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# The Structure of Bromotris(triphenylphosphine)nickel(I), $C_{54}H_{45}BrNiP_3$

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**Abstract.** $M_r = 925{\cdot}50$, trigonal, $P3$, $a = 19{\cdot}110\,(5)$, $c = 10{\cdot}653\,(4)$ Å, $V = 3369\,(2)$ Å$^3$, $Z = 3$, $D_x = 1{\cdot}37$ Mg m$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}51$ mm$^{-1}$, $F(000) = 1431$, room temperature, final $R = 0{\cdot}049$ for 1571 reflections. The molecular structure consists of tetrahedral $Ni^I$ atoms coordinated by three triphenylphosphine molecules and one Br atom. The three independent molecules all have $C_3$ crystallographic symmetry.

**Introduction.** In the course of a research project that in the past has led to the synthesis of interesting cyclopropenium metal complexes (Mealli, Midollini, Moneti, Sacconi, Silvestre & Albright, 1982; Mealli, Midollini, Moneti & Albright, 1983) the reaction between triphenylcyclopropenyl bromide and ethylenebis(triphenylphosphine)nickel was attempted. A crop of yellow crystals separated from a solution of benzene and methanol over a period of two weeks. The compound analyzed as $(PPh_3)_3NiBr$. In spite of the fact that the compound has been known for some time (Heimbach, 1964; Porri, Gallazzi & Vitulli, 1967; Green & Smith, 1971), no detailed crystal structure has been reported. We present here the crystal structure analysis results for the title compound.

**Experimental.** Philips PW 1100 diffractometer, lattice parameters determined using 20 reflections, 4474 measured reflections, $2\theta \le 50°$, $0 \le h \le 15$, $0 \le k \le 15$, $-12 \le l \le 12$; 1571 unique reflections with $I \ge 3\sigma(I)$; three standard reflections, no appreciable variation of their intensities; Lp correction, no absorption correction because of small size of crystal which had a hexagonal prismatic shape with dimensions $0{\cdot}30 \times 0{\cdot}03 \times 0{\cdot}4$ mm; scattering factors for non-hydrogen atoms (*International Tables for X-ray crystallography,* 1974) and for H atoms (Stewart, Davidson & Simpson, 1965). Patterson and Fourier methods, full-matrix least-squares refinement, $\sum w(|F_o|-|F_c|)^2$ minimized, anisotropic thermal parameters for Br, Ni and P atoms, isotropic for the remaining atoms. Phenyl groups refined as $D_{6h}$ rigid bodies, H atoms at calculated positions (C—H = 0·95 Å). Final $R = 0{\cdot}049$, $R_w = 0{\cdot}048$, $w = 1/\sigma(F_o)^2$; maximum least-squares shift to error 0·3, maximum height in final difference Fourier map 0·3 e Å$^{-3}$; SEL 32/70 computer; programs *SHELX*76 (Sheldrick, 1976) and *PLUTO* (Motherwell, 1978).

**Discussion.** Atomic parameters are given in Table 1.* There are three independent $(PPh_3)_3NiBr$ molecules in the unit cell, all having $C_3$ crystallographic symmetry. Inspection of Table 2 is suggestive of the complete equivalence of the molecules, one of which is shown in Fig. 1.

As anticipated by preliminary X-ray work (Porri, Gallazzi & Vitulli, 1967) the geometry of the Ni atom is tetrahedral with $L$—Ni—$L$ angles which deviate from the ideal value of 109·47° by not more than ± 1·5°. There are few crystal structures of monomeric paramagnetic $Ni^I$ compounds in the literature. An appropriate comparison can be made with those complexes which are tetracoordinated by three phosphine groups and a fourth ligand which can be either a $\pi$-acceptor or a $\pi$-donor atom or group. The Br atom in this compound as well as I in the complex (triphos)NiI (1), triphos = $CH_3C(CH_2PPh_2)_3$ (Dapporto, Fallani & Sacconi, 1974) and the $SH^-$ group in (triphos)NiSH (2) (Bianchini, Masi, Mealli & Meli, 1982) belong to the latter category. Examples of $\pi$ acceptors are found in the complex $(pp_3)Ni^+$ (3), $pp_3 = P(CH_2CH_2PPh_2)_3$ (Midollini, Moneti, Orlandini & Sacconi, 1980) and in $(PMe_3)_4Ni^+$ (4) (Gleizes, Dartiguenave, Dartiguenave, Galy & Klein, 1977).

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38461 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional parameters* ($\times 10^4$) *and isotropic thermal parameters* ($Å^2 \times 10^3$)

For Br, Ni and P atoms $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

| | $x$ | $y$ | $z$ | $U_{eq}$ or $U_{iso}$ |
|---|---|---|---|---|
| Br(1) | 0 | 0 | 0 | 57 (2) |
| Ni(1) | 0 | 0 | −2287 (6) | 29 (2) |
| Br(2) | 3333 | 6667 | 671 (4) | 59 (2) |
| Ni(2) | 3333 | 6667 | 2958 (6) | 28 (3) |
| Br(3) | 6667 | 3333 | 2931 (5) | 49 (2) |
| Ni(3) | 6667 | 3333 | 648 (6) | 31 (3) |
| P(1) | 1208 (3) | 158 (3) | −3032 (7) | 33 (4) |
| P(2) | 4227 (3) | 7953 (3) | 3720 (6) | 28 (4) |
| P(3) | 5412 (3) | 2999 (3) | −128 (6) | 36 (4) |
| C(1) | 1769 (9) | −222 (9) | −2126 (11) | 50 (6) |
| C(2) | 2477 (9) | −167 (9) | −2591 (11) | 66 (8) |
| C(3) | 2916 (9) | −415 (9) | −1852 (11) | 60 (7) |
| C(4) | 2646 (9) | −719 (9) | −649 (11) | 63 (7) |
| C(5) | 1938 (9) | −774 (9) | −184 (11) | 78 (8) |
| C(6) | 1499 (9) | −526 (9) | −923 (11) | 64 (7) |
| C(7) | 2009 (8) | 1212 (8) | −3169 (11) | 28 (5) |
| C(8) | 2579 (8) | 1506 (8) | −4134 (11) | 50 (6) |
| C(9) | 3159 (8) | 2325 (8) | −4181 (11) | 61 (7) |
| C(10) | 3169 (8) | 2850 (8) | −3262 (11) | 63 (7) |
| C(11) | 2600 (8) | 2557 (8) | −2297 (11) | 58 (7) |
| C(12) | 2020 (8) | 1738 (8) | −2250 (11) | 42 (6) |
| C(13) | 1137 (8) | −278 (8) | −4593 (11) | 31 (5) |
| C(14) | 1023 (8) | −1056 (8) | −4703 (11) | 45 (6) |
| C(15) | 882 (8) | −1423 (8) | −5879 (11) | 55 (7) |
| C(16) | 857 (8) | −1013 (8) | −6945 (11) | 57 (7) |
| C(17) | 971 (8) | −235 (8) | −6835 (11) | 45 (6) |
| C(18) | 111 (8) | 133 (8) | −5659 (11) | 39 (6) |
| C(19) | 5158 (7) | 8632 (6) | 2826 (12) | 26 (5) |
| C(20) | 5281 (7) | 8422 (6) | 1625 (12) | 46 (6) |
| C(21) | 5960 (7) | 8958 (6) | 935 (12) | 49 (6) |
| C(22) | 6517 (7) | 9705 (6) | 1446 (12) | 62 (7) |
| C(23) | 6394 (7) | 9916 (6) | 2646 (12) | 56 (7) |
| C(24) | 5715 (7) | 9379 (6) | 3336 (12) | 47 (6) |
| C(25) | 3768 (8) | 8595 (8) | 3768 (11) | 26 (5) |
| C(26) | 3963 (8) | 9197 (8) | 4663 (11) | 53 (7) |
| C(27) | 3592 (8) | 9666 (8) | 4627 (11) | 70 (8) |
| C(28) | 3025 (8) | 9533 (8) | 3695 (11) | 54 (7) |
| C(29) | 2830 (8) | 8930 (8) | 2800 (11) | 58 (7) |
| C(30) | 3202 (8) | 8461 (8) | 2836 (11) | 46 (6) |
| C(31) | 4598 (7) | 7973 (8) | 5317 (12) | 33 (5) |
| C(32) | 5353 (7) | 8040 (8) | 5494 (12) | 41 (6) |
| C(33) | 5611 (7) | 7995 (8) | 6701 (12) | 70 (8) |
| C(34) | 5114 (7) | 7883 (8) | 7731 (12) | 60 (7) |
| C(35) | 4360 (7) | 7816 (8) | 7554 (12) | 58 (7) |
| C(36) | 4102 (7) | 7861 (8) | 6346 (12) | 48 (7) |
| C(37) | 4468 (10) | 2286 (10) | 707 (10) | 37 (5) |
| C(38) | 3713 (10) | 1942 (10) | 128 (10) | 52 (6) |
| C(39) | 3014 (10) | 1458 (10) | 819 (10) | 65 (7) |
| C(40) | 3070 (10) | 1316 (10) | 2090 (10) | 79 (8) |
| C(41) | 3825 (10) | 1660 (10) | 2669 (10) | 68 (7) |
| C(42) | 4524 (10) | 2145 (10) | 1978 (10) | 44 (6) |
| C(43) | 5263 (8) | 3880 (9) | −145 (12) | 36 (6) |
| C(44) | 5590 (8) | 4423 (9) | 852 (12) | 53 (6) |
| C(45) | 5479 (8) | 5091 (9) | 912 (12) | 63 (7) |
| C(46) | 5042 (8) | 5215 (9) | −24 (12) | 56 (7) |
| C(47) | 4716 (8) | 4672 (9) | −1020 (12) | 65 (7) |
| C(48) | 4826 (8) | 4004 (9) | −1081 (12) | 68 (8) |
| C(49) | 5190 (8) | 2575 (7) | −1731 (11) | 29 (5) |
| C(50) | 4795 (8) | 1739 (7) | −1898 (11) | 47 (6) |
| C(51) | 4702 (8) | 1417 (7) | −3102 (11) | 63 (7) |
| C(52) | 5003 (8) | 1930 (7) | −4138 (11) | 47 (6) |
| C(53) | 5398 (8) | 2765 (7) | −3970 (11) | 44 (6) |
| C(54) | 5491 (8) | 3088 (7) | −2767 (11) | 39 (6) |

Table 2. *Selected bond lengths* (Å) *and angles* (°)

C(*i*), C(*ii*) and C(*iii*) atoms correspond to atoms C(1), C(7), C(13) in the first molecule, to atoms C(19), C(25), C(31) in the second molecule and to atoms C(37), C(43), C(49) in the third molecule.

| | Molecule (1) | Molecule (2) | Molecule (3) |
|---|---|---|---|
| Ni—Br | 2·437 (6) | 2·436 (6) | 2·432 (6) |
| Ni—P | 2·313 (6) | 2·328 (6) | 2·304 (6) |
| P—C(*i*) | 1·840 (15) | 1·857 (14) | 1·858 (14) |
| P—C(*ii*) | 1·828 (15) | 1·830 (15) | 1·842 (15) |
| P—C(*iii*) | 1·834 (13) | 1·836 (14) | 1·847 (16) |
| Br—Ni—P | 110·1 (2) | 110·4 (2) | 111·0 (2) |
| P—Ni—P′ | 108·9 (2) | 108·5 (2) | 107·9 (2) |
| C(*i*)—P—C(*ii*) | 98·3 (7) | 99·1 (6) | 97·9 (6) |
| C(*i*)—P—C(*iii*) | 102·8 (6) | 103·6 (6) | 101·2 (6) |
| C(*ii*)—P—C(*iii*) | 105·0 (6) | 105·7 (6) | 106·6 (6) |

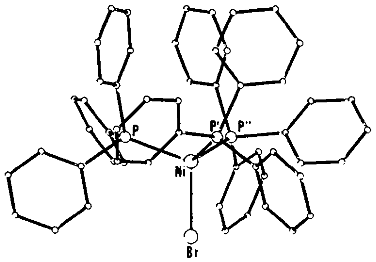

Fig. 1. A perspective view of the title compound.

While compounds (1)–(3) all have $C_{3v}$ symmetry, the symmetry of (4) is almost $D_{2d}$. This is not surprising for both symmetries are calculated to be stable for $d^9$ metal complexes (Burdett, 1980). The P—Ni—P angles, that in the present compound have almost the ideal tetrahedral value, can be as small as ~ 90° in (1) and (2) and as great as ~120° in (3). All the latter angular values are imposed by the steric requirements of the polydentate ligands. Note that (3) has the geometry reminiscent of a trigonal pyramid. Associated with these angular differences are the Ni—P distances of 2·315 (7) Å in the present complex, ~ 2·26 (1) Å in (2) and ~ 2·20–2·21 (1) Å in (1) and (3). The large distance in our compound is probably because for a tetrahedron there is maximum antibonding between metal *d* orbitals and the P lone pairs in the $t_2$ set. Distortion from the tetrahedral geometry towards a trigonal pyramid or in the opposite sense should reduce the effect with a consequent shortening of the Ni—P distances (Elian & Hoffmann, 1975).

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