Synthesis and Reactions of Osmium(III) Chloro Carboxylates. *X*-Ray Crystal Structure of Tetra(μ-n-butyrato)-dichlorodiosmium(III) (*Os–Os*) †

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The interaction of the hexachloroosmate(IV) ion, $OsCl_6^{2-}$, with acetic acid–acetic anhydride mixtures gives the compound $Os_2(\mu\text{-}O_2CMe)_4Cl_2$. This brown insoluble paramagnetic compound on treatment with other carboxylic acids forms the exchanged compounds $Os_2(\mu\text{-}O_2CR)_4Cl_2$ (R = Et, Pr^n, or CH_2Cl) that are more soluble in organic solvents. The binuclear bridged carboxylate structure has been established for the butyrate by *X*-ray diffraction. The crystals are monoclinic, space group $P2_1/n$, with $a = 6.789(2)$, $b = 11.790(1)$, $c = 14.923(1)$ Å, $\beta = 98.211(18)°$, and $Z = 2$. The Os–Os distance is 2.301(1) Å and Os–Cl is 2.417(3) Å. The interaction of $Os_2(\mu\text{-}O_2CMe)_4Cl_2$ with various acids, sodium dimethyldithiocarbamate, aromatic amines, tertiary phosphines, and alkyl isocyanides has been studied.

Although ruthenium carboxylates containing the units $[Ru_2(O_2CR)_4]$ [1] and $[Ru_3O(O_2CR)_6L_3]$ [2] have long been known the osmium analogues are not. Indeed, few osmium carboxylates are known and with the exception of $K[OsO_2(O_2CMe)_3]$,[3a] whose structure has recently been confirmed by *X*-ray diffraction study,[3b] $[Os_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2X_4(PR_3)_2]$,[4] $[OsO_2(NH_2CH_2CO_2)_2]$,[5] and $[OsX_2(O_2CR)(PPh_3)_2]$,[6] the rest are carbonyls of types such as $[Os(O_2CR)_2(CO)(PPh_3)_3]$, $[\{Os(O_2CR)(CO)_3\}_2]$, $[\{Os(O_2CR)(CO)_2L\}_2]$, and $[OsH(O_2CMe)(CO)_2(PR_3)_2]$.[7]

We now give details of the synthesis and characterisation of the acetate and other carboxylates of the type $Os_2(O_2CR)_4Cl_2$ and some reactions thereof. Preliminary reports of these studies have been made.[8]

Results and Discussion

Tetra(μ-*acetato*)-*dichlorodiosmium*(III).—This compound was first obtained [8a] by refluxing sodium hexachloroosmate(IV) in glacial acetic acid containing acetic anhydride and a small amount of concentrated hydrochloric acid for *ca.* 2 days. The brown microcrystalline product precipitates from the reddish brown solution; the nature of this residual solution has not been ascertained but no precipitates were obtained on addition of large cations $[N(PPh_3)_2^+]$ or anions (BPh_4^- or ClO_4^-). However, this method of synthesis proved unreliable since the yields vary between 25 and 70% and even zero with some samples of $Na_2[OsCl_6]$. The reaction also fails with lithium, ammonium, or potassium hexachloroosmates and with the $OsBr_6^{2-}$ ion, probably due to the very low solubility of the salts. The best procedure has been that using hydrochloric acid solutions of the $OsCl_6^{2-}$ ion obtained by the reduction of OsO_4 with iron(II) chloride.[9] The resulting dark red solution was then extracted with diethyl ether to remove much of the iron(III) chloride produced in the course of the reaction, evaporated to near dryness, and the residue heated in glacial acetic acid containing acetic anhydride for *ca.* 10 h. Reproducible and high yields of the acetate can be obtained on a substantial scale. After removal of the insoluble osmium compound, evaporation of the solution and recrystallisation of the solid gives red crystals, which, from *X*-ray crystallographic studies,[10] are the salt $[Fe_3O(O_2CMe)_6(thf)_3][FeCl_4]$ (thf = tetrahydrofuran).

The procedure is effective only for the acetate probably because it is very insoluble and precipitates from the reaction mixture and cannot be used as a general method for synthesis of other dimeric carboxylates. This is in part due to the high solubility of the oxo-centred iron complex which interferes with the isolation of the higher, more soluble, carboxylates. Other reducing agents for OsO_4 in HCl such as ethanol have so far not given useful procedures.

The acetate, $Os_2(O_2CMe)_4Cl_2$, is insoluble in all common organic solvents except pyridine, with which it reacts, so that its molecular weight could not be determined in solution. However, it was sufficiently volatile for a weak parent-ion peak to be observed (at *m/e* 687) in its mass spectrum; fragmentation peaks due to successive loss of chloride ion were also clearly observed. Further fragmentation resulted in the loss of a variety of organic fragments, the nature of which will be discussed elsewhere.[11] The i.r. spectrum (Nujol mull) shows strong bands at 1 450 and 1 380 cm^{-1}, indicating symmetrically co-ordinated acetate groups.[12] The spectrum also shows bands at 392 and 345 cm^{-1}, probably attributable to Os–O and Os–Cl stretches respectively. The structure is presumably the usual tetra-acetate-bridged structure with terminal chlorine atoms, similar to that of $Re_2(O_2CMe)_4Cl_2$ [13] and of the osmium(III) n-butyrate discussed below.

Other Osmium(III) *Carboxylates.*—Although we have been unable to synthesise other osmium carboxylates by direct reactions as above, certain of these can be obtained by exchange reactions with $Os_2(O_2CMe)_4Cl_2$ at elevated temperatures. Thus, heating the acetate to 140—160 °C in propionic or n-butyric acid gives dark green solutions which upon cooling yield the compounds $Os_2(O_2CR)_4Cl_2$ (R = Et or Pr^n). The binuclear nature of these species which are more soluble than the acetate in organic solvents has been confirmed by a variety of techniques. Thus, both compounds show mass spectral patterns containing strong parent-ion peaks corresponding to the binuclear cations $[Os_2(O_2CR)_4Cl_2]^+$. The loss of two successive chloride ions from these parents is observed, as is the loss of more complex organic fragments.[11] The butyrate is sufficiently soluble in benzene for its molecular weight to be determined by osmometry. Values obtained at a variety of concentrations agree well with the dimeric formulation.

Infrared spectra of these compounds are similar to those of

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† *Supplementary data available* (No. SUP 23659, 11 pp.): structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. units employed: B.M. ≈ 9.27×10^{-24} A m^2; atm = 101 325 Pa.

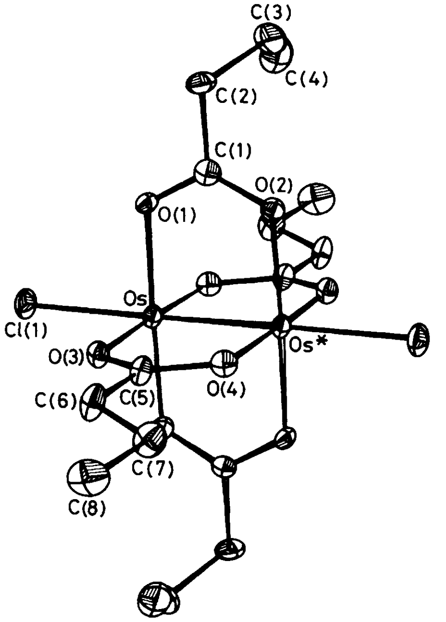

Figure 1. ORTEP diagram at 30% probability level of the molecular structure of $Os_2(O_2CPr^n)_4Cl_2$

the acetate with peaks at 1 478 and 1 375 cm^{-1} (R = Et) and 1 471 and 1 358 cm^{-1} (R = Pr^n) indicative of symmetrically co-ordinated carboxylato-groups.[12] Bands in the regions 340—350 and 390—400 cm^{-1} may be attributed to the Os–Cl or Os–O vibrations respectively.

The compound $Os_2(O_2CCH_2Cl)_4Cl_2$ can be obtained from the reaction of $Os_2(O_2CMe)_4Cl_2$ with molten monochloroacetic acid. This complex is only slightly more soluble than the acetate and hence no solution data could be obtained. However, it does show the mass spectral pattern and i.r. spectrum characteristic of the other osmium carboxylates.

X-*Ray Crystal Structure of* $[Os_2(O_2CPr^n)_4Cl_2]$.—Crystallographic details are given in the Experimental section. Final atomic parameters are given in Table 1, selected bond lengths and angles in Table 2, and a view of the molecule in Figure 1. The molecule is a dimer lying on a crystallographic inversion centre with each osmium ion exhibiting octahedral co-ordination. The Os–Os distance, 2.301(1) Å, is greater than that found in comparable diruthenium(II,III) compounds (2.248—2.292 Å) [14a] despite the greater formal bond order (3.0 *vs.* 2.5). The Os–Cl distance, 2.417(3) Å, is significantly less than those of related ruthenium complexes [14a] which is in accord with the weak co-ordination of axial ligands in $Ru_2^{II,III}$ carboxylates. The observed Os–Os and Os–Cl distances are significantly less than those of the closely related $[Os_2(NC_5H_4O\text{-}2)_4Cl_2]\cdot 2MeCN$ ($NC_5H_4O\text{-}2$ = 2-hydroxypyridine anion), namely 2.357(1) and 2.505(5) Å respectively.[15] The twist angles O(1)–Os–Os*–O(2) and O(3)–Os–Os*–O(4) of 0.3 and 0.6°, respectively, are less than the average of 5.5° reported for the pyridin-2-olato-complex. The reason for this is probably that in the carboxylato-complexes there is little or no repulsive interaction between bridging and terminal ligands. The twisting reported in the pyridin-2-olato-compound arose from the interaction between the hydrogen in the 6-position on the pyridine rings and the terminal chloride ions. This twisting may give rise to less orbital overlap and hence a slight increase in the Os≡Os distance compared to that reported here; that is, the less distorted ligands allow the metal atoms to lie closer together. Finally, the n-butyrate groups exhibit both *gauche* [C(4)–C(3)–C(2)–C(1) 54°] and *trans* [C(8)–C(7)–C(6)–C(5) 176°] conformations.

Table 1. Fractional co-ordinates of atoms with standard deviations in parentheses

Atom	*x*	*y*	*z*
Os	0.088 28(6)	0.440 36(4)	0.459 44(3)
Cl(1)	0.284 5(6)	0.317 1(3)	0.377 6(3)
O(1)	−0.120 8(12)	0.462 2(7)	0.350 4(6)
O(2)	−0.292 1(12)	0.576 7(6)	0.429 2(6)
C(1)	−0.266 4(18)	0.523 8(10)	0.356 5(8)
C(2)	−0.420 5(20)	0.542 3(13)	0.273 6(10)
C(3)	−0.329 5(28)	0.594 2(19)	0.198 9(12)
C(4)	−0.215 2(30)	0.697 9(16)	0.221 9(15)
O(3)	0.234 4(13)	0.573 6(6)	0.419 2(6)
O(4)	−0.067 2(12)	0.309 2(6)	0.501 5(6)
C(5)	0.197 7(18)	0.670 9(11)	0.446 1(9)
C(6)	0.312 3(20)	0.765 9(11)	0.411 3(12)
C(7)	0.236 6(23)	0.880 9(14)	0.428 7(13)
C(8)	0.357 6(27)	0.967 5(14)	0.384 0(13)

Table 2. Bond lengths (Å) and angles (°) in $Os_2(O_2CPr^n)_4Cl_2$

Os–Os	2.301(1)	C(3)–C(4)	1.462(26)
Os–Cl(1)	2.417(3)	Os–O(3)	1.996(7)
Os–O(1)	2.018(8)	Os*–O(4)	2.022(8)
Os*–O(2)	2.015(8)	C(5)–O(3)	1.252(14)
C(1)–O(1)	1.241(14)	C(5)–O(4)	1.284(15)
C(1)–O(2)	1.284(15)	C(5)–C(6)	1.499(18)
C(1)–C(2)	1.518(25)	C(6)–C(7)	1.486(21)
C(2)–C(3)	1.482(21)	C(7)–C(8)	1.523(25)
Cl(1)–Os–Os*	177.96(10)	O(1)–C(1)–O(2)	119.41(8)
O(1)–Os–Os*	89.27(23)	O(1)–C(1)–O(2)	123.5(10)
O(2)–Os–Os*	88.55(23)	C(1)–O(2)–Os*	119.2(7)
O(3)–Os–Os*	89.79(24)	Os–O(3)–C(5)	119.6(8)
O(4)–Os–Os*	88.23(23)	O(3)–C(5)–O(4)	123.3(11)
Os–O(1)–C(1)	119.41(8)	C(5)–O(4)–Os*	119.04(8)

* Represents the atom related by $\bar{x}, \bar{y}, \bar{z}$.

Unlike the majority of other binuclear transition-metal carboxylates, variable-temperature magnetic measurements from 300 to 188 K on dichloromethane solutions of the butyrate and propionate (by Evans' method [16]) show that both compounds are paramagnetic. However, the magnitude of $\mu_{eff.}$ (*e.g.* for R = Pr^n, $\mu_{eff.}$ decreases from 1.15 B.M. per Os at 300 K to 1.02 B.M. per Os at 188 K) is indicative of considerable antiferromagnetic interaction between the osmium(III) ions.* Solid-state magnetic measurements follow a similar pattern, *e.g.* for R = Me, $\mu_{eff.}$ at 288 K is 1.17 B.M. per Os falling to 0.95 B.M. per Os at 209 K. Hence it seems reasonable to suggest for these $Os_2(O_2CR)_4Cl_2$ complexes that there is an appreciable population of a spin-triplet state (perhaps corresponding to the electronic configuration $\sigma^2\pi^4\delta^2\pi^{*2}$ † or $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*1}$) at ambient temperature with the singlet ground state (arising from the $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration) becoming increasingly favoured as the temperature is lowered.

In contrast, the isoelectronic $Re_2^{II,II}Cl_4(PR_3)_4$ are not paramagnetic, suggesting a $\sigma^2\pi^4\delta^2\delta^{*2}$ ground state.[14b] This difference in behaviour between complexes containing iso-

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* Under the same conditions *mer*-$[OsCl_3(PMe_2Ph)_3]$ shows the behaviour expected for a magnetically dilute osmium(III) compound,[17] *i.e.* $\mu_{eff.}$ = 1.70 B.M. (almost temperature invariant).

† In support of this proposal, recent SCF-Xα-SW calculations [18] on $[Ru_2(O_2CH)_4]^+$ and related species indicate an electronic ground-state configuration $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*1}$ with very small energy separation between the π* and δ* orbitals.

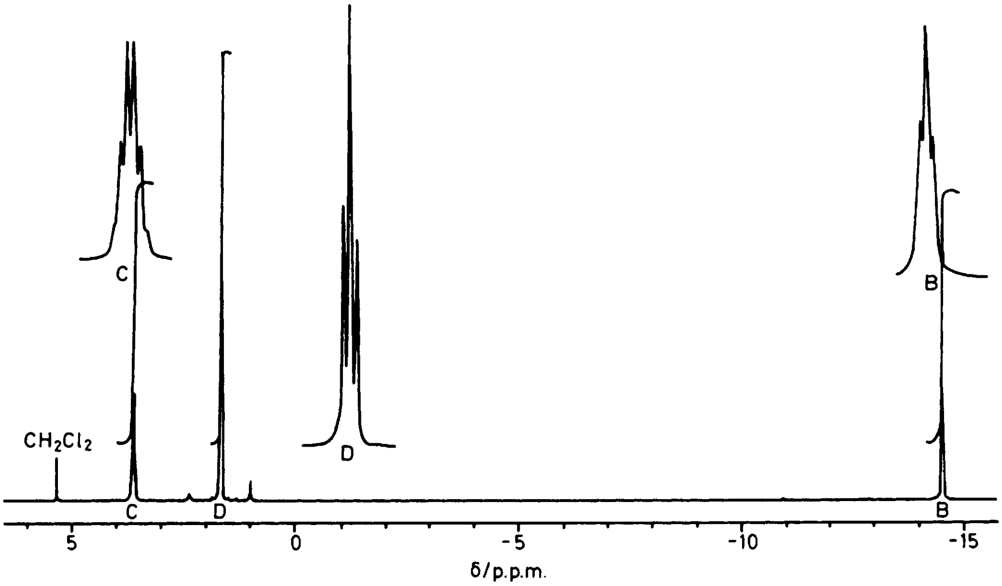

Figure 2. Hydrogen-1 n.m.r. spectrum of $Os_2(O_2CCH^B{}_2CH^C{}_2CH^D{}_3)_4Cl_2$ in CD_2Cl_2 at 297 K: δ −14.53 (H^B), 1.64 (H^D), and 3.59 (H^C) p.p.m.

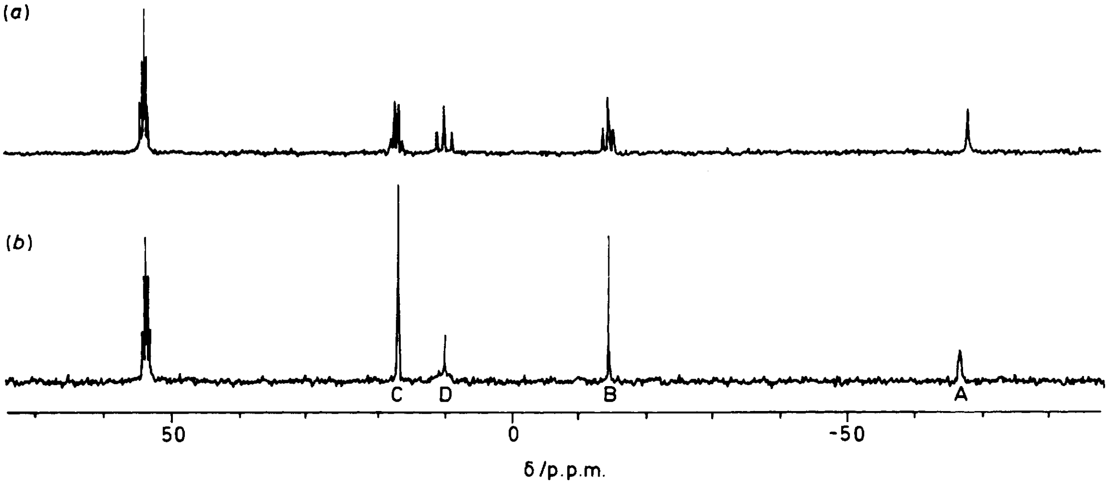

Figure 3. Carbon-13 n.m.r. spectrum of $Os_2(O_2C^AC^BH_2C^CH_2C^DH_3)_4Cl_2$ in CD_2Cl_2 at 296 K: (*a*) proton coupled; (*b*) proton decoupled; δ −66.80 (C^A), −14.48 (C^B), 9.99 (C^D), and 16.87 p.p.m. (C^C)

electronic Re_2^{4+} and Os_2^{6+} cores could be due to the higher positive charge on the latter, causing weaker interactions between the osmium(III) centres and hence producing a low-lying spin-triplet level. In support of this, the Re≡Re distance in $Re_2Cl_4(PEt_3)_4$ is only 2.232(5) Å.[14b]

Further evidence for the presence of significant amounts of unpaired electron density in these $Os_2(O_2CR)_4Cl_2$ compounds is the occurrence of contact-shifted resonances in both the ^1H (Figure 2) and ^{13}C (Figure 3) n.m.r. spectra of $Os_2(O_2CPr^n)_4Cl_2$. All the resonances are displaced to lower frequency compared to their positions in a diamagnetic environment with those lying closest to the osmium(III) centres (H^B and C^A respectively) experiencing by far the largest shift. A more detailed analysis of these spectra will be given elsewhere.[11] In view of these shifted but sharp n.m.r. resonances, it is not surprising that no e.s.r. signals were observed down to liquid-nitrogen temperatures.

Both the propionate and butyrate are sufficiently soluble for their electrochemical behaviour to be studied. Cyclic (c.v.) and alternating current (a.c.v.) voltammetric measurements in CH_2Cl_2–0.25 mol dm^{-3} NBu_4BF_4 at 293 K show that both compounds undergo a facile one-electron, reversible, oxidation at +0.57 and +0.53 V respectively.* In addition the propionate exhibits irreversible oxidation (+1.89 V) and reduction (−1.32 V) waves and the butyrate shows similar peaks at +1.84 and −1.00 V. On cooling, some return-wave characteristics develop but even at 213 K these processes never attain full reversibility. Hence this electrochemical evidence suggests that the formally mixed valence $[Os_2^{II,III}(O_2CR)_4Cl_2]^-$ anions are unstable (*cf.* the corresponding $Cs[Ru_2(O_2CMe)_4Cl_2]$ whose *X*-ray structure has been reported.[14a]).

It was also hoped that controlled-potential electrogeneration of the $Os_2^{III,IV}$ cations, $[Os_2(O_2CR)_4Cl_2]^+$ would enable their magnetic and spectroscopic properties to be determined. However, preliminary studies indicate that on

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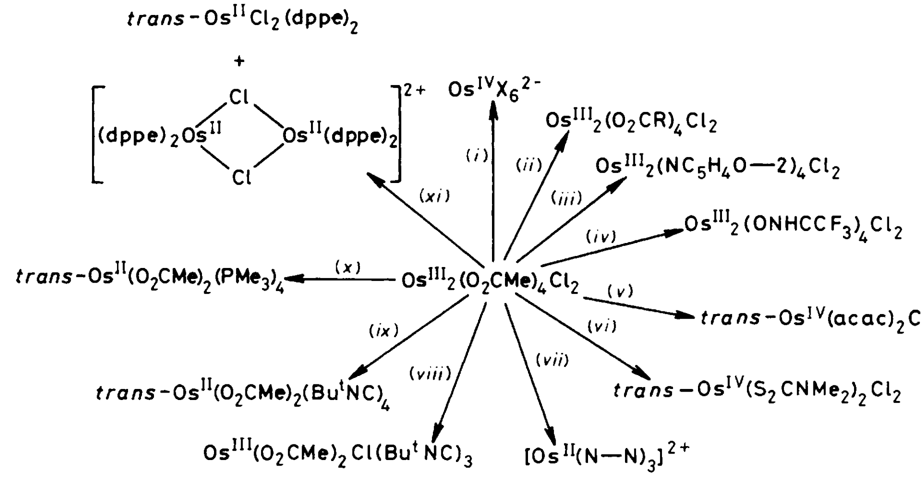
* All these $E_{\frac{1}{2}}$ values are measured with respect to a Ag–AgI reference electrode at which ferrocene is oxidised at +0.60 V.



Scheme. Some reactions of $Os_2(O_2CMe)_4Cl_2$. (*i*) HCl, HBr (aq); (*ii*) RCO_2H; (*iii*) 2-hydroxypyridine; (*iv*) 2,2,2-trifluoroacetamide (from butyrate); (*v*) acetylacetone; (*vi*) $Na[S_2CNMe_2]$; (*vii*) N–N = 2,2′-bipyridyl or 1,10-phenanthroline; (*viii*) Bu^tNC; (*ix*) Na + Bu^tNC; (*x*) PMe_3; (*xi*) $Ph_2P[CH_2]_2PPh_2$

bulk electrogeneration these cations are too unstable at 228 K for even *in situ* measurements of their properties to be obtained.

Finally, for identification purposes, the electronic absorption spectra of these various $Os_2(O_2CR)_4Cl_2$ are listed in the Experimental section. These will be fully discussed elsewhere, together with their resonance-Raman spectra.[19]

Some Reactions of $Os_2(O_2CR)_4Cl_2$ *Compounds.*—Reactions of binuclear transition-metal carboxylates fall into three categories: (1) those in which the terminal ligands are displaced and the bridging RCO_2^- groups are left intact; (2) reactions in which the bridging ligands are partially or completely replaced by other bridging ligands; and (3) reactions which destroy the bridges and give monomeric products.

To date, we have only found examples of reactions of $Os_2(O_2CR)_4Cl_2$ in categories (2) and (3). Moreover, it appears that these diosmium compounds are very reactive and most reagents totally disrupt their structure. In fact, only two examples of reactions in which bridge exchange (other than carboxylate) has occurred have so far been discovered.

(*a*) *Reactions with acids.* The acetate reacts with excess of 2-hydroxypyridine in methanol to yield a dark red-purple solid for which analytical and mass spectral data indicate that it is the known $Os_2(NC_5H_4O\text{-}2)_4Cl_2$ previously made [15] by direct reaction of $OsCl_3$ with 2-hydroxypyridine in ethanol. This compound is also paramagnetic with values of $\mu_{eff.}$ in CH_2Cl_2 (1.44 B.M. per Os at 300 K falling to 1.22 B.M. per Os at 195 K) indicating that antiferromagnetic interactions between osmium(III) centres may be a general phenomenon in binuclear $Os_2^{III,III}$ complexes.

Electrochemical studies on $Os_2(NC_5H_4O\text{-}2)_4Cl_2$ in CH_2Cl_2–0.25 mol dm^{-3} NBu_4BF_4 at 293 K reveal both oxidation (+1.36 V) and reduction (+0.26 V) waves. Neither process is, however, fully reversible (or becomes so on lowering the temperature) as shown by the peak-to-peak separation of 100—120 mV in the cyclic voltammagram and the broad peaks (>90 mV at half-height) in the alternating current voltammagram.

The other example of bridge exchange is in the reaction of $Os_2(O_2CPr^n)_4Cl_2$ with an excess of molten 2,2,2-trifluoroacetamide. It is necessary to use the butyrate rather than acetate here because the product formed, $[Os(ONHCCF_3)_2Cl]_n$, is so insoluble that it cannot be separated from unreacted, equally insoluble osmium acetate. In fact, the low solubility and lack of volatility makes it impossible to determine unequivocally the structure of this complex although by analogy with studies on $Rh_2(ONHCCF_3)_4$[20] it is probably binuclear.

In all the other reactions we have studied, cleavage of the Os≡Os triple bond occurs. For example, $Os_2(O_2CMe)_4Cl_2$ dissolves in concentrated hydrochloric acid to give a yellow solution from which, on addition of $[PPh_3(CH_2Ph)]Cl$, is formed a lemon-yellow precipitate, identical in its i.r. spectrum and electrochemical behaviour to $[PPh_3(CH_2Ph)]_2[Os^{IV}Cl_6]$, prepared by direct reaction of $[PPh_3(CH_2Ph)]Cl$ with $Na_2[OsCl_6]$.[21a] Similarly, treatment of the acetate with aqueous HBr containing some KBr, followed by addition of $[PPh_3(CH_2Ph)]Cl$, gives a high yield of $[PPh_3(CH_2Ph)]_2[Os^{IV}Br_6]$.

Reaction of the acetate with neat acetylacetone (Hacac) under reflux gives a deep red solution from which, on cooling, a small amount of a rather insoluble microcrystalline red solid could be isolated. Analytical and mass spectral data indicate that this is the monomeric complex $Os^{IV}(acac)_2Cl_2$. This osmium(IV) formulation is supported by its electrochemical behaviour in CH_2Cl_2 which shows a reversible one-electron reduction at +0.32 V and an irreversible reduction at −1.51 V. The magnetic moment of 1.29 B.M. at 288 K is also typical of an osmium(IV) complex.[21a] The single ν(OsCl) band at 340 cm^{-1} in the i.r. spectrum indicates a *trans* configuration.

The reaction of an aqueous suspension of the acetate with an excess of $Na[S_2CNMe_2]\cdot 3H_2O$ gives a small amount of dark red powder. The electrochemistry of this material in CH_2Cl_2 which shows only reduction waves (a reversible one at −0.54 V and an irreversible one at −1.37 V) strongly suggests that $Os^{IV}(S_2CNMe_2)_2Cl_2$ {and not $[Os(S_2CNMe_2)_2Cl]_n$ as originally suggested [8b]} is formed.

Thus, it would appear that reaction of the osmium(III) carboxylates with HX and Hacac leads to oxidation of the osmium(III) centres and concomitant bridge cleavage (*cf.* the tendency for quadruply bonded ditungsten species to undergo facile oxidative-addition reactions on treatment with acids [22]).

(*b*) *Reactions with donor ligands.* In contrast to the above reactions, interaction of the acetate with donor ligands such as 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen), and $Ph_2P[CH_2]_2PPh_2$ leads to osmium(II) complexes. Thus, if the acetate is refluxed with an excess of bipy in methanol and the resulting green solution treated with $Na[BPh_4]$, the well known green $[Os(bipy)_3][BPh_4]_2$ is precipitated. Likewise, treatment with phen gives $[Os(phen)_3][BPh_4]_2$. The formulations are based on analytical data and comparison of their electrochemical behaviour and electronic spectra with those previously reported.[21b,23] Although the acetate readily dissolves in pyridine to give a dark red solution, we have so far been unable to isolate any pure species and the solution appears to contain a mixture of compounds with both unidentate and bidentate acetate groups.

The reactions with tertiary phosphines can be complicated. Thus, although the acetate will react with PPh_3, $PMePh_2$, and PMe_2Ph, again no pure compounds could be isolated. However, the acetate dissolves in PMe_3 to give a bright yellow solution from which yellow, air-sensitive crystals could be isolated, and for which analytical and spectroscopic data confirm the formulation *trans*-$Os^{II}(O_2CMe)_2(PMe_3)_4$. The i.r. spectrum of this compound shows a strong band at 1 620 cm^{-1}, indicative of unidentate acetato-groups;[12] the ^{31}P-$\{^1H\}$ n.m.r. spectrum shows a singlet at -38.4 p.p.m. and the ^1H n.m.r. spectrum singlets at δ 1.92 (O_2CMe) and 1.40 (PMe_3) in accord with *trans*-acetato-groups. The similar ruthenium complex, *cis*-$Ru(O_2CMe)_2(PMe_3)_4$, has also been made recently.[24]

This osmium phosphine acetate is an excellent source material for synthesis of other osmium compounds and reactions with alkylating and other reagents will be discussed separately.[25]

The acetate reacts with the diphosphine $Ph_2P[CH_2]_2PPh_2$ (dppe) in methanol to give a low yield of a pale yellow product identified as *trans*-$[OsCl_2(dppe)_2]$ [26] on the basis of analytical data, mass spectrum, i.r., and ^{31}P-$\{^1H\}$ n.m.r. spectroscopy (see Experimental section). Treatment of the dark grey filtrate from the reaction with $Na[BPh_4]$ gives a higher yield of a blue-grey precipitate which on the basis of elemental analysis, ^{31}P-$\{^1H\}$ n.m.r. spectrum, and conductivity measurements in CH_3NO_2 over a concentration range, is formulated as the binuclear osmium(II) complex $[(dppe)_2Os(\mu\text{-}Cl)_2Os(dppe)_2][BPh_4]_2$. The way in which these compounds are formed is far from clear at present.

Isocyanides also react with the acetate. With Bu^tNC in diethyl ether there is a slow reaction (3 d) to give a purple solid for which analytical and spectroscopic data indicate the formulation $Os(O_2CMe)_2Cl(Bu^tNC)_3$ with octahedral osmium(III). When the same reaction is carried out in the presence of sodium amalgam a yellow crystalline material is obtained, for which analytical and spectroscopic data confirm the formulation *trans*-$Os^{II}(O_2CMe)_2(Bu^tNC)_4$. Both compounds show characteristic i.r. bands for isocyanide at 2 060 and 1 200 cm^{-1} and for unidentate acetate at *ca.* 1 620 cm^{-1}. The ruthenium(II) analogue is known.[27] It may be noted that reduction of $[OsCl_2(1,5\text{-}C_8H_{12})]_n$ by potassium amalgam in the presence of t-butyl isocyanide gives $Os(1,5\text{-}C_8H_{12})(Bu^tNC)_3$;[28] $Os(Bu^tNC)_5$ has not yet been made.

The reactions of $[\{Os(O_2CMe)_2Cl\}_2]$ described above are summarised in the Scheme.

Experimental

Microanalyses were by Imperial College, University of Edinburgh, B.M.A.C., and Pascher laboratories. Molecular weights were determined in benzene on a Perkin-Elmer-Hitachi (model 115) osmometer calibrated with benzil. Mass spectra were obtained on an A.E.I. MS902 spectrometer (all peaks quoted for ^{190}Os isotope). Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

Infrared spectra were recorded in the region 4 000—200 cm^{-1} on a Perkin-Elmer 557 grating spectrometer using Nujol or hexachlorobutadiene mulls on caesium iodide plates or potassium bromide discs. N.m.r. spectra (^1H, ^{13}C) were obtained on Bruker WH-360 or WM-250 spectrometers (chemical shifts quoted in p.p.m. to high frequency of $SiMe_4$) and ^{31}P-$\{^1H\}$ spectra on a JEOL-FX60Q spectrometer operating in the pulse and Fourier-transform mode at 22.24 MHz, or on a Bruker WM-250 at 101.27 MHz. Chemical shifts are reported in p.p.m. to high frequency of 85% H_3PO_4. Magnetic measurements were made on a Faraday balance (solid) and in solution by the Evans' method on a Varian Associates HA-100 n.m.r. spectrometer equipped with a variable-temperature probe. Electronic spectra were obtained on Pye-Unicam SP8-400 (solution) and Beckman Acta MIV (solid) spectrophotometers and e.s.r. spectra on a Varian E4 spectrometer employing 100-kHz magnetic field modulation. Electrochemical studies employed a PAR model 170 potentiostat and programmer and NBu_4BF_4 solutions (0.25 mol dm^{-3}) in CH_2Cl_2 (293—213 K) with platinum working and auxiliary electrodes and a Ag–AgI reference electrode (against which ferrocene is oxidised at $E_{\frac{1}{2}} = +0.60$ V). Scan rates were 50-500 mV s^{-1} (c.v.) and 10 mV s^{-1} (a.c.v.) with the frequency of the sinusoidal alternating voltage modulation = 205 Hz.

Conductivity measurements were made in CH_3NO_2 at 303 K using a model 310 Portland Electronics conductivity bridge. Conductivity *vs.* concentration data were obtained over a range of concentrations (1.0×10^{-3}—0.2×10^{-3} mol dm^{-3}) and a plot of Λ_e *vs.* $c_e^{\frac{1}{2}}$ (concentration in mol equivalents) gave a straight line which on extrapolation to $c_e^{\frac{1}{2}} = 0$ gave Λ_0. A subsequent plot of $\Lambda_0 - \Lambda_e$ *vs.* $c_e^{\frac{1}{2}}$ gave a straight line whose slope is a function of the ionic charges.[29] Thus, the slopes obtained were compared with those for known 1 : 1 and 1 : 2 electrolytes and hence the electrolyte type could be determined.

The compounds OsO_4 and $Na_2[OsCl_6]$ were from Johnson Matthey PLC. Analytical data for the osmium compounds are given in Table 3.

Tetra-μ-acetato-dichlorodiosmium(III).—*Method A.* Osmium tetroxide (5 g) was dissolved in concentrated hydrochloric acid (150 cm^3) and anhydrous iron(II) chloride (10 g) added. The mixture was stirred on a steam-bath for *ca.* 4 h, then allowed to cool to room temperature. The solution was extracted several times with diethyl ether and then evaporated to near dryness on a rotary evaporator. To the resulting dark red product was added acetic acid (50 cm^3) and acetic anhydride (50 cm^3) and the solution refluxed for *ca.* 12 h. The precipitate was then collected, washed with methanol, water, diethyl ether, and light petroleum (b.p. 40—60 °C), and dried *in vacuo*. Yield *ca.* 70%.

Method B. Sodium hexachloroosmate (1.0 g), acetic acid (20 cm^3), acetic anhydride (20 cm^3), and concentrated hydrochloric acid (2 cm^3) were refluxed for *ca.* 48 h. The mixture was then filtered and the product washed as above. The yields are very variable but can be as high as 70%. Yields up to *ca.* 40% may also be obtained when sodium hexachloroosmate (0.45 g), sodium acetate (1.0 g), acetic acid (25 cm^3), and ethanol (20 cm^3) are refluxed for *ca.* 48 h.

The compound is insoluble in organic solvents other than those like pyridine with which it reacts. I.r.: $\nu_{asym}(CO_2)$ 1 450 cm^{-1}, $\nu_{sym}(CO_2)$ 1 380 cm^{-1}; $\Delta(\nu_{asym} - \nu_{sym}) = 70$ cm^{-1}. Mass spectrum: *m/e* 687 $[Os_2(O_2CMe)_4Cl_2]^+$; 652, $[Os_2(O_2CMe)_4Cl]^+$; 617, $[Os_2(O_2CMe)_4]^+$. Magnetic moment (solid); $\mu_{eff.}$ 1.17 B.M. per Os (288 K) to 0.95 B.M. per Os (209 K). Electronic spectrum (200—900 nm, solid state reflectance): 260 (br) and 370 nm (br).

Table 3. Analytical data for new compounds

Compound	M.p./°C	Analysis (%)[a] C	H	Cl
$Os_2(O_2CMe)_4Cl_2$	273—275	14.1 (14.0)	1.7 (1.7)	10.5 (10.3)
$Os_2(O_2CEt)_4Cl_2$	238—240	19.2 (19.4)	2.7 (2.7)	9.6 (9.6)
$Os_2(O_2CPr^n)_4Cl_2$	169—171 (decomp.)	24.2 (24.0)	3.5 (3.5)	9.0 (8.9)
$Os_2(O_2CCH_2Cl)_4Cl_2$	251—253	11.7 (11.5)	1.0 (1.0)	23.2 (25.5)
$Os(acac)_2Cl_2$	268—270 (decomp.)	26.5 (26.1)	2.9 (3.1)	15.0 (15.5)
$Os_2(ONHCCF_3)_4Cl_2$	>270	10.9 (10.7)	0.6 (0.5)	N 6.0 (6.2)
$Os(S_2CNMe_2)_2Cl_2$	>250	15.6 (14.4)	2.5 (2.4)	N 5.8 (5.6)
$Os(O_2CMe)_2(PMe_3)_4$[b]	141	31.2 (31.3)	6.9 (6.9)	P 18.7 (20.2)
$[Os_2Cl_2(dppe)_4][BPh_4]_2$	171 (decomp.)	66.5 (68.0)	5.1 (5.1)	
$Os(O_2CMe)_2Cl(Bu^tNC)_3$	>360	38.6 (38.5)	5.7 (5.6)	6.2 (7.0) N 7.0 (7.1)
$Os(O_2CMe)_2(Bu^tNC)_4$[c]	142	44.0 (44.9)	6.6 (6.6)	N 8.3 (8.7)

[a] Required values in parentheses. [b] *M* (cryoscopy in benzene) 580 (612). [c] *M* (cryoscopy in benzene) 605 (640).

*Dichlorotetra-*μ*-propionato-diosmium*(III).—The acetate (0.12 g, 0.17 mmol) was heated in n-propionic acid (15 cm^3) at *ca.* 140 °C for 6 h, then cooled slowly to yield a dark green solid which was collected, washed with methanol and diethyl ether, and dried *in vacuo*. Yield 0.03 g (23%). The compound is soluble in CH_2Cl_2 and sparingly soluble in Me_2CO.

I.r.: $\nu_{asym}(CO_2)$ 1 478 cm^{-1}, $\nu_{sym}(CO_2)$ 1 375 cm^{-1}; $\Delta(\nu_{asym} - \nu_{sym}) = 103$ cm^{-1}. Mass spectrum: *m/e* 743, $[Os_2(O_2CEt)_4Cl_2]^+$; 708, $[Os_2(O_2CEt)_4Cl]^+$; and 673, $[Os_2(O_2CEt)_4]^+$. Magnetic moment in CH_2Cl_2; $\mu_{eff.}$ 1.13 B.M. per Os (300 K) to 1.02 B.M. per Os (188 K) (Curie–Weiss constant $\theta = -173$ K). Electronic spectrum (200—900 nm in CH_2Cl_2): 222 ($\varepsilon = 15\,600$), 244 (sh), 277 (5 800), 364 (sh), and 392 nm (10 800 dm^3 mol^{-1} cm^{-1}).

*Tetra-*μ*-n-butyrato-dichlorodiosmium*(III).—This was prepared as above from the acetate and n-butyric acid (yield 57%). The compound is soluble in CH_2Cl_2, C_6H_6, and Me_2CO. Molecular weight (osmometrically in C_6H_6): 832 (1.20×10^{-3}); 786 (0.85×10^{-3}); 777 (0.51×10^{-3} mol dm^{-3}); requires 799. I.r.: $\nu_{asym}(CO_2)$ 1 471 cm^{-1}, $\nu_{sym}(CO_2)$ 1 358 cm^{-1}; $\Delta(\nu_{asym} - \nu_{sym}) = 113$ cm^{-1}. Mass spectrum: *m/e* 799, $[Os_2(O_2CPr^n)_4Cl_2]^+$; 764, $[Os_2(O_2CPr^n)_4Cl]^+$; and 729, $[Os_2(O_2CPr^n)_4]^+$. Magnetic moment in CH_2Cl_2: $\mu_{eff.}$ 1.15 B.M. per Os (300 K) to 1.02 B.M. per Os at 188 K (Curie–Weiss constant $\theta = -260$ K). Electronic spectrum (200—900 nm) in CH_2Cl_2: 223 ($\varepsilon = 15\,800$), 260 (sh), 278 (6 100), 360 (sh), and 392 nm (10 400 dm^{-3} mol^{-1} cm^{-1}).

*Tetra-*μ*-chloroacetato-dichlorodiosmium*(III).—The acetate (0.11 g, 0.16 mmol) was heated with an excess of molten monochloroacetic acid (8 g) at 120 °C for 3 h; the cooled solid was washed with diethyl ether and the green microcrystalline residue dried *in vacuo*. Yield 0.06 g (45%). The compound rapidly decomposes in CH_2Cl_2 and is insoluble in other solvents. I.r.: $\nu_{asym}(CO_2)$ 1 467 cm^{-1}, $\nu_{sym}(CO_2)$ 1 388 cm^{-1}; $\Delta(\nu_{asym} - \nu_{sym}) = 79$ cm^{-1}. Mass spectrum: *m/e* 825, $[Os_2(O_2CCH_2Cl)_4Cl_2]^+$; 790, $[Os_2(O_2CCH_2Cl)_4Cl]^+$; and 755, $[Os_2(O_2CCH_2Cl)_4]^+$. Electronic spectrum (200—900 nm, solid-state reflectance): 260 (br) and 357 nm (br).

Reactions of the Acetate.—(1) *With* 2-*hydroxypyridine*. The acetate (0.10 g, 0.14 mmol) was refluxed in degassed methanol (30 cm^3) containing an excess of 2-hydroxypyridine (1.0 g) for 3 h when the volume was reduced to 20 cm^3 and the resulting dark red-purple solid collected was washed with methanol and diethyl ether and dried *in vacuo*. Yield, 0.06 g (51%). M.p. >250 °C. The compound is soluble in CH_2Cl_2, Me_2CO, and MeCN (Found: C, 28.0; H, 1.9; N, 6.7. Calc. for $C_{20}H_{16}Cl_2N_4O_4Os_2$: C, 29.0; H, 2.0, N, 6.8%). Mass spectrum: *m/e* 827, $[Os_2(NC_5H_4O\text{-}2)_4Cl_2]^+$; 792, $[Os_2(NC_5H_4O\text{-}2)_4Cl]^+$; and 757, $[Os_2(NC_5H_4O\text{-}2)_4]^+$. Magnetic moment in CH_2Cl_2: $\mu_{eff.}$ 1.44 B.M. per Os (300 K) to 1.22 B.M. per Os (195 K). Electronic spectrum (200—900 nm) in CH_2Cl_2: 222 ($\varepsilon = 27\,000$), 282 (16 100), and 488 nm (5 700 dm^3 mol^{-1} cm^{-1}).

(2) trans-*Bis*(*acetylacetonato*)*dichloroosmium*(IV). The acetate (0.10 g, 0.14 mmol) was refluxed in acetylacetone (5 cm^3) for 6 h to give a dark red solution which deposits on cooling a microcrystalline red solid. The latter was collected, washed with water, methanol, and diethyl ether, and dried *in vacuo*. Yield 0.01 g (15%). The compound is slightly soluble in CH_2Cl_2. I.r.: ν(OsCl) 340 cm^{-1}. Mass spectrum: *m/e* 459, $[Os(acac)_2Cl_2]^+$; and 424, $[Os(acac)_2Cl]^+$. Magnetic moment (solid state): $\mu_{eff.} = 1.29$ B.M. (288 K). Electronic spectrum (200—900 nm) in CH_2Cl_2: 275 ($\varepsilon = 11\,600$), 343 (6 700), 362 (sh), and 544 nm (2 600 dm^3 mol^{-1} cm^{-1}).

(3) *Dichlorotetra-*μ*-2,2,2-trifluoroacetamido-diosmium*(III). The butyrate (0.10 g, 0.13 mmol) was heated in an excess of molten 2,2,2-trifluoroacetamide (3.0 g) at 110 °C for 1.5 h. The cooled melt was washed with diethyl ether to remove the trifluoroacetamide and with methylene chloride to remove any unreacted osmium butyrate. The orange-brown product was then dried *in vacuo*. Yield 0.02 g (18%). The compound is insoluble in all common solvents.

(4) *With hydrochloric acid*. The acetate (0.15 g, 0.22 mmol) was warmed in hydrochloric acid (20 cm^3, 18 mol dm^{-3}) to give a yellow solution. Addition of $[PPh_3(CH_2Ph)]Cl$ led to the slow precipitation of the crystalline $[PPh_3(CH_2Ph)]_2[OsCl_6]$ which was collected, washed with water, methanol, and diethyl ether, and dried *in vacuo*. Yield 0.31 g (64%) (Found: C, 53.7; H, 3.9. Calc. for $C_{50}H_{44}Cl_6OsP_2$: C, 54.1; H, 4.0%). The same compound was precipitated by treating an aqueous solution of $Na_2[OsCl_6]$ with $[PPh_3(CH_2Ph)]Cl$. Electrochemistry (293 K): −0.54 V (one electron reversible reduction), −1.62 V (irreversible reduction), and +1.40 V (one-electron reversible oxidation).

(5) *With hydrobromic acid*. The acetate (0.10 g, 0.14 mmol) was stirred with warming in concentrated hydrobromic acid (15 cm^3) containing KBr (1.0 g) to give a deep red solution. After addition of $[PPh_3(CH_2Ph)]Cl$ the product was extracted into methylene bromide. This was evaporated to dryness and the solid recrystallised from methanol. Yield 0.14 g (35%) (Found: C, 43.7; H, 3.3. Calc. for $C_{50}H_{44}Br_6OsP_2$: C, 43.6; H, 3.2%). Electrochemistry (293 K): −0.32 V (one-electron reversible reduction), −1.70 V (irreversible reduction) and +1.46 V (one-electron reversible oxidation).

(6) *Dichlorobis*(N,N-*dimethyldithiocarbamato*)*osmium*(IV). The acetate (0.15 g, 0.21 mmol) was refluxed with an aqueous solution of $Na[S_2CNMe_2]\cdot 3H_2O$ (0.55 g, 2.5 mmol in 15 cm^3 water) for 6 h. The dark red powder formed was collected, washed with water, ethanol, and diethyl ether, and then dried *in vacuo*. Yield 0.02 g (18%).

(7) *With* 2,2′-*bipyridyl or* 1,10-*phenanthroline*. The acetate (0.12 g, 0.17 mmol) was refluxed with an excess of 2,2′-

bipyridyl (1.0 g) in degassed methanol (25 cm^3) for 3 h to give a dark green solution which was filtered. Sodium tetraphenylborate (0.30 g) was added and the precipitated green solid collected, washed with methanol, and then recrystallised from CH_2Cl_2. Yield 0.25 g (56%) (Found: C, 70.9; H, 4.8; N, 6.4. Calc. for $C_{78}H_{64}BN_6Os$: C, 72.2; H, 5.0; N, 6.5%). Electrochemistry (293 K): reversible one-electron reductions at -1.05, -1.31, and -1.64 V; irreversible oxidation at $+1.06$ V. Similarly prepared was $[Os(phen)_3][BPh_4]_2$.

(8) trans-*Bis(acetato)tetrakis(trimethylphosphine)osmium*(II). The acetate (*ca.* 1.0 g) was stirred in PMe_3 (5 cm^3) under nitrogen for 24 h at room temperature, then the excess PMe_3 was removed and the residue extracted several times with diethyl ether. The filtered solution was reduced in volume and cooled to -10 °C to give air-sensitive yellow crystals. Yield 80%. N.m.r.: ^{1}H (in C_6D_6 at 301 K), δ 1.92 (O_2CMe), 1.40 p.p.m. (PMe_3); ^{31}P-{^{1}H}, δ -38.4 p.p.m. (PMe_3).

The same compound is also obtained when $Os_2(O_2CMe)_4Cl_2$ suspended in thf containing excess of PMe_3 is stirred in the presence of sodium amalgam under 5 atm hydrogen for *ca.* 12 h.

(9) *With* 1,2-*bis(diphenylphosphino)ethane*. The acetate (0.15 g, 0.22 mmol) was refluxed with $Ph_2P[CH_2]_2PPh_2$ (1.0 g) in degassed methanol (20 cm^3) for 4 h. The solution was cooled and the pale yellow *solid* filtered off, washed with methanol and diethyl ether, and then dried *in vacuo*. Yield 0.04 g (9%). M.p. $>$275 °C (Found: C, 60.8; H, 4.6. Calc. for $C_{52}H_{48}Cl_2OsP_4$: C, 59.9; H, 4.6%). I.r.: ν(OsCl) 343 cm^{-1}. Mass spectrum: *m/e* 1 057, $[OsCl_2(dppe)_2]^+$; 1 022, $[OsCl(dppe)_2]^+$; and 987, $[Os(dppe)_2]^+$. ^{31}P-{^{1}H} n.m.r. in CD_2Cl_2 at 301 K: δ 7.30 (s) p.p.m. The compound is sparingly soluble in CH_2Cl_2.

Addition of $Na[BPh_4]$ (0.40 g) to the dark grey filtrate gave a blue-grey precipitate of $[Os_2Cl_2(dppe)_4][BPh_4]_2$, which was collected, washed with methanol and diethyl ether, and dried *in vacuo*. Yield 0.18 g (31%). ^{31}P-{^{1}H} N.m.r. in CD_2Cl_2 at 301 K: δ 36.5 (t) and 5.5 (t) p.p.m., ^2J(P–P) 4.4 Hz. Conductivity in CH_3NO_2 at 303 K: slope of $\Lambda_0 - \Lambda_e$ *vs.* $c_e^{\frac{1}{2}}$ plot = 735 (typical of 1 : 2 electrolyte).[29] The compound is also soluble in acetone.

(10) *Bis(acetato)chlorotris(t-butyl isocyanide)osmium*(III). t-Butyl isocyanide (0.5 cm^3) was added to a suspension of $Os_2(O_2CMe)_4Cl_2$ (0.5 g) in diethyl ether (30 cm^3) and the mixture stirred at room temperature for 3 d. The solution was then filtered, the filtrate evaporated in vacuum, and the solid extracted with methanol (10 cm^3). After filtration and concentration to 3 cm^3, cooling to -20 °C gave a purple solid which was collected, washed with hexane, and vacuum dried. Yield 0.1 g (29%). N.m.r.: ^{1}H, δ 1.30 (CMe_3) and 1.15 p.p.m. (O_2CMe).

(11) *Bis(acetato)tetrakis(t-butyl isocyanide)osmium*(II). To a suspension of the acetate (0.4 g) in thf (40 cm^3), left stirring over an excess of sodium amalgam for *ca.* 15 min, was added excess of Bu^tNC. The solution was left to stir at room temperature for 24 h, then filtered, and the filtrate evaporated in vacuum. The resulting solid was extracted with diethyl ether to give a deep yellow solution from which $Os(O_2CMe)_2(Bu^tNC)_4$ was isolated on cooling. Yield 0.37 g (50%). N.m.r.: ^{1}H (in C_6D_6 at 301 K), δ 2.05(1) (O_2CMe) and 1.41(6) ($NCBu^t$); ^{13}C-{^{1}H}, δ 22.3 (O_2CMe), 3.1 ($CNCMe_3$), and 57.7 (CNC).

Crystallographic Studies.—Crystal data. $C_{16}H_{28}Cl_2O_8Os_2$, $M = 799$, Monoclinic, dark green needles, $a = 6.789(2)$, $b = 11.790(1)$, $c = 14.923(1)$ Å, $\beta = 98.211(18)°$, $U = 1\,182$ Å^3, $Z = 2$, $D_c = 2.25$ g cm^{-3}, $F(000) = 748$, space group $P2_1/n$ [alternative setting for $P2_1/c$ (no. 14)], Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 116.8$ cm^{-1}.

A crystal of dimensions 0.35 × 0.18 × 0.04 mm was used to collect 2 100 unique data out to $\theta = 25°$ on a Nonius CAD-4 diffractometer. The position of the Os atoms was determined from a Patterson map. Subsequent difference-Fourier synthesis revealed all non-hydrogen atoms in the molecule. Structure refinement was carried out using SHELX.[30] In the final cycles of least-squares refinement Os, O, C, and Cl were given anisotropic vibration parameters. No hydrogen atoms were included. The weighting scheme $w = 1.0/[\sigma^2(F) + 0.000\,89F^2]$ was applied. The final R factor was 0.044 based on 1 686 reflections with $I > 2.5\sigma(I)$.

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