −0.9 (sbr); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 218 K): δ −2.4 (sbr). IR (Nujol, cm^{-1}): 2411w, 1590w, 1495m (C=C + C=N), 549br, 520w, 454mbr, 427w (Ar_3P). Anal. Found: C, 66.96; H, 6.21; N, 10.60. Calc.for $C_{46}H_{48}BCuN_6P_2$; C, 67.28; H; 5.89; N, 10.23%.

Compound 5. Compound **5** was prepared similarly to compound **2**, by using CuCl (0.099 g, 1.0 mmol), *p*-$tolyl_3P$ (0.609 g, 2 mmol) and $K[H_2B(tz)_2]$ (0.188 g, 1.0 mmol) in CH_3CN–methanol (1 : 3) solution. Re-crystallisation from $CHCl_3$–petroleum ether (1 : 3) gave complex **5** as a micro-crystalline solid in 63% yield. mp 105–108 °C. ^1H NMR ($CDCl_3$, 293 K): δ 2.27 (s, 18H, CH_3), 6.94–6.98 (mc, 24H, C*H*), 7.35 (s, 2H, 3- or 5-C*H*), 8.07 (s, 2H, 3- or 5-C*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ −3.3 (s); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 218 K): δ −4.1 (s). IR (Nujol, cm^{-1}): 2404w (BH), 1596w, 1500w (C=C + C=N), 507s (Ar_3P), 432w, 420w, 356w, 281w. Anal. Found: C, 67.01; H, 6.01; N, 10.04. Calc. for $C_{46}H_{48}BCuN_6P_2$; C, 67.28; H; 5.89; N, 10.23%.

Compound 6. Compound **6** was prepared similarly to compound **1**, by using CuCl (0.099 g, 1.0 mmol), $MePh_2P$ (0.400 g, 2 mmol) and $K[H_2B(tz)_2]$ (0.188 g, 1.0 mmol) in CH_3CN–methanol (1 : 3). Re-crystallisation from $CHCl_3$ gave complex **6** as a micro-crystalline solid in 68% yield. mp 67–70 °C. ^1H NMR ($CDCl_3$, 293 K): δ 1.52 (s, 6H, CH_3), 7.20–7.26 (m, 20H, C*H*), 7.51 (s, 2H, 3- or 5-C*H*), 8.14 (s, 2H, 3- or 5-C*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): −18.2 (s); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 218 K): δ −18.8 (s). IR (Nujol, cm^{-1}): 2426br (BH), 1585m, 1570m, 1495m (C=C + C=N), 560w, 511sbr, 481s, 436s, 416s, (Ar_3P), 335s 280w, 251w. Anal. Found: C, 58.48; H, 5.56; N, 13.91%. Calc. for $C_{30}H_{32}BCuN_6P_2$; C, 58.79; H; 5.26; N, 13.71.

Compound 7. Compound **7** was prepared similarly to compound **2**, by using CuCl (0.099 g, 1.0 mmol), cy_3P (0.561 g, 2 mmol), and $K[H_2B(tz)_2]$ (0.188 g, 1.0 mmol) in CH_3CN–methanol (1 : 3). Re-crystallisation from CH_3OH–CH_3CN gave complex **7·MeOH** as a micro-crystalline solid in 49% yield. mp 175–178 °C. ^1H NMR ($CDCl_3$, 293 K): δ 1.21–1.93 (m, 33H, C_6H_{11}), δ 7.93 (s, 2H, 3- or 5-C*H*), 8.11 (s, 2H, 3- or 5-C*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 21.0 (s); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 218 K): δ 22.3 (s). IR (Nujol, cm^{-1}): 2430w (BH), 1590w (C=C + C=N), 518m, 473m, 460m, 444w, 431w, 415w, 393w, 381 (Ar_3P). Anal. Found: C, 52.31; H, 8.08; N, 16.16. Calc. for $C_{23}H_{43}BCuN_6OP$; C, 52.62; H; 8.26; N, 16.01%.

Compound 8. $K[HB(tz)_3]$ (0.255 g, 1.0 mmol) was added to a CH_3CN solution (50 ml) of CuCl (0.099 g, 1.0 mmol) and Ph_3P (0.262 g, 1 mmol) at room temperature. After the addition, the

solution was stirred for 2 h and subsequently the solvent was removed with a rotary evaporator. Chloroform (50 ml) was added. The suspension was filtered and the organic layer was 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 $CHCl_3$–diethyl ether (1 : 3) gave complex **8** as a micro-crystalline solid in 68% yield. mp 178–181 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.40–7.45 (m, 15H, C*H*), 7.62 (s, 3H, 3- or 5-C*H*), 8.26 (s, 3H, 3- or 5-C*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ −4.7 (s), 7.3 (sbr); ^{31}P{^{1}H} NMR ($CDCl_3$, 218 K): δ −4.3 (s), 7.8 (s). IR (Nujol, cm^{-1}): 2500w, 2357w (BH), 1511w (C=C + C=N), 526s, 508s, 491s (Ar_3P), 431m. Anal. Found: C, 53.51; H, 4.05; N, 23.06. Calc. for $C_{24}H_{22}BCuN_9P$; C, 53.20; H; 4.09; N, 23.27%.

Compound 9. Compound **9** was prepared similarly to compound **8**, by using CuCl (0.099 g, 1.0 mmol), Bn_3P (0.304 g, 1.0 mmol) and K[HB(tz)$_3$] (0.255 g, 1.0 mmol) in CH_3CN–methanol (1 : 2) solution. Re-crystallisation from $CHCl_3$–diethyl ether (1 : 3) gave complex **9** as a micro-crystalline solid in 87% yield. mp 115 °C dec. ^{1}H NMR ($CDCl_3$, 293 K): δ 3.10 (d, 6H, CH_2), 6.97 (s, 3H, 3- or 5-C*H*), 7.11–7.19 (m, 15H, C*H*), 8.15 (s, 3H, 3- or 5-C*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ −4.4 (sbr), 8.0 (s br); ^{31}P{^{1}H} NMR ($CDCl_3$, 218 K): δ −6.2 (s br), 7.5 (s br). IR (Nujol, cm^{-1}): 2472br (BH), 1597w, 1497s (C=C + C=N), 524s, 510s, 504s (Ar_3P), 434w, 422w. Anal. Found: C, 55.21; H, 5.07; N, 21.51. Calc. for $C_{27}H_{28}BCuN_9P$; C, 55.54; H, 4.83; N, 21.59%.

Compound 10. Compound **10** was prepared similarly to compound **8**, by using CuCl (0.099 g, 1.0 mmol), *o*-tolyl$_3$P (0.304 g, 1 mmol) and K[HB(tz)$_3$] (0.255 g, 1.0 mmol) in CH_3CN–methanol (1 : 2) solution. Re-crystallisation from $CHCl_3$–CH_3CN (1 : 1) gave complex **10·½CHCl$_3$** as a micro-crystalline solid in 67% yield. mp 207–208 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 2.48 (s, 9H, CH_3), 6.96–7.35 (mc, 14H, C*H*), 7.40 (s, 3H, 3- or 5-C*H*), 8.22 (s, 3H, 3- or 5-C*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ −13.9 (sbr); ^{31}P{^{1}H} NMR ($CDCl_3$, 218 K): δ −29.1 (s), −17.3 (sbr). IR (Nujol, cm^{-1}): 2427w (BH), 1590w (C=C + C=N), 569m, 555m, 516m, 458s (Ar_3P), 398w, 375w, 351w, 325w, 303w, 279w, 247w. Anal. Found: C, 51.51; H, 4.52; N, 19.33. Calc. for $C_{27.5}H_{28.5}BCl_{1.5}CuN_9P$; C, 51.32; H; 4.46; N, 19.59%.

Compound 11. Compound **11** was prepared similarly to compound **8**, by using CuCl (0.099 g, 1.0 mmol), *m*-tolyl$_3$P (0.304 g, 1 mmol) and K[HB(tz)$_3$] (0.255 g, 1.0 mmol) in CH_3CN–methanol (1 : 1) solution. Re-crystallisation from $CHCl_3$–*n*-hexane (1 : 4) gave complex **11** as a micro-crystalline solid in 71% yield. mp 181–184 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 2.31 (s, 18H, CH_3), 7.20–7.33 (mc, 24H, C*H*), 7.63 (sbr, 3H, 3- or 5-C*H*), 8.26 (s, 3H, 3- or 5-C*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ 5.7 (sbr); ^{31}P{^{1}H} NMR ($CDCl_3$, 218 K): δ 7.1 (sbr). IR (Nujol, cm^{-1}): 2360w (BH), 1590w, 1495m (C=C + C=N), 546br, 448s (Ar_3P), 352w, 284w. Anal. Found: C, 64.72; H, 6.01; N, 13.88. Calc. for $C_{48}H_{49}BCuN_9P_2$; C, 64.90; H; 5.56; N, 14.19%.

Compound 12. Compound **12** was prepared similarly to compound **8**, by using CuCl (0.099 g, 1.0 mmol), *p*-tolyl$_3$P (0.304 g, 1 mmol) and K[HB(tz)$_3$] (0.255 g, 1.0 mmol) in CH_3CN–methanol (1 : 3) solution. Re-crystallisation from $CHCl_3$–*n*-hexane (1 : 4) gave complex **12** as a micro-crystalline solid in 59% yield. mp 151–155 °C dec. ^{1}H NMR ($CDCl_3$, 293 K): δ 2.31 (s, 9H, CH_3), 7.11–7.42 (mc, 12H, C*H*), 7.60 (s, 3H, 3- or 5-C*H*), 8.35 (s, 2H, 3- or 5-C*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): Δ 5.9 (sbr); ^{31}P{^{1}H} NMR ($CDCl_3$, 218 K): δ 5.2 (s). IR (Nujol, cm^{-1}): 3118w, 3060w (CH), 2500br (BH), 1508m, 1490m (C=C + C=N), 521s, 510s, 431m, 422w (Ar_3P), 365w, 259w. Anal. Found: C, 55.67; H, 4.96; N, 21.32. Calc. for $C_{27}H_{28}BCuN_9P$; C, 55.54; H; 4.83; N, 21.54%.

Compound 13. Compound **13** was prepared similarly to compound **8**, by using CuCl (0.099 g, 1.0 mmol), $MePh_2P$ (0.200 g, 1 mmol) and K[HB(tz)$_3$] (0.255 g, 1.0 mmol) in CH_3CN–methanol (1 : 3) solution. Re-crystallisation from $CHCl_3$–diethyl ether (1 : 3) gave complex **13** as a micro-crystalline solid in 45% yield. mp 193–196 °C dec. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.99 (d, 3H, CH_3), 7.39–7.65 (mc, 10H, C*H*), 7.71 (s, 3H, 3- or 5-C*H*), 8.21 (s, 3H, 3- or 5-C*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ −12.0 (sbr); ^{31}P{^{1}H} NMR ($CDCl_3$, 218 K): δ −12.1 (s). IR (Nujol, cm^{-1}): 2453w (BH), 1585w, 1505w (C=C + C=N), 504s, 477s (Ar_3P), 434w, 409sh. Anal. Found: C, 47.5; H, 4.5; N, 26.6. Calc. for $C_{19}H_{20}BCuN_9P$; C, 47.6; H; 4.2; N, 26.3%.

Compound 14. Compound **14** was prepared similarly to compound **8**, by using CuCl (0.099 g, 1.0 mmol), cy_3P (0.280 g, 1 mmol) and K[HB(tz)$_3$] (0.255 g, 1.0 mmol) in CH_3CN–methanol (1 : 3) solution. Re-crystallisation from $CHCl_3$–diethyl ether (1 : 3) gave complex **14** as a micro-crystalline solid in 73% yield. mp: 239–243 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.28–1.98 (m, 33H, C_6H_{11}), δ 7.92 (s, 3H, 3- or 5-C*H*), 8.24 (s, 3H, 3- or 5-C*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ 24.7 (sbr). ^{31}P{^{1}H} NMR ($CDCl_3$, 218 K): δ 24.6 (s). IR (Nujol, cm^{-1}): 3111w (CH), 2475w (BH), 1557s, 1538w, 1499s (C=C + C=N), 518s, 473m, 460m, (Ar_3P) 444w, 431w, 415w, 393w, 381w. Anal. Found: C, 51.28; H, 7.40; N, 22.19. Calc. for $C_{24}H_{40}BCuN_9P$; C, 51.48; H; 7.20; N, 22.51%.

Structure determinations

Full spheres of low-temperature CCD area-detector diffractometer data were measured (Bruker AXS instrument, ω-scans, $2\theta_{max} = 75°$; monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; *T ca.* 153 K) yielding $N_{t(otal)}$ independent reflections, merging to *N* unique (R_{int} quoted) after 'empirical'/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ considered 'observed' and used in the full matrix least squares refinement, refining anisotropic thermal parameter forms for the non-hydrogen atoms, together with $(x, y, z, U_{iso})_H$. Conventional residuals *R*, R_w (weights: $(\sigma^2(F) + 0.0004\ F^2)^{-1}$) are cited at convergence, neutral atom complex scattering factors being employed within the context of the Xtal 3.7 program system.[17] Pertinent results are given below and in Tables 1 and 2 and Figs. 2–4, the latter showing non-hydrogen atoms with 50% displacement amplitude envelopes, hydrogen atoms having arbitrary radii of 0.1 Å. Individual variations in procedure are cited as 'variata'.

Crystal/refinement data. *Compound 1.* ≡ $C_{40}H_{36}BCuN_6P_2$, *M* = 737.1. Monoclinic, space group $P2_1/c$, (C_{2h}^5, No 14), $a = 8.5706(5)$, $b = 19.252(1)$, $c = 21.293(1)$ Å, $\beta = 93.471(2)°$, $V = 3507$ Å^3. D_c ($Z = 4$) = 1.39_6 g cm^{-3}. $\mu_{Mo} = 7.5$ cm^{-1}; specimen: 0.40 × 0.25 × 0.15 mm; '$T'_{min,max} = 0.72, 0.83$. $N_t = 73173$, $N = 18468$ ($R_{int} = 0.051$), $N_o = 11373$; $R = 0.040$, $R_w = 0.036$. $|\Delta\rho_{max}| = 1.1(2)$ e Å^{-3}.

Compound ***2·2MeOH***. ≡ $C_{48}H_{56}BCuN_6O_2P_2$, *M* = 885.3. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 10.1223(6)$, $b = 14.0189(8)$, $c = 16.0319(9)$ Å, $\alpha = 84.151(1)$, $\beta = 86.363(1)$, $\gamma = 84.819(1)°$, $V = 2251$ Å^3. D_c ($Z = 2$) = 1.30_6 g cm^{-3}. $\mu_{Mo} = 6.0$ cm^{-1}; specimen: 0.45 × 0.45 × 0.19 mm; '$T'_{min,max} = 0.74, 0.83$. $N_t = 45831$, $N = 22975$ ($R_{int} = 0.021$), $N_o = 16191$; $R = 0.037$, $R_w = 0.036$. $|\Delta\rho_{max}| = 0.8(1)$ e Å^{-3}.

Compound ***7·MeOH***. ≡ $C_{23}H_{43}BCuN_6OP$, *M* = 525.0. Monoclinic, space group $P2_1/n$ (C_{2h}^5, No. 14; variant), $a = 13.727(1)$, $b = 10.1806(9)$, $c = 19.682(2)$ Å, $\beta = 105.600(2)°$, $V = 2649$ Å^3. D_c ($Z = 4$) = 1.31_6 g cm^{-3}. $\mu_{Mo} = 9.1$ cm^{-1}; specimen: 0.50 × 0.45 × 0.25 mm; '$T'_{min,max} = 0.62, 0.86$. $N_t = 53690$, $N = 6982$ ($R_{int} = 0.075$), $N_o = 5652$; $R = 0.057$, $R_w = 0.072$. $|\Delta\rho_{max}| = 2.15(4)$ e Å^{-3}.

Table 1 Selected geometries, mononuclear species

Atoms	Parameter	Atoms	Parameter
(a) The $(tz)_2BH_2$ complexes; the two values in each entry are for **1**, **2** (ital.)			
Distances (Å)			
Cu–P(1)	2.2686(4), *2.2642(4)*	Cu–N(12)	2.050(1), *2.106(1)*
Cu–P(2)	2.2697(4), *2.2647(4)*	Cu–N(22)	2.110(1), *2.138(1)*
Angles (degrees)			
P(1)–Cu–P(2)	121.42(2), *135.69(1)*	N(12)–Cu–N(22)	93.17(5), *90.01(4)*
P(1)–Cu–N(12)	117.60(4), *99.25(3)*	P(2)–Cu–N(12)	106.63(4), *115.90(3)*
P(1)–Cu–N(22)	100.06(4), *102.16(3)*	P(2)–Cu–N(22)	114.33(4), *103.85(3)*
Deviations δCu (Å) of copper from C_2N_3 tz planes			
δCu(trz(1))	0.121(3), *0.031(2)*	δCu(trz(2))	0.670(3), *0.394(2)*
Torsion angles (degrees)[a]			
Cu–P(1)–C(11x)–C(11y)	42.2(1), *52.9(1)*	Cu–P(2)–C(21*x*)–C(21*y*)	−53.1(1), *−70.0(1)*
Cu–P(1)–C(12x)–C(12y)	4.8(1), *39.7(1)*	Cu–P(2)–C(22*x*)–C(22*y*)	−45.6(1), *−141.2(1)*
Cu–P(1)–C(13x)–C(13y)	48.5(1), *172.3(1)*	Cu–P(2)–C(23*x*)–C(23*y*)	−46.8(1), *−53.0(1)*
P(1)–C(110)–C(111)–C(112)	—, *−73.7(1)*	P(2)–C(210)–C(211)–C(212)	—, *79.1(1)*
P(1)–C(120)–C(121)–C(122)	—, *−75.8(1)*	P(2)–C(220)–C(221)–C(222)	—, *−81.8(1)*
P(1)–C(130)–C(131)–C(132)	—, *−81.3(1)*	P(2)–C(230)–C(231)–C(232)	—, *−89.8(1)*
(b) The $(tz)_3BH$ complexes; the three values in each entry are for **14**, **10**, **12**			
Distances (Å)			
Cu–P	2.1817(3), 2.166(24), 2.1562(4)	Cu–N(12)	2.1433(8), 2.096(6), 2.071(1)
		Cu–N(22)	2.1029(8)), 2.093(5), 2.100(1)
		Cu–N(32)	2.1047(7), 2.075(7), 2.097(1)
Angles (degrees)			
P–Cu–N(12)	127.29(2), 124.3(2), 121.91(3)	N(12)–Cu–N(22)	88.20(3), 88.6(2), 90.04(5)
P–Cu–N(22)	127.52(2), 128.3(2), 128.69(3)	N(12)–Cu–N(32)	88.37(3), 90.3(3), 91.05(5)
P–Cu–N(32)	123.02(3), 125.0(1), 125.48(4)	N(22)–Cu–N(32)	90.49(3), 88.6(2), 88.48(4)
Deviations δCu (Å) of copper from C_2N_3 tz planes			
δCu(trz(1))	0.296(2), 0.13(1), 0.116(3)		
δCu(trz(2))	0.273(2), 0.12(1), 0.089(3)		
δCu(trz(3))	0.003(2), 0.11(1), 0.084(3)		
Torsion angles (degrees)			
Cu–P–C(11)–C(12)	−26.47(7),[b] −47.2(7), −24.4(2))		
Cu–P–C(21)–C(22)	−46.67(7),[c] −47.9(5), −45.6(1)		
Cu–P–C(31)–C(32)	−62.80(7),[d] −45.0(8), −48.7(1))		

[a] For **1**, $x = 1$, $y = 2$; for **2**, $x = 0$, $y = 1$. The tz(1)/tz(2) interplanar dihedral angles are 49.50(7), *54.12(5)*°. [b] Counterpart value: −153.48(6)°. [c] Counterpart value: −173.37(7)°. [d] Counterpart value: 59.50(7)°.

Compound ***10*·½*CHCl*$_3$**. ≡ $C_{27.5}H_{28.5}BCl_{1.5}CuN_9P$, M = 643.6. Monoclinic, space group $C2/c$ (C_{2h}^6, No. 15), a = 15.708(5), b = 14.299(4), c = 27.283(8) Å, β = 95.611(8)°, V = 6099 Å^3. D_c (Z = 8) = 1.40$_2$ g cm^{-3}. μ_{Mo} = 9.4 cm^{-1}; specimen: 0.35 × 0.25 × 0.16 mm; *'T'*$_{min,max}$ = 0.49, 0.83. N_t = 62156, N = 5045 (R_{int} = 0.11), N_o = 3583; R = 0.076, R_w = 0.078. $|\Delta\rho_{max}|$ = 1.39(4) e Å^{-3}.

Variata. Difference map residues were modelled in terms of chloroform of solvation, disordered over two sets of sites about the crystallographic *2*-axis, geometries constrained. $(x, y, z, U_{iso})_H$ were constrained at estimates throughout. $2\theta_{max}$ was 62.5°.

Compound ***11***. ≡ $C_{48}H_{49}BCuN_9P_2$, M = 888.3. Orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), a = 10.2010(8), b = 19.550(2), c = 22.391(2) Å, V = 4465 Å^3. D_c (Z = 4) = 1.32$_1$ g cm^{-3}. μ_{Mo} = 6.1 cm^{-1}; specimen: 0.30 × 0.20 × 0.15 mm; *'T'*$_{min,max}$ = 0.73, 0.86. N_t = 23479, N = 12705 (R_{int} = 0.076), N_o = 7496; R = 0.045, R_w = 0.043. $|\Delta\rho_{max}|$ = 1.3(3) e Å^{-3}. x_{abs} = −0.01(1). $(x, y, z, U_{iso})_H$ constrained at estimates.

Compound ***12***. ≡ $C_{27}H_{28}BCuN_9P$, M = 583.9. Triclinic, space group $P\bar{1}$, a = 10.9114(9), b = 11.852(1), c = 12.317(1) Å, α = 70.986(2), β = 75.079(2), γ = 71.896(2)°, V = 1410 Å^3. D_c (Z = 2) = 1.37$_6$ g cm^{-3}. μ_{Mo} = 8.7 cm^{-1}; specimen: 0.39 × 0.25 × 0.05 mm; *'T'*$_{min,max}$ = 0.64, 0.86. N_t = 28965, N = 14446 (R_{int} = 0.028), N_o = 9722; R = 0.037, R_w = 0.035. $|\Delta\rho_{max}|$ = 0.8(2) e Å^{-3}.

Compound ***14***. ≡ $C_{24}H_{40}BCuN_9P$, M = 560.0. Monoclinic, space group $P2_1/c$, a = 9.2098(5), b = 14.5388(7), c = 21.045(1) Å, β = 101.377(1)°, V = 2763 Å^3. D_c (Z = 4) = 1.34$_6$ g cm^{-3}. μ_{Mo} = 8.8 cm^{-1}; specimen: 0.35 × 0.35 × 0.16 mm; *'T'*$_{min,max}$ = 0.74, 0.83. N_t = 55604, N = 14503 (R_{int} = 0.028), N_o = 10960; R = 0.027, R_w = 0.030. $|\Delta\rho_{max}|$ = 0.6(1) e Å^{-3}.

CCDC reference numbers 176916–176922.

See http://www.rsc.org/suppdata/dt/b2/b200200k/ for crystallographic data in CIF or other electronic format.

Discussion

The interaction between a tertiary phosphine R_3P (R = Ph, Bn, *o*-, *m*-, or *p*-tolyl, or cy) or $MePh_2P$, copper chloride and the potassium salt of $[H_2B(tz)_2]^-$ in acetonitrile or in methanol at room temperature readily gives the complexes **1**–**7** in good yields, in accordance with the following general eqn. 1.

$$K[H_2B(tz)_2] + CuCl + nR_3P \longrightarrow [Cu(R_3P)_n\{(tz)_2BH_2\}] + KCl \quad (1)$$

1: $R_3P = Ph_3P$, n = 2; **2**: $R_3P = Bn_3P$, n = 2; **3**: $R_3P = (o\text{-tolyl})_3P$, n = 1; **4**: $R_3P = (m\text{-tolyl})_3P$, n = 2; **5**: $R_3P = (p\text{-tolyl})_3P$, n = 2; **6**: $R_3P = MePh_2P$, n = 2; **7**: $R_3P = cy_3P$, n = 1

Table 2 Selected geometries (Å, degrees) polymeric species (**7**, **11**). Primed atoms are generated by $3/2 - x, y - 1/2, 3/2 - z$ (**7**), $x - 1/2, 1/2 - y, 2 - z$ (**11**)

Atoms	Parameter	Atoms	Parameter
(a) Compound **7**			
Cu–P	2.231(1)	Cu–N(12)	2.175(3)
Cu–N(14′)	2.091(3)	Cu–N(22)	2.101(3)
P–Cu–N(12)	117.91(8)	N(12)–Cu–N(22)	88.7(1)
P–Cu–N(22)	126.93(9)	N(12)–Cu–N(14′)	104.9(1)
P–Cu–N(14′)	112.91(8)	N(22)–Cu–N(14′)	101.4(1)
Cu–N(12)–N(11)	117.9(2)	Cu–N(22)–N(21)	119.2(2)
Cu–N(12)–C(13)	136.0(2)	Cu–N(22)–N(23)	136.0(2)
Cu–N(14′)–C(13′)	128.2(2)	Cu–N(14′)–C(15′)	127.4(2)
(b) Compound **11**			
Cu–P(1)	2.263(1)	Cu–N(14)	2.096(3)
Cu–P(2)	2.279(1)	Cu–N(24′)	2.079(3)
P(1)–Cu–P(2)	116.98(4)	P(2)–Cu–N(14)	109.97(9)
P(1)–Cu–N(14)	107.70(9)	P(2)–Cu–N(24′)	109.2(1)
P(1)–Cu–N(24′)	114.40(9)	N(14)–Cu–N(24′)	96.6(1)
Cu–N(14)–C(13)	131.9(2)	Cu–N(24′)–C(23′)	130.4(3)
Cu–N(14)–C(15)	124.8(3)	Cu–N(24′)–C(25′)	126.8(3)

In **7**, Cu lies 0.453(5), 0.380(6), 0.381(5) Å out of tz planes 1, 2, 1′; in **11**, Cu lies 0.265(6), 0.199(6) Å out of tz planes 1, 2′. In **7**, torsion Cu–P–C(1*n*1)–C(1*n*2) (*n* = 1–3) are −165.3(2), 32.3(3), 61.6(3) with Cu–P–C(1*n*1)–C(1*n*6) −34.8(2), −90.7(3), −62.6(3)°. In **11**, Cu–P–C(*mn*1)–C(*nm*2) are (*m* = 1) 147.0(3), −42.3(3), −44.4(4), (*m* = 2) 78.1(3), 0.5(4), −158.6(3)°.

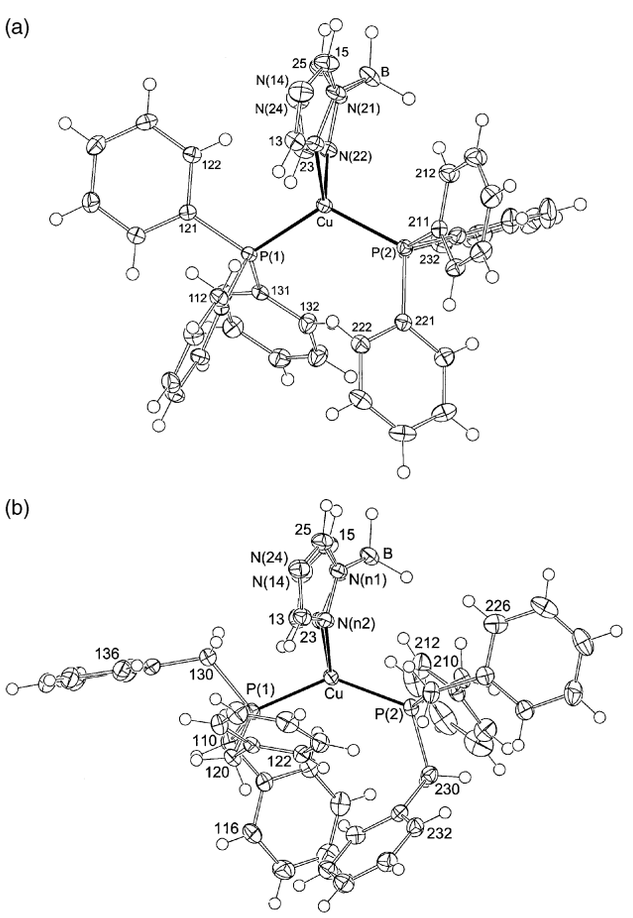

Fig. 2 Projections of (a) **1** and (b) **2**, normal to their CuP_2 planes.

The 1 : 1 adducts **3** and **7** have been obtained only by using sterically hindered cy_3P or $(o\text{-tolyl})_3P$. No 2 : 1 adducts containing these two P-donors have been obtained even when a large excess of ligand was employed. Analogously only 2 : 1 adducts have been obtained when Ph_3P, Bn_3P, $MePh_2P$, $(m\text{-tolyl})_3P$ or $(p\text{-tolyl})_3P$ were employed, *i.e.* the stoichiometry of this kind of complex is essentially independent of the ligand-to-metal ratio employed. Mononuclear structures for all the 2 : 1 derivatives and polynuclear structures for the 1 : 1 adducts have been found in the solid state (see below).

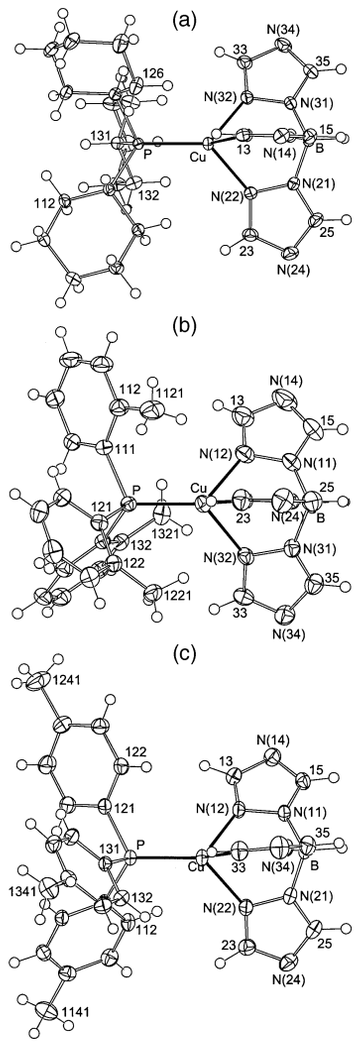

Fig. 3 Projections of (a) **14**, (b) **10**, (c) **12**, normal to their P–Cu bonds.

The interaction between R_3P, copper chloride and the potassium salt of $[HB(tz)_3]^-$ under the same reaction conditions gives the complexes **8**–**14** in good yields, in accordance with the following general eqn. 2:

$$K[HB(tz)_3] + CuCl + nR_3P \longrightarrow [Cu(R_3P)_n\{(tz)_3BH\}] + KCl \quad (2)$$

8: $R_3P = Ph_3P$, $n = 1$; **9**: $R_3P = Bn_3P$, $n = 1$; **10**: $R_3P = (o\text{-tolyl})_3P$, $n = 1$; **11**: $R_3P = (m\text{-tolyl})_3P$, $n = 2$; **12**: $R_3P = (p\text{-tolyl})_3P$, $n = 1$; **13**: $R_3P = MePh_2P$, $n = 1$; **14**: $R_3P = cy_3P$, $n = 1$

In this case a 2 : 1 adduct has been obtained only when $(m\text{-tolyl})_3P$ was employed as the ancillary P-donor ligand, whereas in all the other cases 1 : 1 adducts were obtained independently of the reaction conditions employed. Mononuclear structures have been found in the solid state in the case of the 1 : 1 adducts, whereas a polynuclear complex is obtained in the case of the 2 : 1 adduct (see below).

All of the colorless compounds **1**–**14** 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

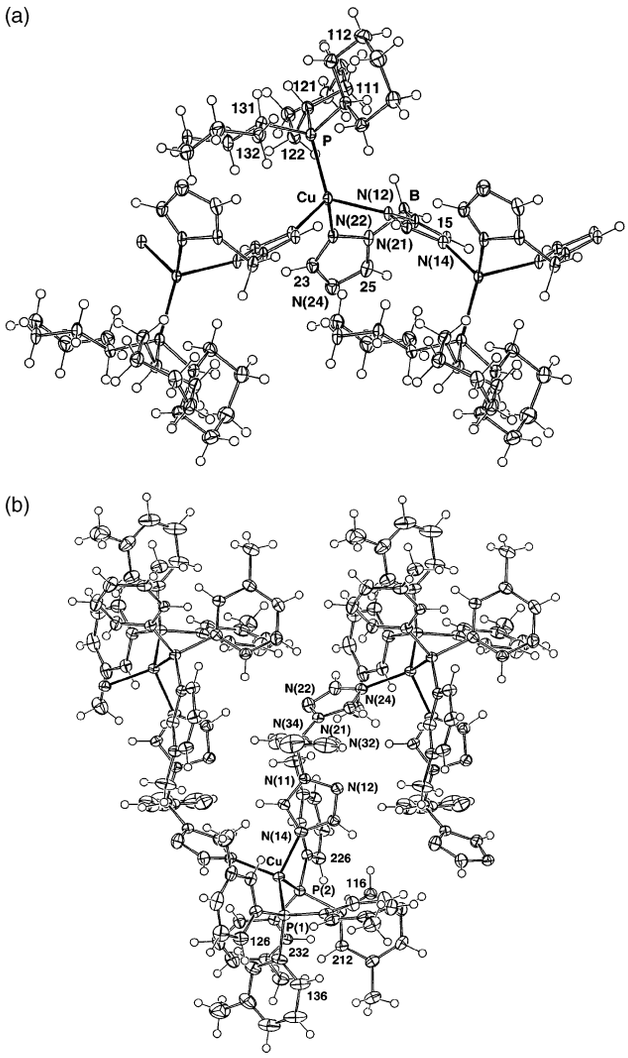

Fig. 4 Views of the polymers of (a) **7** (the polymer axis horizontal in the page), and (b) **11**.

proposed in eqn. 3 appears likely also on the basis of vaporimetric molecular determinations (for example the ratio between calculated and vaporimetric molecular weight for compound **1** is 0.72 at concentration 0.07 %w/w and for compound **9** is 0.65 at concentration 0.08 %w/w) and ^{31}P NMR data (see below).

$$[Cu(R_3P)_n\{(tz)_{3-x}BH_x\}] \rightleftharpoons [Cu(R_3P)_{n-1}\{(tz)_{3-x}BH_x\}] + PR_3 \quad (3)$$

Spectroscopy

The infrared spectra show all the bands required by the presence of the organic nitrogen donor and the phosphine ligand. For all the derivatives **1**–**14** the BH stretches generally appear as a single peak in the expected regions. Upon coordination these bands are slightly shifted to higher frequency with respect to the same absorption observed for free hydrotris(1,2,4-triazolyl)-borate ligands. In the far IR spectra of all the derivatives, we have assigned, on the basis of a previous report on phosphino copper(I) complexes, the broad absorptions near 500 cm^{-1} and those at *ca.* 450 cm^{-1} to Whiffen's *y* and *t* vibrations.[18] In some cases weak to medium bands at *ca.* 350 cm^{-1} appeared, similar to those described for copper-azolato complexes,[19] which are tentatively assigned to ν(Cu–N) stretching vibrations.

The room temperature proton spectra of **1**–**14** in $CDCl_3$ (see Experimental section) are very similar to each other and also to the potassium salts of tris- and bis-(1,2,4-triazolyl)borate in respect of their chemical shift.[6b,20]

The BH signal was not observed in any case, presumably due to broadening of the resonance because of quadrupolar coupling and relaxation effects from the boron atom.[21]

The ^{1}H NMR room temperature spectra exhibit one set of signals for the protons of the triazolyl groups, suggesting highly fluxional species with either a rocking motion of the triorganophosphine copper(I) moiety between the two or three nitrogen atoms of the poly(triazolyl)borate ligand or complete dissociation and reassociation of the triazolyl nitrogen, which occurs rapidly even at low temperature. In fact, on cooling the $CDCl_3$ solutions of selected samples, no additional signal appeared.

The metallacycle of compounds **1**, **2** and **4**–**6**, may be subject to boat inversion as already noted.[22] The phosphorus atoms may be used as a probe for fluxionality, since inversion renders them inequivalent so that two sets of signals should be observed, with the ^{31}P NMR spectrum serving this purpose. In the ^{31}P NMR spectrum of **1** and **4**–**6** only one peak is observed at 293 and 223 K, indicating that, unless there is fortuitous synchronicity, boat inversion is operative, not only at room, but also at low temperature. A different behaviour has been found for the Bn_3P complex **2**, for which one signal at room temperature, and four different signals at 223 K were detected, consistent with the disappearance of fluxionality and the occurrence of equilibria such as in eqn. 3. The four signals in the low temperature ^{31}P-NMR spectrum of complex **2** can be ascribed to the three not equivalent Bn_3P species hypothesized in eqn. 3, and also to a fourth species likely containing the $(tz)_2BH_2$ ligand in a different hapticity. Also the room temperature ^{31}P NMR spectra of complexes **3** and **7**–**14** invariably show single broad resonances, attributed to fluxional behavior in these complexes. The magnitude of Δ ($= \delta^{31}P_{complex} - \delta^{31}P_{free\ ligand}$) decreases with decreasing basicity, also correlating with steric bulk of the ligands. For example the Δ for **7**, **13** and **14**, which contain the more basic phosphines, are the greatest, whereas the smaller values of Δ have been observed for the triarylphosphine derivatives **1**, **4** and **5** containing two phosphorus donors. In fact, as previously observed, the chemical shift is dependent on the stoichiometric ratio N : Ag : P.[16b]

Structure determinations

Adducts of the $tz_2BH^-_2$ ligand have been defined in two forms, namely (a) discrete mononuclear $[Cu(R_3P)_2\{(tz)_2BH_2\}]$, exemplified by **1**, **2**, R = Ph, Bn, which contain four-coordinate copper in a CuP_2N_2 environment, the tz_2BH_2 ligands chelating through their pairs of N(n2) nitrogens (Fig. 2), and (b) unusually, one-dimensional polymeric $[Cu(cy_3P)(tz)BH_2(tz)]_{(\infty|\infty)}$, **7**, also containing four-coordinate copper atoms but now $CuPN_3$, the tz_2BH_2 ligand still chelating through N(n2), but also now bridging successive screw-related copper atoms in the polymer strand N(14) (Fig. 4a). In all three complexes, one formula unit (accompanied by two or one methanol solvent molecules in **2**, **7**), comprises the asymmetric unit of the structure. In **1**, **2**, the CuN_4B rings adopt 'boat' conformations, Cu, B lying 0.476(2), 0.642(3) (**1**), 0.660(2), 0.650(2) Å (**2**) out of the N_4 planes (χ^2 4415, 3290), respectively. In **1**, PPh_3 ligand 2 conforms closely to the C_3-symmetry paradigm, ligand 1 (of opposite chirality) less so (Table 1); in **2**, the benzyl rings, rather than closing around the metal-donor bond 'umbrella' fashion, as is often the case, with Cu–P–C–C *ca.* 90°, in complexes of this ligand, adopt unsymmetrical/irregular dispositions, the two ligands grossly similar but of opposite chirality. In both **1** and **2**, the PR_3 substituent dispositions deviate from potential *m* molecular symmetry, *m* passing through P_2CuB (Fig. 2). The Cu–P distances are very similar, but P–Cu–P are quite disparate between the two compounds. In **2**, the methanol hydrogens hydrogen-bond to the uncoordinated tz N(4) nitrogens (H(1) ··· dN(14) 1.89(3), H(2) ··· N(24) 1.97(3) Å).

The metal environments in **1** and **2** (Table 1), are similar to those found in $[Cu(MePh_2P)_2\{pz)_2BH_2\}]$[16b] (pzH = pyrazole)

(Cu–P 2.2480(5), 2.2730(5), Cu–N 2.045(1), 2.073(1) Å; P–Cu–P 115.48(2), N–Cu–N 90.47(5), P–Cu–N 109.59(3)–113.61(4)°) and $[Cu(Ph_3P)_2\{(pz)_2B(pz_2)\}]$[23] (Cu–P 2.273(1), 2.359(1), Cu–N 2.051(3), 2.087(3) Å; P–Cu–P 119.82(4), N–Cu–N 92.6(1), P–Cu–N 99.21(9)–119.76(9)°), the latter perhaps influenced by the increased anion bulk. It is interesting to note that the metal atom environments in $[(cy_3P)Cu\{(Mepz)_2B(Mepz)_2\}]$,[16b] $[Cu(^tBu_3P)(^tBuPh,Mepz)_3BH)]$[24] and $[Cu(Ph_3P)_2\{((F_3C)_2pz)BH_2(pz(CF_3)_2)\}]$[25] are essentially trigonal planar with, respectively, $CuPN_2$ and CuP_2N arrays.

The present complexes of tz_3BH also fall into two classes, again (a), a mononuclear form, $[Cu(R_3P)\{(tz)_3BH\}]$ with four-coordinate $CuPN_3$ metal environments and the tz_3BH ligand as tripodal N_3 tridentate, exemplified by compounds **14** (R = cy), **10** (R = *o*-tolyl), **12** (R = *p*-tolyl) (Fig. 3), and (b) a one-dimensional polymer $[Cu(m\text{-}tolyl_3P)\{(tz(BHtz)tz)\}]_{(\infty|\infty)}$ **11** in which one of the ligand tz rings is uncoordinated and the other two bridge, not through N(2) but through N(4), to successive copper atoms in the polymer string (Fig. 4b); in each compound one formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. In none of the discrete molecules is the potential *3m* symmetry of the array realized crystallographically, the symmetry being broken by the PR_3 substituent disposition, but in **10** and **12**, the molecular symmetry, inclusive of PR_3 substituents, is a good approximation to *3*, the axis coincident with the Cu–P bond. The substituent disposition in **14** is the common *R* form for that ligand (that in **7** is closer to *M*);[26] in **14**, both Cu–P and (< >) Cu–N are slightly elongated *cf.* **10**, **12**, in which Cu–N are generally comparable with those in numerous other adducts of tris(five-membered N-donor)X(H) tripod systems.[16b,23–25,27–30]

Compound **11** is curious, adducts of PR_3, R = *o*-, *p*-tolyl giving mononuclear adducts of the above form, whereas here, for R = *m*-tolyl, a different stoichiometry with different ligand donor atoms is found, tz coordination occurring through N(4) of two of the three rings, the third not interacting at all; Cu–P, N are comparable with counterpart values in the CuP_2N_2 systems above. Whereas the exocyclic angles at the chelating nitrogens in the mononuclear $tz_{2,3}BH_{2,1}$ systems differ appreciably as expected, the exocyclic angles at the bridging N(4) of **7**, are, unsurprisingly, essentially equivalent (Table 2). However, in the present compound **11**, significant differences are observed, presumably a consequence of 'packing forces'. The polymer here is generated by a 2_1 screw of a chiral space group. The large displacement envelopes of the uncoordinated tz ring may simply be a consequence of its uncoordinated status but perhaps also/or rotational disorder over the two orientations possible about the pendant B–C bond.

Conclusion

We have prepared and characterized a series of copper(I) phosphine complexes with poly(1,2,4-triazolyl)borate ligands, employing X-ray crystallography and NMR spectroscopy to examine how the coordination environment is dependent not only on the cone angle and basicity of the triorganophosphine, but also on the nature of the azole ring. The compounds obtained show an interesting, and in some cases, unpredictable, structural variety, both in the local coordination environment and in the overall geometry. The poly(triazolyl)borate ligands were found capable of functioning either as chelating ligands or as bridges between metal centers. We have found that not only N(2), but also N(4) of the triazole ring can engage in metal coordination to give polymeric complexes, presently one-dimensional. We have also demonstrated that the stoichiometry of the complexes obtained from the reaction of Cu(phosphine) acceptors and poly(triazolyl)borate ligands are dependent not, primarily, on the reaction conditions but, rather, on the nature of the P-donor. The stability of the complexes is strongly dependent on the nature of the phosphine donors. Solution data are consistent with a partial dissociation of complexes occurring through breaking of both Cu–N and Cu–P bonds.

Acknowledgements

We thank the MIURST, CARIMA Foundation and the University of Camerino for financial help.

References

1 S. Trofimenko, *J. Am. Chem. Soc.*, 1966, **88**, 1842.
2 (*a*) S. Trofimenko, *Chem. Rev.*, 1993, **93**, 943; (*b*) S. Trofimenko, *Prog. Inorg. Chem.*, 1986, **34**, 115.
3 (*a*) N. Kitajima and W. B. Tolman, *Prog. Inorg. Chem.*, 1995, **43**, 419; (*b*) P. K. Byers, A. J. Canty and R. T. Honeyman, *Adv. Inorg. Chem.*, 1995, **42**, 291; (*c*) D. L. Reger, *Coord. Chem. Rev.*, 1996, **147**, 571; (*d*) M. Etienne, *Coord. Chem. Rev.*, 1996, **156**, 201.
4 S. Trofimenko, *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, 1999.
5 T. Desmond, F. J. Lalor, G. Ferguson, B. Ruhl and M. Parvez, *J. Chem. Soc., Chem. Commun.*, 1983, 55.
6 (*a*) C. Janiak, T. G. Scharmann, T. Bräuniger, J. Holubová and M. Nádvorník, *Z. Anorg. Allg. Chem.*, 1998, **624**, 769 and references therein; (*b*) C. Janiak, T. G. Scharmann, J. C. Green, R. P. G. Parkin, M. J. Kolm, E. Riedel, W. Mickler, J. Elguero, R. M. Claramunt and D. Sanz, *Chem. Eur. J.*, 1996, **2**, 992.
7 (*a*) F. Lalor, S. M. Miller and N. Garvey, *J. Organomet. Chem.*, 1988, **356**, C57; (*b*) F. Lalor, S. M. Miller and N. Garvey, *Polyhedron*, 1990, **9**, 63; (*c*) K.-B. Shiu, F.-M. Shen, S.-L. Wang and S.-C. Wei, *J. Organomet. Chem.*, 1989, **372**, 251; (*d*) P. Cecchi, G. Gioia Lobbia, D. Leonesi, C. Pettinari, C. Sepe and V. Vinciguerra, *Gazz. Chim. Ital.*, 1993, **123**, 569; (*e*) S. Anderson, A. Harman and A. F. Hill, *J. Organomet. Chem.*, 1995, **498**, 251; (*f*) J. Cartwright, A. Harman and A. F. Hill, *J. Organomet. Chem.*, 1990, **396**, C31.
8 (*a*) C. Santini, G. Gioia Lobbia, C. Pettinari, M. Pellei, G. Valle and S. Calogero, *Inorg. Chem.*, 1998, **37**, 890; (*b*) A. F. Hill, G. R. Owen, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed.*, 1999, **38**, 2759; (*c*) P. A. Slavin, J. Reglinski, M. D. Spicer and A. R. Kennedy, *J. Chem. Soc., Dalton Trans.*, 2000, 239 and references therein; (*d*) C. Santini, C. Pettinari, G. Gioia Lobbia, R. Spagna, M. Pellei and F. Vallorani, *Inorg. Chim. Acta*, 1999, **285**, 81; (*e*) C. Kimblin, B. M. Bridgewater, T. Hascall and G. Parkin, *J. Chem. Soc., Dalton Trans.*, 2000, 891.
9 (*a*) S. Trofimenko, *J. Am. Chem. Soc.*, 1967, **89**, 3903; (*b*) G. J. A. A. Koolhaas, W. L. Driessen, J. Reedijk, H. Kooijman and A. L. Spek., *J. Chem. Soc., Chem. Commun.*, 1995, 517; (*c*) R. Gregorzik, U. Hartmann and H. Vahrenkamp, *Chem. Ber.*, 1994, **127**, 2117; (*d*) U. Hartmann, R. Gregorzik and H. Vahrenkamp, *Chem. Ber.*, 1994, **127**, 2123; (*e*) W. E. Lynch, D. M. Kurtz, S. Wang and R. A. Scott, *J. Am. Chem. Soc.*, 1994, **116**, 11030; (*f*) S. Chen, J. F. Richardson and R. M. Buchanan, *Inorg. Chem.*, 1994, **33**, 2376; (*g*) W. Klaui, C. Piefer, G. Rheinwald and H. Lang, *Eur. J. Inorg. Chem.*, 2000, 1549; (*h*) C. Kimblin, B. M. Bridgewater, D. G. Churchill and G. Parkin, *J. Chem. Soc., Dalton Trans.*, 2000, 2191.
10 S. Trofimenko, *J. Am. Chem. Soc.*, 1967, **89**, 3170.
11 (*a*) Z. Xiao, R. W. Gable, A. G. Wedd and C. G. Young, *J. Chem. Soc., Chem. Commun.*, 1994, 1295; (*b*) I. T. Macleod, E. R. T. Tiekink and C. G. Young, *J. Organomet. Chem.*, 1996, **506**, 301; (*c*) K.-B. Shiu., J. Y. Lee, Y. Wang, M.-C. Cheng, S.-L. Wang and F.-L. Liao, *J. Organomet. Chem.*, 1993, **453**, 211.
12 (*a*) C. Janiak, T. G. Scharmann, P. Albrecht, F. Marlow and R. MacDonald, *J. Am. Chem. Soc.*, 1996, **118**, 6307 and references therein; (*b*) C. Janiak, S. Temizdemir, T. G. Scharmann, A. Schmalstieg and J. Demtschuk, *Z. Anorg. Allg. Chem.*, 2000, **626**, 2053 and references therein.
13 (*a*) I. Goldberg, *Top. Curr. Chem.*, 1988, **149**, 2; (*b*) F. H. Herbstein, *Top. Curr. Chem.*, 1987, **140**, 107; (*c*) C. Janiak, *J. Chem. Soc., Chem. Commun.*, 1994, 545.
14 (*a*) F. T. Edelmann, *Angew. Chem., Int. Ed.*, 2001, **40**, 1656; (*b*) B. E. Hanson, *Coord. Chem. Rev.*, 1999, **185–186**, 795; (*c*) N. Navon, H. Cohen, P. Paoletti, B. Valtancoli, A. Bencini and D. Meyerstein, *Ind. Eng. Chem. Res.*, 2000, **39**, 3536.
15 (*a*) C. Santini, G. Gioia Lobbia, M. Pellei, C. Pettinari, G. Valle and S. Calogero, *Inorg. Chim. Acta*, 1998, **282**, 1; (*b*) C. Santini, C. Pettinari, G. Gioia Lobbia, D. Leonesi, G. Valle and S. Calogero, *Polyhedron*, 1998, **17**, 3201; (*c*) Effendy, G. Gioia Lobbia, C. Pettinari, C. Santini, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1998, 2739.

16 (*a*) Effendy, G. Gioia Lobbia, M. Pellei, C. Pettinari, C. Santini, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2001, 528; (*b*) M. Pellei, C. Pettinari, C. Santini, B. W. Skelton, N. Somers and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2000, 3416; (*c*) G. Gioia Lobbia, M. Pellei, C. Pettinari, C. Santini, B. W. Skelton and A. H. White, *Inorg. Chim. Acta*, submitted.
17 The Xtal 3.7 System, ed. S. R. Hall, D. J. du Boulay and R. Olthof-Hazekamp, University of Western Australia, 2001.
18 G. B. Deacon and R. A. Jones, *Aust. J. Chem.*, 1963, **16**, 499; K. Shobatake, C. Postmus, J. R. Ferraro and K. Nakamoto, *Appl. Spectrosc.*, 1969, **12**, 23.
19 B. C. Cornilsen and K. Nakamoto, *J. Inorg. Nucl. Chem.*, 1974, **36**, 2467; C. Pettinari, F. Marchetti, A. Lorenzotti, G. Gioia Lobbia, D. Leonesi and A. Cingolani, *Gazz. Chim. Ital.*, 1994, **124**, 51.
20 C. Janiak, *Chem. Ber.*, 1994, **127**, 1379.
21 R. K. Harris, *Nuclear Magnetic Resonance Spectroscopy*, Pitman, London, ch. 5–14, pp. 138–141.
22 F. G. Herring, D. J. Patmore and A. Storr, *J. Chem. Soc., Dalton Trans.*, 1975, 711.
23 P. Cecchi, B. Bovio, G. G. Lobbia, C. Pettinari and D. Leonesi, *Polyhedron*, 1995, **14**, 2441.
24 R. R. Conry, G. Ji and A. A. Tipton, *Inorg. Chem.*, 1999, **38**, 906.
25 H. V. R. Dias and H.-L. Lu, *Inorg. Chem.*, 2000, **39**, 2246.
26 G. A. Bowmaker, C. L. Brown, R. D. Hart, P. C. Healy, C. E. F. Rickard and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1999, 881.
27 G. Gioia Lobbia, C. Pettinari, C. Santini, M. Colapietro and P. Cecchi, *Polyhedron*, 1997, **16**, 207.
28 N. Kitajima, T. Koda, S. Hashimoto, T. Kitagawa and Y. Moro-oka, *J. Am. Chem. Soc.*, 1991, **113**, 5664.
29 G. Gioia Lobbia, C. Pettinari, F. Marchetti, B. Bovio and P. Cecchi, *Polyhedron*, 1996, **15**, 881.
30 H. V. R. Dias, W. Jin, H.-J. Kim and H.-L. Lu, *Inorg. Chem.*, 1996, **35**, 2317.