

other pyrromethene derivatives (Sheldrick, Borkenstein, Struckmeier & Engel, 1978). The shortness of the outer N—C bonds [average 1.35 (1) Å] in comparison to the inner N—C bonds [average 1.41 (1) Å] is explicable in terms of valence tautomers. On this basis, the former bond possesses a formal bond order of 1.5, the latter of 1.0.

The dimeric structure of (1) is considerably less strained than a cyclic monomer would be. It has, however, been suggested that a cyclic monomeric biladiene-*a,c*-metal complex is formed in the initial stages of the cyclization of biladienes-*a,c* (Johnson, 1975). If such dimeric complexes, as observed for (1), are of significance in solution, this would provide support for the hypothesis (Fuhrhop, 1978) that any template effect of the metal cation is relatively unimportant in the base-catalysed cyclization behaviour of biladienes-*a,c*. It appears that a metal cation must be capable of accepting an electron pair if ring closure is to occur. The Zn²⁺ cation cannot function as an electron sink and so no cyclization is observed in its case.

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Bis(azobenzenido)dicarbonylosmium(II)

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Abstract. C₂₆H₁₈N₄O₂Os, [Os(CO)₂(C₆H₄NNC₆H₅)₂], monoclinic, *P*2₁/*c*, *a* = 10.746 (3), *b* = 12.516 (4), *c* = 17.136 (5) Å, β = 90.63 (2)°, *U* = 2304.6 Å³, *Z* = 4, *D*_c = 1.754 Mg m⁻³, μ(Mo Kα) = 5.54 mm⁻¹; final *R* = 0.033 for 3433 unique diffractometer data. The Os^{II} atom displays slightly distorted octahedral coordination geometry. The two CO ligands are *cis* with respect to each other. The azobenzenido ligands have undergone *ortho* metallation, and are arranged such that the coordinated N atom of one ligand is *trans* to the coordinated C atom of the other.

Introduction. The reaction of Os₃(CO)₁₂ with azobenzene in refluxing octane affords two major products and a number of low-yield minor products. One of the

major products has been characterized as [HOs₅(CO)₁₃(C₆H₅NC₆H₄N)] (Dawoodi, Mays & Raithby, 1980). To establish the molecular structure of the other, which was obtained as red-orange crystals by recrystallization from warm hexane after separation from the reaction mixture by thin-layer chromatography (10% CH₂Cl₂/hexane eluant), this X-ray analysis was undertaken.

4173 intensities were measured for 3.0 < 2θ ≤ 55.0° on a Stoe four-circle diffractometer with graphite-monochromated Mo Kα radiation, an ω-θ scan technique, and a crystal 0.32 × 0.29 × 0.27 mm. Lp corrections and a semi-empirical absorption correction based on a pseudo-ellipsoid model with 334 azimuthal scan data from 9 independent reflections were applied;

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Table 1. Atom coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

	x	y	z	U_{eq}^*
Os(1)	7148 (1)	1678 (1)	2393 (1)	38 (1)
C(1)	5870 (8)	1319 (6)	3087 (4)	47 (4)
O(1)	5022 (6)	1136 (5)	3461 (4)	72 (4)
C(2)	7687 (9)	2846 (7)	3041 (5)	59 (5)
O(2)	7984 (9)	3544 (5)	3439 (5)	94 (6)
N(1)	8204 (5)	2111 (5)	1404 (3)	41 (3)
N(2)	7695 (6)	2577 (5)	835 (4)	47 (4)
C(3)	5965 (7)	2618 (6)	1744 (4)	44 (4)
C(4)	6459 (7)	2867 (6)	1001 (5)	48 (4)
C(5)	5808 (8)	3440 (6)	425 (5)	55 (5)
C(6)	4630 (8)	3783 (7)	577 (5)	56 (5)
C(7)	4113 (8)	3598 (7)	1313 (6)	60 (5)
C(8)	4768 (7)	3010 (6)	1876 (5)	51 (5)
C(9)	9491 (7)	1819 (6)	1261 (4)	47 (4)
C(10)	9798 (9)	1337 (7)	555 (6)	65 (6)
C(11)	11026 (10)	1093 (8)	427 (7)	76 (7)
C(12)	11930 (10)	1336 (9)	977 (7)	83 (7)
C(13)	11614 (9)	1823 (10)	1666 (7)	84 (8)
C(14)	10381 (8)	2052 (8)	1816 (6)	64 (5)
N(3)	8501 (6)	476 (5)	2745 (4)	42 (3)
N(4)	8515 (6)	-406 (5)	2372 (4)	48 (4)
C(15)	6678 (7)	311 (6)	1738 (4)	46 (4)
C(16)	7547 (6)	-522 (6)	1838 (4)	50 (4)
C(17)	7463 (9)	-1491 (6)	1449 (5)	57 (5)
C(18)	6466 (10)	-1661 (7)	936 (5)	67 (5)
C(19)	5603 (10)	-891 (8)	841 (5)	71 (6)
C(20)	5688 (8)	104 (8)	1223 (5)	58 (5)
C(21)	9492 (7)	587 (6)	3306 (5)	50 (4)
C(22)	10657 (8)	158 (7)	3149 (6)	64 (5)
C(23)	11615 (9)	309 (9)	3717 (8)	90 (8)
C(24)	11369 (12)	810 (9)	4402 (8)	95 (9)
C(25)	10216 (11)	1213 (8)	4550 (6)	80 (7)
C(26)	9258 (9)	1108 (7)	4003 (5)	57 (5)

$$* U_{eq} = (U_1 U_2 U_3)^{1/3}.$$

transmission factors ranged from 0.540 to 0.961. The data were averaged to give 3433 unique observed reflections [$F > 3\sigma(F)$]. Cell dimensions were derived from the angular measurements of 20 strong reflections in the range $20 < 2\theta < 30^\circ$.

The Os atom was located from a Patterson synthesis, and all other non-hydrogen atoms were found from a subsequent difference synthesis. The structure was refined by full-matrix least squares, with the Os, N, O, and C atoms assigned anisotropic thermal parameters. The H atoms were constrained to lie in geometrically idealized positions (C-H 1.08 Å, C-C-H 120.0°), and were assigned a common isotropic temperature factor. Complex neutral-atom scattering factors (*International Tables for X-ray Crystallography*, 1974) were employed, with the weighting scheme $w = 0.7425/[\sigma^2(F) + 0.001071|F_o|^2]$ for the final stages of refinement. The final $R = 0.033$ and $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.035$. Final atomic coordinates and equivalent isotropic temperature factors

Table 2. Bond lengths (Å) and angles (°)

C(1)—Os(1)	1.881 (8)	O(1)—C(1)	1.143 (9)
C(2)—Os(1)	1.921 (9)	O(2)—C(2)	1.151 (10)
C(3)—Os(1)	2.051 (7)	N(2)—N(1)	1.257 (8)
C(15)—Os(1)	2.106 (7)	N(4)—N(3)	1.276 (8)
N(1)—Os(1)	2.120 (6)	C(9)—N(1)	1.454 (9)
N(3)—Os(1)	2.173 (6)	C(4)—N(2)	1.409 (10)
C(4)—C(3)	1.420 (10)	C(21)—N(3)	1.434 (9)
C(8)—C(3)	1.397 (10)	C(16)—N(4)	1.385 (10)
C(5)—C(4)	1.402 (11)	C(16)—C(15)	1.409 (11)
C(6)—C(5)	1.364 (11)	C(20)—C(15)	1.398 (11)
C(7)—C(6)	1.402 (12)	C(17)—C(16)	1.387 (10)
C(8)—C(7)	1.398 (12)	C(18)—C(17)	1.393 (13)
C(10)—C(9)	1.396 (11)	C(19)—C(18)	1.347 (14)
C(14)—C(9)	1.372 (12)	C(20)—C(19)	1.410 (12)
C(11)—C(10)	1.374 (12)	C(22)—C(21)	1.391 (11)
C(12)—C(11)	1.380 (16)	C(26)—C(21)	1.386 (11)
C(13)—C(12)	1.375 (15)	C(23)—C(22)	1.422 (14)
C(14)—C(13)	1.382 (12)	C(24)—C(23)	1.359 (17)
C(26)—C(25)	1.391 (12)	C(25)—C(24)	1.364 (16)
C(2)—Os(1)—C(1)	92.0 (4)	O(1)—C(1)—Os(1)	174.0 (7)
N(1)—Os(1)—C(1)	165.3 (3)	O(2)—C(2)—Os(1)	178.4 (9)
N(1)—Os(1)—C(2)	96.1 (3)	N(2)—N(1)—Os(1)	120.5 (5)
C(3)—Os(1)—C(1)	91.6 (3)	C(9)—N(1)—Os(1)	126.1 (5)
C(3)—Os(1)—C(2)	93.3 (3)	C(9)—N(1)—N(2)	113.1 (6)
C(3)—Os(1)—N(1)	75.7 (3)	C(4)—N(2)—N(1)	111.4 (6)
N(3)—Os(1)—C(1)	98.6 (3)	C(4)—C(3)—Os(1)	112.1 (5)
N(3)—Os(1)—C(2)	99.8 (3)	C(8)—C(3)—Os(1)	132.8 (6)
N(3)—Os(1)—N(1)	92.1 (2)	C(8)—C(3)—C(4)	115.0 (7)
N(3)—Os(1)—C(3)	163.0 (3)	C(3)—C(4)—N(2)	119.2 (7)
C(15)—Os(1)—C(1)	88.3 (3)	C(5)—C(4)—N(2)	117.0 (7)
C(15)—Os(1)—C(2)	174.7 (3)	C(5)—C(4)—C(3)	123.7 (7)
C(15)—Os(1)—N(1)	84.7 (2)	C(6)—C(5)—C(4)	118.9 (8)
C(15)—Os(1)—C(3)	91.9 (3)	C(7)—C(6)—C(5)	119.8 (8)
C(15)—Os(1)—N(3)	75.0 (3)	C(8)—C(7)—C(6)	120.4 (8)
N(4)—N(3)—Os(1)	118.1 (5)	C(7)—C(8)—C(3)	122.0 (8)
C(21)—N(3)—Os(1)	127.5 (5)	C(10)—C(9)—N(1)	119.3 (7)
C(21)—N(3)—N(4)	114.1 (6)	C(14)—C(9)—N(1)	119.2 (7)
C(16)—N(4)—N(3)	114.2 (6)	C(14)—C(9)—C(10)	121.5 (8)
C(16)—C(15)—Os(1)	112.4 (6)	C(11)—C(12)—C(9)	118.1 (10)
C(20)—C(15)—Os(1)	131.5 (7)	C(12)—C(11)—C(10)	120.8 (10)
C(20)—C(15)—C(16)	116.0 (7)	C(13)—C(12)—C(11)	120.4 (10)
C(15)—C(16)—N(4)	119.7 (7)	C(14)—C(13)—C(12)	119.9 (11)
C(17)—C(16)—N(4)	117.0 (8)	C(13)—C(14)—C(9)	119.3 (9)
C(17)—C(16)—C(15)	123.3 (8)	C(26)—C(21)—C(22)	121.4 (8)
C(18)—C(17)—C(16)	118.8 (9)	C(23)—C(22)—C(21)	117.5 (10)
C(19)—C(18)—C(17)	119.4 (8)	C(24)—C(23)—C(22)	120.4 (10)
C(20)—C(19)—C(18)	122.3 (9)	C(25)—C(24)—C(23)	121.2 (11)
C(19)—C(20)—C(15)	120.1 (9)	C(26)—C(25)—C(24)	120.5 (11)
C(22)—C(21)—N(3)	119.7 (8)	C(25)—C(26)—C(21)	119.0 (9)
C(26)—C(21)—N(3)	118.9 (7)		

for the non-hydrogen atoms are given in Table 1, bond lengths and angles in Table 2.*

Discussion. The analysis shows that the title compound (Fig. 1) is analogous to the Fe complex prepared by the reaction of azoanisole with $\text{Fe}(\text{CO})_5$ (Bagga, Flan-

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond angles involving H have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35687 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

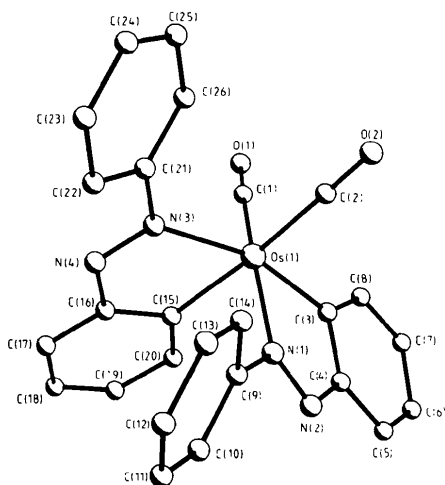


Fig. 1. The molecular structure of $[\text{Os}(\text{CO})_2(\text{C}_6\text{H}_4\text{NNC}_6\text{H}_5)_2]$.

nigan, Knox & Pauson, 1969). Related Os complexes with $(\text{CH}_3\text{NCHC}_6\text{H}_4-)$ (Choo Yin & Deeming, 1977) and benzo[*h*]quinoline (Bruce, Goodall & Stone, 1973) as the ligands have also been prepared from $\text{Os}_3(\text{CO})_{12}$.

Two coordinated azobenzene ligands have also been observed in the structure of bis(azobenzene)-rhodium acetate (Craik, Knox, Pauson, Hoare & Mills, 1971). However, in the Rh complex the two *ortho*-metallated C bonds are *cis* to each other while the Rh–N bonds are *trans*. In the title compound the Os atom displays a slightly distorted octahedral coordination geometry, with the largest deviation caused by the bite requirement of the azobenzene ligand, but the two Os–N bonds are *cis* to each other as are the two Os–C bonds of the chelating ligand. The two carbonyl ligands are also *cis* to each other. The Os–C(carbonyl) bond *trans* to the coordinated N atom is significantly shorter than the Os–C bond *trans* to the *ortho*-

metallated C atom. This suggests that the azobenzene C atom is involved in π -bonding to the metal with competition between the two *trans* C atoms for the π -electron density on the Os, giving rise to the longer Os–C bond. Both Os–N bonds are longer than the terminal Os–N distance of 1.94 (3) Å in $[\text{HOs}_2(\text{CO})_{13}(\text{C}_6\text{H}_5\text{NC}_6\text{H}_4\text{N})]$ (Dawoodi, Mays & Raithby, 1980) where π -donation is considered to be present.

The N–N lengths in the title compound are similar to the value in $[\text{Rh}(\text{O}_2\text{CCH}_3)(\text{C}_6\text{H}_5\text{NNC}_6\text{H}_4)_2]$ (Craik, Knox, Pauson, Hoare & Mills, 1971), and indicate the presence of considerable multiple N–N bonding. The geometry of the remainder of the ligand corresponds closely to the expected values.

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Structure of the Flavone-3-monophosphate–Magnesium Complex

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Abstract. $\text{C}_{15}\text{H}_9\text{O}_6\text{P}^{2-} \cdot \text{Mg}^{2+} \cdot 5\text{H}_2\text{O}$, monoclinic, $C2/c$, $a = 40.877$ (3), $b = 6.296$ (1), $c = 14.139$ (1) Å, $\beta = 101.72$ (1)°, $Z = 8$, $D_m = 1.60$, $D_c = 1.604$ Mg m $^{-3}$ ($T = 295$ K). The structure was solved by direct methods and refined by the block-diagonal least-

squares method to a final R value of 0.041 for 2721 reflections measured on a diffractometer. The crystal consists of hydrophobic layers, containing the aromatic portions of the flavone molecule, separated by hydrophilic layers which contain the phosphate group, the