Electrochemically induced Ligand Substitutions on [OsCl$_3$(PMe$_2$Ph)$_3$]: Rational Pathways to Osmium(II) Complexes

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Following electroreduction of [OsCl$_3$(PMe$_2$Ph)$_3$] it is possible to stabilise and characterise the reactive monoanion [OsCl$_3$(PMe$_2$Ph)$_3$]$^-$. This monoanion readily releases chloride to give a detectable five-co-ordinate intermediate which further reacts with a donor solvent or available ligands to produce [OsCl$_2$(PMe$_2$Ph)$_3$L] (L = MeCN, dimethylformamide, dimethyl sulphoxide, PhCN, CO, N$_2$, or C$_2$H$_4$), initially as the *trans* isomer. The latter can be converted into the *cis* form. When L = PMe$_2$Ph, the '*trans* isomer' formed is not *trans*-[OsCl$_2$(PMe$_2$Ph)$_4$] and should be formulated as *trans*-[OsCl$_2$(PMe$_2$Ph)$_3$(P'Me$_2$Ph)] with a unique weakly bound phosphine. In non-co-ordinating media, concentrated solutions of [OsCl$_2$(PMe$_2$Ph)$_3$] undergo further reactions to form doubly and triply bridged binuclear species such as [Os$_2$Cl$_4$(PMe$_2$Ph)$_6$] and [Os$_2$Cl$_3$(PMe$_2$Ph)$_6$]$^+$. This series of electroinitiated reactions of *mer*-[OsCl$_3$(PMe$_2$Ph)$_3$] has so far yielded over 20 separate complexes individually identified by both spectroscopic methods and voltammetric data.

In order to complement detailed studies on redox-active binuclear ruthenium complexes in this laboratory,$^{1-3}$ we have examined the chemistry of *mer*-[OsCl$_3$(PMe$_2$Ph)$_3$] (**1**) as a possible starting point for rational syntheses of triply halide-bridged diosmium complexes such as [(PMe$_2$Ph)$_3$Os-Cl$_3$Os(PMe$_2$Ph)$_3$]$^+$ and [(PMe$_2$Ph)$_2$ClOsCl$_3$Os(PMe$_2$Ph)$_3$]. Chemical reduction of (**1**) results ultimately in the triply halide-bridged diosmium complex.^{4} However, the mechanistic pathway is unknown and the chemical by-products complicate identification of the reduction products. Thus we have used electrochemical methods in parallel with spectroscopic techniques to elucidate the problem.

The monomer (**1**) has a rewarding electrochemical response, and we have been able to prepare the anion *mer*-[OsCl$_3$(PMe$_2$Ph)$_3$]$^-$ (**2**) together with several [OsCl$_2$(PMe$_2$Ph)$_3$L] complexes [where L = dimethylformamide (dmf), PhCN, MeCN, *etc.*] in both *cis*- and *trans*-dichloro-forms. The *trans* isomer is that initially formed by electrogeneration, in contrast to chemical reduction which generally yields only the thermodynamically favoured *cis* isomers. Furthermore, under appropriate conditions diosmium complexes are indeed the ultimate products. All the various osmium(II) compounds have been individually characterised by i.r., n.m.r., and voltammetric measurements.

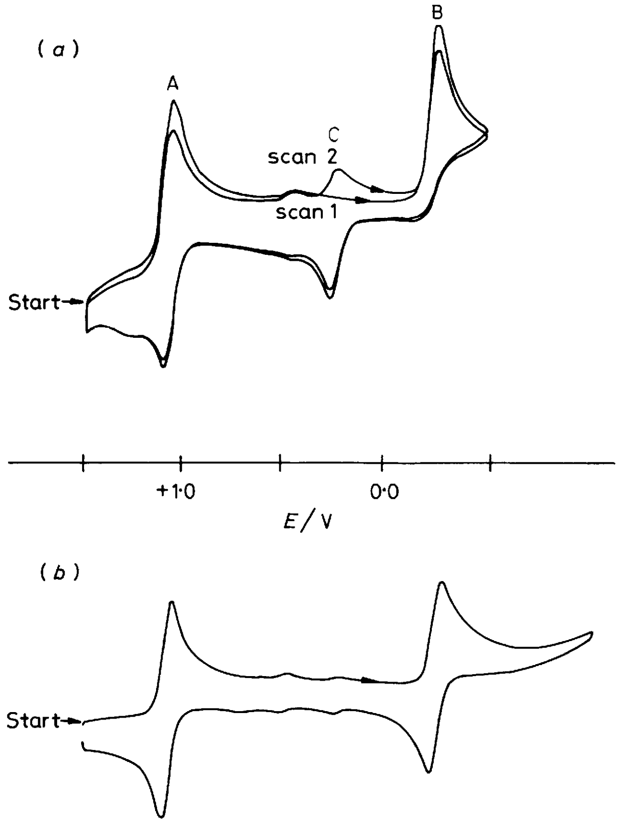


Figure 1. Cyclic voltammograms of *mer*-[OsCl$_3$(PMe$_2$Ph)$_3$] in CH$_2$Cl$_2$–[NBu$_4$][BF$_4$] under argon *vs.* Ag–AgCl (scan rate 100 mV s^{-1}) at 293 (*a*) and 233 K (*b*)

Results and Discussion

A cyclic voltammogram of *mer*-[OsCl$_3$(PMe$_2$Ph)$_3$] in CH$_2$Cl$_2$ under argon at room temperature is shown in Figure 1(*a*). The oxidation [A in Figure 1(*a*)] is assigned as an $\mathrm{Os^{III}} \longrightarrow \mathrm{Os^{IV}}$ + e electrode process and the reduction (B) as an $\mathrm{Os^{III}}$ + e $\longrightarrow \mathrm{Os^{II}}$ electrode process with a rapid 'chemical' (*i.e.* homogeneous) subsequent reaction. Figure 1 also shows that when the solution temperature is decreased to 233 K then the reduction becomes totally reversible (the ratio of the anodic to cathodic peak currents is 1.0 and the anodic-to-cathodic peak separation is 50 mV, compared with the theoretical value of 44 mV for a Nernstian one-electron wave at 233 K). It is therefore possible to stabilise the anion [OsCl$_3$(PMe$_2$Ph)$_3$]$^-$ (**2**) for some seconds simply by altering the temperature. However, adequate characterisation of the anion demands a much longer lifetime, and this has been achieved by variation of the solvent/electrolyte composition. A fully reversible voltammogram [resembling Figure 1(*b*)] can be obtained at room temperature in CH$_2$Cl$_2$ by replacing the supporting electrolyte [NBu$_4$][BF$_4$] by [NR$_3$Me][BF$_4$] (R = C$_8$H$_{17}$ to C$_{10}$H$_{21}$), or by using tetrahydrofuran (thf) with [NBu$_4$][BF$_4$]. Remarkably, either system allows bulk electrogeneration under argon of (**2**) which is bright yellow [(**1**) is dark red], with no loss of the product even

Table. N.m.r. and electrochemical data for derivatives of $[OsCl_3(PMe_2Ph)_3]$

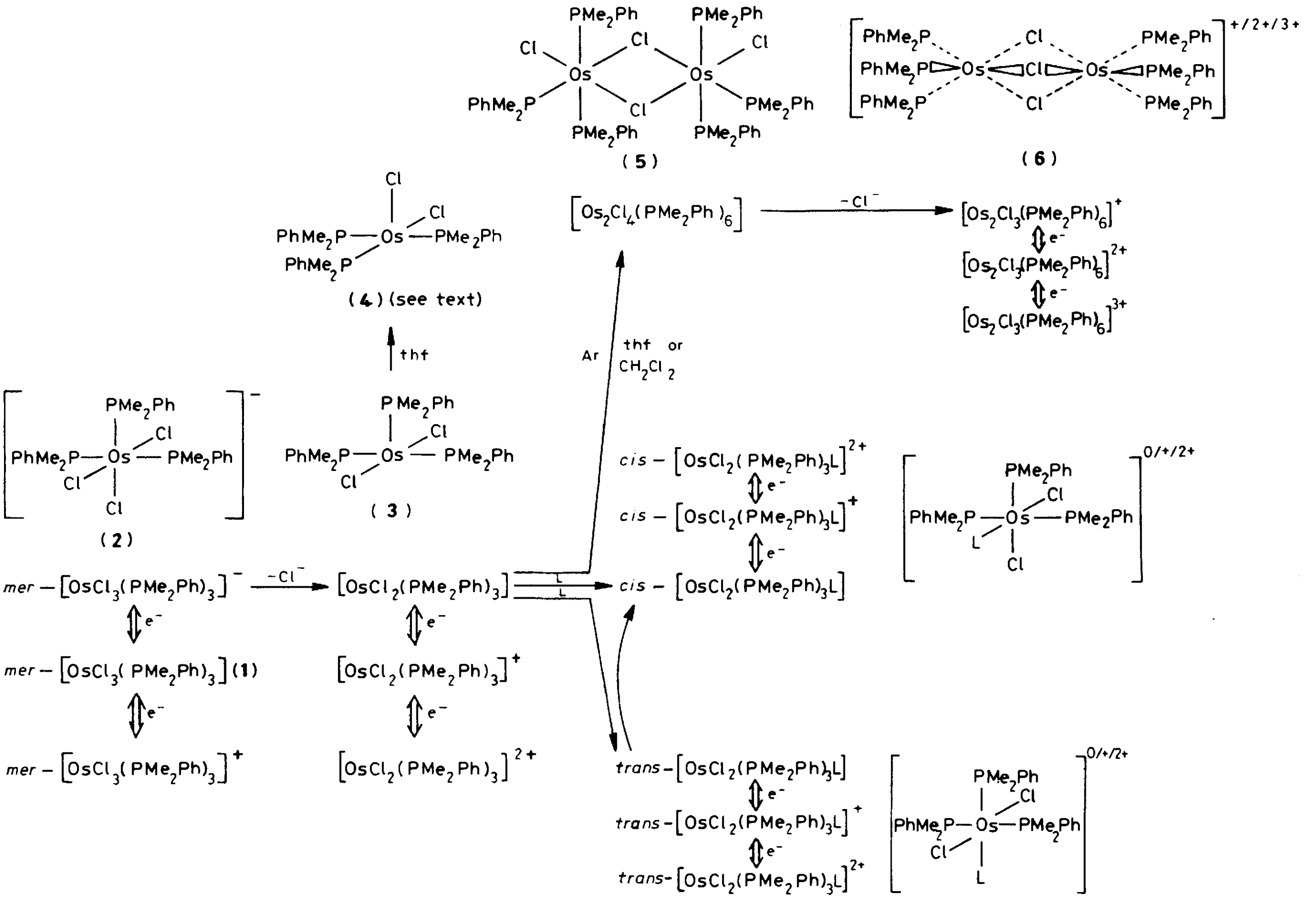
Compound	Solvent	^{31}P-$\{^1H\}$ N.m.r.[a]			$E_{\frac{1}{2}}$ $(Os^{II}$–$Os^{III})$[b]
		δ_A/p.p.m.	δ_B/p.p.m.	J_{AB}/Hz	
trans-$[OsCl_3(PMe_2Ph)_3]^-$	thf[c]	−42.7	−45.1	12.2[d]	−0.36
trans-$[OsCl_2(PMe_2Ph)_3]$	CH_2Cl_2[e]	−46.7	−33.6	22.0[d]	+0.03
	thf[c]	−44.8	−32.8	17.1[d]	+0.03
cis-$[OsCl_2(PMe_2Ph)_3]$	thf[c]	−49.4	−27.6	17.1[d]	
trans-$[OsCl_2(PMe_2Ph)_3(MeCN)]$	CH_2Cl_2	−47.7	−35.9	22.0[d]	+0.25
cis-$[OsCl_2(PMe_2Ph)_3(MeCN)]$	MeCN	−31.3	−31.9	20.6[f]	+0.25
trans-$[OsCl_2(PMe_2Ph)_3(dmf)]$	CH_2Cl_2	−47.5	−28.6	18.3[d]	+0.02
cis-$[OsCl_2(PMe_2Ph)_3(dmf)]$	dmf	−30.5	−31.3	15.0[f]	+0.02
trans-$[OsCl_2(PMe_2Ph)_3(dmso)]$	dmso	−44.1	−38.7	17.1[d]	+0.02
trans-$[OsCl_2(PMe_2Ph)_3(PhCN)]$	PhCN	−47.3	−38.3	22.0[d]	*ca.* +0.26
cis-$[OsCl_2(PMe_2Ph)_3(PhCN)]$	PhCN	−31.3	−31.5	n.a.	*ca.* +0.26
trans-$[OsCl_2(PMe_2Ph)_3(CO)]$	CH_2Cl_2	−46.4	−43.5	30.1[f]	+0.83
trans-$[OsCl_2(PMe_2Ph)_3(C_2H_4)]$	CH_2Cl_2	−48.5	−39.1	15.9[d]	+0.54
trans-$[OsCl_2(PMe_2Ph)_3(N_2)]$	thf	−47.8	−37.3	22.0[d]	+0.16
cis-$[OsCl_2(PMe_2Ph)_3(N_2)]$	thf	−36.3	−34.9	15.1[f]	
trans-$[OsCl_2(PMe_2Ph)_4]$	CH_2Cl_2	−52,5[g]			+0.28
cis-$[OsCl_2(PMe_2Ph)_4]$	CH_2Cl_2	−43.8	−44.9	13.4[f]	+0.75
$[Os_2Cl_4(PMe_2Ph)_6]$	CH_2Cl_2[e]	−44.8	−40.0	17.1[d]	+0.48
$[Os_2Cl_3(PMe_2Ph)_6]^+$	CH_2Cl_2	−36.7[g]			+1.09

[a] All resonances lie to high frequency of the H_3PO_4 reference. All values determined at room temperature (except where specified). [b] All values are measured with respect to a Ag–AgCl, $[NBu_4][BF_4]$–CH_2Cl_2 reference electrode, against which ferrocene is oxidised at +0.55 V in CH_2Cl_2. Values measured in solvents other than CH_2Cl_2 (see Table) include uncorrected junction potentials. The latter were checked in MeCN and dmf and found to be negligible (< 10 mV). [c] Measured at 230 K. [d] Triplet (δ_A) and doublet (δ_B) at 24.2 MHz. [e] Measured at 200 K. [f] AB_2 pattern at 24.2 MHz. [g] Singlet.

after several hours. The ^{31}P-$\{^1H\}$ n.m.r. spectrum of complex (**2**) consists of a typical triplet and doublet (see Table), indicating that the anion retains a *mer* configuration, in common with its osmium(III) precursor.

In contrast, if the electrosynthesis is carried out at room temperature in CH_2Cl_2–$[NBu_4][BF_4]$ or thf–$Li[ClO_4]$ under argon a yellowish green solution is formed. This solution contains no $[OsCl_3(PMe_2Ph)_3]$ or $[OsCl_3(PMe_2Ph)_3]^-$; however, it is diamagnetic and is found to contain free chloride and a new osmium(II) complex, represented respectively by an irreversible oxidation wave at +1.20 V and a reversible oxidation wave at +0.03V. The chloride can be removed from solution by addition of 1 mol equivalent of sodium tetrafluoroborate. Thus the rapid chemical reaction which occurs after reduction of complex (**1**) is loss of a chloride ligand to give $[OsCl_2(PMe_2Ph)_3]$, (**3**). The exact nature of (**3**) is uncertain but our various observations (see below) support the monomeric formulation shown. The analogous complex $[RuCl_2(PPh_3)_3]$ has square-pyramidal co-ordination both in the solid and in solution.[5,6] La Placa and Ibers [5] suggest that the stability of this structure arises from intramolecular blocking of the vacant sixth site by a phosphine phenyl ring, whereas Brookhart and Green [7] have argued for an 'agostic' bonding interaction involving the metal centre and an *ortho*-hydrogen atom of the adjacent phenyl group. Equally for (**3**), a *trans* dichloro-square-pyramidal arrangement is consistent with its ^{31}P n.m.r. spectrum (Table) and with its further reactions (see below). The designation 'five-co-ordinate' herein should be taken to embrace the possibility of special axial interactions. In thf, where the n.m.r. spectroscopic data are better defined, a further clear-cut rearrangement of complex (**3**) is observed. This is tentatively assigned to the *trans*- to *cis*-dichloro-conversion of (**3**) in to (**4**) (Scheme), although weak binding of thf is not excluded by the available data. In summary, as shown in the Scheme, *mer*-$[OsCl_3(PMe_2Ph)_3]$ on reduction loses the chloride ligand *trans* to phosphine to give the intermediate species (**3**), which exhibits its own distinctive redox behaviour [see Table and process C in Figure 1(*a*)]. This is an example of an electrochemical e.c.e. mechanism, *i.e.* an electron transfer, followed by a chemical change, followed by an electron transfer.[8]

We have extended our electrochemical studies of compound (**1**) to a variety of co-ordinating solvents such as acetonitrile (MeCN), dimethylformamide (dmf), dimethyl sulphoxide (dmso), and benzonitrile (PhCN). The redox behaviour and the peak potentials for the Os^{III}–Os^{IV} and Os^{II}–Os^{III} couples of (**1**) itself are independent of solvent and the voltammograms are similar in appearance to those in Figure 1. However, when determined by slow-scan voltammetry or after bulk reduction of compound (**1**), $E_{\frac{1}{2}}$ for the Os^{II}–Os^{III} couple of the *chemically altered* osmium(II) product is dependent on the solvent, occurring for example at +0.02 V in dmf but at 0.26 V in PhCN (Table). Conveniently, the product formed by electroreduction of (**1**) in MeCN largely precipitates from solution. This yellow product, with stoicheiometry $[OsCl_2(PMe_2Ph)_3(MeCN)]$, darkens and decomposes over several days in air. Its configuration is established as the *trans* isomer (Scheme) from its ^1H n.m.r. spectrum in CD_2Cl_2 which shows a triplet (intensity 2) and a doublet (intensity 1) for the methyl resonances (see Experimental section).[9] The MeCN ligand remains firmly bound to the osmium(II) centre as shown by the singlet ^1H n.m.r. signal at δ 1.30 p.p.m. and there is no evidence for free MeCN (singlet at δ 2.00 p.p.m.). The ^{31}P-$\{^1H\}$ n.m.r. spectrum of the *trans* isomer in CH_2Cl_2 shows the expected doublet and triplet [Table, Figure 2(*a*)]. The same signals are observed in the mother-liquor immediately after electroreduction of compound (**1**) since the *trans* product is slightly soluble in MeCN. However, if the solution is left standing at 293 K in the absence of air, these signals decrease in intensity and new ones steadily emerge until only the new signals [an AB_2 pattern, Figure 2(*b*)] are present after 16 h. This final, almost colourless, solution shows no evidence of free PMe_2Ph or Cl^- (beyond the 1 mol equivalent released during the electrosynthesis) and has an electrochemistry almost indistinguishable from the *trans* isomer. This indicates that the sparingly soluble *trans* isomer is the kinetically favoured product and this slowly converts in solution into the thermodynamically favoured *cis* isomer. Accordingly, in the ^1H



Scheme. L = PMe_2Ph (see text), PhCN, MeCN, dmf, N_2, C_2H_4, CO, or dmso

n.m.r. spectrum in CD_3CN[9] the initial triplet and doublet for the *trans* isomer are replaced by two triplets and a doublet (intensity 1:1:1) characteristic of the *cis* isomer (see Experimental section). The *cis* isomer was not isolated but it is noticeably more stable towards aerial oxidation in solution than the *trans* isomer.

Parallel behaviour is found when dmf is used as the electrochemical solvent. Thus the yellow *trans* isomer $[OsCl_2(PMe_2Ph)_3(dmf)]$ precipitates as electroreduction of (**1**) proceeds but the material remaining in solution converts into the *cis* isomer over several hours. N.m.r. and voltammetric data for both isomers are given in the Table. The i.r. spectrum of the *trans* isomer [ν(CO) 1 630 cm^{-1}] indicates O-bonded dmf. In CH_2Cl_2 at *ca.* 200 K the dmf isomer is indefinitely stable, however at room temperature the voltammetry, $^{31}P-\{^1H\}$ n.m.r. and i.r. spectra all change steadily until, after *ca.* 2 h, only signals for a new species are observed. Thus the $E_{\frac{1}{2}}$ value shifts from + 0.02 to +0.20 V, the $^{31}P-\{^1H\}$ n.m.r. spectrum now consists of a doublet at δ −36.2 and a triplet at −47.9 p.p.m., and the i.r. spectrum shows the ν(CO) band shifted to 1 660 cm^{-1}. Since free dmf absorbs at 1 675 cm^{-1}, we tentatively suggest that the dmf ligand is no longer oxygen-bound, but rather nitrogen-bound to the osmium atom. A similar phenomenon is observed in dmso; the initial, presumably oxygen-bound, dmso in the *trans* complex quickly arranges to the thermodynamically favoured sulphur-bound *trans* analogue. The poor affinity of the osmium(II) centre for O-donor ligands is also reflected in the observation that neither thf nor propylene carbonate binds to complex (**3**).

A direct consequence of the reaction sequence postulated in the Scheme is that the rate of chloride loss from the anion (**2**) to form the five-co-ordinate $[OsCl_2(PMe_2Ph)_3]$ (**3**) should be independent of solvent (*i.e.* the products are formed *via* a dissociative mechanism, rather than by an associative mechanism involving solvent co-ordination). The rate of chloride loss (k_f) was measured according to the method of Nicholson and Shain[10] in CH_2Cl_2–$[NBu_4][BF_4]$, MeCN–$[NBu_4][BF_4]$, or dmf–$[NBu_4][BF_4]$ and in every case k_f = 5 s^{-1} at 288 K. The 'following reaction',[8] uptake of L to form $[OsCl_2(PMe_2Ph)_3L]$, ranges from very fast (when L = MeCN, where the five-co-ordinate intermediate could not be observed under any conditions) to rates at which the intermediate was detectable using fast-scanning techniques (*e.g.* L = N_2, see below). The rate of chloride loss can of course be retarded by decreasing the temperature, as noted above.

Other complexes of type $[OsCl_2(PMe_2Ph)_3L]$ (L = CO, N_2, or C_2H_4) can readily be prepared from solutions of electrogenerated (**3**) in CH_2Cl_2–$[NBu_4][BF_4]$ continuously saturated with the relevant gas (see Table for $^{31}P-\{^1H\}$ n.m.r. and voltammetric data). When L = CO, the *trans* isomer is formed [ν(CO) 1 950 cm^{-1} in electrolyte solution; lit.,[4] ν(CO) 1 947 (*trans*), 1 930 cm^{-1} (*cis*)]. There is no evidence of rearrangement even after several days in solution at ambient temperature, but on heating the solution the *cis* isomer is readily produced.

Previous attempts to prepare *trans*-$[OsCl_2(PMe_2Ph)_3(N_2)]$ have been unsuccessful, with only the *cis* isomer being formed.[4,11] This failure was ascribed to the dinitrogen having too weak a σ-donor function to bind *trans* to a high *trans*-influence ligand such as PMe_2Ph. However we find that on

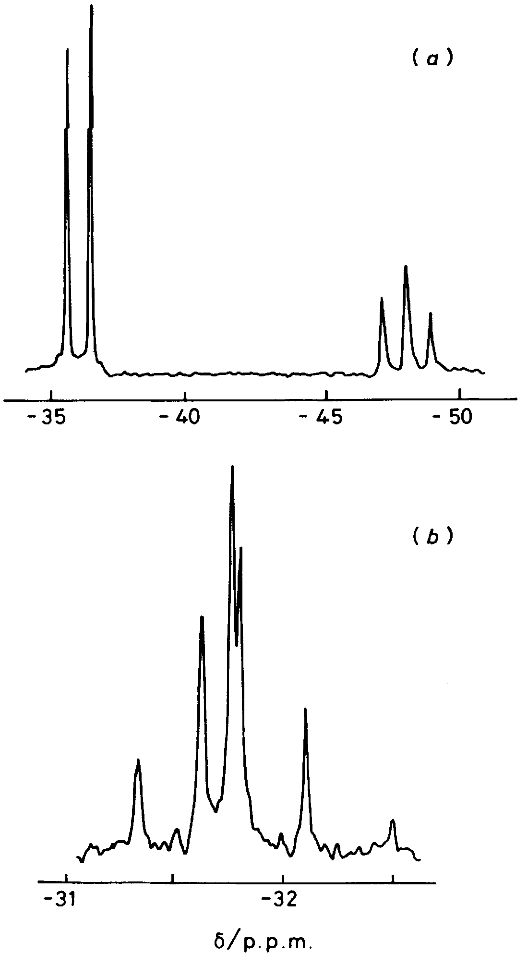


Figure 2. ^{31}P-$\{^1H\}$ N.m.r. spectra at 297 K of (*a*) *trans*-$[OsCl_2(PMe_2Ph)_3(MeCN)]$ in CH_2Cl_2 and (*b*) *cis*-$[OsCl_2(PMe_2Ph)_3(MeCN)]$ in MeCN

treating a solution of complex (**3**) (normally stored under argon) with dinitrogen a new complex is formed which we have assigned as *trans*-$[OsCl_2(PMe_2Ph)_3(N_2)]$, see Table. The *cis* isomer[12] gives a very different ^{31}P-$\{^1H\}$ n.m.r. spectrum. This *trans* complex has a low-intensity, relatively high-energy N–N stretching vibration at 2 280 cm^{-1} [$\nu(N_2)$ 2 078 (*cis*), 2 331 cm^{-1} (gas) (Raman)] indicating that the N_2 group is only weakly bound and not strongly polarised. It should be noted that, despite the low intensity of the observed $\nu(N_2)$ absorption, the emphatic nature of the voltammetric changes and the complementary ^{31}P-$\{^1H\}$ n.m.r. data (Table) establish that *trans*-$[OsCl_2(PMe_2Ph)_3(N_2)]$ is the exclusive osmium complex present in solution. Insertion of N_2 in the *trans* position is relatively slow and by using fast-scanning techniques (100 V s^{-1} at room temperature) the Os^{II}–Os^{III} couples for both the five-coordinate monomer (**3**) and the *trans* N_2 complex can be observed. At slower more conventional scan speeds (100 mV s^{-1}) only the nitrogen complex is observed. Recently, Armstrong and Walton[13] described the electrochemistry in CH_2Cl_2 of related *mer*-$[OsCl_3(PR_3)_3]$ monomers (PR_3 = $PMePh_2$, $PEtPh_2$, PEt_2Ph, PEt_3, $PPr^n{}_3$, or $PBu^n{}_3$) in CH_2Cl_2. All of these complexes were reported to have a reversible (or nearly reversible) oxidation and a completely irreversible reduction similar to $[OsCl_3(PMe_2Ph)_3]$ [Figure 1(*a*)]. It was further noted that, following the reduction, an unidentified chemical product with a well-defined electrochemistry could be detected. We suggest that the unexplained voltammetric behaviour can be attributed to generation of *trans*- $[OsCl_2(PR_3)_3(N_2)]$ complexes since N_2 was used to deoxygenate the cell solutions.

In summary, for every L we have examined, the $[OsCl_2(PMe_2Ph)_3L]$ product formed initially by electroreduction is the *trans* isomer (in accord with the *trans* effect) which is converted into the thermodynamically stable *cis* isomer on standing or on heating. Chemical reduction of $[OsCl_3(PMe_2Ph)_3]$ and related systems generally does not offer this degree of control.[4]

If a concentrated solution (>4 × 10^{-3} mol dm^{-3}) of $[OsCl_2(PMe_2Ph)_3]$ (**3**) is generated in CH_2Cl_2 or thf under argon (*i.e.* with no ligands L present) then, ultimately, as shown in the Scheme we observe the binuclear complex $[Os_2Cl_3(PMe_2Ph)_6]^+$. This cation has also been synthesised by a separate route as an isolated salt (see Experimental section) with indistinguishable n.m.r. and voltammetric properties. We are presently extending our studies of $[Os_2Cl_3(PMe_2Ph)_6]^{+/2+/3+}$ by comparing the magnetic and spectral data for each of the accessible oxidation states, *i.e.* $Os_2{}^{II,II}$, $Os_2{}^{II,III}$, and $Os_2{}^{III,III}$. The $Os_2{}^{II,III}$ mixed-valence complex can be generated from the oxidation of $Os_2{}^{II,II}$ either electrochemically or chemically (by Cl_2) with indistinguishable ^{31}P n.m.r., voltammetric, and u.v., visible, and near-i.r. absorption spectra.[14]

If the formation of $[Os_2Cl_3(PMe_2Ph)_6]^+$ (**6**) from the $[OsCl_2(PMe_2Ph)_3]$ solution is continuously monitored by ^{31}P-$\{^1H\}$ n.m.r. spectroscopy and voltammetry, then an intermediate species (**5**) is observed (see Scheme). Recently Caulton and co-workers[15] photolysed $[OsH_4(PMe_2Ph)_3]$ in thf to produce $[Os_2H_4(PMe_2Ph)_6]$, which underwent a further reaction when dissolved in diethyl ether to give the $[Os_2H_3(PMe_2Ph)_6]^+$ cation. They proposed an initial photoproduct $[OsH_2(PMe_2Ph)_3]$ to explain their reaction mechanism. The two systems are strikingly similar and we suggest that the intermediate observed above is probably the doubly chloride-bridged $[Os_2Cl_4(PMe_2Ph)_6]$. The observed ^{31}P-$\{^1H\}$ n.m.r. spectrum and voltammetry are in agreement with this formulation (Table) and further work is in progress to isolate and characterise fully this complex. It is also formed when $[OsCl_3(PMe_2Ph)_3]$ is reduced by zinc amalgam in a non-coordinating medium. However the concentration of complex (**1**) must be greater than 4 × 10^{-3} mol dm^{-3}, otherwise dimerisation is unfavoured and $[OsCl_2(PMe_2Ph)_3]$ is the sole product.

When the reduction of $[OsCl_3(PMe_2Ph)_2]$ is carried out in CH_2Cl_2 to which an excess of free PMe_2Ph has been added, then a new product can be identified by ^{31}P-$\{^1H\}$ n.m.r. spectroscopy and voltammetry. This was initially formulated as *trans*-$[OsCl_2(PMe_2Ph)_4]$ in parallel with all the other electrogeneration reactions (see Scheme) and consistent with the singlet in its room-temperature ^{31}P-$\{^1H\}$ n.m.r. spectrum. This '*trans* isomer' was also prepared by Zn–Hg reduction of $[OsCl_3(PMe_2Ph)_3]$–PMe_2Ph[16] and by reaction of ethanolic solutions of Na_2OsCl_6 with PMe_2Ph (see Experimental section). All three methods give spectroscopically indistinguishable products. It is interesting to note that with other PR_3 ligands such as PEt_2Ph and $PEtPh_2$ the latter reaction gives only the binuclear species $[Os_2Cl_3(PR_3)_6]Cl$.

In common with other *trans*-$[OsCl_2(PMe_2Ph)_3L]$ complexes, isomerisation of the tetrakis-PMe_2Ph derivative to the *cis* isomer occurs in solution over a few hours at room temperature. Hence the ^{31}P-$\{^1H\}$ n.m.r. spectrum in $CDCl_3$ changes from a singlet to the known A_2B_2 (AA'BB' at 200 MHz) pattern of the *cis* isomer as independently prepared and shown in the Table.* However the voltammetric data for the two isomers, instead of being almost superimposable as for all other examples of L, are

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* Note that in CD_2Cl_2 the ^{31}P-$\{^1H\}$ n.m.r. spectrum of the *cis* isomer is a singlet due to accidental degeneracy of the P resonances.

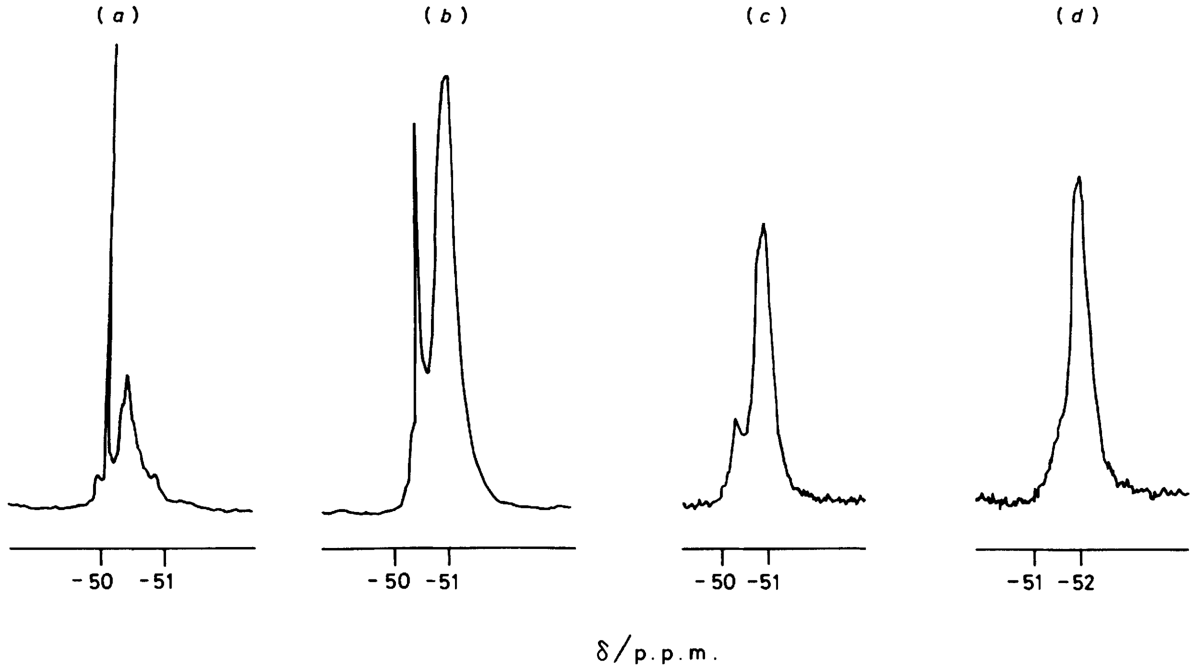

Figure 3. $^{31}P-\{^{1}H\}$ N.m.r. spectra of '*trans*'-[$OsCl_2(PMe_2Ph)_4$] in CD_2Cl_2 at 203 (*a*), 243 (*b*), 253 (*c*), and 263 K (*d*)

separated by more than 400 mV (*cis*, +0.75; '*trans*,' +0.28 V). Furthermore, the $^{31}P-\{^{1}H\}$ n.m.r. signal of the '*trans*' isomer changes dramatically as the temperature is decreased (Figure 3); at 193 K the simple room-temperature singlet at δ −52.5 p.p.m. has become a sharp singlet at −50.0 p.p.m. superimposed on a poorly defined complex pattern (intensity ratio *ca.* 1:3). This process is reversible with temperature and is concentration independent. A variable-temperature ^{1}H n.m.r. study of the '*trans*' complex showed only one set of signals in the methyl and phenyl regions at room temperature, suggesting four magnetically equivalent phosphine ligands, but as the temperature is lowered the spectrum becomes complicated. At 203 K, signals whose positions are independent of temperature are observed at δ 1.60 and 7.37 p.p.m. In addition, in the methyl region two singlets appear at δ 0.68 and 1.90 p.p.m. and in the phenyl region four multiplets centred at δ 5.65, 6.05, 6.65, and 8.46 p.p.m. The ratio of integrals of the combined new signals to the unshifted signals is *ca.* 1:3 for both the methyl and phenyl regions. Thus we conclude that the complex is not a genuine *trans*-[$OsCl_2(PMe_2Ph)_4$] isomer but rather has only three of its PMe_2Ph ligands conventionally bound to the osmium centre through the phosphorus atom. Equally, the ^{13}C (90.2-MHz) n.m.r. spectrum is indicative of very low overall molecular symmetry and non-equivalent phosphines. We suggest that the fourth phosphine is not Os–P bound but rather interacts with the metal atom either through the phenyl-ring π system or through an agostic[7] hydrogen atom from the phenyl or the methyl groups. Hence the complex should be reformulated as *trans*-[$OsCl_2(PMe_2Ph)_3(P'Me_2Ph)$]. Unfortunately all attempts to date to obtain an *X*-ray crystallographic analysis of this compound have proved unsuccessful; the preliminary results indicate a highly disordered structure. The fourth ligand is only weakly bound since it is easily displaced, for example by MeCN to give the previously discussed *trans*-[$OsCl_2(PMe_2Ph)_3(MeCN)$]. It should be noted that such displacement reactions do not occur for the corresponding *cis* isomer with four conventionally bound phosphines. Conversely, excess of PMe_2Ph displaces MeCN from *trans*-[$OsCl_2(PMe_2Ph)_3(MeCN)$] in CH_2Cl_2 yielding the pseudo-*trans* isomer. The failure to observe the true *trans*-[$MCl_2(PR_3)_4$] isomer for *trans*-[$OsCl_2(PMe_2Ph)_4$] is not restricted to this complex. Preliminary studies on *trans*-[$RuCl_2(PMe_2Ph)_4$] also show similar ^{31}P and ^{1}H n.m.r. behaviour. However genuine *trans*-[$MCl_2(PR_3)_4$] complexes do exist; for example, *trans*-[$OsCl_2(PMe_3)_4$] shows a singlet in its $^{31}P-\{^{1}H\}$ n.m.r. spectrum at all temperatures, consistent with its *X*-ray crystal structure,[17] and thus the phenomenon must be intimately linked with the particular substituent groups on PMe_2Ph. Further work is now in progress on variation of the substituents on PR_3 and related ligands, for example $P(OR)R_2$, to see what factors determine the mode of bonding by the fourth phosphine to the metal centre. We are hopeful that definitive *X*-ray crystal data may yet be obtained.

Experimental

Microanalyses were performed by the University of Edinburgh Chemistry Department. Infrared spectra were recorded on a Perkin-Elmer 557 grating spectrometer, using Nujol mulls on CsI plates and solution cells with NaCl windows. Variable-temperature ^{1}H and $^{31}P-\{^{1}H\}$ n.m.r. spectra were run on JEOL FX60Q [with $(CD_3)_2CO$ as capillary lock] and Bruker WP 200SY pulsed Fourier-transform spectrometers.

Investigative electrochemistry was performed using a PAR model 170 potentiostat and programmer with platinum working and auxiliary electrodes and a Ag–AgCl reference electrode. Fast-scan voltammograms ($v > 1$ V s^{-1}) were monitored using a digital Physical Data Inc. model 512A transient store in conjunction with a Telequipment model D66A oscilloscope, with subsequent playback to a Hewlett-Packard 704A X-Y recorder. Low-temperature studies (273–203 K) were carried out in a jacketed cell cooled by a Haake F3Q refrigerated circulation unit.

Electrosyntheses were carried out in a three-compartment cell with a platinum-gauze working electrode using a Hi-Tek potentiostat, type DT2101, in conjunction with a Hi-Tek waveform generator, type PPR1.

Chemicals.—Acetonitrile was purified by the method of Walter and Ramaley[18] and was freshly distilled from P_2O_5 before use. Methylene chloride was allowed to stand for 1 week over KOH pellets and dried by distillation over P_2O_5. Tetrahydrofuran was dried by distillation over sodium wire. All other solvents were used as supplied without further purification. The salts $[NR_3Me][BF_4]$ ($R = C_8H_{17}$ to $C_{10}H_{21}$) were prepared by metathesis of Adogen 464, $[NR_3Me]Cl$ (Aldrich Chemicals), with $Na[BF_4]$ in MeCN. Osmium tetroxide was supplied by Johnson Matthey Chemicals Ltd. and Na_2OsCl_6 was prepared by standard methods.

mer-*Trichlorotris(dimethylphenylphosphine)osmium*(III).—This was prepared by the literature method of Leigh and co-workers[19] (Found: C, 40.8; H, 4.5. Calc. for $C_{24}H_{33}Cl_3OsP_3$: C, 40.6; H, 4.6%).

cis-*Dichlorotetrakis(dimethylphenylphosphine)osmium*(II).—The complex *mer*-$[OsCl_3(PMe_2Ph)_3]$ (0.57 g) and PMe_2Ph (0.5 cm^3) were heated under reflux in degassed 2-methoxyethanol (40 cm^3) for 30 min until the red colour had completely changed to a golden yellow. After volume reduction, addition of acetone, and cooling, the pale cream product precipitated and was washed well with acetone and diethyl ether and dried. Yield of *cis*-$[OsCl_2(PMe_2Ph)_4]$: 0.51 g, (60%) (Found: C, 47.3; H, 5.2. Calc. for $C_{32}H_{44}Cl_2OsP_4$: C, 47.2; H, 5.4%).

trans-*Dichlorotetrakis(dimethylphenylphosphine)-osmium*(II).—The *trans* complex was prepared by a variation of the method of Bell *et al.*,[16] namely; Na_2OsCl_6 and PMe_2Ph were heated under reflux in aqueous ethanol for 1 h (Found: C, 46.7; H, 5.4. Calc for $C_{32}H_{44}Cl_2OsP_4$: C, 47.2; H, 5.4%).

trans-*Dichlorotris(dimethylphenylphosphine)(methyl cyanide)-osmium*(II).—The complex *mer*-$[OsCl_3(PMe_2Ph)_3]$ (0.1 g) was dissolved in degassed MeCN–0.1 mol dm^{-3} $[NBu_4][BF_4]$ (10 cm^3) and electroreduced at -0.60 V until the current decayed to $< 5\%$ of its initial value. The yellow product which precipitated was filtered off under nitrogen, washed with diethyl ether, dried and stored *in vacuo*. Yield of $[OsCl_2(PMe_2Ph)_3(MeCN)]$: 0.07 g (70%) (Found: C, 42.4; H, 5.0; N, 1.9. Calc. for $C_{26}H_{36}Cl_2NOsP_3$: C, 43.5; H, 5.0; N, 1.9%). ^{1}H N.m.r. spectra: *trans*-$[OsCl_2(PMe_2Ph)_3(MeCN)]$ in CD_2Cl_2, $\delta = 1.72$ (d), 1.55 (t), and 1.30 p.p.m. (s, MeCN); *cis*-$[OsCl_2(PMe_2Ph)_3(CD_3CN)]$ in CD_3CN, $\delta = 1.87$ (t), 1.73 (t), and 1.36 (d) p.p.m.

Tri-μ-chloro-hexakis(dimethylphenylphosphine)diosmium(II,II) *Chloride.*—The complex *cis*-$[OsCl_2(PMe_2Ph)_4]$ (0.135 g) was heated under reflux in degassed Bu^{t}OH (30 cm^3) for 24 h. On reduction in volume and cooling, the pale yellow product precipitated as the chloride salt. Yield of $[Os_2Cl_3(PMe_2Ph)_6]Cl$: 0.095 g (85%) (Found: C, 42.8; H, 4.8. Calc. for $C_{48}H_{66}Cl_4Os_2P_6$: C, 42.7; H, 4.8%).

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