Crystal Structure of *trans*-Dibromobis(5-methyl-5*H*-dibenzophosphole)-nickel(II)

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The structure of the title compound has been determined by *X*-ray diffraction methods. The unit cell is monoclinic, $a = 6.66(1)$, $b = 10.15(1)$, $c = 17.96(2)$ Å, $\gamma = 108.9°$, space group $P2_1/b$, $Z = 2$. The structure has been solved by the heavy-atom method from diffractometer data and refined by full-matrix least squares to R 0.052 for 1 881 reflections. The molecule is centrosymmetric, but has no other symmetry. The Br–Ni–P interbond angle is 92.6°.

IN the series of five-co-ordinate compounds $[ML_3X_2]$ (M = Ni, Pd, or Pt; L = 5-alkyl-5*H*-dibenzophosphole; X = Cl, Br, or CN) the geometric form of the co-ordination of the metal varies with variation in M, L, and X.[1,2] Part of the variation can be related to simple steric effects. The structure of the title compound was determined because, if the molecule adopted a square-planar arrangement of nickel bonds, the steric interactions between its ligands should be a simplified analogue of those in the five-co-ordinate bromides. In particular, it might be possible to estimate minimum internal contact distances to be used in a critical discussion of the five-co-ordinate geometry.

RESULTS AND DISCUSSION

The whole molecule is shown in Figure 1. It is centrosymmetric and therefore has the *trans* configuration with all four bonds involving the nickel atom being coplanar. The agreement between the length of chemically equivalent bonds is good.

The Dibenzophosphole Ligand.—The mean P–C_α (see ref. 2 for atom designations) bond length (1.81 Å) falls within the published range for similar bonds. The P–C_γ distance (1.84 Å) follows the observed[2] trend that this bond is marginally longer than P–C_α. The C_α–$C_{\beta'}$ bond (1.47) is similar to the $C(sp^2)$—$C(sp^2)$ single bond in the planar biphenyl[3] and in the non-planar 4,4'-bitolyl.[4]

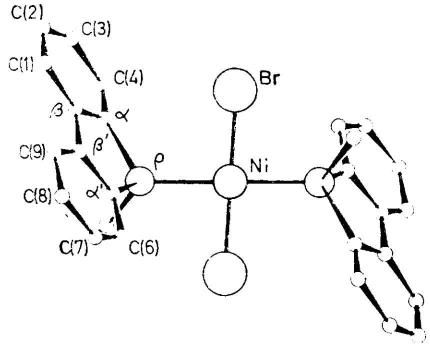

FIGURE 1 Projection of the molecule on the plane through the five central atoms

There is the possibility that some delocalisation of electrons occurs over the whole quasiplanar system, the inclusion of the phosphorus *d*-electron orbitals accounting for the slight shortening of the P–C_α bonds. Although each benzenoid residue is planar, there are deviations from the mean plane passing through both residues. These deviations are not individually significant but they conform to a trend observed for other phosphole ligands,[1] and correspond to a dihedral angle of 2.7° between the benzenoid rings. Molecular dimensions are not available for the free ligand because it is a viscous liquid which forms a glass on cooling.

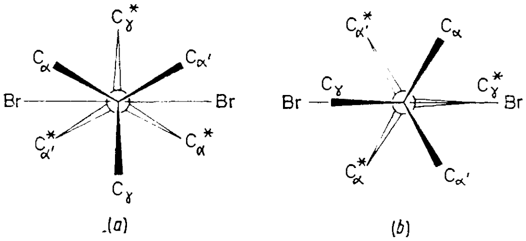

FIGURE 2 Two symmetrical structures projected down the P–Ni–P bond

Geometry at Nickel.—The bond angle Br–Ni–P is 92.6°, Ni–P 2.27, and Ni–Br 2.29 Å. These parameters are similar to those found in the square-planar form of bis(benzyldiphenylphosphine)dibromonickel(II).[5] The molecule does not have the approximate plane of symmetry normal to the Br–Ni–Br bonds which would be possible if the angle at nickel were 90° and the ligand took up the appropriate orientation [Figure 2(*a*)], nor the alternative plane of symmetry including the bromine atoms, with a different orientation of the ligands [Figure 2(*b*)]. The first of these two situations produces two Br $\cdots$ C_α distances of 3.41 Å and a Br $\cdots$ C_γ distance of 4.24 Å, taking mean observed bond distances and angles. The second situation produces two distances of 3.78 and one of 3.26 Å. The first hypothetical structure gives non-bonded contacts longer than the minimum observed (3.39 Å), and so in principle is feasible. In the observed structure the ligand is rotated about the Ni–P bond by *ca.* 16° from the orientation in Figure 2(*b*), presumably to meet intermolecular packing requirements, and the Br–Ni–P angle is distorted slightly from a right angle. The asymmetric relation between the dibenzophosphole ligand and the bromine atoms results in slight inequalities between the Ni–P–C_α and Ni–P–$C_{\alpha'}$ angles (Table 1). If molecular packing forces determine the general disposition of the ligands about the nickel atom, then it seems possible that the ligand distortion to give large Ni–P–C_α and Ni–P–C_γ angles is a result of the relatively short Br $\cdots$ C_α and

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Br $\cdots$ $C_{\beta'}$ distances, *i.e.* that these values are near the minimum equilibrium distances for the crowded system (Table 2). Although the Br $\cdots$ P distances are asymmetric (3.15 and 3.30 Å), these differences themselves cannot be the source of the distortion of the ligand. The shorter of these distances is similar to those found in dibromotris(5-methyl-5*H*-dibenzophosphole)nickel(II)[6] (3.16, 3.20, 3.21, 3.23, and 3.24 Å). Table 2 also lists molecular distances <3.5 Å. They are not unusually short, but compatible with a well packed molecular solid. They are all between atoms in molecules related by a unit-cell shift parallel to *a*.

TABLE 1

Interbond angles (°), with estimated standard deviations in parentheses

P–Ni–Br	92.6(1)	C_α–P–$C_{\alpha'}$	91.1(3)
Ni–P–C_α	120.9(2)	C_α–P–C_γ	103.5(4)
Ni–P–$C_{\alpha'}$	112.9(2)	$C_{\alpha'}$–P–C_γ	106.4(4)
Ni–P–C_γ	118.2(2)		
P–C_α–C_β	110.9(5)	P–$C_{\alpha'}$–C_β	111.4(5)
P–C_α–C(4)	128.6(5)	P–$C_{\alpha'}$–C(6)	127.6(5)
C_α–C_β–$C_{\beta'}$	113.8(6)	C_α–$C_{\beta'}$–C_β	112.8(6)
C_α–C_β–C(1)	120.2(6)	C_α–$C_{\beta'}$–C(9)	121.1(6)
$C_{\beta'}$–C_β–C(1)	126.1(6)	C_β–$C_{\beta'}$–C(9)	126.1(6)
C_β–C(1)–C(2)	118.7(6)	$C_{\beta'}$–C(9)–C(8)	117.9(6)
C(1)–C(2)–C(3)	121.4(6)	C(9)–C(8)–C(7)	121.1(6)
C(2)–C(3)–C(4)	119.4(6)	C(8)–C(7)–C(6)	121.8(6)
C(3)–C(4)–C_α	119.8(6)	C(7)–C(6)–$C_{\alpha'}$	117.1(6)

TABLE 2

(*a*) Interatomic distances (Å), with estimated standard deviations in parentheses

Ni–Br	2.293(1)	P–$C_{\alpha'}$	1.813(7)
Ni–P	2.272(2)	P–C_γ	1.837(7)
P–C_α	1.813(7)		
C_α–C_β	1.41(1)	$C_{\alpha'}$–$C_{\beta'}$	1.41(1)
C_β–C(1)	1.40(1)	$C_{\beta'}$–C(9)	1.39(1)
C(1)–C(2)	1.39(1)	C(9)–C(8)	1.39(1)
C(2)–(C3)	1.39(1)	C(8)–C(7)	1.39(1)
C(3)–C(4)	1.41(1)	C(7)–C(6)	1.40(1)
C(4)–C_α	1.37(1)	C(6)–$C_{\alpha'}$	1.39(1)
C_β–$C_{\beta'}$	1.47(1)	Br $\cdots$ C_γ	3.45
Br $\cdots$ C_α	3.39	Br $\cdots$ $C_{\alpha'}$	3.86

(*b*) Intermolecular contacts <3.5 Å

C(3) $\cdots$ C(6^{I})	3.43	C(3) $\cdots$ $C_{\alpha'}{}^{\text{I}}$	3.47
C(4) $\cdots$ C(6^{I})	3.45	C(2) $\cdots$ C(8^{I})	3.48

Superscript I denotes molecule at $x + 1, y, z$.

EXPERIMENTAL

The crystals were obtained in small yield as dark red prisms by thermal decomposition of dibromotris(5-methyl-5*H*-dibenzophosphole)nickel(II) in chlorobenzene. The space group and approximate cell dimensions were determined from Weissenberg photographs ($hk0$, $k = 2n + 1$; $00l$, $l = 2n + 1$). Intensity data were measured on a Hilger and Watts Y 290 four-circle diffractometer from a prismatic crystal (0.15 × 0.35 × 0.7 mm), by ω–2θ scan and a modified ordinate-analysis method.[7] The setting angles of 10 reflections were measured on both the positive and negative side of the beam and used in a least-squares calculation to determine accurate cell parameters. Of 3 555 observed reflections, there were 2 523 independent reflections of which 1 881 had $\bar{I} \geqslant 2\sigma(\bar{I})$. The merging $R(= \Sigma|I - I_i|/\Sigma I_i)$ was 0.045. Lorentz, polarisation, and an empirical absorption correction,[8] using the $4\bar{2}0$ and $6\bar{6}0$ reflections, were applied. The structure was solved by the heavy-atom method and refined by full-matrix least squares with anisotropic temperature factors for all the atoms. Hydrogen atoms were not sought. The reflection weights were unity for those reflections with $|F_o| < 188$, and $188/|F_o|$ for those with $|F_o| > 188$, $|F_o|$ being on the scale of the published structure factors. The final R factor was 0.052. Scattering factors were taken from ref. 9. Observed structure amplitudes and structure factors calculated from the atomic parameters in Table 3 are listed in Supplementary Publication No. SUP 21785 (13 pp., 1 microfiche),* together with the anisotropic temperature factors.

TABLE 3

Atomic co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses

	x/a	y/b	z/c
Ni	10 000	10 000	0
Br	678(1)	8,671(1)	−942(1)
P	7 269(3)	8.127(2)	335(1)
C_α	5 466(9)	8 247(6)	1 069(4)
C_β	5 595(10)	7 398(6)	1 677(4)
C(1)	4 329(11)	7 341(7)	2 308(4)
C(2)	2 910(11)	8 098(7)	2 309(4)
C(3)	2 750(11)	8 921(7)	1 707(4)
C(4)	4 055(11)	8 987(7)	1 078(4)
$C_{\alpha'}$	8 104(10)	6 868(6)	865(4)
$C_{\beta'}$	7 095(10)	6 612(6)	1 564(4)
C(6)	9 583(10)	6 219(7)	661(4)
C(7)	9 967(12)	5 277(7)	1 171(5)
C(8)	8 948(12)	5 013(8)	1 854(4)
C(9)	7 522(11)	5 689(7)	2 066(4)
C_γ	5 512(12)	7 155(8)	−400(4)

Crystal Data.—$C_{26}H_{22}Br_2NiP_2$, $M = 615$, Monoclinic, $a = 6.66(1)$, $b = 10.15(1)$, $c = 17.96(2)$ Å, $\gamma = 108.89(3)°$, $U = 1\,148.5$ Å^3, $Z = 2$, $D_c = 1.78$. Space group $P2_1/b$ (C^5_{2h}, no. 14). Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) $= 46.8$ cm^{-1}. Balanced filters $\theta < 15°$, β filter $15 \leqslant \theta < 30°$.

[6/138 *Received, 22nd January, 1976*]

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* For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue.

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