Chemistry of the Group 1B Metals. Part 15.[1] Some Diphenylbis(pyrazolyl)borate Complexes of Silver, and the Crystal and Molecular Structures of $[Ag\{P(C_6H_4Me\text{-}p)_3\}\{BPh_2(pz)_2\}]$ ‡ (pz = pyrazolyl)

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The preparation and properties of $[Ag\{P(C_6H_4Me\text{-}p)_3\}\{BH_2(pz)_2\}]$, pz = pyrazolyl, and of $[AgL\{BPh_2(pz)_2\}]$ [L = $P(C_6H_4Me\text{-}p)_3$, $CNBu^t$, $P(OPh)_3$, or $\frac{1}{2}(Ph_2PCH_2PPh_2)$] are described, together with the structure of $[Ag\{P(C_6H_4Me\text{-}p)_3\}\{BPh_2(pz)_2\}]$, which has been determined by a single-crystal *X*-ray study. Crystals are triclinic, space group $P\bar{1}$, with $a = 16.984(5)$, $b = 10.813(3)$, $c = 10.029(3)$ Å, $\alpha = 104.18(3)$, $\beta = 102.85(2)$, $\gamma = 94.63(2)°$, and $Z = 2$. The structure has been refined by least-squares methods using 4 110 independent reflections, to a conventional R of 0.039. The silver atom is pseudo-three-co-ordinate, with the $BPh_2(pz)_2$ ligand attached by one normal [2.194(4) Å] and one long [2.411(4) Å] Ag–N bond; the angle P–Ag–N is 160°.

WE have previously described the preparation and properties of poly(pyrazolyl)borate complexes of silver(I) containing the anions $[B(pz)_4]^-$, $[BH(pz)_3]^-$, and $[BH(dmpz)_3]^-$ (pz = pyrazolyl, dmpz = 3,5-dimethylpyrazolyl) together with ligands containing Group 5 donor atoms.[2] The ^1H n.m.r. spectra of these complexes, together with their analyses and molecular weights, suggest that in them the silver atom is approximately tetrahedrally co-ordinated, with structures similar to those of some related complexes of copper(I), *e.g.* $[Cu(CO)\{BH(pz)_3\}]$.[3] We have also reported some copper(I) complexes containing the $[BH_2(pz)_2]^-$ and $[BPh_2(pz)_2]^-$ anions that are formally three-co-ordinate, such as $[Cu(PPh_3)\{BH_2(pz)_2\}]$ and $[Cu(CNBu^t)\{BPh_2(pz)_2\}]$.[4] In the present paper we describe similar complexes of silver(I), together with the crystal and molecular structures of $[Ag\{P(C_6H_4Me\text{-}p)_3\}\{BPh_2(pz)_2\}]$.

EXPERIMENTAL

Reactions were normally carried out in a nitrogen atmosphere, but no special precautions were taken to exclude oxygen during work-up of the reaction products. Solvents for reactions were dried over sodium and distilled from calcium hydride under nitrogen.

Spectra were obtained with Jasco IRA2 (i.r.), Varian Associates T60 or HA100 (^1H n.m.r. at 60 or 100 MHz respectively), and GEC-AEI MS3074 (mass, at 70 eV § ionising energy, 8 kV accelerating potential) instruments.

Dihydrobis(1-*pyrazolyl*)*borate Complexes*.—(a) $[Ag\{P(C_6H_4Me\text{-}p)_3\}\{BH_2(pz)_2\}]$. Silver nitrate (83 mg, 0.5 mmol) was added to a solution of $Na[BH_2(pz)_2]$ (92 mg, 0.5 mmol) and $P(C_6H_4Me\text{-}p)_3$ (152 mg, 0.5 mmol) in diethyl ether (50 cm^3), and the mixture was stirred in the dark for 1 h at room temperature. The copious black precipitate that formed was filtered off, and the brown filtrate was evaporated. The residue was crystallized from aqueous acetone to give $[Ag\{P(C_6H_4Me\text{-}p)_3\}\{BH_2(pz)_2\}]$ (1) (50 mg, 15%) as a buff *solid* (Found: C, 66.5; H, 5.9; N, 6.45. $C_{27}H_{29}AgBN_4P$ requires C, 66.6; H, 5.8; N, 6.5%). Infrared ($CHCl_3$): ν(BH) 2 400mbr, 2 280w cm^{-1}. ^1H n.m.r. δ($CDCl_3$) 2.39, s, 9 H, Me; 6.16, m, 7.15—7.5 m, and 8.84 m, 18 H, C_6H_4 + pz.

(b) $[Ag(CNBu^t)\{BH_2(pz)_2\}]$. The attempted preparation of this complex by a method similar to the above resulted in decomposition and precipitation of metallic silver.

Diphenylbis(1-*pyrazolyl*)*borate Complexes*.—(a) $[Ag\{P(C_6H_4Me\text{-}p)_3\}\{BPh_2(pz)_2\}]$. Silver nitrate (83 mg, 0.5 mmol) was added to a solution of $P(C_6H_4Me\text{-}p)_3$ (152 mg, 0.5 mmol) in diethyl ether (50 cm^3), and the mixture stirred until solution resulted (2 h, room temperature). The compound $Na[BPh_2(pz)_2]$ (150 mg, 0.5 mmol) was then added, and the mixture stirred for 12 h in the dark. Filtration, evaporation, and recrystallisation of the residue (aqueous acetone) afforded $[Ag\{P(C_6H_4Me\text{-}p)_3\}\{BPh_2(pz)_2\}]$ (2) (170 mg, 50%) as a white *solid*, m.p. 196—197 °C [Found: C, 64.4; H, 5.2; N, 7.9%. *M* (osmometric), 765. $C_{39}H_{37}AgBN_4P$ requires C, 65.8; H, 5.2; N, 7.9%. *M*, 710]. ^1H n.m.r. δ($CDCl_3$) 2.44, s, 9 H, Me; 6.27, t, 2 H, pz; 6.87—7.64, m, 26 H, Ph + pz. See text for further discussion.

(b) $[Ag\{P(OPh)_3\}\{BPh_2(pz)_2\}]$. Silver nitrate (83 mg, 0.5 mmol) was added to $P(OPh)_3$ (155 mg, 0.5 mmol) in diethyl ether (40 cm^3). After 2 h $Na[BPh_2(pz)_2]$ (150 mg, 0.5 mmol) was added, and the mixture was stirred for 12 h in the dark. Filtration, evaporation, and recrystallisation of the residue (aqueous acetone) gave $[Ag\{P(OPh)_3\}\{BPh_2(pz)_2\}]$ (3) (180 mg, 50%) as white *crystals*, m.p. 126—127 °C (Found: C, 60.1; H, 4.4; N, 7.8. $C_{36}H_{31}AgBN_4O_3P$ requires C, 60.25; H, 4.3; N, 7.8%). ^1H n.m.r. δ($CDCl_3$) 6.08, t, 2 H, pz; 6.57—7.67, m, 29 H, Ph + pz.

(c) $[Ag(CNBu^t)\{BPh_2(pz)_2\}]$. The compound $Na[BPh_2(pz)_2]$ (150 mg, 0.5 mmol) was added to a slurry of silver nitrate (83 mg, 0.5 mmol), t-butyl isocyanide (42 mg, 0.5 mmol), and diethyl ether (30 cm^3), and the mixture was stirred for 2 h in the dark. Filtration, evaporation, and crystallisation of the residue (aqueous acetone) gave $[Ag(CNBu^t)\{BPh_2(pz)_2\}]$ (4) (95 mg, 40%) as a white *solid*, m.p. >260 °C [Found: C, 56.0; H, 5.3; N, 14.1%. *M* (osmometric), 522. $C_{23}H_{25}AgBN_5$ requires C, 56.3; H, 5.1; N, 14.3%. *M*, 490]. Infrared (Nujol): ν(CN) 2 180 cm^{-1}. ^1H n.m.r. δ($CDCl_3$) 1.46, s, 9 H, C*Me*$_3$; 6.22, t, 2 H, pz; 6.83—7.70, m, 14 H, Ph + pz.

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‡ [Diphenylbis(1-pyrazolyl)borato-$N^2,N^{2'}$](tri-*p*-tolylphosphine)silver(I).

§ Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

(d) $[\{Ag[BPh_2(pz)_2]\}_2(dppm)]$. A mixture of $Na[BPh_2(pz)_2]$ (150 mg, 0.5 mmol), bis(diphenylphosphino)methane (dppm) (192 mg, 0.5 mmol), and silver nitrate (83 mg, 0.5 mmol) in diethyl ether (50 cm^3) was stirred for 12 h in the dark. Work-up as above gave white *crystals* of $[\{Ag[BPh_2(pz)_2]\}_2(dppm)]$ (5) (140 mg, 45%), m.p. *ca.* 240 °C [Found: C, 60.9; H, 4.65; N, 9.25%. *M* (osmometric), 1 128. $C_{61}H_{54}Ag_2B_2N_8P_2$ requires C, 61.1; H, 4.5; N, 9.35%. *M*, 1 198]. ^{1}H n.m.r. δ([$^2H_6$]acetone) 3.70, m, 2 H, CH_2; 6.11, t, 4 H, pz; 6.77—7.8, m, 48 H, Ph + pz.

Crystallography.—Crystal data for (2). $C_{39}H_{37}AgBN_4P$, *M* 711.4, Triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 16.984(5)$, $b = 10.813(3)$, $c = 10.029(3)$ Å, $\alpha = 104.18(3)$, $\beta = 102.85(2)$, $\gamma = 94.63(2)°$, $U = 1\,723(1)$ Å^3, $D_c = 1.37$ g cm^{-3}, $Z = 2$, $F(000) = 732$, monochromatic Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 6.3$ cm^{-1}, specimen size 0.10 × 0.30 × 0.34 mm (plate).

Structure determination. A unique data set, gathered to $2\theta_{max.}$ 50° by the conventional θ—2θ scan mode on a Syntex $P\bar{1}$ four-circle diffractometer, yielded 6 097 independent reflections. Of these, 4 110 with $I > 3\sigma(I)$ were considered ' observed ' and used in the structure determination and refinement after analytical absorption correction. Refinement was basically by 9 × 9 block-diagonal least squares; the parameters of Ag and P were refined in a single block, all non-hydrogen atoms being thermally anisotropic. All hydrogen-atom positions were determined from difference maps and ' improved ' to idealised sites, and included in the refinement as invariants with $U_H = 1.25 \langle U_{ii}(\text{parent C})\rangle$ to economise on refinement costs. The final residuals were $R = 0.039$, $R' = 0.047$, and $S = 1.31$, reflection weights being $[\sigma^2(F_o) + 0.000\,5(F_o)^2]^{-1}$. Neutral-atom scattering factors (for Ag and P) were corrected for anomalous dispersion (f', f'').[5-7] Computation was carried out using the ' *X*-RAY '76 ' program system,[8] implemented on a CYBER 73 computer. Material deposited as Supplementary Publication No. SUP 22949 (31 pp.) * comprises structure factor amplitudes, thermal parameters, hydrogen-atom parameters, and ring planes. Fractional atomic coordinates are given in Table 1. Non-hydrogen atom numbering is as in Figure 1; hydrogen atoms are numbered according to the parent atom, suffixed α, β, γ in the case of the methyl groups.

TABLE 1

Non-hydrogen atomic fractional cell co-ordinates

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Ag	0.250 44(2)	0.090 96(3)	0.171 14(4)
P	0.295 53(7)	0.197 26(10)	0.017 65(11)
C(111)	0.348 0(2)	0.319 4(4)	0.111 8(4)
C(112)	0.382 4(3)	0.401 6(4)	0.239 7(5)
C(113)	0.449 0(3)	0.493 6(4)	0.315 8(5)
C(114)	0.518 9(3)	0.505 0(4)	0.268 7(5)
C(1141)	0.591 6(3)	0.603 8(5)	0.354 8(6)
C(115)	0.519 1(3)	0.422 2(5)	0.140 2(5)
C(116)	0.453 8(3)	0.330 8(4)	0.062 6(4)
C(121)	0.331 8(2)	0.084 9(4)	−0.114 9(4)
C(122)	0.377 9(3)	−0.003 3(4)	−0.069 4(5)
C(123)	0.406 0(3)	−0.093 3(5)	−0.164 3(5)
C(124)	0.388 5(3)	−0.099 6(4)	−0.306 2(5)
C(1241)	0.418 7(3)	−0.202 0(5)	−0.408 5(6)
C(125)	0.343 5(3)	−0.011 6(5)	−0.351 5(5)
C(126)	0.314 6(3)	0.080 6(4)	−0.257 5(4)
C(131)	0.225 1(2)	0.277 5(4)	−0.084 0(4)
C(132)	0.144 2(3)	0.221 9(4)	−0.134 9(5)
C(133)	0.090 0(3)	0.275 3(5)	−0.220 8(5)
C(134)	0.113 3(3)	0.384 1(5)	−0.257 4(5)
C(1341)	0.053 6(4)	0.442 2(6)	−0.351 8(6)
C(135)	0.193 9(3)	0.441 3(4)	−0.202 6(5)
C(136)	0.249 3(3)	0.388 8(4)	−0.117 1(5)
B	0.193 4(3)	−0.192 7(5)	0.201 7(5)
N(211)	0.333 7(2)	−0.056 8(4)	0.258 3(4)
N(212)	0.289 1(2)	−0.174 8(3)	0.228 0(4)
C(213)	0.336 7(3)	−0.266 7(5)	0.204 4(5)
C(214)	0.414 3(3)	−0.209 9(6)	0.222 2(6)
C(215)	0.409 4(3)	−0.080 9(6)	0.254 9(6)
N(221)	0.180 3(2)	0.042 0(3)	0.314 9(3)
N(222)	0.169 4(2)	−0.084 1(3)	0.315 4(3)
C(223)	0.129 6(3)	−0.093 5(4)	0.415 4(4)
C(224)	0.115 0(3)	0.025 5(5)	0.480 6(5)
C(225)	0.148 5(3)	0.107 6(4)	0.415 9(5)
C(231)	0.153 0(2)	−0.176 1(4)	0.045 7(4)
C(232)	0.194 0(3)	−0.191 0(4)	−0.061 3(4)
C(233)	0.157 3(3)	−0.179 0(5)	−0.195 7(5)
C(234)	0.078 4(3)	−0.152 9(5)	−0.225 3(5)
C(235)	0.036 6(3)	−0.136 4(4)	−0.121 5(5)
C(236)	0.073 8(3)	−0.147 6(4)	0.012 2(5)
C(241)	0.167 5(2)	−0.331 8(4)	0.225 1(4)
C(242)	0.114 3(3)	−0.430 4(4)	0.120 8(5)
C(243)	0.096 5(3)	−0.551 2(4)	0.141 0(5)
C(244)	0.131 7(3)	−0.576 3(5)	0.266 2(6)
C(245)	0.183 8(3)	−0.482 3(5)	0.371 8(6)
C(246)	0.201 7(3)	−0.360 5(4)	0.352 3(5)

RESULTS

Bis(pyrazolyl)borate anions have been likened to anions derived from enolisable 1,3-dicarbonyl compounds or their imine analogues in their electronic and geometric features, and certain parallels between metal derivatives of the borate anions and the analogous acetylacetonates have been noted.[9] From our experience with the tris- and tetrakis-(pyrazolyl)borate anions, which in some instances behave as bidentate ligands, it seemed reasonable to expect that analogous bis(pyrazolyl)borate complexes would also contain bidentate boron ligands. Copper(I) complexes containing these ligands, however, are formally three-co-ordinate.[4] We have therefore prepared several representative silver(I) complexes, and have determined the crystal and molecular structures of one of them.

Dihydrobis(1-pyrazolyl)borate Complexes.—Silver complexes containing the $BH_2(pz)_2$ ligand are significantly less stable than the complexes so far described,[2] a property related to the presence of two hydrogens attached to the boron, and consequent high reducing power. The normally white complexes more or less rapidly change colour to brown or black, even in cold, anaerobic surroundings and when protected from light. We have characterised the complex $[AgL\{BH_2(pz)_2\}]$ [L = $P(C_6H_4Me\text{-}p)_3$] (1) which was obtained in low yield, accompanied by much silver metal. In several other experiments in which we attempted to prepare related complexes with, for example, L = $CNBu^t$, the reaction mixture rapidly turned black and precipitated metallic silver.

In the i.r. spectrum of (1), several ν(BH) bands confirmed the presence of the $BH_2(pz)_2$ ligand. Although only two BH stretching modes would be expected, the presence of both ^{10}B and ^{11}B in natural boron results in a multiplicity of bands. Other properties of this complex were consistent with the presence of the $P(C_6H_4Me\text{-}p)_3$ ligand, *e.g.* the Me resonance at δ 2.39. The complex is formally three-co-ordinate, and the probable structure is considered below.

Diphenylbis(1-pyrazolyl)borate Complexes.—Total substitution of the boron hydrogens by phenyl and pyrazolyl groups gives a ligand which forms silver derivatives which are stable towards reduction. White complexes of general formula $[AgL\{BPh_2(pz)_2\}]$ [L = $P(C_6H_4Me\text{-}p)_3$ (2), $P(OPh)_3$

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

(3), and CNBu^t (4)] and the binuclear [{Ag[BPh$_2$(pz)$_2$]}$_2$(dppm)] (5) were readily obtained and characterised by conventional analytical and spectroscopic methods. The phenyl resonances cover the lower-field pyrazolyl signals in the ^{1}H n.m.r. spectra, and only the signal due to the central proton can be unambiguously assigned, although the total signal in the aromatic region integrates to the correct proton count. The characteristic ν(CN) absorption at 2 180 cm^{-1} was present in the i.r. spectrum of (4), and the ^{1}H n.m.r. spectra contained resonances assigned to the C$_6$H$_4$*Me* protons [in (2)], and to the C*Me*$_3$ protons [in (4)].

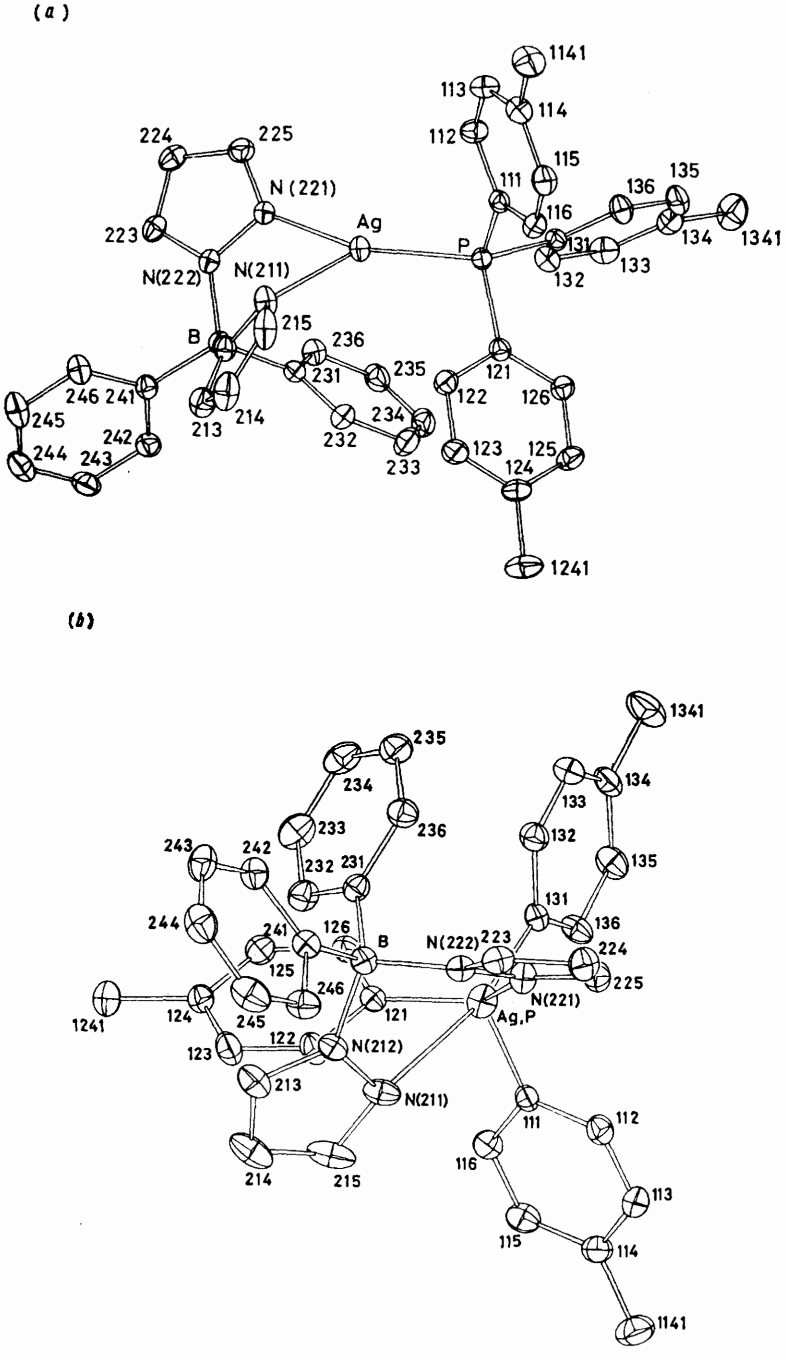

FIGURE 1 (*a*) View of the molecule showing non-hydrogen atom labelling. (*b*) Molecular projection down the Ag–P bond

As with the dihydrobis(pyrazolyl)borate complex (1) described above, the BPh$_2$(pz)$_2$ complexes are formally three-co-ordinate. This apparent co-ordination unsaturation is preserved even when a potentially chelating bis(tertiary phosphine) ligand is present, such as dppm, which gives the binuclear complex (5), the binuclear formulation of which was confirmed by an osmometric molecular-weight determination. To resolve the questions concerning co-ordination about the silver atom, the structure of complex (2) has been determined.

Molecular Geometry.—Molecules of (2) are monomeric, and the molecular structure and atom numbering are shown in Figure 1; Figure 2 shows the unit-cell contents. Important bond lengths are summarised in Table 2. Each silver atom is bonded to a tri(*p*-tolyl)phosphine ligand by an Ag–P bond, and to the diphenylbis(pyrazolyl)borate ligand by two Ag–N bonds, which differ significantly in length, although the second nitrogen is close enough to have a weak interaction with the metal, and to distort the N–Ag–P co-ordination from linear to bent [160.3(1)°]. There are no other atoms within any reasonable bonding distance.

The Ag–P bond distance is 2.351(1) Å. No other monomeric silver–tertiary phosphine complexes have been studied, so that direct comparisons are difficult. However, the shortest Ag–P distance reported, in a distorted tetrahedrally co-ordinated silver complex, [{AgCl(PPh$_3$)}$_4$] is 2.382 Å; [10] other reported Ag–P distances range from 2.422 Å in [{AgBr(PPh$_3$)}$_4$] [10] to 2.519 Å in [Ag(PPh$_3$)$_2$]$_2$-[Ni{S$_2$C=C(CN)$_2$}$_2$].[11]

The Ag–N *Bonds*.—In contrast to other complexes containing the BPh$_2$(pz)$_2$ anion, in which it behaves as a bidentate ligand akin to acetylacetonate, the present complex contains the ligand strongly bound to silver by only one nitrogen atom. The Ag–N(221) distance is 2.194(4) Å, which may be compared to those found in [Ag(imidazole)$_2$]$^+$ [2.120(8), 2.132(8) Å],[12] *catena*-(μ-9-methyladenine)silver (2.163 Å),[13] bis[(nitrato)(pentamethylenetetrazole)silver] (2.216, 2.233 Å),[14] and [Ag(1-Ph-3,5-Me$_2$C$_3$N$_2$H)$_3$]$^+$ [2.243(3) Å]; [15] in the former the silver is two-co-ordinate, while the latter two contain three-co-ordinate silver. The second nitrogen is 2.411(4) Å distant from the metal atom, which implies a very weak bonding interaction. A similar situation is found in [HgMe(bipy)]$^+$, in which the mercury is irregularly co-ordinated to the 2,2′-bipyridyl (bipy) ligand, with Hg–N distances of 2.24(3) and 2.43(3) Å.[16] It is interesting to note that the angle at the metal atom in the silver complex [160.3(1)°] is also virtually the same as found for the mercury derivative [164(1)°]. In the related gold complex [Au(PPh$_3$)(bipy)]$^+$, the two Au–N bonds are 2.166 and 2.406 Å, with a P–Au–N angle of 157.1°.[17]

The Diphenylbis(1-*pyrazolyl*)*borate Ligand*.—The molecular structure of two other complexes containing the BPh$_2$(pz)$_2$ ligand have been reported, namely [Ni{BPh$_2$(pz)$_2$}$_2$] [18] and [Mo(CO)$_2$(η^3-C$_4$H$_7$){BPh$_2$(pz)$_2$}].[19] With the exception of the differing metal–N distances, the ligands are similar, the opening of the chelate ring apparently occurring by a rotation of the pyrazolyl group (21) [*i.e.* N(211,212)] about the B–N bond so that the silver atom lies well out of the ring plane (1.21 Å) in this case; in the case of the other pyrazolyl ring it is only 0.12 Å out of the ring plane. In the case of pyrazolyl groups (21) and (22) [*i.e.* N(221,222)], the boron atom lies slightly out of the plane (0.18, 0.12 Å). The dihedral angle between the two pyrazolyl ring planes is 49.1°. About N(221), the angle sum is 359.8°; about N(211) it is 348.2°, *i.e.* the array about N(211) has trigonal-pyramidal tendencies. In spite of these differences in the nature of the co-ordination of the two pyrazolyl groups, the internal distances and angles are affected only trivially, with one exception, in pyrazolyl (21) the internal angle at N(211) is considerably diminished relative to those at the other three analogous nitrogen atoms. At all nitrogen atoms we find substantial discrepancies in the exocyclic angles, those lying exocyclic to the Ag(N$_2$)$_2$B ring being *ca.* 130°, while those

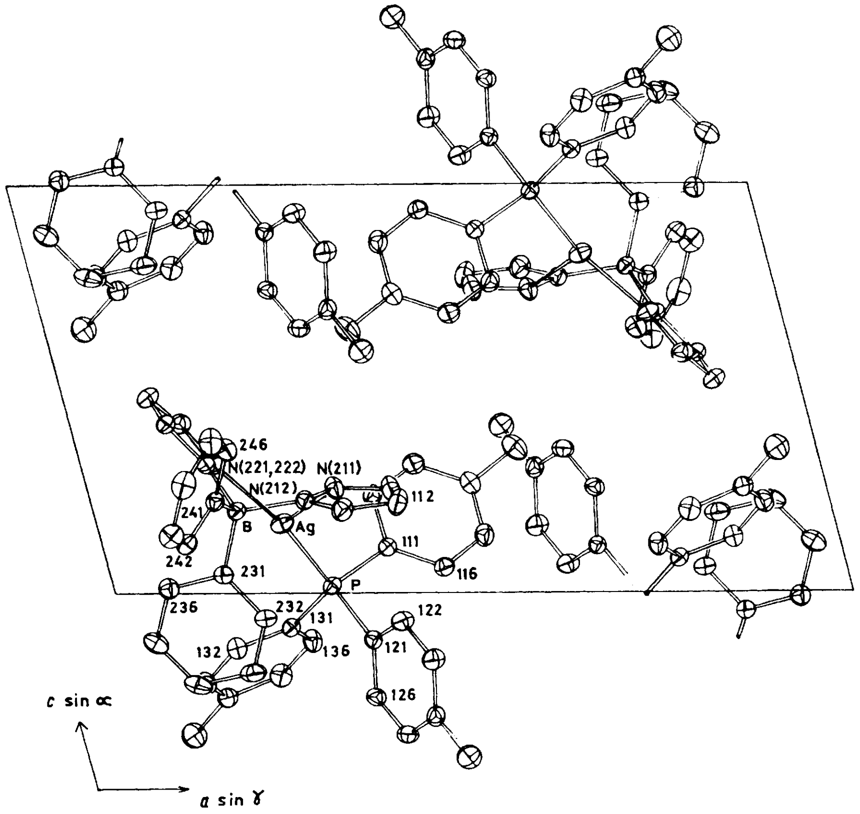

FIGURE 2 Unit-cell contents projected down *b* showing non-hydrogen atoms with 20% thermal ellipsoids

Table 2

Molecular non-hydrogen geometry *

(*a*) Distances (Å)	
P–C(111,121,131)	1.825(4), 1.821(4), 1.811(4)
P–Ag	2.351(1)
Ag–N(211,221)	2.411(4), 2.194(4)
B–C(231,241)	1.622(7), 1.620(7)
B–N(212,222)	1.576(6), 1.573(6)
N(1)–N(2)	1.359(5), 1.363(5)
N(1)–C(5)	1.340(6), 1.333(6)
N(2)–C(3)	1.340(7), 1.346(6)
C(3)–C(4)	1.363(7), 1.362(7)
C(4)–C(5)	1.367(9), 1.378(8)
(*b*) Angles (°)	
C(111)–P–C(121)	104.4(2)
C(111)–P–C(131)	105.3(2)
C(121)–P–C(131)	104.6(2)
Ag–P–C(111)	111.6(2)
Ag–P–C(121)	110.4(2)
Ag–P–C(131)	119.3(2)
C(231)–B–N(212)	109.2(4)
C(241)–B–N(212)	106.2(4)
C(231)–B–N(222)	108.1(4)
C(241)–B–N(222)	109.3(4)
C(231)–B–C(241)	115.2(3)
N(212)–B–N(222)	108.9(3)
Ag–N(1)–N(2)	110.5(2), 117.0(3)
Ag–N(1)–C(5)	133.0(4), 135.8(3)
B–N(2)–N(1)	121.8(3), 121.4(4)
B–N(2)–C(3)	127.7(3), 130.1(4)
N(2)–N(1)–C(5)	104.8(4), 107.0(4)
N(1)–N(2)–C(3)	109.8(4), 108.1(3)
N(2)–C(3)–C(4)	109.1(5), 109.6(4)
C(3)–C(4)–C(5)	104.3(5), 104.8(5)
C(4)–C(5)–N(1)	112.1(5), 110.4(4)
P–Ag–N(211,221)	117.8(1), 160.3(1)
N(211)–Ag–N(221)	81.4(1)

* Phenyl ring geometries are given in SUP 22949. For the pyrazole rings the values are for rings (21), (22) respectively.

endocyclic are *ca.* 120°. With the exception of the C(2)–C(1)–C(6) angles which are diminished below the trigonal value (mean, 118.5°) and the adjacent endocyclic angles at C(2,6) in each ring which are correspondingly enlarged, the geometry of the phenyl rings is normal. However, significant differences are observed in their exocyclic angles at C(1). The probable reason for this lies in contacts between these and other phenyl systems; in order to assist in evaluating these we tabulate *ortho*-hydrogen $\cdots$ (H,C,N) distances less than the van der Waals sum [H $\cdots$ (X) = 1.2 + 1.2 (H), 1.5 (C,N) Å]. All contacts listed are intramolecular; there do not appear to be any significant intermolecular contacts of this type. Both B-phenyl groups have contacts which presumably account for their C(1) exocyclic angular distortion.

The p-*Tolyl Phosphine Ligand.*—In triphenylphosphine, the C–P–C angles are 103.0° (mean); the mean in the present compound is appreciably greater (104.8°), but there are no spectacular deviations from this. Given 104.8° as the mean C–P–C angle and assuming the silver atom is bonded along the pseudo-three-fold axis, Ag–P–C should be 113.8°; two of the angles are much less than this and one much greater [Ag–P–C(131), 119.3(2)°]. While such an irregularity might be caused by packing forces, we have examined the *p*-tolyl array to see whether any intramolecular explanation presents itself. Compared to the B-phenyl groups, the reduction of C(2)–C(1)–C(6) below 120°, although consistent among the three rings, is small (C–C–C, 118.5°); the unsymmetrical nature of the exocyclic angles, however, is very pronounced. Examining the *ortho*-hydrogen contacts, we find that each ring has one such hydrogen atom directed toward C(1) of the next in the cyclic array 1,2,3. In each case, the angle enclosed by that side of the ring associated with that hydrogen is consistently the larger of the two exocyclic C(1) angles. Examining the *ortho*-hydrogen atoms further, we find that their closest contacts to the silver atom are H(112, 122, 136) $\cdots$ Ag: 3.29, 3.13, 3.35 Å. These do not correlate with the variation in Ag–P–C angle; the only reasonable intramolecular cause that we can find for this distortion is associated with the fact that, because the boron atom lies well off the Ag–P molecular axis, the bulk of the pyrazolyl ligand lies well off the axis also, being disposed in that sector which lies near ring 13. However, there do not appear to be any unusually close contacts in this area which might account directly for the anomalously large Ag–P–C(13) angle.

DISCUSSION

In this paper, we have described the synthesis of some asymmetric three-co-ordinate complexes containing silver, and the molecular structure of one of them.

The ^{1}H n.m.r. spectrum of this complex (2) has been obtained at temperatures between 20 and −60 °C, and shows no inequivalence of the pyrazolyl protons at these temperatures. These results, taken with the structural findings, suggest that the molecule is fluxional, with either (*i*) a rocking motion of the R_3PAg moiety between the two nitrogens, or (*ii*) a complete dissociation and re-association of the pyrazolyl nitrogens, occurring rapidly even at lower temperatures, making the two pyrazolyl groups equivalent. We cannot distinguish between the two cases at this stage.

However, we note that there are now many examples of complexes whose structures are related to that of complex (2), in that they contain a d^{10} metal ion (Ag^{I}, Cu^{I}, Au^{I}, Hg^{II}) co-ordinated to two ligands with a nearly linear L–M–L arrangement (*ca.* 160—170°), with a third donor atom considerably further away from the metal, but still close enough to admit of some weak bonding interaction.

An early rationalisation of this type of structure suggested a second-order Jahn–Teller effect, of a type predicted by Orgel and applied by him to tetrahedral and octahedral co-ordination of d^{10} ions.[20] This involves bonding of ligands *via* sd_{z^2} hybrid orbitals, rather than sp hybrids which would have been expected intuitively. However, photoelectron spectroscopy of some mercury(II) compounds suggests that sd_{z^2} hybridisation is not a strong effect, since the d_σ electrons are most tightly bound.[21] The alternative explanation is that the two more tightly bound ligands interact with sp hybrid orbitals, with the third ligand, at a greater distance, weakly bonding *via* a interaction with the metal p orbital. Rapid oscillation of the two pyrazolyl nitrogens between these orbitals would be expected, and is observed.

Data recently reported [22] for the series of complexes of MCl (M = Cu, Ag, or Au) with the bidentate ligand 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene show a striking increase of the P–M–P angles from 132° (Cu) to 141° (Ag) to 176° (Au), which has been related to a shortening and strengthening of the M–P bonds down the series. These data also correlate with the stereochemical changes that occur in the model minimum-energy pathway relating two- and three-coordinate complexes; the structure found for complex (2) may be a minimum energy (as determined by crystal packing forces) conformation of the fluxional species indicated by n.m.r. spectroscopy.

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