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SYNTHESIS AND CHARACTERIZATION OF COPPER(I) DERIVATIVES WITH NITROGEN-DONOR LIGANDS—II.† DIHYDRIDOBIS- AND TETRAKIS(1*H*-PYRAZOL-1-YL)BORATE. THE X-RAY CYRSTAL STRUCTURE OF $[pz_2B\text{-}(\mu\text{-}pz)_2\text{-}Cu(PPh_3)_2]$

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Abstract—Bis(triarylphosphine)copper(I) derivatives with the anionic tetrakis(1*H*-pyrazol-1-yl)borato (pzTp) or dihydridobis(1*H*-pyrazol-1-yl)borato (Bp) have been prepared from $(Ar_3P)_2CuNO_3$ and KpzTp or KBp, and characterized through IR and ^1H, ^{13}C and ^{31}P NMR. The complexes contain tetrahedral Cu^I and a bidentate ligand. The pzTp ones are fluxional in solution with all pyrazolyl groups equivalent down to ~ −60°C. The X-ray crystal structure of $(Ph_3P)_2CupzTp$ has been resolved. The Cu^I atom has distorted tetrahedral cordination and shows Cu—N distances of 2.087(3), 2.051(3) Å and Cu—P distances of 2.273(1), 2.359(1) Å; the N—Cu—N and P—Cu—P angles are 92.6(1)° and 119.82(4)°, respectively, whereas the N—Cu—P angles range from 99.21(9) to 119.76(9)°. The six-membered $B(NN)_2Cu$ ring adopts the boat form.

There has been considerable recent interest in the chemistry of triaryl- or trialkylphosphine copper(I) derivatives because these compounds show a wide variety of structural features[1] and play an important role in the micro-electronics industry.[2] Copper(I) phosphines are involved in a number of catalytic systems[3] and copper(I) compounds in general are useful in organic synthesis;[4] the well-documented importance of copper(I) centres as the active sites in a number of proteins has been recognized.[5] Phosphine Cu^I poly(pyrazolyl)borates have been investigated but no crystal structure has been reported. Furthermore, at least for complexes containing simple (non-chelating) phosphines, the reported stoichiometry is (phosphine)CuTp$^\#$ with the copper four-coordinate [Tp$^\#$ = Tp (hydridotris(1*H*-pyrazol-1-yl)borato, Tp* hydridobis(3,5-dimethyl-1*H*-pyrazol-1-yl)borato, or pzTp] or (pseudo) three-

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† Part I is ref. 9.

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coordinate ($Tp^{\#}$ = Bp, Ph_2Bp)[6] with additional H (or Ph)–Cu interactions.

Nevertheless, although the syntheses of $(PPh_3)_2Cu^I$ chelates with the very common acetylacetonates[7] have been reported and those with the bis(azolyl)alkanes have also been studied,[8,9] $(Ph_3P)_2Cu^I$ derivatives featuring anionic poly(pyrazolyl)borato ligands have rarely been considered up to now[10] and no crystal structure reported. In the present paper, bis(phosphine)copper(I) derivatives with pzTp or Bp are investigated together with the crystal structure of $(Ph_3P)_2Cu(\mu\text{-pz})_2(pz)_2B$.

RESULTS AND DISCUSSION

The interaction between bis(triphenylphosphine)copper(I) nitrate with potassium salts of tetrakis(1*H*-pyrazol-1-yl)borate (pzTp) or dihydridobis(1*H*-pyrazol-1-yl)borate (Bp) in dichloromethane readily gives the corresponding compounds **1**–**6** listed in Table 1, according to the following general equation:

$$(Ar_3P)_2CuNO_3 + KTp^{\#} \longrightarrow KNO_3 + (Ar_3P)_2Cu \cdot Tp^{\#}$$

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

In this case the reaction is not simply metathetic but implies the disruption by $Tp^{\#}$ of the chelation from the bidentate nitrato group. All the compounds are colourless and thermally stable in the solid state, while in solution, above room temperature, they are readily oxidized unless an inert atmosphere is used. They were characterized through analytical and conductivity data (Table 1), IR (Table 2), ^1H and ^{13}C NMR spectra (Tables 3 and 4, respectively).

Conductivity

As it can be seen in Table 1, all the compounds are non-electrolytes in acetone solution and this precludes their dissociation, even if fluxional.

IR spectra

The IR spectra of the complexes **1**–**6** (Table 2) show the bands usually associated with the poly(pyrazolyl)borato ligands: weak and medium vibrations at *ca* 3000 cm^{-1}, and other, more intense bands between 1600 and 1500 cm^{-1} typical of ring breathing;[10] in addition, in the spectra of compounds **4**–**6** the ν(B—H) absorptions are also detected, which are only slightly shifted with respect to the same bands in the free ligands. In the far-IR spectra of all our copper(I) phosphine derivatives, two groups of vibrations are always evident: we assign the first group (around 500 cm^{-1}) to Whiffen's *y*-vibrations of Ar_3P (out-of-plane bending of the phenyl rings), whereas the second group, (around 430 cm^{-1}) can be assigned to P—C(Ph) stretching modes (Whiffen's *t*-vibration).[12] In the far-IR spectra of our compounds it is difficult to

Table 1. Yields, analyses and physical properties of compounds

	Compound[a]	M.p. (°C)	Yield (%)	Elemental analysis (Found/Calc.) (%) C	H	N	Λ[b]
1	$[(Ph)_3P]_2Cu \cdot pzTp$	168–170	88	66.2	5.1	12.9	2.4
				66.5	4.9	12.9	(0.99)
2	$[(p\text{-tolyl})_3P]_2Cu \cdot pzTp$	172–174	76	67.9	5.9	11.4	2.7
				68.2	5.7	11.8	(1.10)
3	$[(m\text{-tolyl})_3P]_2Cu \cdot pzTp$	[c]	69	68.0	6.0	11.5	3.9
				68.2	5.7	11.8	(1.00)
4	$[(Ph)_3P]_2Cu \cdot Bp$	190–192	79	68.3	5.4	7.3	5.1
				68.6	5.2	7.6	(1.00)
5	$[(p\text{-tolyl})_3P]_2Cu \cdot Bp$	159–161	66	69.9	6.1	6.6	5.6
				70.4	6.2	6.8	(1.00)
6	$[(m\text{-tolyl})_3P]_2Cu \cdot Bp$	116–118	58	70.2	6.0	6.5	9.8
				70.4	6.2	6.8	(1.00)

[a] pzTp is tetrakis(1*H*-pyrazol-1-yl)borate, $C_{12}H_{12}N_8B$; Bp is dihydridobis(1*H*-pyrazol-1-yl)borate, $C_6H_8N_4B$.

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

[c] Below room temperature.

Table 2. Selected IR data (cm^{-1})[a] of the ligands and the copper(I) derivatives

Compound	>3000 cm^{-1}	1600–1500 cm^{-1}	<600 cm^{-1}	Other data
[CuNO$_3$(Ph$_3$P)$_2$][b]	3063w	1588w, 1579w	533m, 521m, 503m, 444w, 430w 281w, 248w, 227w	ν(NO$_3$): 1470s, 1280s
[CuNO$_3${(*p*-tolyl)$_3$P)$_2$}][b]	3050w	1598m, 1559w	516m, 505m, 495m, 436m, 421m, 356m, 317w br, 237br	ν(NO$_3$): 1460s, 1288s
[CuNO$_3${(*m*-tolyl)$_3$P)$_2$}][b]	3050w	1589m	553m, 545m, 455m	ν(NO$_3$): 1470s, 1286s
KpzTp	3146w, 3110w, 3080w	1560m, 1539w	490m, 397m, 351m, 344m, 328m 315w, 280m, 253m, 248m	
[(Ph$_3$P)$_2$pzTp]Cu	3129w 3051w	1586w, 1570w 1505m	542w, 523m, 518s, 507s, 491m 443w, 428wn, 413w, 360w, 290w	
[{(*p*-tolyl)$_3$P)$_2$}pzTp]Cu	3145w, 3129w 3098w	1597m, 1558w 1540w, 1500s	542vw, 526sh, 517s, 509m, 501m 432w, 360w, 343w, 329vw	
[{(*m*-tolyl)$_3$P)$_2$}pzTp]Cu	3129w	1600w, 1580w, 1570w, 1540w	568sbr, 524m, 490m, 478s, 453s, 360w, 275w, 214w	
KBp	3140w, 3110w 3090w	1590w, 1557m 1505m	349w, 321m, 278m, 265m, 255m 248m	ν(B—H): 2400br, 2370m 2354m, 2280m
[(Ph$_3$P)$_2$Bp]Cu	3100w 3070w	1587w, 1568w 1500sh	560w, 543w, 515sh, 510s, 493s 435w, 420w, 410w, 281w; 248w	ν(B—H): 2397m, 2366m 2337sh, 2278w
[{(*p*-tolyl)$_3$P)$_2$}Bp]Cu	3104w, 3067w 3040w	1596m, 1570w 1500m	512s, 498s, 442w, 429m, 410sh 352w, 325w, 280vw, 190w	ν(B—H): 2440w, 2406m br 2333w, 2274w
[{(*m*-tolyl)$_3$P)$_2$}Bp]Cu	3147w, 3100w	1595m, 1568w	568s, 545sbr, 520s, 490s, 451s, 423m, 380m, 368m, 352m, 220m br	ν(B—H): 2395s br, 2333m, 2284m

[a] Nujol mull.

[b] From Ref. 25b.

assign the Cu—P and Cu—N stretching bands because both PPh$_3$[13] and poly(pyrazolyl)borato[10] ligands exhibit a number of ligand vibrations in the low-frequency region. However, in the spectra of **1**, **4** and **6**, some bands of weak to medium intensity appeared at around 300 cm^{-1}, which are not present in the spectra of ligands and the starting copper(I) derivatives. On the basis of previous assignments reported in the literature for metal derivatives of nitrogen-donor ligands,[14] we tentatively assign them to Cu—N stretching vibrations.

^{1}H *and* ^{13}C *NMR*

The chemical shifts of the pyrazole moieties do not show significant changes in comparison with those of the potassium salts of the ligands.

Table 3. ^{1}H and ^{31}P NMR data[a]

No.	Compound	H(3) or H(5)		H(4)	Others	^{31}P
1	[(Ph)$_3$P]$_2$Cu·pzTp	7.45 d	7.28 d	6.12 t	7.35, 7.34, 7.32 m	+0.41
2	[(*p*-tolyl)$_3$P]$_2$Cu·pzTp	7.48 d	7.32 d	6.18 t	*p*-Me : 2.36, 7.10–7.27 m	−2.10
3	[(*m*-tolyl)$_3$P]$_2$Cu·pzTp	7.48 d	7.35 d	6.18 t	*m*-Me : 2.30, 7.08–7.29 m	+1.39
4	[(Ph)$_3$P]$_2$Cu·Bp	7.60 d	7.05 d	5.98 t	7.38, 7.30, 7.22 m	−1.92
5	[(*p*-tolyl)$_3$P]$_2$Cu·Bp	7.62 d	7.28 d	6.06 t	*p*-Me : 2.36, 7.05–7.23 m	−3.59
6	[(*m*-tolyl)$_3$P]$_2$Cu·Bp	7.65 d	7.34 d	6.10 t	*m*-Me : 2.20, 7.07–7.27 m	−1.13

[a] In ppm from internal TMS, solvent CDCl$_3$.

Table 4. ^{13}C NMR data[a]

No.	Compound	C(3) or C(5)		C(4)	Others
1	[(Ph)$_3$P]$_2$Cu·pzTp	141.4[b]	134.8	104.7	133.8, 133.5, 129.3, 128.6, 128.5
		141.4[c]	134.8	104.6	133.8, 133.5, 129.3, 128.7, 128.5
		142.2[d]	133.5	105.0	133.7, 129.4, 128.5
		143.0[e]	136.6	105.6	134.2, 133.6, 132.3, 129.4, 128.5
		142.2		104.8	
2	[(*p*-tolyl)$_3$P]$_2$Cu·pzTp	142.0	139.8	105.2	135.3, 134.3, 133.9, 130.0, 129.7 Me: 21.8
3	[(*m*-tolyl)$_3$P]$_2$Cu·pzTp	141.9	138.6	105.2	135.1, 134.7, 131.4, 131.1, 128.8 Me: 21.9
4	[(Ph)$_3$P]$_2$Cu·Bp	141.0	134.4	103.8	134.6, 134.1, 129.7, 129.0, 128.8
5	[(*p*-tolyl)$_3$P]$_2$Cu·Bp	141.1	139.6	103.8	135.4, 134.3, 134.0, 129.7, 129.5 Me: 21.8
6	[(*m*-tolyl)$_3$P]$_2$Cu·Bp	140.5	138.2	103.2	134.6, 134.3, 130.4, 128.5, 128.3 Me: 21.3

[a] In ppm from Me$_4$Si calibration from internal deuterium solvent lock.

[b] Room temperature.

[c] +50°C.

[d] −50°C.

[e] −80°C.

The ^{1}H and ^{13}C spectra of compounds **1**–**3** (those with pzTp) in CDCl$_3$ solution show only one set of signals for the pyrazole rings (sharp for ^{1}H but slightly broadened for ^{13}C). The latter should therefore be equivalent in the NMR time scale. This means that the compounds are fluxional at room temperature with one or more pz ring(s) not engaged in copper ligation. Indeed, the ^{13}C spectrum of **1** run at +50°C shows very sharp lines at the same chemical shifts; in contrast, at −50°C some pyrazole peaks are very broad [8, 14 and 35 Hz at half height for C(5), C(4) and C(3), respectively]. By cooling to −60°C, the splitting of C(3) and C(4) (two peaks of equal intensity for each one) is barely detectable, while at −70°C it becomes evident, and at −80°C the separated peaks are fairly sharp.

Compounds **4**–**6** may also be subject to boat inversion, as already noted.[15] In principle either the boron-bonded hydrogens or the phosphorus atoms may be used as a probe for fluxionality, since the inversion makes them non-equivalent to each other and two sets of signals should be observed. The ^{31}P signals, at variance with the B—H ones, which are extremely broad, may serve this purpose. In the ^{31}P spectra only one sharp peak is observed, indicating that, unless there is fortuitous synchronicity, the boat inversion is operating at room temperature.

X-ray crystal structure of the complex [pz$_2$B-(μ-pz)$_2$-Cu(PPh$_3$)$_2$]

The crystal structure of the complex consists of discrete monomeric molecules without any Cu···Cu interaction. An ORTEP[16] view along *a* is shown in Fig. 1 with its numbering scheme. Selected bond distances and angles are given in Table 5. The packing of the molecules in the crystal is determined by normal van der Waals contacts. The shortest intermolecular distances are between the molecule x, y, z and the equivalent: $1+x, y, z$; $-x, -y, 1-z$; $-x, 1/2+y, 1/2-z$; $1-x, -1/2+y, 1/2-z$.

The copper(I) atom has a distorted tetrahedral coordination: the angles range from 92.6(1) to 119.82(4)°. The remarkable deviation from the ideal angle can be explained by the need to accommodate the bulky Ph$_3$P and pzTp groups.

The Cu—P bond distances [2.273(1) and 2.359(1) Å] are slightly longer than the sum of covalent radii (2.27 Å) and than the values reported for other phosphine–copper(I) complexes, ranging between 2.15 and 2.30 Å.[16]

In the phosphine ligands the P—C bonds [weighted average 1.823(4) Å] are slightly longer than the 1.77–1.83 Å values found in Ph$_3$PAu(6-methylpyridonato-*N*)[17] and in (Ph$_3$PAu)$_2$diethylbarbituric acid,[18] owing to the interligand repulsions; the

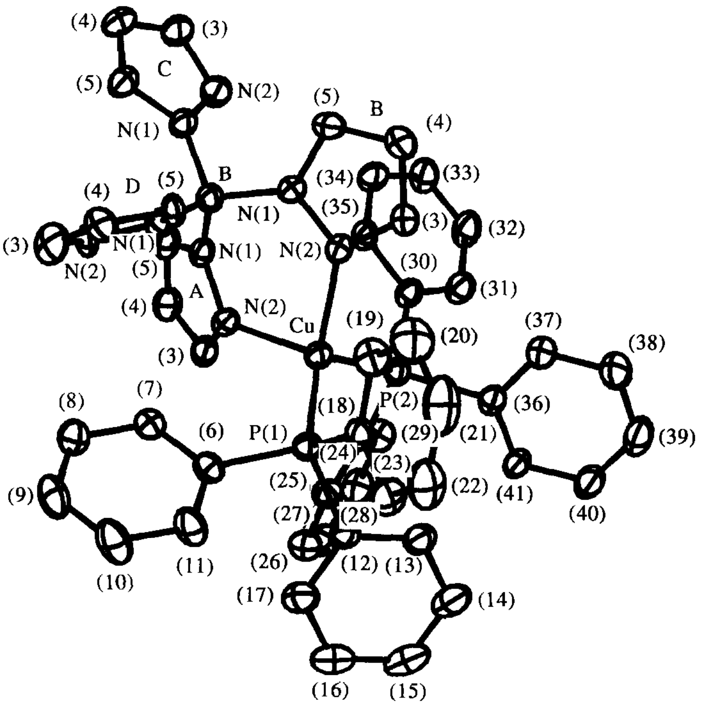

Fig. 1. ORTEP plot and numbering scheme of atoms. Thermal ellipsoids enclose 25% of the electron density. Hydrogen atoms are omitted for clarity.

C—P—C angles [weighted average 102.4(9)°] are comparable with the value of 102.8(7)° found in Cu(PPh$_3$)(Tp*)[19] and 102.9(1)° found in the Cu^{I}(PPh$_3$)$_2$ moiety of the complex Cu$_2$[P(*m*-tolyl)$_3$]$_3$I$_2$;[20] the Cu—P—C angles [weighted average 115.7(1.6)°] are comparable with the values, ranging from 110.5 to 117.7°, found in the bis(triphenylphosphine)copper(I) fluoroacetates.[21]

The Cu—N bonds [2.087(3) and 2.051(3) Å] are larger than the sum of covalent radii (1.87 Å) and comparable with the average values of 2.098 (12), 2.094(7) and 2.009(10) Å found in Cu(PPh$_3$) (Tp*), [Cu(Tp*)]$_2$(OH$_2$) and [Cu(Tp*)]$_2$(CO$_3$), respectively.[19]

The pyrazole rings are non-planar, with the probability $P = 94.4\%$ for the N(1A)—C(5A) ring [maximum displacement $-0.007(4)$ Å for C(3A)], $P > 99\%$ for the N(1B)—C(5B) ring [maximum displacement $-0.010(4)$ Å for C(3B)], $P = 58.5\%$ for the N(1C)—C(5C) ring [maximum displacement $-0.004(4)$ Å for C(5C)] and $P > 99\%$ for the N(1D)—C(5D) ring [maximum displacement $-0.006(4)$ Å for N(2D)]. Inside the pyrazole rings, the rules about the pattern of values for the angles[22] apply and the external angles at N(1) also follow the quoted rules.

The six-membered B(NN)$_2$Cu ring adopts the boat form; the copper atom forms the stern [displacement from the plane of the nitrogen atoms 0.1045(5) Å] and the boron atom the bow [displacement from the plane of the nitrogen atoms 0.559(5) Å]; the Cu···B fold angle is 154.1(3)°. The puckering parameters calculated according to Cremer and Pople[23] are: $Q = 0.458$, $\theta = 70.4°$, $\phi = 349.0°$. The pure boat conformation corresponds to $\theta = 90°$ and $\phi = 360°$. The distortion from the pure boat is remarkable (19.6°) and ϕ is smaller than 360°. The boat conformation is distorted in the direction of a half-boat and flattened at the copper apex. The "bite" of the ligand, i.e. the N—Cu—N angle, is 92.6(1)°. The steric demands of ligands determine the stability of complexes, in ligand competition and exchange. It is of value to calculate effective cone angles of ligands from the crystallographic structural data.[24] For pzTp, the middle of the Cu—N vectors is assumed to be the cone axis, and the cone vertex is centred on the copper atom: the angle between the cone axis and the vector which touches the Van der Waals radii of the hydrogen atoms closest to copper ($r = 1.17$ Å for hydrogen) is 102.5° for H(3A) and 103.6° for H(3B). These angles correspond to a total average value of 206.1°.

For the triphenylphosphine ligands, the cone apex centred on the copper atom was located 2.273 Å from the P(1) atom and 2.359 Å from the P(2) atom. The apex angle of the cone, which lies at the van der Waals radii of the outermost atoms, turned

Table 5. Selected interatomic distances (Å) and bond angles (°)

In the coordination sphere			
Cu—N(2A)	2.087(3)	N(2A)—Cu—P(1)	119.76(9)
Cu—N(2B)	2.051(3)	N(2A)—Cu—P(2)	99.21(9)
Cu—P(1)	2.273(1)	N(2B)—Cu—P(1)	115.91(9)
Cu—P(2)	2.359(1)	N(2B)—Cu—P(2)	105.05(9)
N(2A)—Cu—N(2B)	92.6(1)	P(1)—Cu—P(2)	119.82(4)
In the tetrakis(pyrazol-1-yl)borate ligand			
N(1A)—B	1.529(5)	N(1B)—B	1.534(6)
N(1A)—N(2A)	1.365(4)	N(1B)—N(2B)	1.364(4)
N(2A)—C(3A)	1.340(5)	N(2B)—C(3B)	1.336(5)
C(3A)—C(4A)	1.384(6)	C(3B)—C(4B)	1.379(6)
C(4A)—C(5A)	1.371(6)	C(4B)—C(5B)	1.370(7)
C(5A)—N(1A)	1.357(5)	C(5B)—N(1B)	1.358(5)
N(1C)—B	1.534(5)	N(1D)—B	1.539(6)
N(1C)—N(2C)	1.372(5)	N(1D)—N(2D)	1.345(5)
N(2C)—C(3C)	1.339(5)	N(2D)—C(3D)	1.309(6)
C(3C)—C(4C)	1.375(7)	C(3D)—C(4D)	1.381(7)
C(4C)—C(5C)	1.367(6)	C(4D)—C(5D)	1.385(7)
C(5C)—N(1C)	1.350(5)	C(5D)—N(1D)	1.383(5)
N(2A)—N(1A)—C(5A)	109.0(3)	N(2B)—N(1B)—C(5B)	109.1(3)
Cu—N(2A)—N(1A)	122.6(2)	Cu—N(2B)—N(1B)	125.6(2)
Cu—N(2A)—C(3A)	126.1(3)	Cu—N(2B)—C(3B)	127.7(3)
N(1A)—N(2A)—C(3A)	105.6(3)	N(1B)—N(2B)—C(3B)	105.8(3)
N(2A)—C(3A)—C(4A)	112.0(4)	N(2B)—C(3B)—C(4B)	111.8(4)
C(3A)—C(4A)—C(5A)	103.8(4)	C(3B)—C(4B)—C(5B)	104.4(4)
C(4A)—C(5A)—N(1A)	109.5(4)	C(4B)—C(5B)—N(1B)	108.9(4)
N(2C)—N(1C)—C(5C)	111.1(3)	N(2D)—N(1D)—C(5D)	111.2(3)
N(1C)—N(2C)—C(3C)	104.1(3)	N(1D)—N(2D)—C(3D)	105.6(4)
N(2C)—C(3C)—C(4C)	111.9(4)	N(2D)—C(3D)—C(4D)	112.5(4)
C(3C)—C(4C)—C(5C)	105.6(4)	C(3D)—C(4D)—C(5D)	105.3(4)
C(4C)—C(5C)—N(1C)	107.2(4)	C(4D)—C(5D)—N(1D)	105.3(4)
N(1A)—B—N(1B)	112.9(3)	N(1B)—B—N(1C)	107.8(3)
N(1A)—B—N(1C)	108.5(3)	N(1B)—B—N(1D)	110.1(3)
N(1A)—B—N(1D)	109.2(3)	N(1C)—B—N(1D)	108.2(3)
B—N(1A)—N(2A)	122.6(3)	B—N(1C)—N(2C)	120.5(3)
B—N(1A)—C(5A)	128.1(3)	B—N(1C)—C(5C)	128.3(3)
B—N(1B)—N(2B)	123.2(3)	B—N(1D)—N(2D)	120.5(3)
B—N(1B)—C(5B)	127.6(3)	B—N(1D)—C(5D)	126.3(3)
In the phosphine ligands			
P(1)—C(6)	1.833(4)	P(2)—C(24)	1.825(4)
P(1)—C(12)	1.822(4)	P(2)—C(30)	1.825(4)
P(1)—C(18)	1.804(4)	P(2)—C(36)	1.829(4)
Cu—P(1)—C(6)	116.7(1)	Cu—P(2)—C(24)	112.0(1)
Cu—P(1)—C(12)	112.6(1)	Cu—P(2)—C(30)	113.8(1)
Cu—P(1)—C(18)	117.2(1)	Cu—P(2)—C(36)	122.8(1)
C(6)—P(1)—C(12)	105.5(2)	C(24)—P(2)—C(30)	104.8(2)
C(6)—P(1)—C(18)	101.2(2)	C(24)—P(2)—C(36)	101.0(2)
C(12)—P(1)—C(18)	101.8(2)	C(30)—P(2)—C(36)	100.3(2)
In the phenyl rings			
Weighted average of distances and endocyclic angles :			
C(P)—C(*ortho*)	1.390(4)	C(*ipso*)	118.0(3)
C(*ortho*)—C(*meta*)	1.384(3)	C(*ortho*)	120.9(2)
C(*meta*)—C(*para*)	1.373(2)	C(*meta*)	120.1(1)
		C(*para*)	120.0(4)

out to be 172.0, 140.8 and 163.9° with respect to H(7), H(13) and H(19) and 168.0, 173.9 and 127.4° with respect to H(25), H(35) and H(37), respectively. The effective cone angle is the average θ of the outermost hydrogen atoms of the three phenyl groups: 158.9° for the P(1) ligand and 156.4° for the P(2) ligand.

EXPERIMENTAL

Concentration was always carried out *in vacuo* (water aspirator). The samples were dried *in vacuo* to constant weight (20°C, *ca* 0.1 Torr). Carbon, hydrogen and nitrogen analyses were carried out in our Department; IR spectra were recorded from 4000 to 250 cm^{-1} on a Perkin–Elmer 2000 System Series FTIR instrument. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian VX-300 spectrometer operating at room temperature (300 MHz for ^{1}H, 75 MHz for ^{13}C and 121.4 MHz for ^{31}P). The electrical resistance of acetone solutions was measured with a Crison CDTM 522 conductimeter at room temperature.

Nitrato[bis{triarylphosphine}copper(I)]

The starting $(Ph_3P)_2CuNO_3$ or $[(m\text{-tolyl})_3P]_2CuNO_3$ compounds were prepared according to the literature.[25] The compound $[(p\text{-tolyl})_3P]_2CuNO_3$ was obtained when the same preparation was carried out in refluxing methanol and a strong excess of phosphine ligand (ratio 10 : 1) for 2 days and after vacuum concentration to small volume (56% yield).

[Bis{triarylphosphine}copper(I)]tetrakis(1H-pyrazol-1-yl)borato (1–3)

These compounds were prepared by adding a dichloromethane solution (*ca* 25 cm^3) of 1 mmol of the appropriate bis(triphenylphosphine)copper(I) nitrate to a stirring dichloromethane solution/suspension (*ca* 25 cm^3) of 1 mmol (318 mg) of potassium tetrakis (1*H*-pyrazol-1-yl)borate under a stream of N_2. The filtered solution (KNO_3) was evaporated to dryness; the residue was purified from dichloromethane–Et_2O.

[Bis(triarylphosphine]copper(I)]dihydridobis(1H-pyrazol-1-yl)borato (4–6)

A similar procedure was used for **4–6**; after slow evaporation of the solvent, the residue was recrystallized from acetonitrile–Et_2O.

X-ray analysis

A suitable crystal of bis(triphenylphosphine) copper(I) tetrakis(1*H*-pyrazol-1-yl)borate, having approximate dimensions $0.73 \times 0.35 \times 0.14$ mm^3 was used for data collection. Accurate lattice parameters were obtained by least-squares refinement of 25 reflections measured on an Enraf–Nonius CAD4 diffractometer (using graphite monochromated Cu-K_α radiation) of Centro Grandi Strumenti, Pavia, Italy.

The intensities of 7932 independent reflections were corrected for Lorentz and polarization factors and for absorption as specified by North *et al.*,[26] with minimum and maximum absorption factors of 0.8423 and 0.9984, respectively. The structure factors were then placed on an approximate absolute scale by Wilson's method[27] and a mean thermal parameter was thereby obtained. Details of crystal data and intensity collection are listed in Table 6.

Structure determination and refinement

The copper and the two phosphorus atoms were located by the Patterson method. A subsequent three-dimensional difference Fourier synthesis phased on the Cu, P(1) and P(2) atoms revealed the remaining non-hydrogen atoms of the complex molecule. The least-squares refinement of the positional and first isotropic and later anisotropic thermal parameters of the non-hydrogen atoms reduced R to 0.049. The positions of the hydrogen atoms were then calculated from the geometry of the compound and checked in a final difference Fourier map. Further refinement, including the hydrogen atoms with the same isotropic thermal parameters of their bonded atoms, reduced the R index to 0.042 after three cycles. The 4573 observed reflections with $I > 3\sigma(I)$ were given unit weight. Weights obtained from counting statistics did not lead to better results. The final difference Fourier map showed maximum and minimum $\Delta\rho$ values $+0.339$ and -0.259, both close to the copper atoms.

All calculations were carried out with the Enraf–Nonius SDP crystallographic computing package[28] and with local programs.

Supplementary material available

Tables of atomic positional parameters of non-hydrogen atoms and hydrogen atoms, table of anisotropic thermal parameters, tables of bond distances and bond angles involving non-hydrogen atoms and hydrogen atoms, tables of planarity of molecular regions and a listing of observed and calculated structure factors (total of 46 pages).

Table 6. Crystal data, data collection and refinement of the structure

Formula	$C_{48}H_{42}BN_8P_2Cu$
Formula weight	867.22
Space group	$P2_1/c$
Colour	colourless
a (Å)	12.379(3)
b (Å)	18.226(3)
c (Å)	19.462(4)
β (°)	103.35(2)
V_c (Å^3)	4272(2)
Z	4
D_{calc} (g cm^{-3})	1.35
Crystal size (mm)	0.73 × 0.35 × 0.14
μ(Cu-K_α) (cm^{-1})	17.86
Data collection instrument	Enraf–Nonius CAD4
Radiation (monochromated)	Cu-K_α (λ = 1.5418 Å)
Temperature of data collection (K)	293
Scan mode	ω–2θ
Data collection range	$4 < 2\theta < 70$
Standards (measured every 300 min)	−4 −1 4, 1 −3 −6, −1 −5 3
No. of unique reflections measured	7932 ($h, k, +l$)
No. of data with $F_0^2 \geqslant 3\sigma(F_0^2)$	4573
No. of parameters refined	541
R^a and R_w^b	0.042, 0.041

[a] $R = (\Sigma|\,|F_0| - k|F_c|\,|)/\Sigma|F_0|$.

[b] $R_w = [\Sigma w(|F_0| - k|F_c|)^2/\Sigma w|F_0|^2]^{1/2}$.

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