Preparation and Isomerization of Dicarbonyldihalogeno[*o*-phenylenebis-(dimethylarsine)]osmium Complexes

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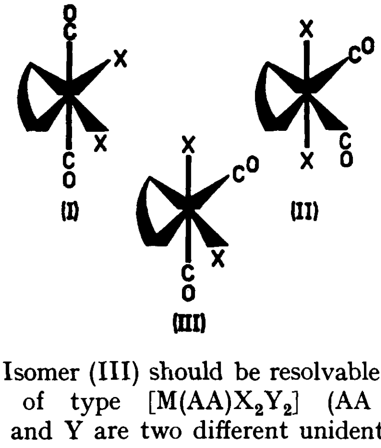
The preparation of the series of osmium(II) complexes [Os(pdma)X$_2$(CO)$_2$] [X = Cl, Br, or I; pdma = *o*-phenylenebis(dimethylarsine)] starting from [OsX$_6$]$^{2-}$ is reported, together with their physical and chemical properties. For X = I all three theoretically possible geometrical isomers of the octahedral complex [these being with *trans*-CO and *cis*-I ligands, (I); with *trans*-I and *cis*-CO ligands, (II); and with *cis*-CO and *cis*-I ligands (III)] have been obtained, and the interconversions (I) → (II) (in 2-methoxyethanol as solvent at 104 °C), (I) → (III) (in nitrobenzene at 104 °C), and (II) → (III) (in ethylene glycol at 165 °C) demonstrated. The thermodynamic stability of the isomers lies in the order (I) < (II) < (III). Based on studies of the interconversions at various temperatures, in various solvents, and in the presence of added ligands, it is suggested for [Os(pdma)I$_2$(CO)$_2$] that the transformation (I) → (II) in 2-methoxyethanol takes place *via* a rhombic-twist mechanism and the transformation (I) → (III) in nitrobenzene by formation of a five-co-ordinate intermediate with unidentate pdma. For X = Cl or Br only isomers (II) and (III) could be obtained, and the conversion (II) → (III) demonstrated.

We have shown in a previous publication that the normally bidentate ligand *o*-phenylenebis(dimethylarsine) (pdma) can show considerable flexibility in its mode of co-ordination when it is attached to the osmium carbonyl group. We were able to obtain complexes with one unidentate pdma ligand, with one uni- and one bidentate pdma, and with two bidentate pdma ligands in *cis* and *trans* configurations.[1] In order to utilize this ability of pdma to form a variety of isomers, we have prepared and investigated complexes of general formula [Os(pdma)X$_2$(CO)$_2$], where X = Cl, Br, or I. For these complexes the three geometrical isomers *cis*-dihalogeno-(*trans*-dicarbonyl)(pdma)osmium, (I), *trans*-dihalogeno-(*cis*-dicarbonyl)(pdma)osmium, (II), and *cis*-dihalogeno-(*cis*-dicarbonyl)(pdma)osmium, (III) (see Figure), are possible. Isomer (III) should be resolvable. Although complexes of type [M(AA)X$_2$Y$_2$] (AA = bidentate ligand; X and Y are two different unidentate ligands) were first investigated by Werner,[2] and their isomerization has been the subject of some theoretical discussion,[3] the preparation of all three possible isomers appears to be an extremely rare event {Bailar and Peppard[4] obtained all three isomers of [Co(en)Cl$_2$(NH$_3$)$_2$]$^+$ (en = ethylenediamine); we have been unable to find another example}. The preparation of one of the possible isomers is on the other hand quite common, although the geometry is not always clearly established. Hales and Irving[5] have in fact briefly described [Os(pdma)I$_2$(CO)$_2$]; as a result of the work described here, we believe the product they obtained was isomer (III). Complexes of the type [MX$_2$Y$_2$Z$_2$] (X, Y, and Z all unidentate), for which five geometrical isomers are possible, are more numerous. For instance, Chatt and Richards and co-workers[6,7] have prepared complexes of type [Os(PR$_3$)$_2$Cl$_2$(CO)$_2$], and were able to obtain four of the possible isomers, although not with the same R group on the phosphine ligand. They were also able to interconvert some of the isomers. However, in general, preparation of more than one isomer is rare,[8,9] and there is no information on the mechanism of the interconversion.



There appear to be three main reasons for the lack of information on the isomers of [M(AA)X$_2$Y$_2$] complexes and their interconversion. First, it is difficult to devise preparative routes to each of the possible isomers; secondly, once obtained, the complexes are rarely robust enough to be isomerized without extensive decomposition; and thirdly, it is often difficult to unequivocally determine the geometry of the isomer(s) obtained. The osmium complexes reported here are readily prepared, are interconvertible without significant decomposition, and the geometry can readily be determined by a combination of i.r. and n.m.r. spectroscopy.

RESULTS AND DISCUSSION

Preparation and Characterization of the Complexes.—The preparation of isomers (I) and (II) [X = I for isomer (I), X = Cl, Br, or I for isomer (II)] from [OsX$_6$]$^{2-}$, CO, and pdma essentially involved initial formation of *cis*- or *trans*-[OsX$_4$(CO)$_2$]$^{n-}$ [n = 1 or 2, *i.e.* complexes of Os^{III} or Os^{II} respectively]. This was followed by substitution of pdma for two X$^-$ ligands, with concomitant reduction of Os^{III} to Os^{II} where appropriate. These two steps were demonstrated by isolation of the appropriate [OsX$_4$(CO)$_2$]$^{n-}$ intermediates and their further reaction with pdma to give the required [Os(pdma)X$_2$(CO)$_2$] products. The CO ligands in the [OsX$_4$(CO)$_2$]$^{n-}$ complexes exert a strong *trans* effect, and this is the reason why the products of substitution of two

X^- ligands in *cis*-$[OsX_4(CO)_2]^{n-}$ by pdma were *trans,cis*-$[Os(pdma)X_2(CO)_2]$, isomer (II), rather than *cis,cis*-$[Os(pdma)X_2(CO)_2]$, isomer (III). The *cis*-$[OsX_4(CO)_2]^{n-}$ complexes were much more stable with respect to loss of CO than their *trans* analogues, and it was even possible to carry out the substitution reactions with pdma without maintaining an atmosphere of CO. When this was tried with the *trans* isomers, monocarbonyl products were obtained. As before [1] the exact nature of the agent which reduces Os^{III} to Os^{II} (where necessary) is unknown.

In the case of *trans*-$[OsI_4(CO)_2]^-$, the high *trans* effect of CO meant that one CO ligand was very readily lost from the complex,[10] and isomer (I) could only be obtained when the pdma substitution reaction was carried out without heating, under an atmosphere of CO, and in the absence of excess of pdma. Under these conditions the reaction was slow, apparently because of the slow reduction of Os^{III} to Os^{II}, and the major reaction products were isomer (I) and an intermediate, apparently $[Os(pdma)I_3(CO)_2]^-$, in which only one I^- ligand has been replaced by unidentate pdma. There was evidence for monocarbonyl by-products also, but not for isomers (II) or (III). The complexes *trans*-$[OsBr_4(CO)_2]^{n-}$ ($n = 1$ or 2) exist,[10] but one CO is extremely labile, and reactions with pdma even under a CO atmosphere gave only the previously described [1] monocarbonyl product $[Os(pdma)_2Br_2(CO)]$ (containing one uni- and one bi-dentate pdma).

Characterization of the complexes

Complex	Analysis (%) [a]			M.p.[b] (θ_c/°C)	I.r.[c] (cm^{-1}) [$\nu(CO)$]	^1H n.m.r.[d] (δ/p.p.m.)
	C	H	X			
(II; X = Cl)	23.8	2.6	11.5	226	2 034, 1 975	1.79 in $[^2H_1]CHCl_3$
	(23.9)	(2.7)	(11.7)			
(III; X = Cl)	23.8	2.6	11.5	273	2 040, 1 962	2.03, 1.95, 1.87, 1.84 in $[^2H_1]CHCl_3$
	(23.9)	(2.7)	(11.7)			
(II; X = Br)	20.6	2.2	23.4	228	2 019, 1 978	1.92 in $[^2H_1]CHCl_3$
	(20.8)	(2.3)	(23.1)			
(III; X = Br)	20.9	2.4	23.3	265	2 038, 1 964	2.10, 2.00, 1.91, 1.85 in $[^2H\ ]$dmso
	(20.8)	(2.3)	(23.1)			2.12, 2.01, 1.94, 1.87 in $[^2H_1]CHCl_3$
(I; X = I)	18.5	2.1	32.5	*e*	1 990, 1 980 (sh)	2.07 in $[^2H_1]CHCl_3$
	(18.3)	(2.0)	(32.3)			
(II; X = I)	18.5	2.1	32.2	250	2 020, 1 974	2.03 in $[^2H_6]$dmso
	(18.3)	(2.0)	(32.3)			2.18 in $[^2H_5]C_6H_5NO_2$
(III; X = I)	18.5	2.1	32.1	247	2 021, 1 966	2.29, 2.27, 1.92 [g] in $[^2H_1]CHCl_3$
	(18.3)	(2.0)	(32.3)			

[a] Calculated values are given in parentheses. [b] Uncorrected, in capillary tubes. [c] As Nujol mulls; all bands are very strong unless otherwise noted. [d] Chemical shifts are for the methyl-on-arsenic resonances relative to $SiMe_4$. [e] Compound softens in the temperature range 130—150 °C; isomerization presumably occurs (see text). [f] 1 995 cm^{-1} in $CHCl_3$ solution. [g] Relative ratio 1 : 1 : 2 respectively.

The various *trans* effects in both the osmium starting materials and the products are not readily understood. Naively one might expect the essentially pure σ-donor X ligands and the strong π-acceptor–weak σ-donor CO ligand to mutually reinforce their bonding to the metal. {There is a clear relation between σ-donor ability, as measured by electronegativity, of X and stability of *trans*-$[OsX_4(CO)_2]^-$ with respect to CO loss in the order I > Br > Cl.} Such a viewpoint would predict that reaction of pdma with *cis*-$[OsX_4(CO)_2]^{n-}$ ($n = 1$ or 2) would give isomer (III), in contrast to the isomer (II) actually observed. It might also be expected on this basis that replacement of X by the more electron-withdrawing pdma would destabilize the complexes with respect to CO loss. In fact none of the $[Os(pdma)X_2(CO)_2]$ complexes shows any tendency to lose either CO, X, or pdma.

Isomer (III) was normally obtained by thermal isomerization of isomer (II). The direct preparation of (III) from $[OsX_6]^{2-}$, CO, and pdma described in the Experimental section actually involved intermediate formation of *fac*-$[OsX_3(CO)_3]^-$,[11] as was shown by the isolation of this complex and its subsequent reaction with pdma. Replacement of one CO and one X ligand in $[OsX_3(CO)_3]^-$ complexes by a polarizable group such as PPh_3 has been reported previously,[11] although the $[Os(PPh_3)_2X_2(CO)_2]$ product appears to have *trans*-PPh_3 groups.[11—13]

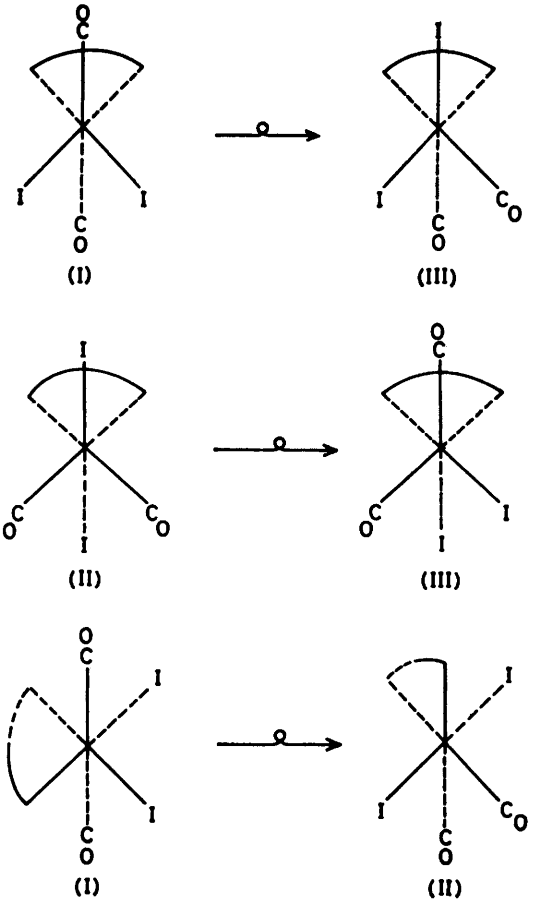
The $[Os(pdma)X_2(CO)_2]$ complexes were characterized, and their geometry determined, by a combination of microanalytical and n.m.r. and i.r. spectroscopic methods. Details are given in the Table. Isomer (I) is expected to show a single methyl-on-arsenic ^1H n.m.r. absorption and one $\nu(CO)$ i.r. absorption, isomer (II) a single ^1H and two i.r. absorptions, and isomer (III) four ^1H and two i.r. absorptions, assuming for isomers (I) and (II) that there is a plane of symmetry through the pdma ligand.[1,14-16] As can be seen from the Table, the expected number of i.r. and ^1H n.m.r. absorptions were observed in each case. It is interesting to note that there was little significant difference in the frequency of $\nu(CO)$ for any of the complexes. We have found previously that in $[Os(pdma)_2X(AB)]^{n+}$ complexes (AB = CO or N_2 for $n = 1$, NO for $n = 2$) $\nu(AB)$ was essentially independent of X, but not of geometry.[1,16] It appears that the requirements of the two CO ligands for π-bonding are satisfied by the one Os(pdma) unit.

The evidence presented below on the isomerization of the complexes indicates that the relative thermodynamic stability of the isomers is (I) < (II) < (III). If the generally accepted order of σ-donor ability, I > As > CO, and of π-acceptor ability, CO > As > I, is assumed, the relative stabilities can be understood in terms of the requirements of the three ligands for σ or π electrons. As expected, the requirement of CO for π electrons makes (I) the most unstable isomer. An alternative explanation for the greater stability of (II) with respect to (I) is that the ligand-field splitting of (II) ($d_{xy} < d_{xz},d_{yz}$) is less than that of (I) ($d_{xy} > d_{xz},d_{yz}$).[17]

Isomerization of the Complexes.—On heating in 2-methoxyethanol at 104 °C for 15 h, isomer (I; X = I) was converted quantitatively into (II). The isomerization was not affected by light (either u.v. or visible); none of the complexes described here was sensitive to light. During the isomerization of (I) into (II) in 2-methoxyethanol the solution remained non-conducting, and when the isomerization was carried out under an atmosphere of CO no tricarbonyl products were observed, neither was the reaction markedly retarded in rate. There was no reaction between pdma and isomer (I) under the isomerization conditions, although at 124 °C in the presence of excess of pdma and Na[BPh$_4$], *trans*-[Os(pdma)$_2$I(CO)][BPh$_4$] [1] was obtained. Addition of excess of iodide ion also had no effect on the isomerization, although on refluxing (124 °C) (I) for 48 h in the presence of excess of Br$^-$, a complicated mixture of products was obtained, some of which contained Br$^-$ as a ligand. At 124 °C in 2-methoxyethanol (I) gave a mixture of (II) (80%) and (III) (20%) within 1 h; (II) was not converted into (III) at 124 °C in this solvent, even on refluxing for 1 week. In dimethyl sulphoxide (dmso) at 104 °C isomer (I) decomposed to a mixture of unidentified products. In nitrobenzene at 104 °C, (I) was quantitatively converted into (III) within 18 h; under the same conditions (II) was less than 20% converted into (III).

The above evidence indicates clearly that at 104 °C in 2-methoxyethanol the isomerization of (I) into (II) proceeded without loss of a unidentate ligand. It also indicates rather less clearly that, in this solvent, formation of a five-co-ordinate intermediate with a unidentate pdma ligand does not occur either. A further important point against the unidentate pdma intermediate is that such a species would have a low-energy barrier to rotation, leading to preferential formation of the thermodynamically most stable isomer (III) [should the energy barrier to rotation be in fact high, the only possibilities would be formation of (III) or no reaction whatever]. Formation of isomer (III) was not observed. We therefore conclude that in 2-methoxyethanol at 104 °C the isomerization of (I) into (II) proceeded *via* an intramolecular rearrangement in which the pdma ligand remained bidentate. At 124 °C in 2-methoxyethanol, since as well as (II) some (III) was formed directly from (I), either two different intramolecular rearrangements, or one rearrangement and simultaneous formation of a five-co-ordinate intermediate, are the possible mechanisms. In nitrobenzene at 104 °C the quantitative conversion of (I) into (III) indicates that in this better co-ordinating solvent the formation of a five-co-ordinate intermediate with unidentate pdma is the most likely mechanism.

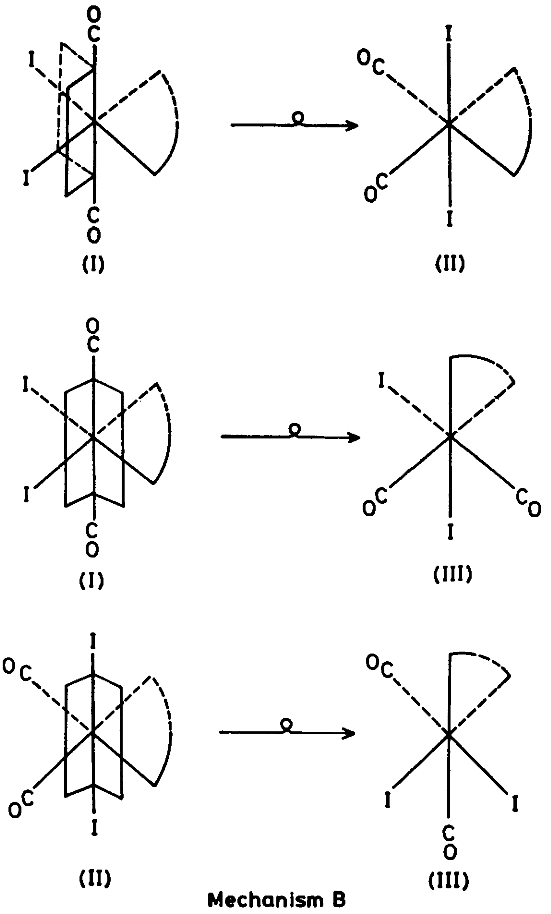
Isomer (II; X = I) was not isomerized in 2-methoxyethanol at 124 °C, whereas the bromo-analogue isomerized completely to (III) after 8 d at this temperature. There was neither noticeable isomerization nor decomposition of (II; X = I) on heating in dmso at 165 °C for 3 h, and, as noted above, (II) was less than 20% converted into (III) in nitrobenzene at 104 °C after 18 h. Isomer (II; X = Cl, Br, or I) was converted quantitatively into (III) by heating at 165 °C in ethylene glycol for 24 h. For X = I isomerization was negligible below 150 °C. When the isomerization of (II; X = I) into (III) at 165 °C was conducted under an atmosphere of CO, no tricarbonyl products could be observed. In comparative experiments at 165 °C it was found that the rate of isomerization of (II) into (III) was in the order I ≪ Br > Cl.



Mechanism A

SCHEME 1 Transformation of isomers by the trigonal-twist mechanism; rotation is about the axis perpendicular to the plane of the paper. Only representative transformations are shown; however, all (I) ⟶ (II) transformations involve the pdma ligand; no (I) ⟶ (III) or (II) ⟶ (III) transformation involves pdma

The evidence does not allow us to decide between a purely intramolecular rearrangement and formation of a five-co-ordinate intermediate as a mechanism for isomerization of (II) to (III), although the stability of (II) in co-ordinating solvents such as nitrobenzene or dmso may indicate a reluctance to become five-co-ordinate. What is surprising is the 60 °C temperature difference between the (I) to (II) and (II) to (III) isomerizations (for X = I). As established above, isomerization (I) to (II) proceeds *via* an intramolecular rearrangement mechanism. The theoretically possible mechanisms of this type for octahedral complexes have been discussed elsewhere.[18] The most important ones are the Bailar or trigonal twist [19] (mechanism A) and the Ray–Dutt or rhombic twist [20] (mechanism B). Inspection of models reveals that the transformation of (I) into (II) (X = I) by mechanism A *always* requires an alteration in the configuration of the pdma group, as well as the CO and I ligands, whereas transformations (I) to (III) or (II) to (III) require only rotations of the CO and I ligands, the pdma remaining fixed (see Scheme 1). The same transformations by mechanism B are exactly opposite; (I) to (II) requires rotation of the CO and I ligands only, whereas (I) to (III) or (II) to (III) require rotation of CO, I, and pdma (see Scheme 2).



SCHEME 2 Transformation of isomers by the rhombic-twist mechanism; rotation occurs in the planes indicated. Only representative transformations are shown; however all (I) ⟶ (II) transformations involve only the CO and I groups; all (I) ⟶ (III) or (II) ⟶ (III) transformations involve the pdma ligand

The extra energy required for the (II) to (III) transformation, when compared to (I) to (II), implies that the steric hindrance in the former transformation is greater than in the latter. This must be true even if the mechanism of the (II) to (III) transformation involves the formation of a five-co-ordinate intermediate, or if it proceeds *via* a (II) to (I) to (III) pathway. The last pathway can be excluded because prolonged heating of (II) at 124 °C does not give (III). As can be seen from Schemes 1 and 2, the (I) to (II) transformation by the rhombic-twist mechanism is the only one in which the closest steric contact in the transition state is between only CO and I; all other transformations involve at least one As–As, I–As, or I–I contact. The smallest steric hindrance in these other transformations is provided by the single As–As contact in the (I) to (III) transformation by the rhombic-twist mechanism; some (I) to (III) transformation does occur at 124 °C, in competition with the (I) to (II) transformation. We propose therefore that the (I) to (II) transformation in 2-methoxyethanol at 104 °C proceeds *via* a rhombic-twist mechanism.

EXPERIMENTAL

The starting materials OsO_4 and $[NH_4]_2[OsCl_6]$ were obtained from Johnson, Matthey, and pdma from Strem Chemicals. All other materials were reagent grade. The OsO_4 was converted into $[NBu^n_4]_2[OsCl_6]$ or $[NBu^n_4]_2[OsBr_6]$ by the method described previously.[1,21] The complexes *cis*-$Cs_2[OsCl_4(CO)_2]$, $[NBu^n_4][OsBr_3(CO)_3]$, *cis*- and *trans*-$[NBu^n_4]_2[OsX_4(CO)_2]$, and *trans*-$[NBu^n_4][OsI_4(CO)_2]$ were prepared by the literature methods.[10–12] Operations involving pdma were conducted under an argon atmosphere; the $[Os(pdma)X_2(CO)_2]$ products were air stable and isomerization experiments were only conducted under an argon atmosphere to confirm that redox processes did not interfere.

The reactions of $[OsX_6]^{2-}$ with CO produce initially monocarbonyl, then dicarbonyl, and finally tricarbonyl complexes.[1,10,11] It is necessary to carefully control the time of this stage of the reaction in order to maximize the yield of the required dicarbonyl complexes.

trans-*Dicarbonyl*-cis-*di-iodo*[o-*phenylenebis*(*dimethylarsine*)]*osmium*, cis,trans-$[Os(pdma)I_2(CO)_2]$ (I).—To *trans*-$[NBu^n_4][OsI_4(CO)_2]$ (0.9 g, 0.81 mmol) in a mixture of methanol (35 cm^3) and acetone (10 cm^3), was added pdma (0.30 g, 1.0 mmol). The solution was stirred at 25 °C under CO for 48 h, then vacuum rotary evaporated to dryness (at 25 °C). The residue was dissolved in the minimum amount of $CHCl_3$, placed on an acidic Alumina column (Woelm, activity grade II), and eluted with hexane–chloroform (2 : 1). The whole of the broad green-yellow band which eluted was collected, the solution evaporated to dryness (25 °C), and the resultant solid recrystallized from chloroform–2-methoxyethanol, yield 0.34 g, 0.37 mmol (38%).

cis-*Dicarbonyl*-trans-*di-iodo*[o-*phenylenebis*(*dimethylarsine*)]*osmium*, trans,cis-$[Os(pdma)I_2(CO)_2]$ (II).—A solution of $[NBu^n_4]_2[OsCl_6]$ (1.0 g, 1.13 mmol) in 2-methoxyethanol (30 cm^3) was refluxed with CO passing through the solution for 5 min. Aqueous HI (55%, 5 cm^3) was added and refluxing under CO continued. After 3.5 h the initially green solution had become brown-yellow. Pdma (0.31 g, 1.08 mmol) was then introduced and the solution refluxed under CO for another 10 min. The solution was then concentrated to *ca.* 3 cm^3 *in vacuo*; the bright yellow precipitate which resulted was filtered off and washed with ethanol (95%, 5 $\mathrm{cm^3}$). The product was recrystallized from chloroform–hexane, yield 0.4 g, 0.44 mmol (45%).

Alternatively, *trans,cis*-$[\mathrm{Os(pdma)I_2(CO)_2}]$ (II) was obtained by heating a saturated solution of *cis,trans*-$[\mathrm{Os(pdma)I_2(CO)_2}]$ (I) in 2-methoxyethanol for 15 h. The solvent was evaporated *in vacuo* and the product recrystallized from chloroform–hexane, yield essentially quantitative.

cis-*Dicarbonyl*-cis-*di-iodo*[o-*phenylenebis*(*dimethylarsine*)]-*osmium*, cis,cis-$[\mathrm{Os(pdma)I_2(CO)_2}]$ (III).—A yellow suspension of *trans,cis*-$[\mathrm{Os(pdma)I_2(CO)_2}]$ (II) (0.07 g, 0.077 mmol) in ethylene glycol (20 $\mathrm{cm^3}$) was refluxed. Decolouration of the suspension was observed after *ca.* 10 min. After 1 h the volume of ethylene glycol was reduced to 5 $\mathrm{cm^3}$ by evaporation (hot plate). The solution was cooled and kept at −20 °C for 24 h. The resultant yellow-white precipitate was filtered off, washed quickly with ethanol (95%), and recrystallized from chloroform–ethanol, yield 0.06 g, 0.066 mmol (86%) of very pale yellow crystals.

trans-*Dibromo*-cis-*dicarbonyl*[o-*phenylenebis*(*dimethylarsine*)]*osmium*, trans,cis-$[\mathrm{Os(pdma)Br_2(CO)_2}]$ (II).—A solution of $[\mathrm{NBu^n_4}]_2[\mathrm{OsBr_6}]$ (1.0 g, 0.87 mmol) in a mixture of 2-methoxyethanol (30 $\mathrm{cm^3}$) and HBr (48%, 3 $\mathrm{cm^3}$) was refluxed with CO passing through the solution for 20 h. The solution was cooled to 25 °C, pdma (0.33 g, 1.15 mmol) added, and the solution stirred at 75 °C under a CO atmosphere until it became yellow-orange (*ca.* 17 h). The solvent was evaporated *in vacuo*, giving a tan coloured oil. On cooling in an ice-bath for 5 h, or on standing for 16 h at room temperature, the oil became crystalline. The yellow crystals were washed with methanol and diethyl ether and recrystallized from acetone–methanol, yield 0.15 g, 1.85 mmol (25%).

cis-*Dibromo*-cis-*dicarbonyl*[o-*phenylenebis*(*dimethylarsine*)]*osmium*, cis,cis-$[\mathrm{Os(pdma)Br_2(CO)_2}]$ (III).—A solution of $[\mathrm{NBu^n_4}]_2[\mathrm{OsBr_6}]$ (1.7 g, 1.47 mmol) in 2-methoxyethanol (50 $\mathrm{cm^3}$) was refluxed with CO passing through the solution for 24 h. The CO supply was discontinued and to the pale yellow, still refluxing solution, was added pdma (0.65 g, 2.27 mmol). Refluxing was continued for 2 h. The solvent was evaporated (25 °C, *in vacuo*), leaving an oil, which was washed with methanol (10 $\mathrm{cm^3}$) to which a few drops of aqueous HBr (48%) had been added. The white crystals which immediately formed were filtered off and recrystallized from chloroform–ethanol, yield 0.5 g, 0.61 mmol (49%).

Alternatively, *cis,cis*-$[\mathrm{Os(pdma)Br_2(CO)_2}]$ (III) could be obtained by heating *trans,cis*-$[\mathrm{Os(pdma)Br_2(CO)_2}]$ (II) (0.065 g, 0.08 mmol) in ethylene glycol (5 $\mathrm{cm^3}$) at 160 °C for 24 h. After addition of water (five drops) to the solution it was set aside in an ice-bath for 16 h. The resultant white precipitate was filtered off and recrystallized from acetone, yield 0.055 g, 0.68 mmol (85%).

cis-*Dicarbonyl*-trans-*dichloro*[o-*phenylenebis*(*dimethylarsine*)]*osmium*, trans,cis-$[\mathrm{Os(pdma)Cl_2(CO)_2}]$ (II).—To a solution of *cis*-$\mathrm{Cs_2[OsCl_4(CO)_2]}$ (0.3 g, 0.39 mmol) in 2-methoxyethanol (30 $\mathrm{cm^3}$) was added pdma (0.13 g, 0.45 mmol), and the solution heated at 105 °C for 2 h. The solution was cooled to 25 °C, filtered to remove CsCl, and the filtrate evaporated to dryness *in vacuo*. The resultant solid was dissolved in acetone, the solution filtered, and the filtrate evaporated *in vacuo* until yellow crystals formed. These were filtered off and washed with ethanol and diethyl ether, yield 0.15 g, 0.21 mmol (54%).

cis-*Dicarbonyl*-cis-*dichloro*[o-*phenylenebis*(*dimethylarsine*)]-*osmium*, cis,cis-$[\mathrm{Os(pdma)Cl_2(CO)_2}]$ (III).—A solution of $[\mathrm{NBu^n_4}]_2[\mathrm{OsCl_6}]$ (1.0 g, 1.13 mmol) in 2-methoxyethanol (30 $\mathrm{cm^3}$) was heated at 110 °C, with a current of CO passing through the solution, for 72 h. The solution was cooled to room temperature, the CO current stopped, and pdma (0.4 g, 1.40 mmol) added. The solution was reheated to 110 °C for 2 h, then evaporated (vacuum rotary) to a volume of *ca.* 3 $\mathrm{cm^3}$. To the oily product, was added water (three drops) and the mixture set aside for 18 h. The resultant white crystals were filtered off, recrystallized from chloroform–ethanol, and washed with ethanol and diethyl ether, yield 0.25 g, 0.34 mmol (37%).

Alternatively, *cis,cis*-$[\mathrm{Os(pdma)Cl_2(CO)_2}]$ (III) could be obtained by refluxing a solution of *trans,cis*-$[\mathrm{Os(pdma)Cl_2(CO)_2}]$ (II) (0.07 g, 0.097 mmol) in ethylene glycol (5 $\mathrm{cm^3}$) for 0.5 h. After cooling, five drops of water were added to the solution, which was then set aside in an ice-bath overnight. The white crystals which formed were filtered off and recrystallized from acetone, yield essentially quantitative.

Instruments used were a Perkin-Elmer 467 i.r. spectrophotometer, spectra being run as Nujol mulls or in solution between KBr or $\mathrm{CaF_2}$ plates, a Varian T60 n.m.r. spectrophotometer, and a Beckman RC-18A conductivity bridge, measurements being made at a concentration of *ca.* 10^{-3} mol $\mathrm{dm^{-3}}$. Microanalyses were by A. Bernhardt, West Germany.

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