Fig. 2. The unit-cell contents projected down the b axis. O atoms are represented by filled circles and hydrogen bonds by dashed lines. The labelling is shown only for N atoms in the cation and for O atoms in the anion related to that defined by the coordinates in Table 2 by the transformation $\frac{1}{2}+x$, $-\frac{1}{2}-y$, $1+z$. H atoms are omitted.

with the large and very anisotropic displacement parameters of the F atoms, may indicate some disorder of the trifluoromethyl group.

The crystal structure consists of layers of $[Ru(tu)_6]^{2+}$ cations with the metal atoms lying exactly on the 001 planes. Anions lie between these layers; each is hydrogen bonded to four cations,

three in the same layer and one in an adjacent layer. Adjacent cations are also directly linked by N—H···S hydrogen bonds (see Fig. 2 and Table 3).

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Structures of
c-Acetonitrile-ab-dibromo-d-carbonyl-ef-bis(triphenylphosphine)osmium(2+) and b-Acetonitrile-af-dibromo-d-carbonyl-ce-bis(triphenylphosphine)osmium(2+)

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Abstract. (II). $[cis\text{-}OsBr_2(C_2H_3N)(CO)\{P(C_6H_5)_3\}_2]$, $M_r = 943.65$, orthorhombic, $P2_12_12_1$, $a = 13.278$ (5), $b = 24.462$ (8), $c = 10.823$ (3) Å, $V = 3515$ (2) Å^3, $Z = 4$, $D_x = 1.783$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 60.03$ cm^{-1}, $F(000) = 1832$, $T = 296$ K, $R = 0.031$, 2802 unique observed reflections. (III) $[trans\text{-}OsBr_2(C_2H_3N)(CO)\{P(C_6H_5)_3\}_2]$, $M_r = 943.65$, monoclinic, $P2_1/n$, $a = 10.326$ (5), $b = 15.461$ (10), $c = 22.961$ (8) Å, $\beta = 91.15$ (5)°, $V = 3665$ (5) Å^3, $Z = 4$, $D_x = 1.710$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 57.58$ cm^{-1}, $F(000) = 1832$, $T = 296$ K, $R = 0.060$, 3089 unique observed reflections. Compounds (II)

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and (III) were prepared by dissolving the bioctahedral precursor, $\{Os(CO)[P(C_6H_5)_3]_2\}(\mu\text{-}Br)_3\{OsBr_2[P(C_6H_5)_3]\}$, (I), in acetonitrile. Compound (II) has an all-*cis* geometry in which the two Br atoms are *cis* to each other, as are the two Os coordinated triphenylphosphines and the CO and acetonitrile ligands. Compound (III) has all-*trans* geometry, where the two Br atoms and triphenylphosphine ligands are *trans* to each other, as are CO and acetonitrile ligands.

Introduction. In this paper we report the preparations and crystal structures of two isomers of $Br_2(CH_3CN)(CO)\{P(C_6H_5)_3\}_2Os^{II}$. These complexes, (II) and (III), are related to a group of monocarbonyl compounds of Os obtained by a reaction in which the metal-bound carbonyl is derived from the reaction solvent, acetic acid/acetic anhydride (Robinson, Hinckley & Ikuo, 1988; Hinckley, Ikuo & Robinson, 1988; Hinckley, Ali & Robinson, 1990). They were prepared by reaction of the bioctahedral precursor, (I), with acetonitrile. Of the several isomers possible with this selection of ligands, only these two were obtained.

(I)   (II)   (III)
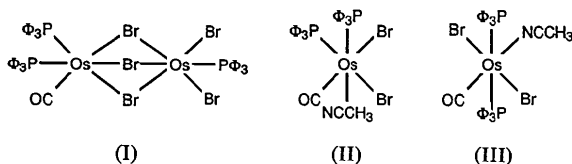
Experimental. The red precursor complex, $\{Os(CO)[P(C_6H_5)_3]_2\}(\mu\text{-}Br)_3\{OsBr_2[P(C_6H_5)_3]\}$, (I), was prepared by refluxing under N_2 a solution containing di(tetra-*n*-butylammonium) hexabromo-osmate(IV) (1·830 g, 1·585 mmol) and triphenylphosphine (1·469 g, 5·60 mmol) in 50 ml mixed acetic acid/acetic anhydride (40/10) solvent for 24 h. Red solid product, (I), was separated by filtration (yield: 1·105 g, 0·693 mmol). Acetonitrile and diethyl ether were used as supplied. Acetonitrile was added to a small amount (0·5 g) of (I) with continuous stirring under N_2. Initial red solution changed to orange with a pale-green precipitate in a few hours. Orange solution was separated from precipitate by decantation and layered with diethyl ether. X-ray-quality orange crystals of (II) were obtained in 3–4 d. Light-green X-ray-quality crystals of (III) were obtained in 24 h from a dichloromethane solution of the complex layered with diethyl ether. Infrared spectra of Nujol mulls exhibited CO stretching absorptions at 1950·2 for (II) and 1924·7 cm^{-1} for (III).

Crystals used for data collection: 0·25 × 0·20 × 0·17 mm, orange, equant (II); 0·35 × 0·15 × 0·03 mm, green, platy (III). Much difficulty was encountered in finding a high-quality crystal of (III); crystal utilized was best of ten surveyed but gave relatively broad and occasionally asymmetric peak shapes; refinement results were not expected to be of the highest quality. Rigaku AFC5S diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω scans, scan speeds 4° min^{-1} (II) and 3° min^{-1} (III), weak reflections [$I < 10\cdot0\sigma(I)$] rescanned (maximum of two rescans) and the counts accumulated to assure good counting statistics. Lattice parameters from least-squares fit of 25 strong reflections in 2θ ranges 36–41 (II) and 24–29° (III). A total of 3476 (II) and 6431 (III) reflections measured [h 0 to 15, k 0 to 29, l 0 to 12 for (II); h 0 to 12, k 0 to 18, l −27 to 27 for (III)], 674 (II) and 3342 (III) reflections considered unobserved with [$I < 3\sigma(I)$], data sets comprised of 2802 (II) and 3089 (III) unique reflections, $(\sin\theta/\lambda)_{max} = 0\cdot60$ Å^{-1}. Three standard reflections [101, 021, 241 (II); 0$\bar{2}$0, $\bar{1}$11, $\bar{1}$15 (III)] changed by 0·9, 1·3 and 1·4% (II) and −1·2, −1·0 and −1·4% (III); no decay corrections applied. Data corrected for Lorentz, polarization, and absorption [empirical ψ scan corrections, five (II) and three (III) reflections, transmission ranges 0·81–1·00 (II) and 0·54–1·00 (III)]. The direct methods program *MITHRIL* (Gilmore, 1984) provided the atomic coordinates of the Os atom for (II) and the Os and Br positions for (III). The phase extension program *DIRDIF* (Beurskens, 1984) used to locate Br and P atoms of (II). The remaining non-H atoms of both (II) and (III) were located by least-squares and difference Fourier syntheses. Full-matrix least-squares refinement was performed to minimize $\Sigma w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$ and $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/Lp^2$ (S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, Lp = Lorentz and polarization factor, and $p = 0\cdot03$). After convergence, phenyl ring and methyl H atoms were placed at idealized positions (C—H = 0·95 Å), and fixed (isotropic B's for H atoms calculated as $1\cdot2 \times B_{eq}$ of associated C atom); rotational orientation of methyl groups obtained from difference Fourier synthesis for both (II) and (III). Final cycles of refinement performed with 415 (II) and 405 (III) variables including all non-H positional and anisotropic thermal parameters [with the exception of the CO ligand of (III), which was refined isotropically] and one scale factor. Convergence of (II) and (III) yielded $R = 0\cdot031$ and 0·060, $wR = 0\cdot032$ and 0·064, $S = 1\cdot04$ and 1·61, and $(\Delta/\sigma)_{max} = 0\cdot06$ and 0·03. Final difference syntheses for (II) and (III) produced $(\Delta\rho)_{max} = 0\cdot72$ and 2·99 e Å^{-3}, and $(\Delta\rho)_{min} = -0\cdot68$ and −1·47 e Å^{-3}, all near the Os position. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 71, 148). All computer programs from the *TEXSAN* package (Molecular Structure Corporation, 1985).

Table 1. *Positional and equivalent isotropic thermal parameters for the non-H atoms and their e.s.d.'s*

$$B_{eq} = (8\pi^2/3)[U_{22} + (1/\sin^2\beta)(U_{11} + 2U_{33} + 2U_{13}\cos\beta)].$$

	x	y	z	B_{eq} (Å²)
Compound (II)				
Os(1)	0·48728 (3)	0·66680 (2)	0·27753 (4)	1·81 (1)
Br(1)	0·41897 (8)	0·76195 (5)	0·2103 (1)	3·09 (4)
Br(2)	0·4343 (1)	0·63363 (6)	0·0590 (1)	3·48 (6)
P(1)	0·5859 (2)	0·5926 (1)	0·3521 (3)	2·4 (1)
P(2)	0·3242 (2)	0·6422 (1)	0·3484 (3)	2·1 (1)
C(1)	0·7222 (8)	0·6116 (5)	0·348 (1)	2·8 (5)
C(2)	0·7932 (8)	0·5788 (5)	0·291 (1)	3·7 (6)
C(3)	0·892 (1)	0·5966 (6)	0·283 (2)	4·7 (7)
C(4)	0·9234 (9)	0·6446 (6)	0·333 (1)	4·2 (7)
C(5)	0·853 (1)	0·6766 (6)	0·391 (1)	4·4 (7)
C(6)	0·7547 (9)	0·6608 (6)	0·399 (1)	3·7 (6)
C(7)	0·5890 (8)	0·5247 (4)	0·278 (1)	2·9 (5)
C(8)	0·602 (1)	0·4779 (7)	0·342 (2)	5·4 (9)
C(9)	0·605 (1)	0·4268 (6)	0·285 (2)	6 (1)
C(10)	0·598 (1)	0·4245 (7)	0·159 (2)	7 (1)
C(11)	0·587 (1)	0·4704 (8)	0·094 (2)	6 (1)
C(12)	0·582 (1)	0·5213 (6)	0·150 (1)	5·1 (8)
C(13)	0·5660 (8)	0·5755 (4)	0·516 (1)	2·4 (5)
C(14)	0·483 (1)	0·5412 (4)	0·547 (1)	3·1 (5)
C(15)	0·460 (1)	0·5307 (6)	0·671 (1)	4·3 (7)
C(16)	0·519 (1)	0·5532 (6)	0·763 (1)	5·2 (7)
C(17)	0·600 (1)	0·5850 (6)	0·732 (1)	5·6 (8)
C(18)	0·625 (1)	0·5966 (5)	0·611 (1)	3·7 (6)
C(19)	0·2934 (8)	0·5684 (5)	0·353 (1)	2·5 (5)
C(20)	0·225 (1)	0·5487 (5)	0·440 (1)	3·8 (6)
C(21)	0·207 (1)	0·4929 (5)	0·447 (1)	4·1 (7)
C(22)	0·255 (1)	0·4568 (6)	0·371 (1)	4·4 (7)
C(23)	0·321 (1)	0·4769 (5)	0·281 (1)	3·6 (6)
C(24)	0·3408 (7)	0·5329 (4)	0·276 (1)	2·6 (5)
C(25)	0·2888 (8)	0·6628 (5)	0·505 (1)	2·4 (5)
C(26)	0·1887 (8)	0·6747 (5)	0·535 (1)	3·1 (6)
C(27)	0·162 (1)	0·6823 (5)	0·659 (1)	4·3 (7)
C(28)	0·231 (1)	0·6783 (5)	0·750 (1)	4·0 (7)
C(29)	0·331 (1)	0·6670 (5)	0·721 (1)	4·0 (6)
C(30)	0·3581 (8)	0·6582 (4)	0·602 (1)	2·5 (5)
C(31)	0·2228 (7)	0·6689 (5)	0·2515 (9)	2·5 (5)
C(32)	0·1880 (8)	0·7222 (5)	0·265 (1)	3·4 (6)
C(33)	0·114 (1)	0·7438 (7)	0·188 (2)	5·5 (9)
C(34)	0·076 (1)	0·7129 (8)	0·097 (1)	5·5 (9)
C(35)	0·109 (1)	0·6586 (7)	0·080 (1)	4·5 (7)
C(36)	0·183 (1)	0·6369 (6)	0·159 (1)	4·4 (7)
C(37)	0·5205 (8)	0·7042 (4)	0·428 (1)	2·5 (5)
O(1)	0·5365 (6)	0·7267 (3)	0·5039 (8)	2·8 (4)
N(1)	0·6157 (7)	0·6906 (4)	0·1817 (8)	2·4 (4)
C(38)	0·6861 (9)	0·6979 (5)	0·124 (1)	3·2 (6)
C(39)	0·778 (1)	0·7090 (6)	0·054 (1)	4·9 (8)
Compound (III)				
Os(1)	0·96184 (7)	0·22537 (5)	0·65042 (4)	2·39 (3)
Br(1)	1·1467 (2)	0·3124 (1)	0·6975 (1)	3·9 (1)
Br(2)	0·8114 (2)	0·1104 (2)	0·6091 (1)	4·8 (1)
P(1)	0·8741 (5)	0·1982 (3)	0·7444 (2)	2·6 (2)
P(2)	1·0535 (5)	0·2443 (3)	0·5566 (2)	2·9 (3)
N(1)	1·091 (2)	0·119 (1)	0·6652 (7)	3·3 (9)
C(1)	0·950 (2)	0·108 (1)	0·780 (1)	3 (1)
C(2)	0·910 (2)	0·021 (1)	0·767 (1)	5 (1)
C(3)	0·975 (3)	−0·046 (2)	0·791 (2)	8 (2)
C(4)	1·075 (4)	−0·035 (3)	0·826 (2)	10 (3)
C(5)	1·117 (3)	0·047 (3)	0·841 (1)	9 (2)
C(6)	1·056 (2)	0·117 (2)	0·815 (1)	6 (1)
C(7)	0·699 (2)	0·174 (1)	0·7490 (9)	2 (1)
C(8)	0·612 (2)	0·210 (1)	0·711 (1)	4 (1)
C(9)	0·478 (2)	0·200 (2)	0·720 (1)	5 (1)
C(10)	0·435 (2)	0·154 (2)	0·765 (1)	5 (1)
C(11)	0·521 (2)	0·114 (2)	0·802 (1)	5 (1)
C(12)	0·654 (2)	0·125 (2)	0·795 (1)	4 (1)
C(13)	0·883 (2)	0·284 (1)	0·7981 (8)	2·5 (9)
C(14)	0·896 (2)	0·369 (1)	0·781 (1)	4 (1)
C(15)	0·888 (2)	0·435 (1)	0·823 (1)	4 (1)
C(16)	0·874 (2)	0·418 (2)	0·881 (1)	5 (1)
C(17)	0·868 (2)	0·332 (2)	0·898 (1)	5 (1)
C(18)	0·873 (2)	0·265 (1)	0·857 (1)	4 (1)
C(19)	1·126 (2)	0·349 (1)	0·536 (1)	4 (1)
C(20)	1·204 (4)	0·356 (2)	0·490 (1)	10 (2)
C(21)	1·258 (5)	0·433 (2)	0·470 (2)	14 (3)
C(22)	1·215 (3)	0·506 (2)	0·499 (1)	7 (2)
C(23)	1·139 (3)	0·504 (1)	0·546 (1)	6 (2)
C(24)	1·093 (2)	0·425 (1)	0·565 (1)	4 (1)
C(25)	1·184 (2)	0·168 (1)	0·547 (1)	4 (1)
C(26)	1·151 (2)	0·081 (1)	0·529 (1)	5 (1)
C(27)	1·243 (4)	0·015 (2)	0·527 (1)	7 (2)

Table 1. (*cont.*)

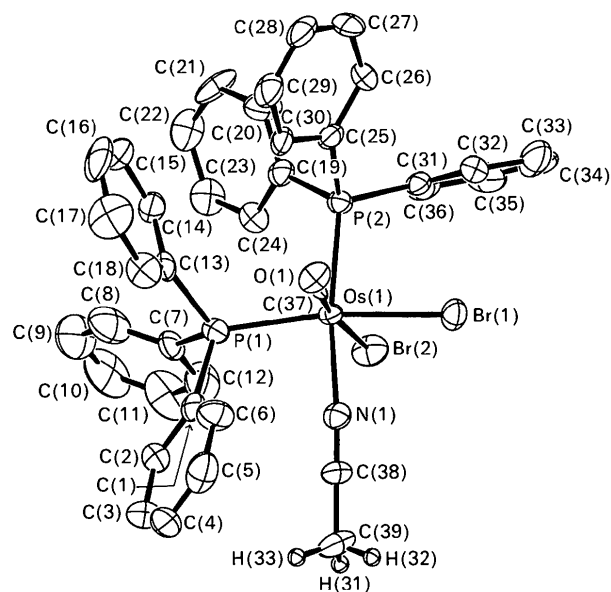|	x	y	z	B_{eq} (Å²)
C(28)	1·366 (3)	0·040 (3)	0·544 (1)	9 (2)
C(29)	1·410 (3)	0·118 (3)	0·563 (1)	8 (2)
C(30)	1·309 (2)	0·184 (2)	0·565 (1)	6 (1)
C(31)	0·949 (2)	0·228 (1)	0·4921 (9)	3 (1)
C(32)	0·998 (3)	0·202 (2)	0·441 (1)	6 (2)
C(33)	0·926 (3)	0·197 (2)	0·391 (1)	7 (2)
C(34)	0·795 (3)	0·216 (2)	0·392 (1)	6 (2)
C(35)	0·741 (2)	0·241 (1)	0·444 (1)	5 (1)
C(36)	0·820 (2)	0·246 (1)	0·493 (1)	4 (1)
C(37)	1·159 (2)	0·064 (2)	0·675 (1)	4 (1)
C(38)	1·243 (2)	−0·006 (1)	0·687 (1)	5 (1)
O(1)	0·793 (1)	0·3682 (8)	0·6314 (5)	1·9 (2)
C(39)	0·840 (2)	0·329 (1)	0·637 (1)	3·8 (5)

Fig. 1. Molecular configuration and atom-numbering scheme for molecule (II). Thermal ellipsoids at the 50% probability level; ring H atoms omitted to improve clarity.

Discussion. The molecular configurations of the title isomers, (II) and (III), are presented in Figs. 1 and 2. Table 1 presents atomic coordinates and equivalent isotropic temperature factors for (II) and (III); selected bond distances and angles for the two structures are given in Table 2.* In both complexes, Os atoms are six coordinate with the bonds arranged in a distorted octahedron. Each Os atom is bound to two Br atoms, two P atoms of coordinating triphenylphosphine ligands, the N atom of an acetonitrile ligand and the C atom of a carbonyl ligand. In the *cis* complex, the two Br atoms are *cis* to one another as are the two triphenylphosphines. The carbonyl

* Lists of structure factors, H-atom coordinates, anisotropic thermal parameters, distances and angles involving the phenyl rings, intermolecular distances, and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53884 (79 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

ligand and the coordinated acetonitrile ligand are also *cis* to one another, so that (II) may be considered 'all *cis*'. The *trans* complex, (III), is 'all *trans*', the Br atoms are *trans*, as are the triphenylphosphines, and the two remaining ligands, carbonyl and acetonitrile.

In (II), the Os—Br bond distances are 2·602 (1) and 2·598 (1) Å, which are somewhat longer than the average distance (2·561 Å) found in similar compounds (Robinson, Hinckley & Ikuo, 1988; Hinckley, Ikuo & Robinson, 1988; Hinckley, Ali & Robinson, 1990). The Os—P distances for the *cis* phosphine ligands in (II) are 2·375 (3) and 2·379 (3) Å, and in (III), where the phosphines ligands are *trans*, these distances are 2·394 (6) and 2·388 (6) Å. Differences between Os—P bond distances in (II) and (III) may be due to electronic effects. In (III), the *trans* phosphines must compete directly for π-bonding electrons, while in (II), *cis* coordination positions the phosphine ligands so that π-bonding electrons are in orthogonal orbitals.

Bond distances involving the acetonitrile ligands in both (II) and (III) are similar, with the largest difference involving the Os—N bonds. In (II), the Os—N distance is 2·079 (9) Å, while that distance in (III) is 2·14 (2) Å. The associated C—N bond in (II) is 1·14 (1) and in (III) is 1·13 (2) Å.

The P—Os—P bond angle in (II) is 101·5 (1)°. This relatively large angle can be attributed to steric

interactions between the *cis*-phosphines. In this structure, the Os coordination sphere adopts a very distorted octahedral geometry. In (III), the P—Os—Br bond angles are near 90° and the P and Br atoms bound to the Os atom are angled away from the carbonyl ligand and towards the coordinated acetonitrile group. The angles in (III) may be affected by substitutional disorder involving Br and the carbonyl ligand. Although evidence for the disorder is not evident on difference Fourier maps, the fact that the carbonyl ligand of (III) could not be refined anisotropically, coupled with the unusually short C—O distance of 0·79 (2) Å suggests that very minor CO ⟷ Br substitution could be taking place. We have observed CO ⟷ Br disorder in similar Os complexes (Robinson, Hinckley & Ikuo, 1988).

Table 2. *Selected bond distances (Å), bond angles (°) and their e.s.d.'s*

Compound (II)

Os(1)—Br(1)	2·602 (1)	P(1)—C(13)	1·84 (1)
Os(1)—Br(2)	2·598 (1)	P(2)—C(19)	1·85 (1)
Os(1)—P(1)	2·379 (3)	P(2)—C(25)	1·83 (1)
Os(1)—P(2)	2·375 (3)	P(2)—C(31)	1·83 (1)
Os(1)—C(37)	1·92 (1)	C(37)—O(1)	1·01 (1)
Os(1)—N(1)	2·079 (9)	N(1)—C(38)	1·14 (1)
P(1)—C(1)	1·87 (1)	C(38)—C(39)	1·46 (2)
P(1)—C(7)	1·84 (1)		

Br(1)—Os(1)—Br(2)	86·01 (5)	Os(1)—P(1)—C(1)	109·5 (4)
Br(1)—Os(1)—P(1)	165·75 (8)	Os(1)—P(1)—C(7)	123·5 (5)
Br(1)—Os(1)—P(2)	89·96 (8)	Os(1)—P(1)—C(13)	114·9 (4)
Br(1)—Os(1)—C(37)	83·7 (3)	C(1)—P(1)—C(7)	101·0 (5)
Br(1)—Os(1)—N(1)	84·0 (2)	C(1)—P(1)—C(13)	102·7 (5)
Br(2)—Os(1)—P(1)	102·67 (8)	C(7)—P(1)—C(13)	102·6 (6)
Br(2)—Os(1)—P(2)	88·18 (8)	Os(1)—P(2)—C(19)	117·2 (4)
Br(2)—Os(1)—C(37)	169·6 (3)	Os(1)—P(2)—C(25)	117·6 (4)
Br(2)—Os(1)—N(1)	81·7 (2)	Os(1)—P(2)—C(31)	113·3 (3)
P(1)—Os(1)—P(2)	101·5 (1)	C(19)—P(2)—C(25)	100·9 (5)
P(1)—Os(1)—C(37)	87·2 (3)	C(19)—P(2)—C(31)	101·6 (5)
P(1)—Os(1)—N(1)	86·1 (3)	C(25)—P(2)—C(31)	104·1 (5)
P(2)—Os(1)—C(37)	93·3 (3)	Os(1)—C(37)—O(1)	176 (1)
P(2)—Os(1)—N(1)	168·5 (2)	Os(1)—N(1)—C(38)	172 (1)
C(37)—Os(1)—N(1)	95·7 (4)	N(1)—C(38)—C(39)	178 (2)

Compound (III)

Os(1)—Br(1)	2·557 (3)	P(1)—C(13)	1·81 (2)
Os(1)—Br(2)	2·533 (3)	P(2)—C(19)	1·85 (2)
Os(1)—P(1)	2·394 (6)	P(2)—C(25)	1·80 (2)
Os(1)—P(2)	2·388 (6)	P(2)—C(31)	1·83 (2)
Os(1)—N(1)	2·14 (6)	C(39)—O(1)	0·79 (2)
Os(1)—C(39)	2·05 (2)	N(1)—C(37)	1·13 (2)
P(1)—C(1)	1·80 (2)	C(37)—C(38)	1·42 (3)
P(1)—C(7)	1·85 (2)		

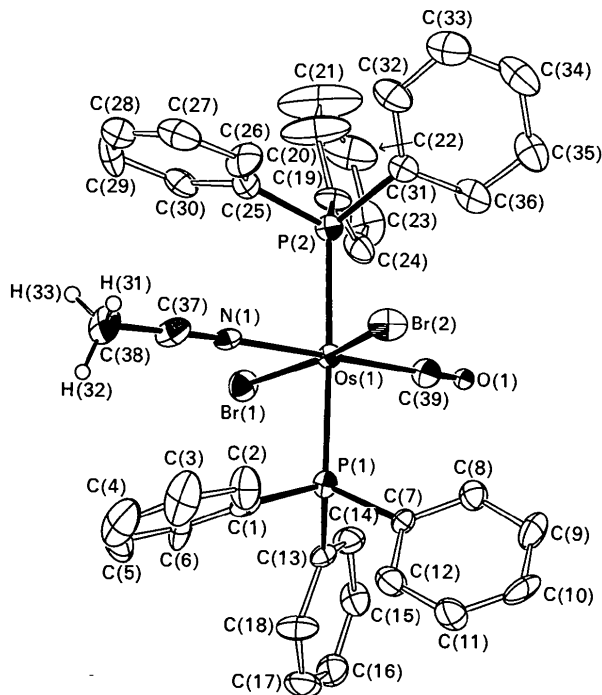|			
Br(1)—Os(1)—Br(2)	167·07 (8)	Os(1)—P(1)—C(1)	112·2 (7)
Br(1)—Os(1)—P(1)	90·2 (1)	Os(1)—P(1)—C(7)	118·3 (7)
Br(1)—Os(1)—P(2)	90·6 (1)	Os(1)—P(1)—C(13)	118·0 (6)
Br(1)—O(1)—N(1)	83·0 (5)	C(1)—P(1)—C(7)	103·8 (9)
Br(1)—Os(1)—C(39)	95·8 (6)	C(1)—P(1)—C(13)	104 (1)
Br(2)—Os(1)—P(1)	88·5 (1)	C(7)—P(1)—C(13)	98·2 (8)
Br(2)—Os(1)—P(2)	90·0 (1)	Os(1)—P(2)—C(19)	120·2 (7)
Br(2)—Os(1)—N(1)	84·1 (5)	Os(1)—P(2)—C(25)	109·8 (8)
Br(2)—Os(1)—C(39)	97·1 (6)	Os(1)—P(2)—C(31)	118·3 (7)
P(1)—Os(1)—P(2)	176·8 (2)	C(19)—P(2)—C(25)	104 (1)
P(1)—Os(1)—N(1)	88·2 (5)	C(19)—P(2)—C(31)	99 (1)
P(1)—Os(1)—C(39)	91·7 (6)	C(25)—P(2)—C(31)	104 (1)
P(2)—Os(1)—N(1)	88·8 (5)	Os(1)—C(39)—O(1)	178 (3)
P(2)—Os(1)—C(39)	91·3 (6)	Os(1)—N(1)—C(37)	178 (2)
N(1)—Os(1)—C(39)	178·7 (8)	N(1)—C(37)—C(38)	179 (3)

Fig. 2. Molecular configuration and atom-numbering scheme for molecule (III). Thermal ellipsoids at the 50% probability level; ring H atoms omitted to improve clarity.

Chemistry and Biochemistry, the College of Science and the Office of Research Development and Administration of SIUC.

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A BF₂-Bridged Cobalt Dimethylglyoxime Complex

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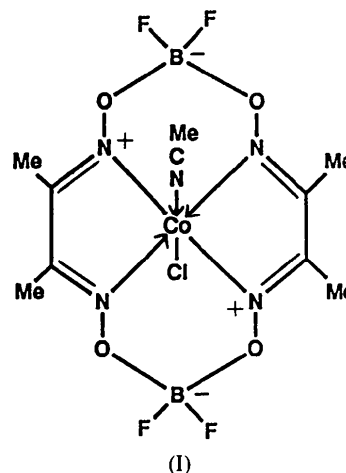
Abstract. (Acetonitrile)chloro(2,2,9,9-tetrafluoro-5,-6,12,13-tetramethyl-1,3,8,10-tetraoxa-4,7,11,14-tetra-aza-1,8-diboracyclotetradeca-4,6,11,13-tetraene-$\kappa^4 N$)cobalt(III), [CoCl(C₂H₃N)(C₈H₁₂B₂F₄N₄O₄)], $M_r = 461\cdot3$, orthorhombic, $P2_12_12_1$, $a = 9\cdot912$ (1), $b = 13\cdot485$ (1), $c = 13\cdot534$ (1) Å, $V = 1809$ Å³, $Z = 4$, $D_x = 1\cdot69$, D_m (flotation) $= 1\cdot67$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0\cdot71069$ Å, μ(Mo $K\alpha$) = 11·5 cm⁻¹, $F = 928$, $T = 292$ K, $R = 0\cdot031$ for 2062 unique observed $[I/\sigma(I) \geq 3\cdot0]$ reflections. The molecule contains octahedrally coordinated Co^{III} with axial Cl and MeCN; Co—N(dimethylglyoxime) 1·885 (3), Co—N(MeCN) 1·898 (3), Co—Cl 2·202 (1) Å. The BF₂ groups are displaced from the equatorial coordination plane, alternately up and down.

Introduction. The use of substituted cobalt glyoxime complexes as dioxygen carriers is handicapped by their rapid autoxidation. It has been shown (Lance, Goldsby & Busch, 1991) that the replacement of the bridging H⁺ atoms in the O···H···O units by BF₂⁺ groups leads to a dramatic reduction in the decomposition rate. We now report the X-ray structure of the parent dimethylglyoxime complex containing BF₂⁺ groups (I).

Experimental. The complex was prepared as described in Lance *et al.* (1991). Red platy crystals were obtained from acetonitrile/ether. Data were collected with a Nicolet $P2_1$ four-circle diffractometer in the ω–2θ mode. Maximum 2θ was 55° with scan range $\pm 1\cdot0°$ (2θ) around the $K\alpha_1$–$K\alpha_2$ angles, scan speed 2–24° min⁻¹, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0·5 of the scan time. hkl ranges were: 0/12, 0/17, 0/17.

Six standard reflections were monitored every 100 reflections, and showed only random fluctuations during data collection. Unit-cell dimensions and standard deviations were obtained by a least-squares fit of 15 reflections ($15 < 2\theta < 25°$). Reflections were processed to give 2321 unique reflections, of which 2062 were considered observed $[I/\sigma(I) \geq 3\cdot0]$. These

(I)