Carbonylhalogeno[*o*-phenylenebis(dimethylarsine)]osmium Complexes, including those containing Unidentate *o*-Phenylenebis(dimethylarsine)

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The preparation of the series of osmium(II) complexes, *trans*- and *cis*-$[\mathrm{Os(pdma)_2X(CO)}][\mathrm{BPh_4}]$ [X = Cl, Br, or I; pdma = *o*-phenylenebis(dimethylarsine)] and $[\mathrm{Os(pdma)_2X_2(CO)}]$ (X = Br or I), is reported, together with their i.r. and n.m.r. spectra. The complexes $[\mathrm{Os(pdma)_2X_2(CO)}]$ contain one uni- and one bi-dentate pdma ligand, and a crystal structure analysis of $[\mathrm{Os(pdma)_2Br_2(CO)}]$ shows that the osmium atom is octahedrally co-ordinated by two *trans*-Br ligands, one CO *trans* to a bidentate pdma, and the arsenic of one unidentate pdma. The unco-ordinated arsenic of the unidentate pdma is 4.36 Å from the osmium. Crystal data: $a = 15.70(1)$, $b = 11.48(1)$, $c = 17.51(1)$ Å, $\beta = 115.89(3)°$, $Z = 4$, space group $P2_1/c$; final R 0.048 for 2 047 observed reflections (by full-matrix refinement). The $[\mathrm{Os(pdma)_2X_2(CO)}]$ complexes give *cis*-$[\mathrm{Os(pdma)_2X(CO)}]^+$ on heating, and the *cis* complexes isomerize to the *trans* on further heating. The preparation and properties of the osmium(III) complexes $[\mathrm{NBu^n_4}][\mathrm{Os(pdma)X_4(CO)}]$ (X = Cl, Br, or I), which also contain a unidentate pdma ligand, are reported.

WE have previously indicated our interest in the synthesis of the series of complexes of general formula *trans*-$[\mathrm{M(pdma)_2X(L)}]^{n+}$ (M = Fe, Ru, or Os; X = Cl, Br, I, or OH; L = NO for $n = 2$, CO or $\mathrm{N_2}$ for $n = 1$, and CN for $n = 0$); the ligand *o*-phenylenebis(dimethylarsine) is here, as previously, abbreviated pdma.[1] In the previous paper we described the synthesis of *trans*-$[\mathrm{Os(pdma)_2X(NO)}]^{2+}$ (X = Cl, Br, or OH) and *trans*-$[\mathrm{Os(pdma)_2Cl(N_2)}]^+$. Our goal in the work described here was *trans*-$[\mathrm{Os(pdma)_2X(CO)}]^+$. The synthesis of these complexes was more difficult than expected. The pdma ligands proved capable of occupying from one to four co-ordination sites around osmium, and of readily giving geometrical isomers. We have thus obtained the first thoroughly characterized and extensive series of complexes containing unidentate pdma,[2,†] as well as complexes containing *cis* and *trans* bis(bidentate pdma). Details of the syntheses, structural characterization, and interconversions of these complexes are reported here.

RESULTS AND DISCUSSION

Preparation and Properties of Carbonylhalogeno[o-*phenylenebis*(*dimethylarsine*)]*osmium Complexes*.—When 1 mol equivalent of pdma was added to acetone solutions of $[\mathrm{OsX_4S(CO)}]^-$ (X = Cl, Br, or I),[‡] at room temperature, the osmium(III) complexes $[\mathrm{Os(pdma)X_4(CO)}]^-$, isolated as the tetra-n-butylammonium salts, were readily obtained. The products were 1 : 1 electrolytes in acetone solution, and paramagnetic ($\mu_{\mathrm{eff.}}$ 2.01 B.M.[§] at room temperature [||]); these results, combined with analyses, indicate that the complexes contain a unidentate pdma ligand (see Table 1 for characterization details of all the complexes described here). In view of the lability of only the one ligand in $[\mathrm{OsX_4S(CO)}]^-$ we assume that the pdma is *trans* to CO. From the reaction between $[\mathrm{OsCl_4S(CO)}]^-$ and the unidentate $\mathrm{PPh_3}$ ligand, $[\mathrm{OsCl_4(PPh_3)(CO)}]^-$ was obtained. The remarkable *trans*-labilizing effect of CO in these $[\mathrm{OsX_4L(CO)}]^-$ complexes is not easy to understand. The single half-filled orbital of $\mathrm{Os^{III}}$ is expected to be the non-bonding d_{xy} orbital (the OsCO axis being taken as z), which will not influence the *trans* ligand. A kinetic *trans* effect seems unlikely given the ease with which the *trans* ligand is lost. The osmium(II) complexes *trans*-$[\mathrm{Os(pdma)_2X(CO)}]^+$ described below are qualitatively orders of magnitude less labile in the *trans* position than $[\mathrm{OsX_4L(CO)}]^-$; we have also found, in attempts to prepare *trans*-$[\mathrm{Os(pdma)_2X(CO)}]^+$ and *trans*-$[\mathrm{Os(pdma)_2X(NO)}]^{2+}$ directly from *trans*-$[\mathrm{Os(pdma)_2X_2}]$ or *trans*-$[\mathrm{Os(pdma)_2X_2}]^+$ (see also ref. 1), that the halides in these complexes are not labile. Hence pdma has a large stabilizing effect on the *trans* ligand, possibly due to its π-acceptor capability.

Attempts to induce the pdma ligand to replace a second X ligand, becoming bidentate, and thus forming $[\mathrm{Os(pdma)X_3(CO)}]$, by heating $[\mathrm{Os(pdma)X_4(CO)}]^-$ under reflux in methanol were unsuccessful. Apart from unchanged starting material the only isolable product obtained was in the case of X = Br. This product had an analysis indicating the stoicheiometry $[\mathrm{Os(pdma)_{1.5}Br_2(CO)}]$, showed one CO vibration in the i.r. spectrum, and three methyl-on-arsenic proton resonances of equal intensity in the ^{1}H n.m.r. spectrum. The only structure which satisfies these results is one in which one pdma acts as a bridging ligand between two $[\mathrm{Os(pdma)Br_2(CO)}]$

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† To our knowledge the only previous report of a complex containing unidentate pdma is a reference (without details) to $[\mathrm{W(pdma)(CO)_4(CS)}]$.[2]

‡ The preparation of $[\mathrm{OsX_5(CO)}]^{2-}$ has been described previously.[3,4] However, in our hands, the products of these preparations were always a mixture of $[\mathrm{OsX_5(CO)}]^{2-}$ and $[\mathrm{OsX_4S(CO)}]^-$ [S = solvent ($\mathrm{H_2O}$, MeOH, or $\mathrm{Me_2CO}$), X = Cl or Br]. In solutions not containing excess of $\mathrm{X^-}$ the complexes were essentially completely in the $[\mathrm{OsX_4S(CO)}]^-$ form, which is therefore used in the text. For X = I only $[\mathrm{OsI_4S(CO)}]^-$ could be obtained. See also Experimental section.

§ Throughout this paper: 1 B.M. $\approx 9.27 \times 10^{-24}$ A m^2; 1 atm = 101 325 Pa.

|| Magnetic moments of similar osmium(III) complexes have seldom been reported; $[\mathrm{OsCl_3(AsMePh_2)_3}]$ has a moment of 1.80—1.95 B.M.; see B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 1964, **6**, 162.

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[2] B. D. Dombek and R. J. Angelici, *Inorg. Chem.*, 1976, **15**, 1089.

[3] M. J. Cleare and W. P. Griffith, *J. Chem. Soc.* (*A*), 1969, 372; 1970, 2788.

[4] W. Preetz and F. H. Johannsen, *J. Organometallic Chem.*, 1975, **86**, 397.

units.* In any event disproportionation and reduction of [Os(pdma)Br$_4$(CO)]$^-$ had occurred.

When 2 mol equivalents of pdma were added to methanol solutions of [OsX$_4$S(CO)]$^-$ (X = Br or I only) at room temperature the osmium(II) complexes [Os(pdma)$_2$X$_2$(CO)] were obtained after several hours. The same products were obtained in higher yield on refluxing the solutions for 10 h. The ^{1}H n.m.r. spectra of these non-electrolyte complexes showed four methyl-on-arsenic proton resonances of equal intensity, which results could only be explained if one of the pdma ligands was acting as a unidentate ligand. This was confirmed by the *X*-ray crystal-structure analysis of [Os(pdma)$_2$Br$_2$(CO)] discussed below, which showed that one of the arsenic donor atoms of one of the pdma ligands was 4.36 Å from the osmium atom, a distance which is clearly non-bonding. This complex is the first fully documented example of pdma acting as a unidentate ligand, and pdma now joins the family of ligands such as 2,2′-bipyridine and 1,10-phenanthroline which, although overwhelmingly bidentate in nature, can be unidentate.[5,6]

TABLE 1

Characterization of the complexes

Complex	Analysis (%) [a] C	H	X	M.p. (θ$_c$/°C) [b]	Λ [c] S cm^2 mol^{-1}	I.r. spectra (cm^{-1}), ν(CO) [d]	^{1}H N.m.r. spectra,[e] δ/p.p.m.
[NBu$^n_4$][OsCl$_4$(OH$_2$)(CO)]	32.9 (34.3)	6.2 (6.2)	22.9 (22.2)	93	88	1 994	
[NBu$^n_4$][Os(pdma)Cl$_4$(CO)]	36.5 (36.4)	5.9 (5.9)	16.0 (15.9)	115	93	1 983	
cis-[Os(pdma)$_2$Cl(CO)][BPh$_4$]	47.2 (47.0)	4.6 (4.6)	3.1 (3.1)	139	92	1 985	1.30, 1.38, 1.55, 1.84, 1.86, 2.00 2.05, 2.22 in [^{2}H$_6$]dmso
trans-[Os(pdma)$_2$Cl(CO)][BPh$_4$]	47.2 (47.1)	4.6 (4.6)	3.1 (3.1)	279	91	1 942, 1 935	1.96, 2.11 in [^{2}H$_6$]dmso
[NBu$^n_4$][OsCl$_4$(PPh$_3$)(CO)]	48.6 (48.7)	6.0 (6.0)	16.4 (16.3)	138		1 995	
[NBu$^n_4$][OsBr$_4$(OH$_2$)(CO)]	25.6 (25.7)	4.8 (4.9)	40.0 (40.3)	159		1 975	
[NBu$^n_4$][Os(pdma)Br$_4$(CO)]	30.4 (30.5)	4.9 (5.0)	30.0 (30.1)	110	114	1 994	
[Os(pdma)$_2$Br$_2$(CO)]	26.5 (26.5)	3.4 (3.4)	16.8 (16.6)	200		1 942	1.24, 1.38, 1.95, 2.13 in [^{2}H$_1$]CHCl$_3$
cis-[Os(pdma)$_2$Br(CO)][BPh$_4$]	45.4 (45.6)	4.4 (4.4)	6.7 (7.0)	133	93	1 984	1.27, 1.38, 1.66, 1.86, 1.97, 2.03, 2.10, 2.20 in [^{2}H$_6$]dmso
trans-[Os(pdma)$_2$Br(CO)][BPh$_4$]	45.4 (45.3)	4.4 (4.3)	6.7 (6.8)	279	91	1 943, 1 936	2.07 in [^{2}H$_6$]dmso
[NBu$^n_4$][Os(pdma)I$_4$(CO)]	25.9 (25.7)	4.2 (4.0)	40.5 (40.7)			1 987	
[Os(pdma)$_2$I$_2$(CO)]	24.1 (24.3)	3.1 (3.0)	24.3 (24.4)	206		1 946	1.25, 1.77, 2.02, 2.22 in [^{2}H$_1$]-CHCl$_3$
cis-[Os(pdma)$_2$I(CO)][BPh$_4$]	43.7 (43.5)	4.3 (4.3)	10.3 (10.1)	137	85	1 984	1.23, 1.41, 1.84, 1.87, 2.07, 2.15, 2.19 [f] in [^{2}H$_6$]dmso
trans-[Os(pdma)$_2$I(CO)][BPh$_4$]	43.7 (43.6)	4.3 (4.2)	10.3 (10.2)	266	95	1 941 (sh), 1 936	2.03, 2.24 in [^{2}H$_6$]dmso

[a] X represents Cl, Br, or I in the corresponding complexes; calculated values are given in parentheses. [b] Uncorrected, ±2 °C. [c] In acetone. [d] All the bands are very strong unless noted as shoulder (sh). [e] Chemical shifts are for the methyl-proton resonances relative to SiMe$_4$. [f] Resonance at 2.19 p.p.m. has relative intensity 2 compared to the other resonances.

When [OsCl$_4$S(CO)]$^-$ in methanol solution was treated, at room temperature, with 2 mol of pdma an oily mixture resulted, from which no characterizable complex could be isolated. On refluxing the methanol solution (*i.e.* at 65 °C) *cis*-[Os(pdma)$_2$Cl(CO)]$^+$ could be isolated in good yield. Conversion of [Os(pdma)$_2$Br$_2$(CO)] into *cis*-[Os(pdma)$_2$Br(CO)]$^+$ was achieved on refluxing in ethanol (78 °C), whereas the conversion for the analogous iodo-complex required 2-methoxyethanol (b.p. 124 °C). (The interconversions of the various complexes described here are conveniently shown in the Scheme.) It is apparent that replacement of a halide ligand [which must be *trans* to the second halide ligand (see the structural analysis below)] in [Os(pdma)$_2$X$_2$(CO)] by the ' dangling ' arsenic requires less energy in the order Cl < Br < I. This is the reverse of the normal order found for predominantly dissociative replacement of X$^-$ by solvent,[7] and indicates an associative mechanism of replacement. This is probably brought about by the relatively close proximity of the ' dangling ' arsenic atom to the inner co-ordination sphere. We note, in this connection, that simple replacement of a halide (*e.g.* by another halide) does not occur under the conditions obtaining here. Dixon [8] has shown that an associative mechanism is operative in the fluxional substitutional behaviour of unidentate 1,10-phenanthroline (phen) and related ligands in *cis*-[PtCl(PR$_3$)$_2$(phen)]$^+$. For a four-co-ordinate square-planar complex such an associative mechanism is much less surprising than for the six-co-ordinate octahedral system described here.

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* A bridging pdma ligand is known in [{(η^5-MeC$_5$H$_4$)Mn(CO)$_2$}-(pdma)] (M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 1964, 395).

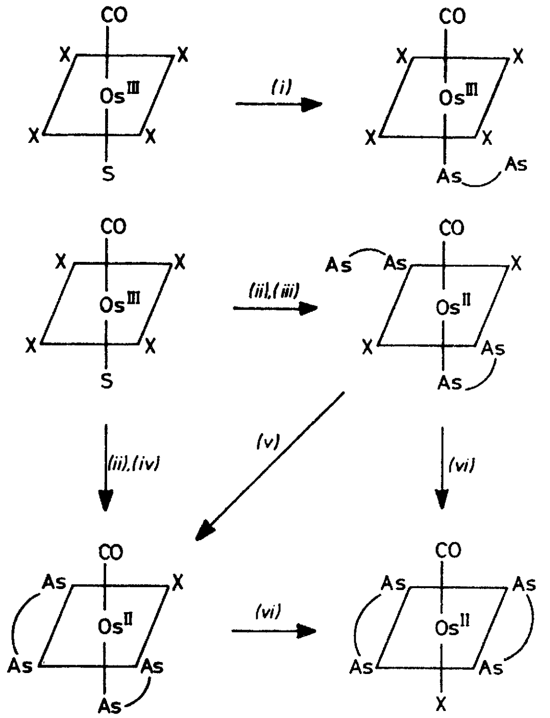
[5] R. J. Watts, J. S. Harrington, and J. Van Houton, *J. Amer. Chem. Soc.*, 1977, **99**, 2179.

[6] G. W. Bushnell, K. R. Dixon, and M. A. Khan, *Canad. J. Chem.*, 1974, **52**, 1367.

[7] F. Basolo and R. G. Pearson, ' Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, p. 165.

[8] K. R. Dixon, *Inorg. Chem.*, 1977, **16**, 2618.

When heated to 240—250 °C all the *cis*-[Os(pdma)$_2$X(CO)][BPh$_4$] complexes first melted at *ca.* 135 °C, then resolidified as the *trans* isomers at *ca.* 240 °C. There was no isomerization on refluxing *cis*-[Os(pdma)$_2$Br(CO)][BPh$_4$] in 2-methoxyethanol (124 °C) for 48 h, and no significant difference in the energies required for the *cis* to *trans* isomerization between the three different halide ligands could be observed. This indicates a purely intramolecular rearrangement process. *trans* to *cis* isomerisation did not occur, indicating, as usual, that the *trans* isomer is thermodynamically more stable.



SCHEME Preparation and chemical transformations of [Os(pdma)$_n$X$_m$(CO)]$^{p+}$. (*i*) 1 mol pdma, 25 °C, acetone (X = Cl, Br, or I); (*ii*) 2 mol pdma, 65 °C, methanol; (*iii*) X = Br or I; (*iv*) X = Cl; (*v*) X = Br (78 °C) or I (125 °C); (*vi*) 250 °C

In the reaction of [OsX$_4$S(CO)]$^-$ with 2 mol equivalents of pdma, reduction of Os^{III} to Os^{II} occurs. The products were obtained in 31—53% yield after recrystallization, and no oxide of pdma was observed in the reaction. Hence, we conclude that pdma is at best catalytically involved in the reduction, which must be caused by the solvent. Attempts to test this hypothesis further by adding a large excess of pdma were not fruitful since this gave oily products which were difficult to work up.

The stereochemistry of the complexes described above was established by the ^{1}H n.m.r. method previously used for pdma complexes.[1,9-13] For *trans* complexes of the [Os(pdma)$_2$X(Y)]$^{n+}$ type, two methyl-on-arsenic proton resonances of equal intensity are expected, whereas for *cis* complexes eight resonances should be observed. Table 1 shows the resonances are generally found as expected for the indicated geometries, and they are in the δ 1.20—2.25 p.p.m. region. One accidental equivalence (at 60 MHz) clearly occurred for *cis*-[Os(pdma)$_2$I(CO)]$^+$, and we assume that the single resonance observed for *trans*-[Os(pdma)$_2$Br(CO)]$^+$ (which was observed in both [^{2}H$_1$]CHCl$_3$ and [^{2}H$_6$]dimethyl sulphoxide) is also due to accidental equivalence.

For [Os(pdma)$_2$X$_2$(CO)] (X = Br or I), containing both uni- and bi-dentate pdma, the ^{1}H n.m.r. spectrum showed four methyl-on-arsenic proton resonances of equal intensity, of which the most shielded proton with a δ value of 1·24 (X = Br) and 1·25 p.p.m. (X = I) can be assigned to the methyl groups attached to the unco-ordinated arsenic atom. It is worth noting that four methyl-on-arsenic proton resonances of equal intensity are also expected from complexes of type *cis*-[M(pdma)$_2$X$_2$]Y, and caution is therefore necessary in assigning the structures of such complexes in the absence of conductivity data.

In the solid state (Nujol-mull spectra) the i.r. spectra of *trans*-[Os(pdma)$_2$X(CO)][BPh$_4$] showed at least two broad ν(CO) absorption bands indicating that solid-state effects, which must act directly on the CO ligand,[14] were present. However, *trans*-[Os(pdma)$_2$X(CO)][BPh$_4$] showed a very broad ν(CO) absorption even in dilute dimethylformamide solution. It has been previously

TABLE 2

Positional parameters * for [Os(pdma)$_2$Br$_2$(CO)]

Atom	*x*	*y*	*z*
Os	0.247 41(6)	0.413 02(7)	0.761 64(5)
Br(1)	0.360 1(1)	0.238 7(2)	0.793 5(2)
Br(2)	0.130 1(1)	0.584 1(2)	0.716 1(1)
As(1)	0.184 9(1)	0.368 3(2)	0.606 1(1)
As(2)	0.119 6(1)	0.286 1(2)	0.751 6(1)
As(3)	0.378 4(1)	0.535 2(2)	0.765 7(1)
As(4)	0.348 4(2)	0.740 3(2)	0.897 8(2)
C(1)	0.275(2)	0.437(2)	0.875(2)
O(1)	0.293(1)	0.446(1)	0.945(1)
C(2)	0.254(2)	0.272(2)	0.565(1)
C(3)	0.143(1)	0.497(2)	0.523(1)
C(4)	0.149(2)	0.137(2)	0.811(1)
C(5)	0.025(1)	0.354(2)	0.780(1)
C(6)	0.436(1)	0.482(2)	0.694(2)
C(7)	0.491(1)	0.532(2)	0.873(1)
C(8)	0.449(2)	0.843(3)	0.962(2)
C(9)	0.253(2)	0.839(2)	0.902(2)
C(10)	0.336(1)	0.783(2)	0.784(1)
C(11)	0.315(1)	0.897(2)	0.756(1)
C(12)	0.306(2)	0.925(2)	0.676(2)
C(13)	0.324(2)	0.844(2)	0.626(1)
C(14)	0.354(1)	0.699(2)	0.736(1)
C(15)	0.306(2)	0.925(2)	0.676(2)
C(16)	0.046(1)	0.234(2)	0.634(1)
C(17)	−0.030(2)	0.160(2)	0.616(1)
C(18)	−0.085(2)	0.127(2)	0.532(2)
C(19)	−0.060(2)	0.164(2)	0.469(1)
C(20)	0.017(2)	0.236(2)	0.488(1)
C(21)	0.072(1)	0.271(2)	0.573(1)

* Estimated standard deviations relating to the least significant figure are given in parentheses.

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[9] P. G. Douglas and R. D. Feltham, *J. Amer. Chem. Soc.*, 1972, **94**, 5254.

[10] T. E. Nappier, R. D. Feltham, J. H. Enemark, A. Kruse, and M. Cooke, *Inorg. Chem.*, 1975, **14**, 806.

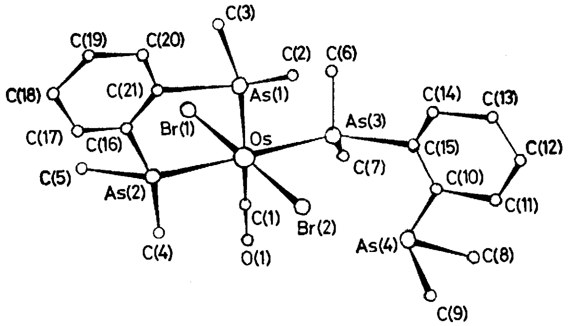
[11] B. K. W. Baylis and J. C. Bailar, *Inorg. Chem.*, 1970, **9**, 641.

[12] P. G. Douglas, R. D. Feltham, and H. G. Metzger, *J. Amer. Chem. Soc.*, 1971, **93**, 84.

[13] J. H. Enemark, R. D. Feltham, J. Riker-Nappier, and K. F. Bizot, *Inorg. Chem.*, 1975, **14**, 624.

[14] J. Chatt, G. J. Leigh, and N. Thankarajan, *J. Chem. Soc.* (*A*), 1971, 3168.

observed that in the solid state the pdma ligands of *trans*-[Co(pdma)$_2$(NCS)(NO)][NCS] are not planar.[13] The *trans*-Co(pdma)$_2$ unit is in the ' chair ' conformation, and in solution must undergo rapid conformational interconversion, since only two, not four, signals are seen in the methyl-on-arsenic region of the ^{1}H n.m.r. spectrum.[13] The only explanation for our observation of a broad ν(CO) absorption even in solution is the presence of both chair and ' boat ' conformations in solution. The *cis*-[Os(pdma)$_2$X(CO)]$^+$ complexes show only one sharp i.r. absorption.



Numbering scheme and geometry for [Os(pdma)$_2$Br$_2$(CO)]

Crystal and Molecular Structure of [Os(pdma)$_2$Br$_2$(CO)].—The positional parameters and standard deviations obtained from the final least-squares cycle of the refinement are given in Table 2, and the hydrogen-atom positions in Table 3. For the numbering scheme see the Figure. Bond distances and angles derived from these positions are given in Table 4. The observed structure amplitudes, and calculated structure factors and the thermal parameters from the last cycle of refinement, are listed in Supplementary Publication No. SUP 22337 (13 pp.).*

TABLE 3

Hydrogen-atom positions for [Os(pdma)$_2$Br$_2$(CO)]

Atom *	*x*	*y*	*z*
H(2a)	0.287	0.207	0.605
H(2b)	0.300	0.315	0.552
H(2c)	0.210	0.231	0.510
H(5a)	−0.027	0.300	0.769
H(5b)	−0.002	0.426	0.747
H(5c)	0.055	0.375	0.841
H(6a)	0.387	0.452	0.640
H(6b)	0.483	0.422	0.722
H(6c)	0.468	0.548	0.679
H(7a)	0.477	0.554	0.921
H(7b)	0.540	0.585	0.873
H(7c)	0.526	0.454	0.892
H(8a)	0.479	0.825	1.024
H(8b)	0.428	0.926	0.957
H(8c)	0.505	0.846	0.947
H(9a)	0.192	0.835	0.848
H(9b)	0.272	0.924	0.907
H(9c)	0.239	0.820	0.949
H(11)	0.305	0.961	0.794
H(12)	0.284	1.007	0.654
H(13)	0.321	0.870	0.569
H(14)	0.359	0.674	0.618
H(17)	−0.046	0.129	0.663
H(18)	−0.144	0.079	0.515
H(19)	−0.098	0.141	0.409
H(20)	0.034	0.263	0.441

* The numbers used to identify the hydrogen atoms are those of the carbon atom to which the hydrogen is attached.

TABLE 4

Intramolecular distances (Å) and angles(°) * for [Os(pdma)$_2$Br$_2$(CO)]

Os–Br(1)	2.567(3)	C(19)–C(20)	1.39(4)
Os–Br(2)	2.570(3)	C(20)–C(21)	1.42(3)
Os–As(1)	2.511(3)	C(21)–C(16)	1.37(4)
Os–As(2)	2.423(3)	As(3)–C(6)	1.93(3)
Os–As(3)	2.465(3)	As(3)–C(7)	1.94(2)
Os–C(1)	1.85(3)	As(3)–C(15)	1.95(2)
C(1)–O(1)	1.15(3)	As(4)–C(8)	1.90(3)
As(1)–C(2)	1.90(3)	As(4)–C(9)	1.91(2)
As(1)–C(3)	1.97(2)	As(4)–C(10)	1.97(3)
As(1)–C(21)	1.96(2)	C(10)–C(11)	1.42(4)
As(2)–C(4)	1.95(2)	C(11)–C(12)	1.37(3)
As(2)–C(5)	1.92(3)	C(12)–C(13)	1.38(4)
As(2)–C(16)	1.96(2)	C(13)–C(14)	1.38(4)
C(16)–C(17)	1.37(3)	C(14)–C(15)	1.39(3)
C(17)–C(18)	1.40(3)	C(15)–C(10)	1.38(3)
C(18)–C(19)	1.38(4)		
Br(1)–Os–Br(2)	175.1(1)	As(1)–Os–As(2)	83.0(1)
Br(1)–Os–As(1)	89.0(1)	As(1)–Os–As(3)	94.2(1)
Br(1)–Os–As(2)	90.9(1)	As(1)–Os–C(1)	170.9(1.0)
Br(1)–Os–As(3)	87.2(1)	As(2)–Os–As(3)	176.7(2)
Br(1)–Os–C(1)	93.7(8)	As(2)–Os–C(1)	88.3(9)
Br(2)–Os–As(1)	86.1(1)	As(3)–Os–C(1)	94.5(9)
Br(2)–Os–As(2)	88.8(1)	Os–C(1)–O(1)	176.7(2.0)
Br(2)–Os–As(3)	92.8(1)	Os–As(3)–C(6)	114.8(7)
Br(2)–Os–C(1)	91.2(8)	Os–As(3)–C(7)	114.5(8)
Os–As(1)–C(2)	120.8(6)	Os–As(3)–C(15)	118.4(6)
Os–As(1)–C(3)	119.5(6)	C(6)–As(3)–C(7)	97.6(1.0)
Os–As(1)–C(21)	108.0(8)	C(6)–As(3)–C(15)	103.5(1.0)
C(2)–As(1)–C(3)	102.6(1.1)	C(7)–As(3)–C(15)	105.4(8)
C(2)–As(1)–C(21)	98.9(1.0)	C(8)–As(4)–C(9)	94.3(1.4)
C(3)–As(1)–C(21)	104.1(8)	C(8)–As(4)–C(10)	97.6(1.2)
Os–As(2)–C(4)	119.4(7)	C(9)–As(4)–C(10)	99.2(1.1)
Os–As(2)–C(5)	116.0(6)	As(1)–C(21)–C(16)	119.4(1.4)
Os–As(2)–C(16)	110.7(7)	As(2)–C(16)–C(21)	118.6(1.4)
C(4)–As(2)–C(5)	104.6(1.1)	As(3)–C(15)–C(10)	117.5(1.9)
C(4)–As(2)–C(16)	100.8(8)	As(4)–C(10)–C(15)	118.8(1.6)
C(5)–As(2)–C(16)	103.0(9)		

* Estimated standard deviations relating to the least significant figure(s) are given in parentheses.

TABLE 5

Equations of means planes and, in square brackets, distances (Å) of atoms from the plane

Plane (1): Os, Br(1), Br(2), As(1), C(1), O(1)

$$12.3892X + 7.0429Y - 5.4510Z = 1.7304$$

[Os 0.092, Br(1) 0.087, Br(2) 0.091, As(1) −0.149, C(1) −0.009, O(1) −0.113]

Plane (2): Os, As(1), As(2), As(3), C(1), O(1)

$$-8.7971X + 9.1298Y + 0.6092Z = 2.0632$$

[Os −0.005, As(1) 0.042, As(2) −0.046, As(3) −0.038, C(1) 0.037, O(1) 0.010]

Plane (3): Os, Br(1), Br(2), As(2), As(3)

$$-2.7391X + 1.9000Y + 16.6229Z = 12.7002$$

[Os 0.067, Br(1) −0.042, Br(2) −0.042, As(2) 0.009, As(3) 0.008]

Plane (4): As(1), As(2), C(16—21)

$$-8.8767X + 9.2765Y + 1.7158Z = 2.8491$$

[As(1) −0.034, As(2) 0.033, C(16) 0.001, C(17) −0.041, C(18) −0.004, C(19) 0.009, C(20) 0.027, C(21) 0.009]

Plane (5): As(3), As(4), C(10—15)

$$13.9122X + 2.5371Y - 0.3574Z = 6.3884$$

[As(3) −0.040, As(4) 0.016, C(10) −0.007, C(11) 0.000, C(12) −0.026, C(13) 0.037, C(14) 0.047, C(15) −0.026]

The structure consists of well separated discrete mole-

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

cules of [Os(pdma)$_2$Br$_2$(CO)]. The closest intermolecular contacts are between the oxygen [O(1)] of the carbonyl group, or the bromine atoms, and various hydrogen atoms, all being *ca.* 3·0 Å. The closest contact to the unco-ordinated arsenic [As(4)] is a hydrogen at 3.45 Å, indicating little interaction between this arsenic and other molecules. An examination of the angles about the osmium atom (Table 4) and a selection of mean planes (Table 5) shows that the osmium atom is essentially octahedrally co-ordinated, with the stereochemistry shown in the Figure. The only angles which differ by more than 2° from 90° are ones involving the carbonyl C atom, which is difficult to locate accurately in a structure involving so many heavy atoms, or those involving the arsenic atoms of the bidentate pdma ligand [As(1) and As(2)]. The As(1)–Os–As(2) angle [83.0(1)°] is clearly due to the restricted 'bite angle' of bidentate pdma. Consideration of the known structures involving the pdma ligand[15-20] shows that the As–M–As angles decrease as the M–As bond distances increase, as would be expected for a rigid bidentate ligand with an essentially fixed bite angle. The long Os–As(1) distance again reflects the strong *trans*-labilizing influence of CO. The unequal Os–As(2) and Os–As(3) distances are probably caused by the combined effects of the *trans*-labilizing influence of CO and the restricted pdma bite angle. The long Os–As(1) bond (2.51 Å) forces As(2) to compromise between a normal bond distance [which is represented by Os–As(3), 2.46 Å] with a consequently very small As(1)–Os–As(2) angle, and a shorter bond distance (found 2.42 Å) with an angle closer to 90°.

The C–O distance [1.15(3) Å] and Os–C–O angle [176.7(2.0)°] are normal. Only one previous structure of a formally osmium(II) carbonyl, that of carbonyl-(α,γ-dimethyl-α,γ-dihydro-octaethylporphinato)-pyridineosmium(II), has been reported;[21] the Os–C distance [1.828(5) Å] is comparable to the 1.85(3) Å reported here. One can estimate an Os^{II}–Br distance to be 2.55 Å {incomplete projection data indicate[22] Os–Br in [OsBr(H)(PPh$_3$)$_3$(CO)] to be 2.60 Å} and an Os–As as 2.47 Å, in agreement with the distances found here. Detailed discussion is not possible because of the lack of comparable structures.

The primary purpose of the investigation, to confirm that one pdma was unidentate, is clearly fulfilled. The Os–As(4) distance [4.363 Å] is 1.8 Å greater than the Os–As bonding distances, and beyond any reasonable interaction distance. There are no significant differences between the $C_6H_4As_2$ units of the uni- and bidentate pdma ligands (see Tables 4 and 5), but there are differences in the angles around the arsenic atoms. The C–As–C angles around the unco-ordinated arsenic [As(4), 94.3—99.2°] are smaller than those around the unidentate arsenic [As(3), 97.6—105.4°], due to the larger effective size of a non-bonded pair as against a lone pair of electrons. The restricted bite angle of the bidentate pdma produces smaller Os–As–C(phenyl) angles [Os–As(1)–C(21) 108.0, Os–As(2)–C(16) 110.7°; the unidentate arsenic has Os–As(3)–C(15) 118.4°], allowing the other angles around the arsenic atoms to open up. This opening is mainly effected by movement of the methyl groups [CH$_3$–As(1)–CH$_3$ 102.6 and CH$_3$–As(2)–CH$_3$ 104.6, *versus* CH$_3$–As(3)–CH$_3$ 97.6; Os–As(1)–CH$_3$ 120.8 and 119.5, and Os–As(2)–CH$_3$ 116.0 and 119.4, *versus* Os–As(3)–CH$_3$ 114.5 and 114.8°]. Within the limits of error there are no significant differences in the As–C distances.

EXPERIMENTAL

Preparation of Complexes.—The starting materials OsO$_4$ and [NH$_4$]$_2$[OsCl$_6$] were obtained from Johnson, Matthey, and pdma from Strem Chemicals. All the other materials were reagent grade. Osmium tetraoxide was converted into [NBu$^n_4$]$_2$[OsBr$_6$] by the method previously described for the preparation of [NH$_4$]$_2$[OsBr$_6$];[23] [NBu$^n_4$]$_2$[OsCl$_6$] was also obtained from [NH$_4$]$_2$[OsCl$_6$] by metathesis using [NBu$^n_4$]Cl. The other carbonylhalogeno-osmium starting materials were obtained as described below. All the operations involving pdma were conducted under a dinitrogen atmosphere; the final products were all stable in air.

Instruments used in this work were a Perkin-Elmer 467 i.r. spectrophotometer, spectra being run as Nujol mulls or in solution between KBr or CaF$_2$ plates, a Varian T60 n.m.r. spectrometer, and a Beckman RC-18A conductivity bridge, measurements being made at a concentration of *ca.* 10^{-3} mol dm^{-3}. Magnetic moments were determined by the Gouy method. Microanalyses were by A. Bernhardt, West Germany.

In describing the syntheses of all the compounds, we give below the most convenient route to each, starting with the commonly available or easily accessible reagents. Where one or more compounds are in fact intermediates in the synthesis of others {*e.g.* [OsX$_4$(OH$_2$)(CO)]$^-$ or [Os(pdma)X$_4$-(CO)]$^-$} their isolation (which was performed for the purposes of understanding the processes described in the Results and Discussion section) is only described where it is necessary for the further synthesis.

Tetra-n-butylammonium trans-*Aquacarbonyltetrachloro-osmate*, [NBu$^n_4$][*trans*-OsCl$_4$(OH$_2$)(CO)]. The salt [NBu$^n_4$]$_2$-[OsCl$_6$] (2.0 g) in 2-methoxyethanol (40 cm^3) was heated under reflux under CO (1 atm pressure) for 6 h. The solution was then evaporated to 10 cm^3 *in vacuo*. Diethyl ether (50 cm^3) was added to precipitate the yellow product, which was recrystallized from acetone–diethyl ether to which a few drops of water had been added, washed with ether, and dried in air, yield 1.2 g (86%).

Tetra-n-butylammonium trans-*aquatetrabromocarbonylosmate*, [NBu$^n_4$][*trans*-OsBr$_4$(OH$_2$)(CO)]. The salt [NBu$^n_4$]$_2$-

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$[\mathrm{OsBr_6}]$ (2.0 g) was heated under reflux in a solution of methanol (50 cm^3) and acetone (50 cm^3) under CO (1 atm) for 6 d. The volume of the solution was reduced to 20 cm^3 *in vacuo* and diethyl ether added until precipitation of the green-brown product was complete. The product was filtered off, recrystallized from methanol to which a little water had been added, and dried in air, yield 0.9 g (65%).

Tetra-n-butylammonium trans-*tetrachloro- and -tetrabromocarbonyl*[o-*phenylenebis*(*dimethylarsine*)]*osmate*, $[\mathrm{NBu^n_4}]$[*trans*-$\mathrm{Os(pdma)Cl_4(CO)}$] *and* $[\mathrm{NBu^n_4}]$[*trans*-$\mathrm{Os(pdma)Br_4(CO)}$]. To $[\mathrm{NBu^n_4}][\mathrm{OsCl_4(OH_2)(CO)}]$ (0.25 g) in acetone (20 cm^3) was added pdma (0.07 cm^3, 0.1 g) at room temperature. The pale yellow solution, which became orange within 5 min, was stirred for 1 h, and its volume then reduced to 5 cm^3 *in vacuo*. Addition of diethyl ether gave the orange product, which was recrystallized (rapidly because of some tendency to lose pdma) from acetone–diethyl ether, washed with diethyl ether, and dried in air, yield 0.18 g (50%). The bromo-complex was obtained by an exactly similar method in 67% yield.

Tetra-n-butylammonium trans-*carbonyltetraiodo*[o-*phenylenebis*(*dimethylarsine*)]*osmate*, $[\mathrm{NBu^n_4}]$[*trans*-$\mathrm{Os(pdma)I_4(CO)}$]. A solution of $[\mathrm{NBu^n_4}][\mathrm{OsCl_6}]$ (2.0 g) in 2-methoxyethanol (20 cm^3) was heated under reflux under CO (1 atm) for 10 h. Aqueous HI (60%, 5 cm^3) was then added and refluxing continued for 30 min. On cooling a bright green solid {presumed to be $[\mathrm{NBu^n_4}][\mathrm{OsI_4(OH_2)(CO)}]$} precipitated, which was filtered off, washed with water, dried in air, and redissolved in acetone (60 cm^3). *o*-Phenylenebis(dimethylarsine) (0.28 cm^3, 0.4 g) was added, the solution stirred for 0.5 h, and then evaporated to dryness *in vacuo*. The green-gray solid was washed with diethyl ether and recrystallized from acetone–diethyl ether, yield 0.8 g (28%).

Tetra-n-butylammonium trans-*carbonyltetrachloro*(*triphenylphosphine*)*osmate*, $[\mathrm{NBu^n_4}]$[*trans*-$\mathrm{OsCl_4(PPh_3)(CO)}$]. To $[\mathrm{NBu^n_4}][\mathrm{OsCl_4(OH_2)(CO)}]$ (0.35 g) in acetone (20 cm^3) was added $\mathrm{PPh_3}$ (0.37 g). The solution was stirred for 0.5 h in an ice-bath, then diethyl ether was added to precipitate the product, which was filtered off and recrystallized from acetone–diethyl ether as yellow crystals, yield 0.4 g (82%).

Dibromocarbonylbis[o-*phenylenebis*(*dimethylarsine*)]*osmium*, $[\mathrm{Os(pdma)_2Br_2(CO)}]$. To $\mathrm{OsO_4}$ (1.0 g) was added aqueous HBr (48%, 36 cm^3), the solution heated under reflux for 2 h and then evaporated to dryness on a steam-bath. The residue was dissolved in methanol (100 cm^3), NaBr (1.0 g) added, and the mixture heated under reflux under CO (1 atm) for 4 d. *o*-Phenylenebis(dimethylarsine) (1.55 cm^3, 2.25 g) was then added, refluxing continued for 10 h, the solution cooled, and the yellow product which precipitated was filtered off, washed well with methanol, recrystallized from chloroform–diethyl ether, and dried in air to give 2.0 g (53%) of the yellow-orange product.

The complex was also obtained directly by heating $[\mathrm{NBu^n_4}][\mathrm{OsBr_4(OH_2)(CO)}]$ under reflux with pdma (1 : 2 mol ratio) in methanol for 10 h and working up as above.

Carbonyldi-iodobis[o-*phenylenebis*(*dimethylarsine*)]*osmium*, $[\mathrm{Os(pdma)_2I_2(CO)}]$. To $[\mathrm{NBu^n_4}][\mathrm{OsBr_4(OH_2)(CO)}]$ (1.0 g) in methanol (20 cm^3) was added aqueous HI (60%, 3 cm^3). The resulting solution was heated under reflux for 1 h, evaporated to *ca.* 5 cm^3 *in vacuo*, and the green precipitate was filtered off. It was redissolved in methanol (20 cm^3), and pdma (0.55 cm^3, 0.8 g) followed by $[\mathrm{NH_4}]\mathrm{I}$ (1.0 g) added. After refluxing for 3 h the solution was cooled in ice, and the resulting orange precipitate was filtered off and recrystallized from chloroform–diethyl ether, yield 0.6 g (46%).

cis-*Carbonylchlorobis*[o-*phenylenebis*(*dimethylarsine*)]*osmium tetraphenylborate*, *cis*-$[\mathrm{Os(pdma)_2Cl(CO)}][\mathrm{BPh_4}]$. The salt $[\mathrm{NBu^n_4}]_2[\mathrm{OsCl_6}]$ (2.0 g) in 2-methoxyethanol (40 cm^3) was heated under reflux under CO (1 atm) for 24 h. To the cooled yellow solution was added a solution of $\mathrm{Na[BPh_4]}$ (3.5 g) in water (40 cm^3). After cooling in an ice-bath for 30 min the white precipitate of $[\mathrm{NBu^n_4}][\mathrm{BPh_4}]$ was filtered off. *o*-Phenylenebis(dimethylarsine) (0.9 cm^3, 1.3 g) was then added to the filtrate and the solution heated under reflux for 24 h. Some of the off-white product precipitated; $\mathrm{Na[BPh_4]}$ was added to the cooled solution until precipitation was complete, and after cooling in an ice-bath the product was filtered off, recrystallized as white crystals from acetone–diethyl ether, washed with ether, and dried in air, yield 0.8 g (31%).

cis-*Carbonylhalogenobis*[o-*phenylenebis*(*dimethylarsine*)]*osmium tetraphenylborate*, *cis*-$[\mathrm{Os(pdma)_2X(CO)}][\mathrm{BPh_4}]$ (X = Br *or* I). The complex $[\mathrm{Os(pdma)_2X_2(CO)}]$ (0.2 g) was heated under reflux in 2-methoxyethanol (40 cm^3). The suspended starting material dissolved and the solution became colourless over 1 d. The solution was evaporated to about half its volume *in vacuo* and $\mathrm{Na[BPh_4]}$ (0.6 g) in water (10 cm^3) was added. The resulting white precipitate was filtered off, washed with water, and dried in air. It was recrystallized from acetone–diethyl ether. Yields were essentially quantitative.

The bromo-complex was also obtained by heating $[\mathrm{NBu^n_4}][\mathrm{OsBr_4(OH_2)(CO)}]$ and pdma (1 : 2 mol ratio) under reflux in ethanol for 24 h, adding $\mathrm{Na[BPh_4]}$, and working up as above.

trans-*Carbonylhalogenobis*[o-*phenylenebis*(*dimethylarsine*)]*osmium tetraphenylborate*, *trans*-$[\mathrm{Os(pdma)_2X(CO)}][\mathrm{BPh_4}]$ (X = Cl, Br, *or* I). These complexes were obtained by heating *cis*-$[\mathrm{Os(pdma)_2X(CO)}][\mathrm{BPh_4}]$. The *cis* complex first melted, then on further heating resolidified as *trans*-$[\mathrm{Os(pdma)_2X(CO)}][\mathrm{BPh_4}]$. The complexes were recrystallized as white crystals from acetone–diethyl ether. Conversion was in each case essentially quantative.

Structure Determination, Solution, and Refinement of $[\mathrm{Os(pdma)_2Br_2(CO)}]$.—Crystals of $[\mathrm{Os(pdma)_2Br_2(CO)}]$ were obtained as described above. Weissenberg and precession photographs uniquely established the space group as monoclinic $P2_1/c$ (C^5_{2h}, no. 14).

Crystal data. $\mathrm{C_{21}H_{32}As_4Br_2OOs}$, $M = 950.2$; $a = 15.699(7)$, $b = 11.488(5)$, $c = 17.508(10)$ Å, $\beta = 115.89(3)°$, $U = 2\,836.9$ Å^3; $D_c = 2.22$, $Z = 4$, $D_m = 2.23$ g cm^{-3} (flotation in $\mathrm{CCl_4}$–$\mathrm{C_2Br_4}$), $F(000) = 1\,776$; Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 126.6 cm^{-1}.

Collection and reduction of intensity data. The crystal used was wedge shaped (*ca.* 0.25 × 0.31 × 0.32 mm) and was mounted in an arbitrary direction on a Picker FACS 1 diffractometer. Cell dimensions were determined from 12 accurately centred reflections with $2\theta > 35°$, and a unique hkl, $\bar{h}kl$ data set was collected to 2θ 40° (2 635 reflections). Instrument settings were as described previously,[24] with the exception that the counter slit width was set at 5 mm. One standard reflection, monitored every 25 reflections, showed no significant change in intensity.

Absorption, Lorentz, and polarization corrections were

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[24] F. Bottomley, *J.C.S. Dalton*, 1972, 2148; 1975, 2538.

applied (transmission factors varied from 5 to 10%).[25] Reflections with a net count of <60 were considered unobserved, leaving 2 047 observed structure amplitudes for the structure solution.

Structure solution and refinement. The structure was solved using direct methods. The scattering-factor curves for all the atoms were taken directly from the '*X*-Ray '76' package.[25] These are essentially the same as those given in International Tables.[26] The Os, As, and Br factors were corrected for both the real and the imaginary parts of the anomalous dispersion. Refinement was by the full-matrix method, minimizing $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme was of the statistical form $1/\sigma^2(F)$ described by Corfield *et al.*[27] Refinement, with all the atoms anisotropic, proceeded normally to R 0.056. Examination of a difference-Fourier synthesis clearly gave all the hydrogen-atom locations except those attached to C(3) and C(4), two carbon atoms attached to the co-ordinated arsenic atoms As(1) and As(2) of the bidentate pdma ligand. Inclusion of the observed hydrogen atoms and further refinement (the H atoms being not refined but adjusted to give C–H bond distances of 0.98 Å and the appropriate tetrahedral or benzene-ring bond angles) gave convergence at R 0.048, R' 0.059. A difference-Fourier at this final stage did not show the missing hydrogen atoms, which were therefore not included in the refinement. The final difference-Fourier showed, as its largest positive and negative peaks, peaks of 1.29 e Å^{-3} at the osmium position and -0.70 e Å^{-3} 1.5 Å along the Os–As(1) vector. Error analysis of the agreement for various reflection groups, and in terms of θ and intensity, showed no trends. The estimated deviation of an observation of unit weight was 1.23 e.

We thank the National Research Council of Canada for support, and Johnson, Matthey for a generous loan of osmium compounds.

[8/319 *Received*, 23*rd February*, 1978]

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