Pergamon

S0277-5387(96)00284-7

Polyhedron Vol. 16, No. 2, pp. 207–215, 1997
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0277-5387/97 $15.00 + 0.00

Synthesis and characterization of copper(I) derivatives with *N*-donor ligands—IV.† Poly(1*H*-pyrazol-1-yl)borates cyclohexylphosphine Cu^I, the X-ray crystal structures of [HB-(μ-pz)$_3$-CuP(Cy)$_3$] and [HB-(μ-3,5 Me$_2$pz)$_3$-CuP(Cy)$_3$]

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(Received 29 February 1996; accepted 5 June 1996)

Abstract—The binding abilities of several polypyrazolylborato ligands (Tp$^{\#}$) toward nitrato bis(cyclohexylphosphine)Cu^I have been investigated. Complexes of empirical formula (Cy$_3$P)$_2$Cu·Tp$^{\#}$ (Tp$^{\#}$ = Bp or pzTp) and (Cy$_3$P)Cu·Tp$^{\#}$ (Tp$^{\#}$ = Tp, Tp^{Me}, Tp* or Tp*^{Cl}) have been synthesized and characterized through analytical and spectral (IR, ^{1}H, ^{13}C and ^{31}P NMR) measurements. The compound (Cy$_3$P)$_2$Cu·pzTp is fluxional at room temperature. In the crystal structure of the title compounds the copper atom is found in a strongly distorted tetrahedral coordination (the N—Cu—N and N—Cu—P angles range from 87.5(1) to 90.8(1)° and from 120.8(1) to 130.3(1)°, respectively. Comparison is made with related phosphino copper(I) derivatives. Copyright © 1996 Elsevier Science Ltd

Keywords: polypyrazol-1-ylborates; cyclohexylphosphine Cu^I; X-ray; ^{31}P; synthesis; derivatives of copper(I).

Metal derivatives containing poly(pyrazolyl)borato ligands have been widely investigated by inorganic, organometallic and bioinorganic chemists [1,2]. Recently, the tris(pyrazolyl)borato ligand system [Tp$^{\#}$] has found widespread use in the study of copper chemistry, a metal which plays a relevant role in the synthesis of catalytic systems [3,4] and models for biomimetic studies [4–8]. Phosphino-copper(I) derivatives have also potential applications in microelectronic technology [9].

In previous papers, the synthesis and characterization of bis(triarylphosphine)copper(I) derivatives with bis(azolyl)alkanes [10] and bis-, tris- and tetrakis(pyrazolyl)borato ligands have been described [11,12]. Now, we have extended our studies to the interaction of poly(pyrazolyl)borato ligands Bp, Tp$^{\#}$ (Tp$^{\#}$ = Tp, Tp^{Me}, Tp*, Tp*^{Cl}) and pzTp (Fig. 1) with a more sterically hindered Cu^I acceptor as (Cy$_3$P)$_2$Cu^I.

In this paper we describe the synthesis and spectroscopic characterization of six new Cu^I derivatives and also the solid state structural study of two of them, namely [HB-(μ-pz)$_3$-CuP(Cy)$_3$] and [HB-(μ-3,5-Me$_2$pz)$_3$-CuP(Cy)$_3$]. We have observed that the diversity of stoichiometries and geometries in these kind of complexes is strongly dependent on the steric and electronic requirements of the donors employed. The factors affecting the stoichiometry and the coordination number are here discussed and rationalized

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† Part III is Reference 12.

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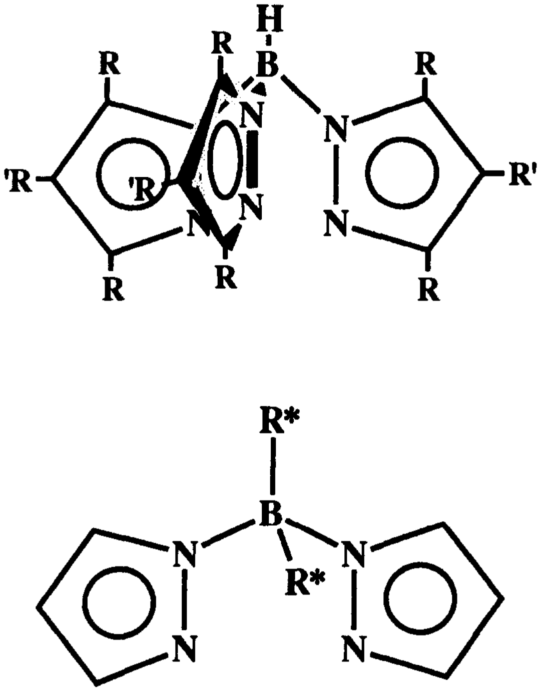

Fig. 1. Structure of the poly(pyrazol-1-yl)borato ligands employed in this work.

on the basis of steric and electronic arguments (for example Tolman's cone angle [13]).

EXPERIMENTAL

All solvents were dried by standard techniques. The reagents were obtained from Aldrich Chemical Co. and from Alfa. The samples were dried *in vacuo* to constant weight (20°C, *ca* 0.1 Torr). Concentration was always carried out under reduced pressure (water aspirator). Elemental analyses were carried out in-house with a Fisons Instruments 1108 CHNS-O Elemental analyzer. IR spectra from 4000 to 100 cm^{-1} were recorded with a Perkin-Elmer System 2000 FT-IR, instrument. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a VX-300 Varian spectrometer operating at room temperature (300 for ^1H, 75 for ^{13}C and 121.4 MHz for ^{31}P) or on a Varian Gemini-200 (200 MHz for ^1H, 50 MHz for ^{13}C). Melting points were taken on an IA 8100 Electrothermal instrument. The electrical resistances of solutions were measured with a Crison CDTM 522 conductimeter at room temperature.

All manipulations of Cu^I complexes were executed under dinitrogen to avoid any oxidation to Cu^{II}.

Synthesis of the donors

The donors Bp, Tp, Tp^{Me}, Tp*, Tp^{*Cl} and pzTp were prepared by published methods [14].

Synthesis of nitrato[bis{tricyclohexylphosphine} copper(I)]

The starting compound $\{(Cy_3P)_2CuNO_3\}$ was prepared according to the literature [15].

[*Bis*(*tricyclohexylphosphine*)*copper*(*I*)*dihydridobis* (*pyrazol*-1-*yl*)*borato*] (**1**)

A dichloromethane solution (25 cm^3) of bis(tricyclohexylphosphine) copper(I)nitrate (680 mg, 1.0 mmol) was added to a stirred dichloromethane suspension (30 cm^3) of potassium dihydrobis(1*H*-pyrazol-1-yl)borate (186 mg, 1 mmol) under a stream of N_2. After 3 h stirring the solid (KNO_3) was filtered and washed with dichloromethane (20 cm^3). The filtered solution was evaporated to dryness; the residue was purified from dichloromethane–heptane affording product **1** (460 mg, 0.6 mmol). Compound **2** was obtained similarly.

[(*Tricyclohexylphosphine*)*copper*(*I*)*hydridotris*(1*H*-*pyrazol*-1-*yl*)*borato*] (**3**)

A dichloromethane solution (25 cm^3) of bis(tricyclohexylphosphine)copper(I)nitrate (680 mg, 1.0 mmol) was added to a stirred dichloromethane suspension (30 cm^3) of potassium hydridotris(1H-pyrazol-1-yl)borate (250 mg, 1.0 mmol) under a stream of N_2. After 3 h stirring the solid (KNO_3) was filtered and washed with dichloromethane (20 cm^3). After slow evaporation of the solvent, the residue was recrystallized from acetonitrile-Et_2O, affording complex **3** (410 mg, 0.74 mmol). Compounds **4**–**6** were prepared similarly.

X-ray crystallography

Crystals and experimental data are summarized in Table 1. Colourless crystals of compound $Cy_3PCu \cdot Tp$ (**3**) were obtained from an acetonitrile/diethyl ether solution. For data collection one sample was used of approximate dimensions 0.2 × 0.2 × 0.3 mm. The cell parameters were refined by least squares from angular position of 12 reflections in the range $7 < 2\theta < 26°$.

Colourless crystals of compound $Cy_3PCu \cdot Tp^* \cdot CH_3CN$ (**5A**) were obtained from an acetonitrile/diethyl ether solution and the data were collected from a crystal of about 0.15 × 0.15 × 0.2 mm. The cell parameters were refined by least squares from angular positions of 14 reflections in the range $7 < 2\theta < 18°$.

Both crystals were mounted on a CS automatic four-circle diffractometer equipped with a Huber goniometer [16] using graphite monochromatized Mo-K_α radiation ($\lambda = 0.710689$ Å). The data were

Table 1. Crystallographic data

Compound	**3**	**5A**
Formula	$C_{27}H_{43}BCuN_6P$	$C_{33}H_{55}BCuN_6P \cdot CH_3CN$
Formula weight	557.1	682.2
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$Pna2_1$
a (Å)	8.519(2)	20.475(4)
b (Å)	18.939(4)	12.470(2)
c (Å)	18.541(4)	14.663(3)
β (°)	103.27(3)	
V (Å^{-3})	2911.6(15)	3744(2)
Z	4	4
D_c (g cm^{-3})	1.271	1.210
μ (cm^{-1})	8.31	6.59
$F(000)$	1184	1464
No. of measured reflections	8454	4100
No. of unique reflections	8454	3564
No. of observed reflections	4187	3350
	$\lvert F_o \rvert > 2\sigma \lvert F_o \rvert$	$\lvert F_o \rvert > 6\sigma \lvert F_o \rvert$
Function minimized	$\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2$	
Variables refined	325	424
$R = \Sigma(\lvert F_o \rvert^2 - \lvert F_c \rvert)^2 / \Sigma F_o^2$	0.029	0.039
$R_w = \Sigma_w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma_w F_o^2$	0.049	0.057
$w^{-1} = \sigma^2(F_o) + KF_o^2$	$K = 0.0025$	$K = 0.0030$

collected at room temperature for $3 < 2\theta < 60°$ using an ω scan technique with a $\Delta\omega = 1°$. The scan rate was automatically chosen according to the peak intensity in the range 2.0–30.0° min^{-1}. Background counts were taken with stationary crystal with an offset of 0.5° at each end of the scan, and a total background to scan time ratio of 0.5. The intensities of three standard reflections were monitored every 97 reflections during the data collections in order to evaluate the decay. Data were corrected for Lorentz and polarization effects and for decay, but not for absorption.

Both of the structures were solved by direct methods by using SIR 92 structure determination package [17]. All the non-hydrogen atoms were refined by full-matrix least-squares methods with anisotropic thermal parameters. For the compound $Cy_3PCu \cdot Tp$ (**3**) the hydrogen atoms were introduced in the final refinement in idealized positions (C—H = 0.96 Å). Each hydrogen atom was assigned arbitrarily the equivalent isotropic temperature factor of the parent carbon atom and allowed to ride on it.

For the compound $Cy_3PCu \cdot Tp^* \cdot CH_3CN$ (**5A**), which crystallizes with a molecule of solvent in the asymmetric unit, the hydrogen atoms of the methyl groups, which are affected by large amplitude thermal motion, were introduced in calculated positions for the two more-populated conformations revealed by the Fourier difference. Their occupancy factor was kept fixed during the final refinement to 0.5. Otherwise each hydrogen atom was treated as described previously for the compound $Cy_3PCu \cdot Tp$ (**3**).

All calculations were carried out on a PC using the SIR CAOS [18] and SHELXTL [19] packages.

RESULTS AND DISCUSSION

The copper(I)polypyrazolylborato complexes **1**–**6** were synthesized from the interaction of bis(cyclohexylphosphine)copper(I)nitrato with potassium salts of the ligands, in dichloromethane suspension in accordance with the following equations:

$$(Cy_3P)_2CuNO_3 + KTp^{\#} \rightarrow KNO_3 + (Cy_3P)_2Cu \cdot Tp^{\#} \quad (I)$$

$(Tp^{\#} = Bp, pzTp)$

$$(Cy_3P)_2CuNO_3 + KTp^{\#} \rightarrow KNO_3 + Cy_3P + (Cy_3P)Cu \cdot Tp^{\#} \quad (II)$$

$(Tp^{\#} = Tp, Tp^{Me}, Tp^*, Tp^{*Cl})$

All reactions resulted in the formation of the desired products in fair yields.

The complexes were generally purified from acetonitrile/Et_2O: $Cy_3PCu \cdot Tp^*$ (**5**) crystallizes also with a molecule of CH_3CN (compound **5A**). It is worth noting that the ligand pzTp, even if it is more sterically hindered with respect to Tp, is not able to act as tridentate donor by displacing a phosphine group.

The compounds **1**–**6** gave satisfactory elemental analyses. They are soluble in CH_2Cl_2, $CHCl_3$, DMSO and acetone. In the last solvent they are non-electrolytes (Table 2). This is in reasonable agreement with the neutral structures proposed in Fig. 2. In $CHCl_3$ (concentration in the range 1.0–2.0×10^{-2} m), the ratio r between the vaporimetric molecular weight

Table 2. Yields, analyses, and physical properties of compounds **1**–**6**

	Compound[a]	M.p.	Yield	Elemental Analysis (Found/Calc.) (%) C	H	N	Λ[b]
1	$[(Cy)_3\text{-}P]_2Cu\cdot Bp$	114–116	61	65.6	9.6	7.2	6.3
				65.4	9.7	7.3	(1.0)
2	$[(Cy)_3\text{-}P]_2Cu\cdot pzTp$	155–157	79	63.7	8.8	12.6	7.8
				63.8	8.7	12.4	(1.0)
3	$[(Cy)_3\text{-}P]Cu\text{-}Tp$	88–90	74	58.4	7.9	14.9	6.7
				58.2	7.8	15.1	(1.1)
4	$[(Cy)_3\text{-}P]Cu\text{-}Tp^{Me}$	194–196[c]	68	60.5	8.0	13.8	6.4
				60.2	8.2	14.0	(1.0)
5	$[(Cy)_3\text{-}P]Cu\text{-}Tp^*$	179–181[c]	70	62.0	8.8	12.9	7.5
				61.8	8.7	13.1	(0.9)
5A	$[(Cy)_3\text{-}P]Cu\text{-}Tp^*\cdot CH_3CN$	179–181[c]	15	61.8	8.8	13.9	7.2
				61.6	8.6	14.4	(0.9)
6	$[(Cy)_3\text{-}P]Cu\text{-}Tp^{*Cl}$	206–208[c]	62	53.6	6.9	11.1	8.7
				53.2	7.0	11.3	(1.0)

[a] Bp is dihydridobis(1*H*-pyrazol-1-yl)borate, $C_6H_8N_4B$; pzTp is tetrakis(1*H*-pyrazol-1-yl)borate, $C_{12}H_{12}N_8B$; Tp is hydridotris(1*H*-pyrazol-1-yl)borate, $C_9H_{10}N_6B$; Tp^{Me} is hydridotris(3-Me-1*H*-pyrazol-1-yl)borate, $C_{12}H_{16}N_6B$; Tp* is hydridotris(3,5Me$_2$-1*H*-pyrazol-1-yl)borate, $C_{15}H_{22}N_6B$; Tp^{*Cl} is hydridotris(3,5-Me$_2$,4-Cl-1*H*-pyrazol-1-yl)borate, $C_{15}H_{19}Cl_3N_6B$.

[b] Specific conductivity in acetone solution ($ohm^{-1}\ cm^2\ mol^{-1}$) at room temperature and the molar concentration × 10^{-3} indicated in parentheses in the lower line.

[c] Melting with decomposition.

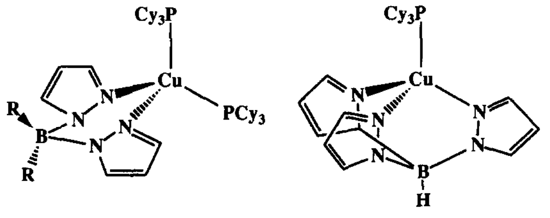

Fig. 2. Structures of the copper(I) derivatives.

and the formula weight for compound **1** lies in the range 0.70–0.80 and indicates that this complex presumably dissociates partly in this solvent in accordance with eq. III:

$$(Cy_3P)_2Cu\cdot Bp \rightleftharpoons (Cy_3P)Cu\cdot Bp + Cy_3P \quad \text{(III)}$$

All the complexes **1**–**6** were characterized through infrared (Nujol mull and chloroform solution) (Table 3) and ^1H, ^{13}C, and ^{31}P NMR spectra (Tables 4–5).

Infrared data

The IR spectra (Table 3) show several bands which may be taken as diagnostic of the poly(pyrazol-1-yl)borato ligands: weak and medium vibrations at about 3100 cm^{-1} due to C—H stretching in the pyrazolic ring, several more intense absorptions between 1600 and 1500 cm^{-1} typical of ring breathing [20] and finally in the derivatives **1** and **3**–**6**, one or two weak bands due to B—H stretching, generally unchanged with respect to those observed in the spectra of potassium salts of the ligands [21]. In the far-IR region the weak bands in the range 400 – 380 cm^{-1} are likely due to P—C stretching modes [22], whereas some weak absorptions at *ca* 300 cm^{-1}, absent in the spectra of both the starting copper(I) derivative and poly(pyrazolyl)borato ligands, are tentatively assigned to Cu—N stretching modes, also on the basis of previous reports in literature [23].

No significant differences were observed between the spectra in Nujol mull and those recorded in chloroform solution.

We have observed that the bis(tricyclohexyl-phosphine)derivatives **1**–**6** were more oxygen sensitive than the previously reported triphenylphosphine analogues [11,12]. Indeed, when the compounds **1**–**6** were dissolved in chloroform and exposed to air, their solutions turned deep green or blue, two characteristic colours of copper(II) derivatives.

^1H, ^{31}P *and* ^{13}C-*NMR spectra*

The ^1H and ^{13}C-NMR spectra (Tables 4 and 5) show the signals due to ligand moieties in the expected position and multiplicity [14] (e.g. for ^1H: two doublets and a pseudo-triplet for the derivatives of Bp, pzTp and Tp, two doublets for the Tp^{Me} pyrazole ring protons, together with a Me singlet, a singlet for 4-H and two singlets for the 3- and -5-Me in the Tp* derivative, and finally two Me singlets for Tp^{*Cl}). On comparison between the chemical shift related to the same type of proton in the starting potassium poly-

Table 3. Selected IR data (cm^{-1})[a]

Compound	No.	>3000	1600–1500	<650	ν(B—H)
[(Cy$_3$P)$_2$Cu·Bp]	**1**	3109w	1502w, 1499w	520w, 510m, 490m, 470m, 396w, 386w, 351w, 325w, 306w, 279w, 247w, 224w	2446m, 2390w
[(Cy$_3$P)$_2$Cu·pzTp]	**2**	3172w, 3148w	1508m, 1499m	519m, 474w, 462w, 420w, 395w, 386w, 360m, 346w, 280w, 247w	
[(Cy$_3$P)Cu·Tp]	**3**	3115w, 3089w, 3134w	1589w, 1050sh, 1496m	520br, 473m, 460sh, 418w, 385w, 333m, 303w, 280w, 247w, 225w	2458m, 2403w
[(Cy$_3$P)Cu·Tp^{Me}]	**4**	3179w, 3115w	1576w, 1506m	520m, 492w, 473w, 395w, 380w, 346w, 326w, 280m, 247w, 212w, 203w	2458w, 2405w
[(Cy$_3$P)Cu·Tp*]	**5**	3115w	1541m	513m, 483m, 469w, 460w, 396w, 383w, 352w, 326w, 303w, 280m, 254m, 247m	2516w
[(Cy$_3$P)Cu·Tp*]·CH$_3$CN	**5A**	3115w	1541m	513m, 483m, 469w, 460w, 396w, 383w, 352w, 326w, 303w, 280m, 254m, 247m	2516w
[(Cy$_3$P)Cu·Tp*^{Cl}]	**6**	3174w	1538m, 1522w, 1505sh	538w, 519m, 490w, 481w, 470w, 426w, 383w, 326vw, 279m, 247w, 226m	2458w, 2405w

[a] Nujol mull and/or CHCl$_3$ solution.

Table 4. ^{1}H and ^{31}P NMR data[a]

No.	Compound[b]	3- or 5-H		4-H	3- or 5-pz-Me		Cy groups	^{31}P
1	[(Cy)$_3$P]$_2$Cu·Bp	7.59 d	7.48 d	6.16 t	—	—	1.90–1.72 m, br 1.42–1.20 m, br	17.92
2	[(Cy)$_3$P]$_2$Cu·pzTp	7.65 d	7.07 d	6.22 t	—	—	1.80 m, br; 1.25 m, br	25.62
3	[(Cy)$_3$P]Cu·Tp	7.62 d	7.47 d	6.10 t	—	—	2.08–1.72 m, br 1.52–1.25 m, br	22.37[c]
4	[(Cy)$_3$P]$_2$Cu·Tp^{Me}	7.42 d	—	5.90 d	2.28	—	1.86–1.64 m, br 1.42–1.20 m, br	21.21
5	[(Cy)$_3$P]$_2$Cu·Tp*	—	—	5.66 s	2.34	2.20	1.89–1.70 m, br 1.45–1.22 m, br	26.34[c]
5A	[(Cy)$_3$P]$_2$Cu·Tp*·CH$_3$CN	—	—	5.68 s	2.34	2.22	1.89–1.70 m, br 1.45–1.22 m, br	
6	[(Cy)$_3$P]$_2$Cu·Tp*^{Cl}	—	—	—	2.32	2.20	1.90–1.74 m, br 1.56–1.24 m, br	24.44

[a] CDCl$_3$ solutions, δ in ppm from Me$_4$Si, calibration from internal deuterium solvent lock.

[b] The NMR data of potassium salts of bis-, tris- and tetrakis(pyrazolyl)borates are in [14].

[c] Recorded at −45°C.

Table 5. ^{13}C NMR data[a]

No.	Compound[b]	3- or 5-C		4-C	Cy	*pz*-Me
1	[(Cy)$_3$P]$_2$Cu·Bp	140.5	135.4	103.9	Cy: 32.6 d, 31.4 s, 28.0 d, 26.9 s	
2	[(Cy)$_3$P]$_2$Cu·pzTp	141.6	134.9	104.6	Cy: 32.1 d, 30.7 d, 27.3d, 26.1 s	
3	[(Cy)$_3$P]Cu·Tp	140.1	134.3	103.9	Cy: 32.8 br, 31.4 s, 28.1 d, 26.9 s	
4	[(Cy)$_3$P]Cu·Tp^{Me}	149.1	135.8	102.2	Cy: 33.0 d, br, 31.9 s, 28.0 d, 26.4 s	Me: 15.1
5	[(Cy)$_3$P]Cu·Tp*	147.1	143.2	104.6	Cy: 33.8 d, 30.9 s, 27.9 d, 26.4 d	Me: 14.8, 12.9
6	[(Cy)$_3$P]Cu·Tp*^{Cl}	145.2	140.4	108.4	Cy: 34.2 d, 32.7 d, 28.4 d, 26.7 s	Me: 13.2, 11.4

[a] CDCl$_3$ solutions, δ in ppm from Me$_4$Si, calibration from internal deuterium solvent lock.

[b] NMR data of potassium tris(pyrazolyl)borates are in [14].

(pyrazol-1-yl)borates and in the corresponding phosphinocopper(I) derivatives **1–6**, generally we have found downfield resonances in the case of H(5), CH_3—C(5) and CH_3—C(3) and upfield resonances in the case of H(4), whereas only a negligible shift was detected in the case of H(3). This is likely due to change in electron density of azole ring upon coordination of the donor to copper ion. Differences in chemical shifts of the cyclohexyl protons with respect to the starting $(Cy_3P)_2CuNO_3$ [15] are not significant. In all the ^1H and ^{13}C we observed one set of signals for each magnetically equivalent nucleus. Assuming that a tetrahedral coordination, similar to that found in the crystal structures of derivatives **3** and **5A**, is operating in solution also in the case of derivative **2**, we hypothesized a fluxional behaviour of this compound which likely requires a fast concomitant breaking and formation of the Cu—N bond. This behaviour is analogous to those observed in the corresponding $(Ar_3)_2Cu(I)\cdot pzTp$ [12]. In the ^{13}C-NMR spectra we found a pattern of chemical shifts in keeping with what has been previously described [14].

The ^{31}P NMR spectra of complexes **1–6** are reported in Table 4. In all the cases we observed only a single resonance. This is due to a fluxional behaviour of these complexes. The signal observed for the (pyrazol-1-yl)boratocopper(I) derivatives **1–6** appears downfield with respect to those observed for the free tricyclohexylphosphine signal (11.8 ppm). $\Delta\delta^{31}P = \delta^{31}P_{complex}-\delta^{31}P_{ligand}$, the difference in shift between the free phosphine and copper(I) complexes is in the order of 6–14 ppm. The shift is smaller than those observed in platinum and gold complexes [24]. These acceptors are more electronegative than phosphorus and inductively they withdraw electron density from the phosphorus atom which experiences a greater net magnetic field. In the ^{31}P NMR spectrum of the derivative **1** we found a broad signal upfield shifted with respect to those reported for derivatives **2–6**. This is likely due to instability of complex **1** in solution which undergoes rapid ligand exchange in accordance with equilibrium III.

Description of the molecular structures of $Cy_3PCu\cdot Tp$ (**3**) *and* $Cy_3PCu\cdot Tp^*\cdot CH_3CN$ (**5A**)

Perspective drawings of $Cy_3PCu\cdot Tp$ (**3**) and $Cy_3PCu\cdot Tp^*\cdot CH_3CN$ (**5A**) are shown in Figs 3 and 4 together with the numbering scheme. Selected interatomic distances and angles are reported in Tables 6 and 7. In both derivatives the copper atom is tetracoordinate, being bonded to one phosphorus atom of Cy_3P and three nitrogen atoms of the tridentate Tp and Tp*. The copper atom is in a strongly distorted tetrahedral environment: the N—Cu—N and N—Cu—P angles are in the range 87.5(1)–90.8(1)° and 120.8(1)–130.3(1)°, respectively. This finding is probably due to remarkable steric hindrance of the tricyclohexylphosphine [13] and Tp ligands. The

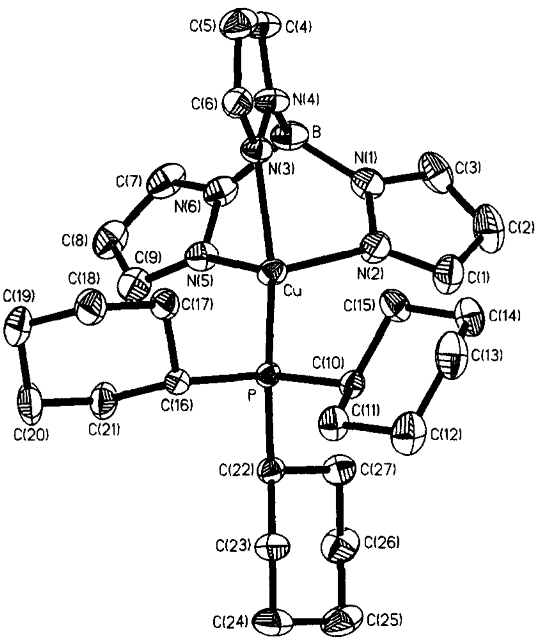

Fig. 3. Molecular structure and labelling scheme for $[(Cy)_3P]_2Cu\cdot Tp$ **3**.

Table 6. Selected bond lengths (Å)

Compound	3	5A
Cu—P	2.170(1)	2.207(1)
Cu—N(2)	2.104(2)	2.133(2)
Cu—N(3)	2.095(2)	2.106(2)
Cu—N(5)	2.093(2)	2.147(2)
P—C(10)	1.864(2)	1.852(5)
P—C(16)	1.847(2)	1.860(5)
P—C(22)	1.860(2)	1.867(4)
N(1)—N(2)	1.361(3)	1.369(5)
N(1)—C(3)	1.338(4)	1.352(6)
N(2)—C(1)	1.332(3)	1.326(6)
N(3)—N(4)	1.364(3)	1.374(4)
N(3)—C(6)	1.326(3)	1.330(5)
N(4)—C(4)	1.334(3)	1.358(5)
N(5)—N(6)	1.351(3)	1.388(5)
N(5)—C(9)	1.325(3)	1.312(6)
N(6)—C(7)	1.350(3)	1.340(6)
C(1)—C(2)	1.385(5)	1.379(7)
C(2)—C(3)	1.351(5)	1.386(7)
C(4)—C(5)	1.376(4)	1.376(6)
C(5)—C(6)	1.379(4)	1.393(6)
C(7)—C(8)	1.354(4)	1.396(7)
C(8)—C(9)	1.383(4)	1.375(6)
C(1)—C(28)		1.504(7)
C(3)—C(29)		1.492(6)
C(4)—C(30)		1.494(6)
C(6)—C(31)		1.510(6)
C(7)—C(32)		1.484(7)
C(9)—C(33)		1.496(1)
N(90)—C(91)		1.086(13)
C(91)—C(92)		1.459(12)

Table 7. Selected bond angles (°)

Compound	**3**	**5A**
P—Cu—N(2)	120.8(1)	125.4(1)
P—Cu—N(3)	130.3(1)	126.9(1)
P—Cu—N(5)	125.5(1)	124.1(1)
N(2)—Cu—N(3)	90.8(1)	90.2(1)
N(3)—Cu—N(5)	87.5(1)	89.5(1)
N(2)—Cu—N(5)	90.6(1)	89.5(1)
Cu—P—C(10)	116.0(1)	112.4(2)
Cu—P—C(16)	114.6(1)	113.2(2)
Cu—P—C(22)	111.5(1)	112.0(1)
N(2)—N(1)—C(3)	109.9(2)	110.1(4)
N(1)—N(2)—C(1)	105.8(2)	106.3(4)
N(4)—N(3)—C(6)	106.0(2)	106.1(3)
N(3)—N(4)—C(4)	109.9(2)	110.6(3)
N(6)—N(5)—C(9)	106.1(2)	106.0(3)
N(5)—N(6)—C(7)	109.6(2)	109.8(3)
N(2)—C(1)—C(2)	110.3(3)	110.8(4)
C(1)—C(2)—C(3)	105.5(3)	105.9(5)
N(1)—C(3)—C(2)	108.6(3)	106.9(4)
N(4)—C(4)—C(5)	108.3(3)	106.5(3)
C(4)—C(5)—C(6)	104.8(2)	106.7(3)
N(3)—C(6)—C(5)	111.1(2)	110.1(3)
N(6)—C(7)—C(8)	108.4(2)	107.2(4)
C(7)—C(8)—C(9)	105.0(2)	105.3(4)
N(5)—C(9)—C(8)	110.9(2)	111.7(4)
N(2)—C(1)—C(28)		121.6(4)
C(2)—C(1)—C(28)		127.7(5)
N(1)—C(3)—C(29)		123.2(4)
C(2)—C(3)—C(29)		129.9(5)
C(5)—C(4)—C(30)		130.8(4)
N(4)—C(4)—C(30)		122.8(4)
C(5)—C(6)—C(31)		128.3(4)
N(3)—C(6)—C(31)		121.5(3)
N(6)—C(7)—C(32)		123.8(5)
C(8)—C(7)—C(32)		129.0(5)
N(5)—C(9)—C(33)		121.6(4)
C(8)—C(9)—C(33)		126.8(5)
N(90)—C(91)—C(92)		178.3(12)

Cu—N bond lengths [**3**: 2.093(2), 2.095(2) and 2.104(2) Å; **5A**: 2.106(2), 2.133 and 2.147(2) Å] are somewhat longer than those observed previously in other copper(I)-azole compounds [25], suggesting a weak bonding interaction between the poly(pyrazol-1-yl)borate and the copper(I) acceptor.

Interesting features involving the metal coordination environment are recognizable comparing the structures of the compounds through some characteristic parameters such as those reported in Table 8. While the bond distances Cu(I)—N and Cu(I)—P are greater in **5A** than in **3**, the mean N—Cu—N (bite angles) and N—Cu—P angles in **5A** and in **3** are similar. In the phosphorus environment, besides the already cited lengthening of the Cu—P bond in **5A**, the C(ipso)—P mean bond distance is slightly greater in **5A** than in **3**, the angles C(ipso)—P—C(ipso) are significantly wider in **5A** than in **3**. Substitution of Me for hydrogen in position 3 of the pyrazole rings clearly makes the $Tp^{\#}$ sterically more demanding. Indeed, methyls show close contacts with the cyclohexyl groups whose shortest values range from 3.868 to 3.723 Å. The widening of C—P—C angles in **5A** at P are a consequence of the longer distance from Cu and are reflected, in part, in the enlarged C(ipso)—P distances.

Comparing the Cu—P bond lengths in the complexes **3** and **5A** with the corresponding ones in the precursors Cy_3P—$CuNO_3$ [15] or Cy_3P—$CuClO_4$ [26] a contraction of such bonds is observed on complex formation. This is to be expected on the basis of the actual oxidation state of Cu. In the precursors the phosphine is bonded to an essentially ionic metal centre, while in the complexes they are bonded to a nearly neutral one. This makes the retrodonation of electron density, from Cu to P low-lying antibonding orbitals, more effective and so the bond is stronger and shorter.

The greater value of Cu—P bond length in **5A** with respect to **3** may indicate that the overall donating power of Tp* is here lower than that of Tp for steric reasons. Since Tp* is known to be a better donor to non-hindered centres (in particular to the proton) this behaviour is likely due to steric hindrance. Indeed, recalling that the Cu—N bond lengths are greater in **5A** than in **3** as well, it may be concluded that the Me substituted ligand Tp* is here somewhat prevented from an approach so close to the bulky metal moiety as that of unsubstituted Tp.

It is also of interest to compare the present structure of **3** with the previously obtained one of $Ph_3PCu\cdot Tp$ [12] besides the N—Cu—N, N—Cu—P, and C—P—C angles which are similar and underscore the homogeneity of the complexes, the Cu—N and Cu—P bond lengths are greater in **3** than in $Ph_3PCu\cdot Tp$. This offers the chance to compare the Cu moieties (instead of the ligand ones, *vide supra*) in their contribution to steric hindrance. Here again the lengthenings observed in **3** (*vs* $Ph_3PCu\cdot Tp$) are accounted for by the same motivations as above. The P—C lengths are not comparable in this case since the carbon atoms have different hybridizations. Although the differences in the angles are slight it may be noted that the increase in N—Cu—P value for **3** is consistent with a consequent decrease of the N—Cu—N one. This, taken together with the C—P—C increase, depict a situation in which the bulky Cy_3PCu moiety demands more space and slightly compresses the Tp moiety.

Supplementary material available

Full tables of bond lengths and angles, tables of atomic coordinates and equivalent displacement coefficients, tables of observed and calculated structural factors, anisotropic thermal parameters for non-H atoms as well as hydrogen atom parameters are available as supplementary material.

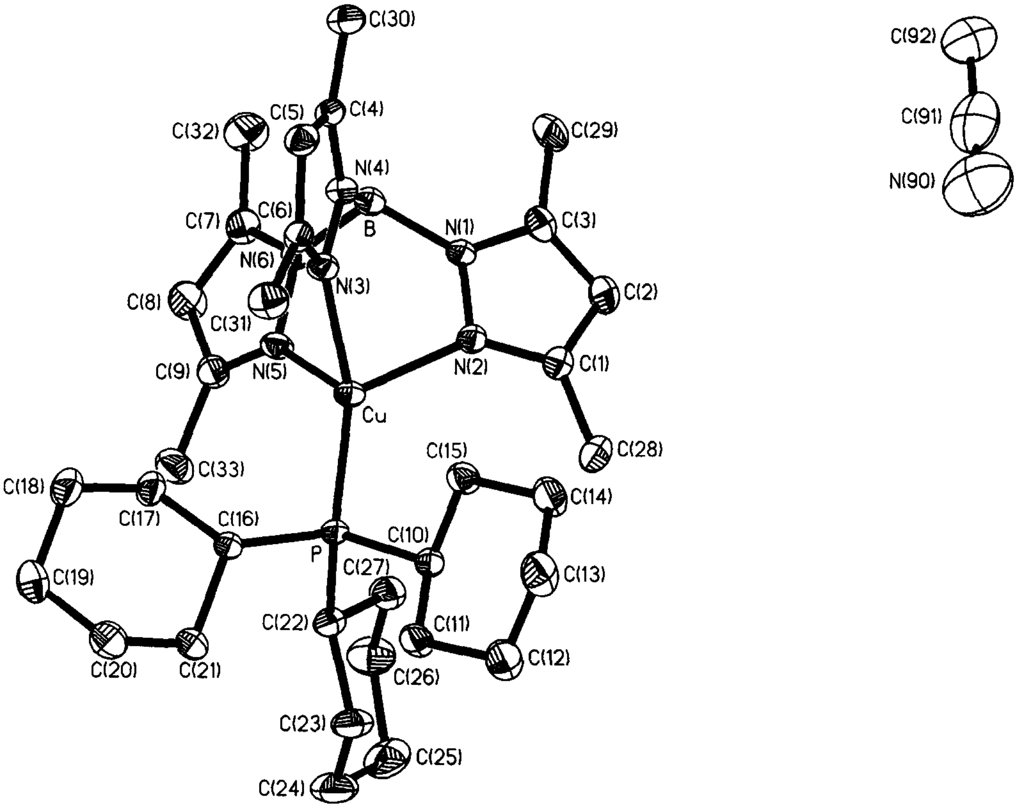

Fig. 4. Molecular structure and labelling scheme for $[(Cy)_3P]_2Cu \cdot Tp^* \cdot CH_3CN$ **5A**.

Table 8. Comparison of significant structural parameters

Compound	Cu—N[a]	Cu—P[a]	P—C[a]	N—Cu—N[b]	N—Cu—P[b]	C—P—C[b]	Reference
$Cy_3PCu \cdot Tp$ (**3**)	2.097	2.170	1.857	89.63	125.53	104.50	—
$Ph_3PCu \cdot Tp$	2.076	2.153	1.829	90.40	125.00	103.70	12
$(Ph_3P)_2Cu \cdot pzTp$	2.069	2.316	1.823	92.60	[d]	102.43	11
$Cy_3PCu \cdot Tp^*$ (**5A**)[c]	2.128	2.207	1.860	89.73	125.47	106.23	—

[a] In Å.

[b] In degrees.

[c] $+CH_3CN$.

[d] There are two different mean values according to the present of two phosphines: 117.84 and 102.13°.

Acknowledgements—Financial support from the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) and the Consiglio Nazionale delle Recerche (C.N.R.-Rome) is gratefully acknowledged. The authors would also like to acknowledge Dr Fabio Marchetti (University di Camerino) for helpful discussion and Professor M. Bonamico (CNR-Montelibretti) for the help in the refinement of complex **5A**.

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