# SHORT STRUCTURAL PAPERS

## cis-Dibromonitrosylbis(triphenyl phosphite)rhodium

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**Abstract.** $RhBr_2(NO)$ $[P(OC_6H_5)_3]_2$, monoclinic, $P2_1/c$, $a=14.78$ (2), $b=13.50$ (2), $c=20.35$ (2) Å, $\beta=109.6$ (2)°, $D_m=1.60$, $D_c=1.59$ g cm$^{-3}$ for $Z=4$. The structure is square pyramidal with a bent nitrosyl group occupying the apical position. The Br atoms are *cis*-disposed.

**Introduction.** Green crystals of the title complex were prepared by a modification of the method of Crooks & Johnson (1970) and recrystallized from dichloromethane/methanol. A crystal $0.20 \times 0.20 \times 0.16$ mm was used for data collection. The cell parameters were obtained from a least-squares analysis of the settings of 25 reflexions measured on a four-circle Philips PW1100 diffractometer. Intensities were measured with

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graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.7107$ Å), $\omega-2\theta$ scan mode (scan width $1.0°\theta$, scan speed $0.03°\theta$ s$^{-1}$). 1788 reflexions were collected in the $2\theta$ range 6 to 36° of which 1688 had $I>2\sigma(I)$ and were considered observed. Three reference reflexions were monitored after every 63 reflexions; their intensities fell, on average, to 73% of their initial value. Lorentz-polarization corrections were applied but no allowance was made for absorption. The Rh and two Br atoms were located from a Patterson map, and a subsequent difference synthesis yielded the positions of the P and O atoms of the triphenyl phosphite ligands, the N atom and two phenyl rings. The remaining atoms were located after further refinement and model building. The final refinement, carried out with the Rh, Br and P atoms anisotropic and all the phenyl rings treated as rigid groups, yielded $R=0.114$. H atoms were not

Table 1. *Fractional atomic coordinates and their e.s.d.'s* ($\times 10^4$) *of the heavy atoms*

Rxy denotes the phenyl ring bonded to oxygen atom O(xy).

| | x | y | z | | x | y | z |
|---|---|---|---|---|---|---|---|
| Rh | 2221 (2) | 5483 (2) | 8311 (4) | R13C(1) | 4072 (12) | 3705 (15) | 8273 (22) |
| Br(1) | 2100 (3) | 4589 (3) | 9376 (5) | R13C(2) | 4759 (12) | 3787 (15) | 7944 (22) |
| Br(2) | 2401 (3) | 7086 (3) | 8995 (5) | R13C(3) | 5721 (12) | 3971 (15) | 8344 (22) |
| P(1) | 2155 (8) | 4017 (7) | 7695 (13) | R13C(4) | 5986 (12) | 4063 (15) | 9064 (22) |
| P(2) | 2728 (7) | 6246 (7) | 7502 (11) | R13C(5) | 5299 (12) | 3980 (15) | 9394 (22) |
| N | 772 (27) | 5693 (27) | 7941 (37) | R13C(6) | 4347 (12) | 3797 (15) | 8994 (22) |
| O(11) | 1628 (17) | 4221 (17) | 6916 (24) | R21C(1) | 4181 (14) | 7354 (19) | 8313 (16) |
| O(12) | 1516 (15) | 3181 (16) | 7870 (20) | R21C(2) | 4432 (14) | 8324 (19) | 8523 (16) |
| O(13) | 3140 (15) | 3450 (16) | 7837 (20) | R21C(3) | 5266 (14) | 8523 (19) | 9078 (16) |
| O(21) | 3366 (14) | 7235 (15) | 7707 (20) | R21C(4) | 5857 (14) | 7742 (19) | 9423 (16) |
| O(22) | 1914 (17) | 6699 (17) | 6828 (21) | R21C(5) | 5616 (14) | 6772 (19) | 9212 (16) |
| O(23) | 3285 (14) | 5523 (15) | 7253 (21) | R21C(6) | 4772 (14) | 6573 (19) | 8658 (16) |
| O(3) | 499 (29) | 5753 (29) | 7287 (34) | R22C(1) | 1635 (20) | 7638 (17) | 6712 (21) |
| R11C(1) | 1365 (22) | 3423 (19) | 6488 (19) | R22C(2) | 1880 (20) | 8065 (17) | 6710 (21) |
| R11C(2) | 430 (22) | 3050 (19) | 6289 (19) | R22C(3) | 1468 (20) | 8962 (17) | 5881 (21) |
| R11C(3) | 145 (22) | 2292 (19) | 5795 (19) | R22C(4) | 811 (20) | 9433 (17) | 6133 (21) |
| R11C(4) | 794 (22) | 1907 (19) | 5500 (19) | R22C(5) | 565 (20) | 9006 (17) | 6675 (21) |
| R11C(5) | 1729 (22) | 2280 (19) | 5699 (19) | R22C(6) | 977 (20) | 8109 (17) | 6964 (21) |
| R11C(6) | 2015 (22) | 3038 (19) | 6193 (19) | R23C(1) | 3588 (25) | 5797 (18) | 6647 (22) |
| R12C(1) | 1807 (16) | 2205 (17) | 8092 (32) | R23C(2) | 2979 (25) | 5757 (18) | 5957 (22) |
| R12C(2) | 2028 (16) | 1501 (17) | 7661 (32) | R23C(3) | 3328 (25) | 5986 (18) | 5413 (22) |
| R12C(3) | 2262 (16) | 531 (17) | 7897 (32) | R23C(4) | 4287 (25) | 6255 (18) | 5569 (22) |
| R12C(4) | 2264 (16) | 267 (17) | 8564 (32) | R23C(5) | 4895 (25) | 6304 (18) | 6259 (22) |
| R12C(5) | 2042 (16) | 958 (17) | 8986 (32) | R23C(6) | 4546 (25) | 6076 (18) | 6793 (22) |
| R12C(6) | 1808 (16) | 1927 (17) | 8750 (32) | | | | |

## Table 2. *Temperature factors*

(a) Temperature factors of the heavy atoms (excluding C atoms) and their e.s.d.'s ($\text{Å}^2 \times 10^3$)

|  | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Rh | 57 (2) | 42 (2) | 334 (12) | −10 (3) | 32 (3) | −8 (2) |
| Br(1) | 92 (3) | 72 (3) | 407 (19) | 0 (6) | 43 (5) | −18 (3) |
| Br(2) | 100 (3) | 58 (2) | 402 (18) | −35 (5) | 73 (5) | −17 (2) |
| P(1) | 62 (7) | 46 (5) | 235 (42) | 17 (12) | 13 (13) | −12 (5) |
| P(2) | 47 (6) | 63 (6) | 190 (35) | −12 (11) | 15 (10) | −7 (5) |

|  | $U$ |  | $U$ |  | $U$ |  | $U$ |
|---|---|---|---|---|---|---|---|
| N | 115 (18) | O(12) | 74 (8) | O(21) | 68 (7) | O(23) | 61 (7) |
| O(11) | 67 (9) | O(13) | 75 (8) | O(22) | 87 (9) | O(3) | 172 (22) |

(b) Average temperature factors of the carbon atoms in each phenyl ring ($\text{Å}^2 \times 10^3$)

| Ring | $U$ | Ring | $U$ | Ring | $U$ |
|---|---|---|---|---|---|
| R11 | 104 (16) | R13 | 70 (13) | R22 | 112 (17) |
| R12 | 127 (21) | R21 | 85 (14) | R23 | 94 (16) |

located. Scattering factors were from Cromer & Mann (1968) and anomalous dispersion corrections were applied for Rh, Br and P. Final positional and thermal parameters are given in Tables 1 and 2.* Fig. 1 shows the molecular configuration and atomic nomenclature and Fig. 2 the coordination round the Rh atom. Tables 3, 4 and 5 list the bond lengths, angles and the relevant least-squares plane.

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\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31910 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

## Table 3. *Bond lengths* (Å)

| | | | |
|---|---|---|---|
| Rh—Br(1) | 2·54 (1) | P(2)—O(21) | 1·61 (2) |
| Rh—Br(2) | 2·54 (1) | P(2)—O(22) | 1·61 (3) |
| Rh—P(1) | 2·33 (2) | P(2)—O(23) | 1·47 (3) |
| Rh—P(2) | 2·27 (2) | O(11)-R11C(1) | 1·36 (4) |
| Rh—N | 2·04 (4) | O(12)-R12C(1) | 1·41 (3) |
| N—O(3) | 1·26 (9) | O(13)-R13C(1) | 1·41 (3) |
| P(1)-O(11) | 1·54 (4) | O(21)-R21C(1) | 1·42 (4) |
| P(1)-O(12) | 1·59 (3) | O(22)-R22C(1) | 1·33 (3) |
| P(1)-O(13) | 1·58 (2) | O(23)-R23C(1) | 1·49 (4) |

## Table 4. *Bond angles and torsion angles* (°)

| | | | |
|---|---|---|---|
| Br(1)-Rh—Br(2) | 87·8 (3) | Rh—P(2)—O(22) | 117 (1) |
| Br(1)-Rh—P(1) | 93·1 (6) | Rh—P(2)—O(23) | 108 (2) |
| Br(2)-Rh—P(1) | 176·6 (3) | P(1)—O(11)—R11C(1) | 117 (2) |
| P(2)—Rh—P(1) | 87·7 (6) | P(1)—O(12)—R12C(1) | 127 (2) |
| P(2)—Rh—Br(1) | 165·7 (3) | P(1)—O(13)—R13C(1) | 130 (2) |
| P(2)—Rh—Br(2) | 90·7 (4) | P(2)—O(21)—R21C(1) | 125 (2) |
| N—Rh—Br(1) | 91 (2) | P(2)—O(22)—R22C(1) | 128 (3) |
| N—Rh—Br(2) | 89 (1) | P(2)—O(23)—R23C(1) | 119 (2) |
| N—Rh—P(1) | 94 (1) | O(11)-R11C(1)-R11C(2) | 121 (2) |
| N—Rh—P(2) | 103 (2) | O(12)-R12C(1)-R12C(2) | 123 (3) |
| O(3)—N—Rh | 109 (5) | O(13)-R13C(1)-R13C(2) | 116 (2) |
| Rh—P(1)-O(11) | 109 (1) | O(21)-R21C(1)-R21C(2) | 116 (1) |
| Rh—P(1)-O(12) | 114 (2) | O(22)-R22C(1)-R22C(2) | 113 (3) |
| Rh—P(1)-O(13) | 116 (1) | O(23)-R23C(1)-R23C(2) | 124 (2) |
| Rh—P(2)-O(21) | 120 (2) | | |

Torsion angles

| | | | |
|---|---|---|---|
| P(1)-Rh-N-O(3) | 59·5 | P(2)-Rh-N-O(3) | 29·1 |

## Table 5. *Least-squares plane*

The equation of the plane is expressed in orthogonalized space as $lX + mY + nZ = P$. $d$ is the perpendicular distance (Å) from each atom to the plane. Atoms marked with an asterisk were not included in the least-squares calculation.

$$(13\cdot0541)X + (-2\cdot0672)Y + (2\cdot4692)Z = 4\cdot0007$$

|  | $d$ |  | $d$ |  | $d$ |
|---|---|---|---|---|---|
| Rh* | −0·1822 | Br(2) | −0·1103 | P(2) | 0·1219 |
| Br(1) | 0·1065 | P(1) | −0·1181 | N* | −2·2088 |
|  |  |  |  | O(3)* | −2·7386 |

**Discussion.** The mode of coordination of the nitrosyl group in transition-metal nitrosyls has been the subject of much argument (Frenz & Ibers, 1972; Enemark & Feltham, 1974). In particular, five-coordination complexes containing this ligand have been discussed. A survey of representative members of this group (ref-
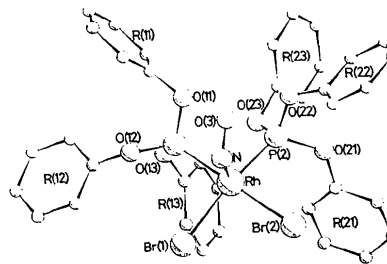


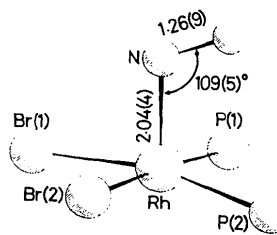Fig. 1. Perspective view of the molecule with atomic and phenyl-ring nomenclature.



Fig. 2. Inner coordination round the rhodium atom.

erences quoted in Vols. 1–7 of *Molecular Structures and Dimensions*, 1935–1975) shows that when the coordination round the metal atom is trigonal bipyramidal, the nitrosyl group coordinates in a linear fashion and the IR absorption band $v(N-O)$ is found between 1770 and 1640 cm$^{-1}$. On the other hand, when the coordination round the metal atom approaches square pyramidal the nitrosyl ligand is found at the apical position and coordinates in a non-linear manner. The characteristic $v(N-O)$ band for this mode of coordination occurs in the range 1630–1654 cm$^{-1}$ for neutral complexes and 1680–1720 cm$^{-1}$ for cationic complexes.

In a study by English & Haines (1976) of a series of five-coordinate nitrosyls RhBr$_2$(NO)L$_2$ where L = P(Ph)$_x$(OPh)$_{3-x}$ it was found that the band $v(N-O)$ in the neutral title compound occurred at the remarkably high frequency of 1750 cm$^{-1}$, suggesting that this neutral complex had a trigonal bipyramidal structure. A structure determination was undertaken to ascertain whether this was in fact the case, or if the increase in $v(N-O)$ from 1630 for RhBr$_2$(NO) (PPh$_3$)$_2$ to 1750 cm$^{-1}$ for the title compound was due to purely electronic effects.

The solution of the structure reveals a square pyramidal geometry with an apical non-linear nitrosyl group. In contrast to IrCl$_2$(NO) (PPh$_3$)$_2$ (Mingos & Ibers, 1971) the halide ligands are *cis*-disposed. The N–O vector is directed between the two Rh–P vectors, that is towards the more crowded part of the molecule. The Rh–N length is among the longest so far observed in a nitrosyl complex and is in accordance with the in-

stability of the complex with respect to decomposition products not exhibiting a $v(N-O)$ band. In IrCl$_2$(NO) (PPh$_3$)$_2$ the Ir–N length is 1·94 (2) Å.

Further work is in progress on the intermediate members of this series, which exhibit intermediate $v(N-O)$ frequencies, in order to elucidate their structures and understand more fully the role of the the P ligands in determining the molecular configuration.

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# Copper Complex of Guanosine-5'-monophosphate

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**Abstract.** [Cu$_3$(C$_{10}$H$_{12}$N$_5$O$_8$P)$_3$(H$_2$O)$_8$].5H$_2$O is orthorhombic, space group $P2_12_12$, with $a = 23·369$ (5), $b = 20·711$ (5), $c = 11·305$ (3) Å, $Z = 4$, $D_m = 1·81$ (3), $D_x = 1·83$ g cm$^{-3}$, Mo $K\alpha$, $\lambda = 0·71069$ Å. There are three Cu(5'-GMP) complexes in the asymmetric unit linked together *via* base–Cu–phosphate bonds forming a polymeric chain. Cu has square pyramidal five-coordination with the binding axially through N(7).

**Introduction.** Single crystals of octahedral habit were obtained by mixing equimolar quantities of disodium guanosine-5'-phosphate and Cu(NO$_3$)$_2$ in water. The amount of crystalline material was not enough to carry out an elementary analysis. A crystal was mounted

along **c** and data within a sphere of reflexions limited at sin $\theta/\lambda = 0·56$ were collected on a Siemens diffractometer. The experimental procedure is described elsewhere (Sletten, 1974). Of the 6460 unique reflexions recorded, 1999 were less than the threshold value.

The structure was solved by *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974) and refined by full-matrix least squares to an $R$ of 0·077. Due to limited computer space each cycle had to be run in three passes. Cu and P were refined anisotropically, the other atoms isotropically. 52 of the 62 H atoms were located in a difference map and included in the structure factor calculations, but not refined. The 10 remaining H atoms belong to the crystal water.