

A New Class of Osmium(IV) Complexes containing both Oxide and Carboxylate Bridges

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Summary The reactions of the Os^{VI} complexes OsO₂X₂(PR₃)₂ (X = Cl or Br) with refluxing carboxylic acids produce a new class of osmium dimers of the type Os₂(μ-O)(μ-O₂CR)₂X₄(PR₃)₂ whose structural details have been confirmed by an *X*-ray diffraction study of Os₂(μ-O)(μ-O₂CCH₃)₂Cl₄(PPh₃)₂.

In contrast with the existence of many osmium complexes containing [Os(μ-N)Os] and [Os(μ-O)₂Os] bridges,¹ compounds containing a single Os–O–Os unit are rare, being restricted to oxyhalogeno-anions of osmium(IV) of the type [Os₂OX₁₀]⁴⁻. Only in the case of Cs₄Os₂OCl₁₀ has this been documented by a crystal structure determination,² although vibrational spectroscopy has been used to support the existence of this structural feature in several halogeno-anions of this same type.³ In the course of investigating the reactions of *trans*-OsX₄(PPh₃)₂ and *trans*-OsO₂X₂(PPh₃)₂ (X = Cl or Br) with ligands such as carboxylic acids and the anions of 2-hydroxypyridine and 2-hydroxy-6-methylpyridine, which can be particularly effective in inducing coupling of metal centres to give complexes containing metal–metal bonds (often of multiple order),⁴ we have discovered a new class of osmium(IV) dimers which are constrained to contain a bent Os–O–Os bridging unit.

When suspensions of *trans*-OsO₂X₂(PPh₃)₂⁵ are refluxed in acetic acid–acetic anhydride mixtures (10:1 by volume), dark-coloured solutions (brown for X = Cl and purple for X = Br) are obtained which upon evaporation to low volume deposit crystals of diamagnetic Os₂(μ-O)(μ-O₂CCH₃)₂X₄(PPh₃)₂ in high yield (80% for X = Cl; 60% for X = Br). These compounds may be recrystallized from dichloromethane–diethyl ether mixtures. Comparable reactions of other phosphine derivatives of the type OsO₂X₂(PR₃)₂ with carboxylic acids lead to similar products,[†] thereby demonstrating that this is an extensive class of complexes in which the halide, carboxylate bridge, and/or phosphine ligands may be varied.

Crystal data: C₄₀H₃₈Cl₄P₂O₅Os₂·C₄H₁₀O, *M* = 1257.0, monoclinic, space group *P*2₁/*c*, *a* = 13.066(3), *b* = 18.124(3), *c* = 19.619(4) Å, β = 107.10(2)°, *U* = 4441 Å³; *Z* = 4; *F*(000) = 2440, μ(Mo-*K*_α) = 58.1 cm⁻¹.‡

The structure of the diethyl ether solvate of Os₂(μ-O)(μ-O₂CCH₃)₂Cl₄(PPh₃)₂ was solved by conventional heavy-atom methods and refined to a final *R* value of 0.044 for 4668 reflections (6 ≤ 2θ ≤ 50° at 296 K) on an Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated Mo-*K*_α radiation. The lattice diethyl ether molecules are disordered and do not interact in any significant

† Satisfactory microanalytical data and spectroscopic properties (i.r., ¹H n.m.r., and e.s.c.a.) were obtained for these complexes.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

way with the osmium(IV) dimer, the structural core of which is shown in the Figure. With the exception of the orientation of the phenyl rings, the molecule exhibits approximate C_2 symmetry.

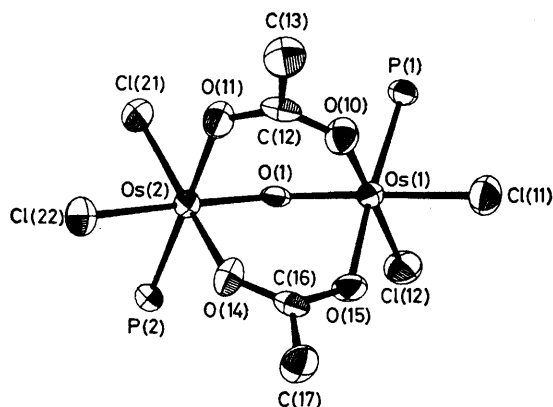


FIGURE. An ORTEP representation of $\text{Os}_2(\mu\text{-O})(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\text{PPh}_3)_2$ with the phenyl rings of the PPh_3 ligands omitted. Important representative bond lengths: $\text{Os}(1)\text{-Os}(2)$ 3.440(2), $\text{Os}(1)\text{-O}(1)$ 1.830(10), $\text{Os}(2)\text{-O}(1)$ 1.828(9), $\text{Os}(1)\text{-O}(10)$ 2.083(9), $\text{Os}(1)\text{-O}(15)$ 2.118(9), $\text{Os}(1)\text{-Cl}(11)$ 2.306(4), $\text{Os}(1)\text{-Cl}(12)$ 2.332(4), $\text{Os}(1)\text{-P}(1)$ 2.374(3) Å. The $\text{Os}(1)\text{-O}(1)\text{-Os}(2)$ angle is $140.2(4)^\circ$. The $\text{Os}(2)$ -ligand distances are equivalent to the corresponding $\text{Os}(1)$ -ligand distances within experimental error.

The $\text{Os}_2(\mu\text{-O})(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\text{PPh}_3)_2$ molecule is best viewed as being derived from the $[\text{Os}_2(\mu\text{-O})\text{Cl}_{10}]^{4-}$ anion^{1,2} through replacement of three of the four $\text{Os-Cl}_{\text{cis}}$ bonds (*cis*, that is, to the Os-O-Os unit) about each six-coordinate Os centre by one phosphine and by one oxygen atom from each of two intramolecular acetate bridges. The constraints imposed by the two carboxylate bridges are such that the Os-O-Os unit becomes bent (140°) with it now serving as an integral part of two fused 'chair-like' OsOOOCO rings. This change from a linear to bent Os-O-Os geometry is accompanied by a lengthening of the associated Os-O bonds from 1.778 to 1.829 Å. This presumably reflects (in part) a decrease in the $\text{Os}(d_\pi)\text{-O}(p_\pi)\text{-Os}(d_\pi)$ overlap which is maximized in the linear arrangement.

As a consequence of the presence of both oxide and carboxylate bridges, the Os-Os distance becomes quite short (3.440 Å), being less than that in the 'parent' chloride OsCl_4 (3.560 Å) in which it can be argued⁶ there is no Os-Os bonding. Whether some degree of metal-metal bonding exists in $\text{Os}_2(\mu\text{-O})(\mu\text{-O}_2\text{CR})_2\text{X}_4(\text{PR}_3)_2$ cannot be inferred from the diamagnetism of these complexes since super-exchange through the ligand bridges may equally well account for this particular property of these molecules.

In contrast with the reductive coupling which occurs upon allowing $\text{OsO}_2\text{X}_2(\text{PR}_3)_2$ to react with $\text{RCO}_2\text{H}-(\text{RCO})_2\text{O}$ mixtures, the reactions between these osmyl complexes and L = the anion of 2-hydroxypyridine or 2-hydroxy-6-methylpyridine afford the magnetically dilute osmium(III) monomers $\text{OsX}_2(\text{L})(\text{PR}_3)_2$. This difference in reaction course might be explained by the greater reducing propensity of these substituted pyridines (compared with carboxylate ligands) and their reluctance to form the distorted type of bridge which is necessary to span two *weakly* interacting osmium(IV) atoms at a long distance from one another. These substituted pyridine ligands are known to be much more effective in stabilizing dinuclear units which contain very short metal-metal bonds,⁴ including the triply-bonded Os_2^{6+} core, as in $\text{Os}_2(2\text{-oxypyridinato})_4\text{Cl}_2$.⁷

The electrochemical redox properties of $\text{Os}_2(\mu\text{-O})(\mu\text{-O}_2\text{CR})_2\text{X}_4(\text{PR}_3)_2$ have been explored using cyclic voltammetry (solutions in 0.2 M Bu_4NPF_6 -dichloromethane). All complexes have a reversible one-electron reduction at $E_{1/2} = \text{ca. } +0.2 \text{ V vs. saturated calomel electrode (S.C.E.)}$ and an irreversible reduction with $E_{\text{p.c}}$ between -0.7 and $-1.0 \text{ V vs. S.C.E.}$, the actual value of which is dependent upon the nature of the halide, carboxylate, and phosphine ligands. Since these molecules may be considered as derivatives of the $[\text{Os}_2(\mu\text{-O})(\mu\text{-O}_2\text{CR})_2]$ core which is itself a fragment of the presently unknown $[\text{Os}_3(\mu\text{-O})(\mu\text{-O}_2\text{CR})_6]^+$ cluster, analogues of which exist for other transition metals including ruthenium(III),^{8,9} it is clear that an understanding of the reduction chemistry and reactivity of $\text{Os}_2(\mu\text{-O})(\mu\text{-O}_2\text{CR})_2\text{X}_4(\text{PR}_3)_2$ may be important in designing synthetic routes to the $[\text{Os}_3(\mu\text{-O})(\mu\text{-O}_2\text{CR})_6]^+$ cluster.

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