Electrophilic Behaviour of Co-ordinated Nitrogen Mono-oxide: Preparation and Reactions of Halogenonitrosylbis[*o*-phenylenebis(dimethylarsine)]osmium Complexes

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The complexes *trans*-$[Os(pdma)_2X(NO)]X_2{\cdot}H_2O$ [X = Cl, Br, or I; pdma = *o*-phenylenebis(dimethylarsine)] were prepared from $[OsX_5(NO)]^{2-}$ and pdma. They react reversibly with $[OH]^-$ to give $[Os(pdma)_2X(NO_2)]$. The complex $[Os(pdma)_2Cl(NO)]Cl_2{\cdot}H_2O$ and hydrazine hydrate give $[Os(pdma)_2Cl(N_3)]$, which reacts with O_2 to give $[Os(pdma)_2Cl(NO_2)]$ and with HCl to give *trans*-$[Os(pdma)_2Cl(N_2)]Cl$. Treatment of a mixture of $[Os(pdma)_2Cl(N_3)]$ and $[Os(pdma)_2Cl(NO_2)]$ with HCl gives *trans*-$[Os(pdma)_2Cl(N_2)]Cl$ and *cis*-$[Os(pdma)_2Cl(NO)]Cl_2$. The complex *cis*-$[Os(pdma)_2Cl(NO)]Cl_2$ and $[OH]^-$ gives *trans*-$[Os(pdma)_2(NO)(OH)]Cl_2$. Treatment of *trans*-$[Os(pdma)_2Cl(NO)]Cl_2{\cdot}H_2O$ with phenylhydrazine gives *trans*-$[Os(pdma)_2Cl(N_2)]Cl$ and $[Os(pdma)_2Cl(ONNNHPh)]$. The latter complex undergoes free-radical reactions with O_2 in various solvents to give $[Os(pdma)_2Cl(N_2)]Cl$, $[Os(pdma)_2Cl(NO_2)]$, or $[Os(pdma)_2Cl(NO)]Cl_2{\cdot}H_2O$, or mixtures of these, depending on the conditions. The complex $[Os(pdma)_2Cl(NO)]Cl_2{\cdot}H_2O$ and hydroxylamine gave *trans*-$[Os(pdma)_2(NO)(OH)]Cl_2$ together with other unidentified products. The physical and chemical properties of all the complexes are reported.

In order to understand the factors governing the electrophilic behaviour of co-ordinated nitrogen mono-oxide, and to extend the known classes of reaction, we have been searching for complexes having nitrosyl groups which are reactive towards nucleophiles.[1] The known reactions of chloronitrosylbis[*o*-phenylenebis(dimethylarsine)]ruthenium,[2,3] $[Ru(pdma)_2Cl(NO)]^{2+}$, and the possibility of similar reactions with the iron analogue,[4] prompted us to synthesise, and investigate the reactions of, the previously unknown osmium complexes $[Os(pdma)_2X(NO)]^{2+}$ (X = Cl, Br, or I), despite our previous experience of the unreactivity of osmium nitrosyls.[5] A second reason for preparing these complexes was that the recent preparation of $[Fe(pdma)_2Cl(NO)]^{2+}$ has revealed the possibility of a complete series of complexes of type $[M(pdma)_2X(AB)]^{n+}$ [M = Fe, Ru, or Os; X = Cl, Br, or I; AB = NO for $n = 2$ (and possibly $n = 0$) and N_2 or CO for $n = 1$]. Other members of such a series, *e.g.* X = $[OH]^-$ and AB = $[CN]^-$, can also be envisaged. Such a series of complexes, which has not before been approached, would be invaluable for investigating such matters as comparative ligand reactivities, the nature of the metal–ligand bonding, and the relative properties of NO, CO, and N_2 as ligands.

In this paper we present the synthesis and chemical and physical properties of $[Os(pdma)_2X(NO)]^{2+}$, reactions of these complexes to give nitro (NO_2), 1-oxo-3-phenyltriazene(1−) (PhNHNNO), azido (N_3), and dinitrogen (N_2) complexes, and some chemical and physical properties of the products. Reactions forming *cis*-$[Os(pdma)_2Cl(NO)]^{2+}$ and *trans*-$[Os(pdma)_2(NO)(OH)]^{2+}$ are also reported.

RESULTS AND DISCUSSION

Preparation and Properties of $[Os(pdma)_2X(NO)]^{2+}$.—Initial attempts at synthesising $[Os(pdma)_2X(NO)]^{2+}$ by reaction of NO with the readily prepared[6] $[Os(pdma)_2Cl_2]^+$ were unsuccessful, the Cl^- of the starting complex being completely inert to substitution in methanol or water, even in the presence of Ag^+. Attempts at a 'one-pot' synthesis using $[NH_4]_2[OsCl_6]$, pdma, and *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide[7] also gave no NO incorporation. The synthesis given in the Experimental section, which used the reaction of pdma with $[OsX_5(NO)]^{2-}$ (ref. 8) in ethanol–water, was simple, but is still not completely satisfactory because of the time consumed, and low yields obtained, in the preparation of $[OsX_5(NO)]^{2-}$ (although this preparation is also simple).

The complexes $[Os(pdma)_2X(NO)]X_2{\cdot}H_2O$ (X = Cl, Br, or I; the anion may also be ClO_4 or N_3) are yellow to orange air-stable solids, soluble to a limited extent in polar organic solvents such as dimethylformamide (dmf) or ethanol and to some degree also in water. The water of crystallisation is very tenaciously bound. The complexes were characterised by analysis, conductivity, i.r. and n.m.r. spectroscopy, and by their chemical reactions. The results of the physical measurements and analyses are in the Table.

The molar conductivities in dmf, some of which were obtained graphically over a range of concentration, were in the range 130—140 S cm^2 mol^{-1}, at the lower end of the range (130—170 S cm^2 mol^{-1}) found for 1 : 2 complexes in dmf.[9] Conductivities of related 1 : 1 complexes, *e.g.* $[Os(pdma)_2Cl(N_2)]^+$, prepared in the present

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Characterisation of the complexes

Complex	Analysis (%)										I.r. spectra (cm^{-1})			δ [b]/p.p.m. (solvent)	Λ in dmf / S cm^2 mol^{-1}
	Calc.					Found									
	C	H	N	X	Other	C	H	N	X	Other	ν(NO) or ν(N_2) in solution (solvent)	ν(NO) or ν(N_2) in Nujol [a]	Other bands (Nujol) [a]		
trans-$[Os(pdma)_2Cl(NO)]X_2\cdot H_2O$ X = Cl	26.2	3.7	1.5		Cl 11.6	26.6	3.8	1.7		Cl 12.1	1 861 (water)	1 872	3 370s, br (H_2O)	2.36, 2.57 (D_2O) [c]	196[d], 50 [e]
Br												1 873			
I												1 854, 1 834 (sh)			
trans-$[Os(pdma)_2Cl(NO)]X_2$ X = ClO_4	23.4	3.1	1.4			23.75	3.1	1.8			1 869 (dmf)	1 840	1 090 (ClO_4)		135
N_3	25.5	3.4	10.4		Cl 3.8	26.2	3.7	10.7		Cl 3.1		1 850	2 005 (N_3)		
Cl[f]												1 886			
trans-$[Os(pdma)_2Br(NO)]X_2\cdot H_2O$ X = Br	22.85	3.2	1.3		Br 22.85	24.4	3.7	1.5		Br 23.4		1 860, 1 815 (sh)			
I	21.0	3.0	1.2			21.4	3.5	1.4			1 867 (dmf)	1 860		2 24, 2 33 ([$^2H_6$]dmso)	132
trans-$[Os(pdma)_2Br(NO)][ClO_4]_2$	22.4	3.0	1.3	6.6	Br 7.5	22.6	3.8	1.5	6.4	Br 6.9		1 850	1 086 (ClO_4)		137
trans-$[Os(pdma)_2I(NO)]I_2\cdot H_2O$	20.15	2.85	1.2		I 32.0	21.0	2.7	1.3		I 31.5	1 859 (dmf)	1 850		2.68, 2.85 ([$^2H_6$]dmso)	136
trans-$[Os(pdma)_2I(NO)][ClO_4]_2$	21.5	2.9	1.25		I 11.4	21.9	3.5	1.4		I 9.1	1 862 (dmf)	1 850	1 095s (ClO_4)		139
trans-$[Os(pdma)_2(NO)(OH)]I_2$	22.6	3.1	1.3	23.9		22.75	3.2	1.2	23.9		1 820 (dmf)	1 835, 1 815 (sh)	3 416s (OH)	2.03, 2.29 (D_2O),[c] 2.12, 2.35 ([$^2H_6$]dmso)	131
cis-$[Os(pdma)_2Cl(NO)]X_2\cdot H_2O$ X = Cl	26.2	3.7	1.5		Cl 11.6	24.4	3.5	1.4		Cl 11.5		1 861, 1 837 (sh)		2.09, 2.30, 2.47, 2.66 (D_2O) [g]	182 [d],47[e]
I	21.8	3.1	1.3		Cl 3.2	22.5	3.1	1.2		Cl 2.9		1 863			
$[Os(pdma)_2X(NO_2)]$ X = Cl	28.5	3.8	1.7	4.2		28.5	4.1	1.75	3.9				1 317s, 1 297 [$\nu_{sym}(NO_2)$]; 1 229 [$\nu_{asym}(NO)_2)$]; 813w [$\delta_{sym}(NO_2)$]		
Br	27.0	3.6	1.6			27.1	3.6	1.95					1 309s, 1 295 [$\nu_{sym}(NO_2)$]; 1 227 [$\nu_{asym}(NO_2)$]; 812w [$\delta_{sym}(NO_2)$]		
I	25.7	3.4	1.5			25.7	3.25	1.6					1 309s, 1 289 [$\nu_{sym}(NO_2)$]; 1 225 [$\nu_{asym}(NO_2)$]; 814w [$\delta_{sym}(NO_2)$]		
$[Os(pdma)_2Cl(N_3)]$	28.6	3.9	5.0	4.2		28.0	3.8	4.6	3.6				2 040 [$\nu(N_3)$]		
trans-$[Os(pdma)_2Cl(N_2)]X$ X = Cl	27.9	3.75	3.25		Cl 8.2	28.1	4.3	3.2		Cl 7.6		2 080		2 07, 2.11 ($CDCl_3$)	
Br	26.5	3.5	3.1	8.8	Cl 3.9	25.9	3.7	3.2	8.8	Cl 3.9		2 080			33
ClO_4												3 088	1 090 (ClO_4)		
$[Os(pdma)_2Cl(ONNNHPh)]$	33.4	4.1	4.5		Cl 3.8	33.7	4.3	4.6		Cl 3.4			3 250w, 1 600s, 1 502s, 1 145s		8

[a] All the bands are very strong (vs) unless noted as strong (s), weak (w), or shoulder (sh). [b] Relative to $SiMe_4$ as standard except where noted. [c] Relative to $Me_3SiCH_2CH_2CH_2SO_3Me$. [d] In water. [e] In ethanol. [f] By dehydration of $[Os(pdma)_2Cl(NO)]Cl_2\cdot H_2O$ at 60 °C *in vacuo* for 4 d. [g] Ratio of resonances is 1 : 1 : 3 : 3.

work were 33 S cm^2 mol^{-1} in ethanol compared to the range (35—45 S cm^2 mol^{-1}) quoted in the literature,[9] and of non-electrolytes, *e.g.* [Os(pdma)$_2$Cl(ONNNHPh)] in dmf, 8 S cm^2 mol^{-1}. Association between anions and cations in solution appears to be somewhat greater than for other complexes.

The n.m.r. technique has been used previously to determine the geometry of six-co-ordinate complexes of pdma,[2,4,10] and the assignments have recently received confirmation from crystal-structure analyses of [Co(pdma)$_2$(NCS)(NO)][NCS] [11] and [Ru(pdma)$_2$Cl(N$_3$)] (see footnote 14 of ref. 2). In the *trans* configuration there are two sets of four equivalent methyl groups on the pdma ligands, giving rise to two methyl singlets of equal intensity in the n.m.r. spectrum. For the *cis* configuration all eight methyl groups are non-equivalent, and eight methyl resonances are expected. The methyl resonances in the pdma complexes were found in the 2.0—2.5 p.p.m. region.[2,4,10] The n.m.r. results (Table) show that the [Os(pdma)$_2$X(NO)]$^{2+}$ complexes all have the *trans* configuration.

The ν(NO) frequency in the i.r. spectra of the complexes (Table) shows that the MNO group must be linear with, formally, [NO]$^+$ co-ordinated to Os$^{\text{II}}$.[12] This conclusion is supported by the chemical properties of the complexes (see below). The ν(NO) frequency was *ca.* 25 cm^{-1} lower than for the analogous ruthenium complexes, reflecting increased π-electron donation by osmium. In solution ν(NO) is almost independent of the X ligand, although for *trans*-[Os(pdma)$_2$(NO)(OH)]$^{2+}$ it is lower. It is perhaps surprising that ν(NO) should not be heavily dependent on the *trans* ligand, but we note that, for all [OsL$_5$(NO)] (L = unidentate or half-bidentate ligand) complexes formally containing [NO]$^+$, ν(NO) lies in the rather narrow range (when compared to the reduction in wavenumber of *ca.* 350 cm^{-1} from the free [NO]$^+$ value of 2 200 cm^{-1}) of 1 800 {[OsBr$_5$(NO)]$^{2-}$} to 1 905 cm^{-1} {[Os(CN)$_5$(NO)]$^{2-}$}.[1,5,13] The range for ruthenium is even narrower, 1 840—1 927 cm^{-1}.[1,13] These narrow ranges occur because the bonding between a metal and [NO]$^+$ depends very heavily on the π component, since [NO]$^+$ is a poor σ donor.[14,15] Therefore, the major influence on the frequency of ν(NO) is the satisfaction of the requirement of [NO]$^+$ for π bonding, and differences in the ability of the ML$_5$ moiety to donate π electrons (produced by the presence of different L ligands) are a minor influence.

From the Table it is seen that ν(NO) is strongly dependent on the environment of the complex; in Nujol the order of ν(NO) with respect to the counter ions is $[\mathrm{ClO_4}]^- < \mathrm{I}^- < \mathrm{Br}^- < \mathrm{Cl}^-$, with a spread of 45 cm^{-1}. There are two ways in which counter ions may affect the frequencies of ligands such as NO: direct repulsion between anions and the ligand electrons, resulting in electron density moving from ligand π^* orbitals back to the metal; and an indirect interaction with the other ligands of the complex, *e.g.* protons on NH$_3$.[16] The indirect interaction is not possible with the ligand pdma, and the order of ν(NO) (the largest anion, which has the smallest repulsive effect, having the lowest frequency) clearly indicates a direct interaction.

Reactions of [Os(pdma)$_2$X(NO)]$^{2+}$.—The complexes reacted rapidly, at room temperature, with a variety of nucleophiles. Except where stated, we investigated reactions of the chloro-complex only; cursory examination showed that reactions of the other halogeno-complexes are similar, but complicated by the lower solubilities of the starting materials. The products of the reactions were characterised by analysis, i.r. and n.m.r. spectroscopy, and conductivity, and the results are collected in the Table. In general we did not investigate the mechanisms of the reactions; reports, in varying detail, of the mechanisms of the reactions between metal nitrosyls and the nucleophiles [OH]$^-$,[17] NH$_2$OH,[18,19] N$_2$H$_4$,[2,18] and N$_2$H$_3$Ph [2] used in this work are available.

There was a rapid reversible reaction between *trans*-[Os(pdma)$_2$X(NO)]$^{2+}$ (X = Cl, Br, or I) and [OH]$^-$ (aqueous, 1 mol dm^{-3}) to form [Os(pdma)$_2$X(NO$_2$)], which is assumed to have *trans* geometry. The equilibrium constants for the reaction could not be measured because no suitable physical property could be found.

In the rigorous absence of dioxygen and light, *trans*-[Os(pdma)$_2$Cl(NO)]$^{2+}$ reacted with hydrazine hydrate in ethanol to form [Os(pdma)$_2$Cl(N$_3$)]. With O$_2$ and light, even in the solid state, [Os(pdma)$_2$Cl(N$_3$)] rapidly formed [Os(pdma)$_2$Cl(NO$_2$)]. Hence, reaction of [Os(pdma)$_2$Cl(NO)]$^{2+}$ with hydrazine hydrate in air and light gave an inseparable mixture of [Os(pdma)$_2$Cl(N$_3$)] and [Os(pdma)$_2$Cl(NO$_2$)]. The nitro-product was identical to that formed from *trans*-[Os(pdma)$_2$Cl(NO)]$^{2+}$ and [OH]$^-$. A similar reaction has been observed between O$_2$ and [Ru(pdma)$_2$Cl(N$_3$)],[2] but the azido-osmium complex appears to be more reactive than its ruthenium analogue. Treatment of [Os(pdma)$_2$Cl(N$_3$)] with aqueous concentrated HCl gave [Os(pdma)$_2$Cl(N$_2$)]$^+$ together with some [Os(pdma)$_2$Cl(NO)]$^{2+}$. The latter must arise from [Os(pdma)$_2$Cl(NO$_2$)] produced by reaction of trace amounts of O$_2$ with [Os(pdma)$_2$Cl(N$_3$)]. The n.m.r. spectrum showed that [Os(pdma)$_2$Cl(N$_2$)]$^+$ has *trans* geometry, and it is therefore assumed [Os(pdma)$_2$Cl(N$_3$)] is also *trans*. However, the same technique showed that the [Os(pdma)$_2$Cl(NO)]$^{2+}$ by-product {which was also obtained in greater yield by treating the mixture of [Os(pdma)$_2$Cl(N$_3$)] and [Os(pdma)$_2$Cl(NO$_2$)], produced from the reaction of hydrazine in air, with HCl} showed

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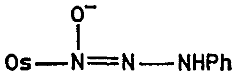
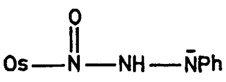
not two methyl resonances but four, in the ratio 1 : 1 : 3 : 3. We consider these to arise from a *cis* isomer with chemical-shift differences for two sets of three methyl groups unresolvable (at 60 MHz). Additional evidence for the formation of a new isomer of $[Os(pdma)_2Cl(NO)]^{2+}$ was given by the i.r. and electronic spectra (Table). With aqueous $[OH]^-$ (1 mol dm^{-3}), *cis*-$[Os(pdma)_2Cl(NO)]^{2+}$ rapidly gave *trans*-$[Os(pdma)_2(NO)(OH)]^{2+}$, in contrast to the $[Os(pdma)_2Cl(NO_2)]$ produced from *trans*-$[Os(pdma)_2Cl(NO)]^{2+}$ and $[OH]^-$. It is clear that the *cis* isomer was formed during reaction of *trans*-$[Os(pdma)_2Cl(NO_2)]$ with HCl, but only when the azido-complex was present. A dimeric species may be involved as an intermediate.

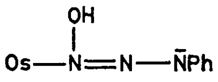
The $\nu(N_2)$ frequency for *trans*-$[Os(pdma)_2Cl(N_2)]^+$ (2 080 cm^{-1}) is 45 cm^{-1} lower than for *trans*-$[Ru(pdma)_2Cl(N_2)]^+$, as for $\nu(NO)$ in $[M(pdma)_2Cl(NO)]^{2+}$. Comparing $[M(NH_3)_5(N_2)]^{2+}$ (refs. 20 and 21) with $[M(pdma)_2Cl(N_2)]^+$,[4] $[M(NH_3)_5(NO)]^{3+}$,[1,5] and $[M(pdma)_2Cl(NO)]^{2+}$ (M = Ru or Os), $\nu(N_2)$ is lower for the ammine complex but $\nu(NO)$ lower for the pdma complex. This reversal of order is again due to the different balance of σ and π effects in $[M(NO)]^+$ or $[M(N_2)]$ bonding. In the $[NO]^+$ complex the major influence is the π bonding, and the greater ability of a *trans*-Cl, compared to NH_3, to donate π electrons will reduce $\nu(NO)$. For N_2 the σ component is more important than for $[NO]^+$, and hence the electron-acceptor ability of pdma,[22] the relative abilities of NH_3, Cl, and N_2 to compete for σ orbitals, and the relative energies of the bonding orbitals on N_2 will all play a large role in determining the amount of π-back bonding, and hence in the frequency of $\nu(N_2)$. In the solid state $\nu(N_2)$ was independent of the Cl^- or Br^- anion. This indicates that the anions are not in close proximity to the N_2 ligand, but detailed structural information is needed to confirm this.


$Os-\overset{O^-}{\overset{|}{N}}=N-NHPh$

(1)


$Os-\overset{O}{\overset{\|}{N}}-NH-\bar{N}Ph$

(2)


$Os-\overset{OH}{\overset{|}{N}}=N-\bar{N}Ph$

(3)

Phenylhydrazine, $PhNHNH_2$, and *trans*-$[Os(pdma)_2Cl(NO)]^{2+}$ formed a mixture of *trans*-$[Os(pdma)_2Cl(N_2)]^+$ and $[Os(pdma)_2Cl(ONNNHPh)]$ in ethanol. The relative yields varied somewhat unpredictably; the dinitrogen complex comprised 40—70% of the product. Nevertheless the reaction was the most convenient for preparing $[Os(pdma)_2Cl(N_2)]^+$, since this could be readily obtained by addition of diethyl ether to the concentrated reaction solution after removal of the immediately precipitated $[Os(pdma)_2Cl(ONNNHPh)]$. The crude product was freed from co-precipitated $[PhNHNH_3]Cl$ by recrystallisation.

The formula of $[Os(pdma)_2Cl(ONNNHPh)]$ was assigned on the basis of analytical and i.r. evidence, initial conductivities (the complex decomposed quite rapidly in solvents suitable for conductivity measurements), and by analogy with its ruthenium analogue,[2] although its chemical properties were different. Attempts to obtain an n.m.r. spectrum failed due to decomposition problems. Because the starting complex and all the reaction products from $[Os(pdma)_2Cl(ONNNHPh)]$ have the *trans* configuration we assume it is *trans*. We also note that three tautomers (1)—(3) of the Os(ONNNHPh) unit exist. The i.r. spectrum of the complex showed a band at 3 250 cm^{-1}, typical for a NH vibration, but no band at higher energy where an OH vibration might be expected. Therefore, tautomer (**3**) seems unlikely, at least in the solid state, but we have no evidence in favour of (1) or (2). Delocalisation and electronegativity considerations make (1) attractive as the lowest-energy tautomer, and this formula is therefore used here.

Feltham and his co-workers[2] found that $[Ru(pdma)_2Cl(ONNNHPh)]$ gave $[Ru(pdma)_2Cl(NO)]^{2+}$ on treatment with HCl.[2] We found that $[Os(pdma)_2Cl(ONNNHPh)]$ gave good yields of $[Os(pdma)_2Cl(N_2)]^+$ on treatment with aqueous concentrated HCl, but no nitrosyl species. On the other hand, in solution the osmium complex was extremely sensitive to dioxygen. In dmf or dimethyl sulphoxide treatment with air gave high yields of $[Os(pdma)_2Cl(NO_2)]$ within minutes, but there was no reaction in days under argon. In $CHCl_3$, in the presence of O_2, a mixture of $[Os(pdma)_2Cl(N_2)]^+$ and $[Os(pdma)_2Cl(NO)]^{2+}$ was rapidly produced. A similar reaction was found in CH_2Cl_2, but was slower. In CCl_4 with O_2 the major product was $[Os(pdma)_2Cl(NO)]^{2+}$ with a lesser yield of $[Os(pdma)_2Cl(NO_2)]$ and a trace amount of $[Os(pdma)_2Cl(N_2)]^+$, the reaction being slower than in CH_2Cl_2. In aqueous suspension, $[Os(pdma)_2Cl(ONNNHPh)]$ and NO rapidly gave $[Os(pdma)_2Cl(NO)]^{2+}$, with a small amount of the N_2 complex as by-product. There was no reaction with $[OH]^-$ or $[CO_3]^{2-}$.

It is obvious that the above reactions are radical in nature. Osmium apparently promotes free-radical reactions of the ligand, since the analytical reagent PhN(OH)N=NPh is stable to air in solution,[23] though it can be oxidised to the radical PhN(O)N=NPh by Ag_2O.[24] It is presumed that the first step in all the reactions of $[Os(pdma)_2Cl(ONNNHPh)]$ is also hydrogen abstraction, but the tautomeric form from which the hydrogen is abstracted may be different in the complex because of the influence of the osmium. The osmium *d*

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orbitals may also allow formation of a low-energy path for hydrogen abstraction *via* a metal hydride. The path of the subsequent reaction of the complex is dependent on the solvent and/or the presence of other radical species. However, a major route in the decomposition of PhN(O)NNPh is loss of N_2 and formation of PhNO,[24] and this appears to be paralleled in reactions of the osmium complex.

Hydroxylamine, $\mathrm{NH_2OH}$, and *trans*-$[\mathrm{Os(pdma)_2Cl(NO)}]^{2+}$ gave a 35% yield of $[\mathrm{Os(pdma)_2(NO)(OH)}]^{2+}$. A mixture of other products, among which were $[\mathrm{Os(pdma)_2Cl(N_2)}]^{+}$ and $[\mathrm{Os(pdma)_2Cl(NO_2)}]$, judging from the i.r. spectra, were also formed but could not be separated. The n.m.r. spectrum showed that $[\mathrm{Os(pdma)_2(NO)(OH)}]^{2+}$ was the *trans* isomer, and the reaction therefore provides an alternative to the *cis*-$[\mathrm{Os(pdma)_2Cl(NO)}]^{2+}$ + $[\mathrm{OH}]^-$ route to the hydroxo-complex. Attempts to obtain this complex by substitution of X^- in *trans*-$[\mathrm{Os(pdma)_2X(NO)}]^{2+}$ gave only $[\mathrm{Os(pdma)_2X(NO_2)}]$. There was no formation of $[\mathrm{Os(pdma)_2(NO_2)(OH)}]$ when $[\mathrm{Os(pdma)_2(NO)(OH)}]^{2+}$ was treated with $[\mathrm{OH}]^-$. The way in which the products of the $\mathrm{NH_2OH}$ reaction were formed is rather mysterious. Reaction of $\mathrm{NH_2OH}$ with co-ordinated NO usually leads to formation of N_2O, either as a ligand,[18] or as an evolved gas.[19,25] In the present work N_2O did not appear as a ligand, nor was any gas evolved. It is unlikely that $\mathrm{NH_2OH}$ promotes simple substitution of $[\mathrm{OH}]^-$ for the strongly bound Cl^-; the only other alternative is loss of NO by reaction with $\mathrm{NH_2OH}$, followed by loss of Cl^- and reformation of NO from $\mathrm{NH_2OH}$. Further work is in progress on this reaction.

There was no reaction between *trans*-$[\mathrm{Os(pdma)_2Cl(NO)}]^{2+}$ and aqueous $\mathrm{NH_3}$, aniline, *p*-methoxyaniline, or azide ion.

In all the reactions of *trans*-$[\mathrm{Os(pdma)_2Cl(NO)}]^{2+}$ the co-ordinated nitrosyl is attacked by a nucleophile as the first step. We have previously shown that a variety of nitrosyl complexes, all with a ν(NO) frequency at $>1\,886$ cm^{-1}, are similarly attacked, whereas others with lower ν(NO) are not.[1] The reactive *trans*-$[\mathrm{Os(pdma)_2X(NO)}]^{2+}$ complexes discussed here have ν(NO) close to 1 865 cm^{-1}, whereas *trans*-$[\mathrm{Os(pdma)_2(NO)(OH)}]^{2+}$ [ν(NO) at 1 820 cm^{-1}] was unreactive. It appears that, within a series of related complexes, ν(NO) is a guide to reactivity, but there is no general frequency range for reactive or unreactive complexes. This parallels the much better known situation for carbonyls, where ν(CO) is, in general, only an indication of which carbonyls could be electrophilic, but where a good correlation between ν(CO) and electrophilicity for a closely related series of complexes exists.[26] To date, related series of nitrosyl complexes such as those discussed here or $[\mathrm{RuX(NH_3)_4(NO)}]^{n+}$ ($X = \mathrm{NH_3}$, $n = 3$; $X = $ Cl, Br, I, or OH, $n = 2$)[18,27] have not shown the gradual variation in electrophilicity observed for carbonyls, probably because the changes in electron density at the nitrogen atom produced by the different ligands have not been small enough to influence reactivity in a subtle way. We are attempting to obtain a series of complexes where this subtle variation occurs.

EXPERIMENTAL

The salt $[\mathrm{NH_4}]_2[\mathrm{OsCl_6}]$ was obtained from Johnson, Matthey. All the other materials were reagent grade. The salts $\mathrm{Cs_2[OsX_5(NO)]}$ (X = Cl, Br, or I) were prepared by a considerably modified version of the literature method.[8]*

Caesium Pentahalogenonitrosylosmate, $\mathrm{Cs_2[OsX_5(NO)]}$ (X = Cl, Br, *or* I).—The salt $[\mathrm{NH_4}]_2[\mathrm{OsCl_6}]$ (1.0 g) was 'activated' by refluxing for 30 min in water (14 cm^3) to which 10 drops of concentrated HCl had been added. To the still warm solution was added $\mathrm{K[NO_2]}$ (5 g) and then NO was passed slowly through the refluxing solution for 3 d. To the resulting dark yellow solution was added concentrated HX until the effervescence ceased; excess of HX (2 cm^3) was then added, the mixture was filtered to remove an unknown white solid, and the solution was warmed until it became completely red. Caesium chloride was then added to the cooled solution until precipitation of $\mathrm{Cs_2[OsX_5(NO)]}$ was complete. Yields were *ca.* 30%. Examination of the i.r. spectrum of the products showed that they were impure; these materials were normally used without further purification in subsequent syntheses. An analytically pure sample of the chloro-complex was obtained, with difficulty, by first washing the crude product with concentrated HCl, in which $\mathrm{Cs_2[OsCl_5(NO)]}$ is only slightly soluble, then thrice recrystallising by reprecipitating with CsCl from water containing a few drops of HCl. The product was washed with ethanol and diethyl ether and dried in air (Found: Cl, 26.7; N, 2.20. Calc. for $\mathrm{Cl_5Cs_2NOOs}$: Cl, 26.75; N, 2.10%). Similar procedures were used for the bromo- and iodo-complexes. We found that ν(NO) for the complexes was at 1 818 {$\mathrm{Cs_2[OsCl_5(NO)]}$}, 1 799 {$\mathrm{Cs_2[OsBr_5(NO)]}$}, and 1 806 cm^{-1} {$\mathrm{Cs_2[OsI_5(NO)]}$}. These values differ from those in the literature,[13] but the purity of the literature samples is unknown.

trans-*Halogenonitrosylbis*[o-*phenylenebis*(*dimethylarsine*)]-*osmium Di-iodide Hydrate*, *trans*-$[\mathrm{Os(pdma)_2X(NO)}]\mathrm{I_2{\cdot}H_2O}$ (X = Cl, Br, *or* I).—To a solution of $\mathrm{Cs_2[OsX_5(NO)]}$ (0.20 g) in water (30 cm^3) was added a solution of pdma (0.3 g) in ethanol (30 cm^3). The resulting mixture was heated under reflux under argon until a clear yellow solution was produced (usually *ca.* 2 d). The solution was evaporated on a steam-bath under argon to a volume of *ca.* 20 cm^3, then NaI was added until precipitation of *trans*-$[\mathrm{Os(pdma)_2X(NO)}]\mathrm{I_2{\cdot}H_2O}$ was complete. The precipitate was removed by filtration, washed with ethanol and diethyl ether, and dried in air. Crude yields were *ca.* 60%. The chloro-complex was recrystallised from nitromethane–diethyl ether, the bromo- and iodo-complexes from dmf–$\mathrm{OEt_2}$. In each case a few drops of water was added, since crystallisation of the complex as a hydrate was greatly facilitated. Recrystallised yields were *ca.* 60% of the crude material.

Chloride, bromide, perchlorate, and azide salts of the

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* *Note added in proof:* A recent preparation of $[\mathrm{OsX_5(NO)}]^{2-}$ differs from that given here in that the intermediate $[\mathrm{Os(NO)(NO_2)_3(OH)}]^{2-}$ is isolated before subsequent reaction with HX. This procedure has not been checked, but may increase yields at the expense of convenience (N. M. Sinitsyn, V. F. Travkin, A. A. Stevlov, and Z. B. Itkina, *Soviet J. Co-ord. Chem.*, 1975, **1**, 82).

[25] F. Bottomley, S. G. Clarkson, and S. B. Tong, *J.C.S. Dalton*, 1974, 2344.

[26] R. J. Angelici and L. J. Blacik, *Inorg. Chem.*, 1972, **11**, 1754.

[27] F. Bottomley and J. R. Crawford, *J.C.S. Dalton*, 1972, 2145.

complexes were prepared from the iodide by metathesis using the following conditions: *

Complex required		Precipitating agent	Solvent	Recrystallised from
trans-[Os(pdma)$_2$Cl(NO)][ClO$_4$]$_2$		Na[ClO$_4$]	Water	Me$_2$CO–OEt$_2$
Cl	Cl$_2$	[NBu$^t_4$]Cl	MeNO$_2$	EtOH–OEt$_2$
Cl	Br$_2$	[NBu$^t_4$]Br	MeNO$_2$	EtOH–OEt$_2$
Cl	[N$_3$]$_2$	Na[N$_3$]	Water	Me$_2$CO–OEt$_2$
Br	Br$_2$	LiBr	dmf	dmf–OEt$_2$
Br	[ClO$_4$]$_2$	Na[ClO$_4$]	dmf	Me$_2$CO–OEt$_2$
I	[ClO$_4$]$_2$	Na[ClO$_4$]	dmf	Me$_2$CO–OEt$_2$

The electronic spectrum of *trans*-[Os(pdma)$_2$Cl(NO)]Cl$_2$·H$_2$O in water showed one band at 295 nm (ε 1 562 dm^3 mol^{-1} cm^{-1}).

Reaction of trans-[Os(pdma)$_2$X(NO)]$^{2+}$ *with Hydroxide Ion: Halogenonitrobis*[o-*phenylenebis*(*dimethylarsine*)]*osmium*, [Os(pdma)$_2$X(NO$_2$)] (X = Cl, Br, *or* I).—The complex [Os(pdma)$_2$Cl(NO)]Cl$_2$·H$_2$O (0.10 g) was dissolved in the minimum quantity of aqueous Na[OH] (5 cm^3, 1 mol dm^{-3}). The solution was stirred at room temperature for 1 h, during which time a pale yellow precipitate of [Os(pdma)$_2$Cl(NO$_2$)] was deposited. This was removed by filtration, washed with water, ethanol, and diethyl ether, and dried *in vacuo* over P$_4$O$_{10}$, yield 0.075 g (83%). The product was recrystallised from chloroform–diethyl ether, yield 0.075 g (83%). The complexes [Os(pdma)$_2$Br(NO$_2$)] and [Os(pdma)$_2$I(NO$_2$)] were prepared analogously from [Os(pdma)$_2$Br(NO)]I$_2$·H$_2$O and [Os(pdma)$_2$I(NO)]I$_2$·H$_2$O in 39 and 58% yield respectively.

Reaction of trans-[Os(pdma)$_2$Cl(NO)]$^{2+}$ *with Hydrazine: Azidochlorobis*[o-*phenylenebis*(*dimethylarsine*)]*osmium*, [Os(pdma)$_2$Cl(N$_3$)].—To a deoxygenated solution of [Os(pdma)$_2$Cl(NO)]Cl$_2$·H$_2$O (1.0 g) in ethanol (150 cm^3) was added, dropwise, hydrazine hydrate (35 cm^3) until precipitation of yellow [Os(pdma)$_2$Cl(N$_3$)] was complete. The product was collected by filtration, washed with water, ethanol, and diethyl ether, and dried under argon, yield 0.78 g (85%). More of the material could be obtained from the filtrate on evaporation, but it was contaminated with [Os(pdma)$_2$Cl(NO$_2$)], as occurred when rigorous precautions against dioxygen were not taken.

Reaction of [Os(pdma)$_2$Cl(N$_3$)] *with Dioxygen.*—Dioxygen was passed through a solution of [Os(pdma)$_2$Cl(N$_3$)] (0.08 g) in chloroform (70 cm^3) for 48 h. Addition of diethyl ether gave a pale yellow precipitate of [Os(pdma)$_2$Cl(NO$_2$)] (0.04 g, 50%) which was purified as before and shown to be identical to [Os(pdma)$_2$Cl(NO$_2$)] obtained from *trans*-[Os(pdma)$_2$Cl(NO)]$^{2+}$ and [OH]$^-$ by analysis and spectroscopy.

Reaction of [Os(pdma)$_2$Cl(N$_3$)] *with Hydrochloric Acid:* trans-*Chloro*(*dinitrogen*)*bis*[o-*phenylenebis*(*dimethylarsine*)]-*osmium Chloride, trans*-[Os(pdma)$_2$Cl(N$_2$)]Cl, *and* cis-*Chloronitrosylbis*[o-*phenylenebis*(*dimethylarsine*)]*osmium Dichloride, cis*-[Os(pdma)$_2$Cl(NO)]Cl$_2$.—The complex [Os(pdma)$_2$Cl(N$_3$)] {containing some [Os(pdma)$_2$Cl(NO$_2$)] as impurity} (0.30 g) was treated directly with concentrated HCl (25 cm^3). There was immediate precipitation of very pale yellow *trans*-[Os(pdma)$_2$Cl(N$_2$)]Cl which was removed by filtration, washed quickly with water, ethanol, and diethyl ether, and dried in air, yield 0.08 g (25%). The green filtrate remaining after removal of *trans*-[Os(pdma)$_2$Cl(N$_2$)]Cl was evaporated to dryness in air. The resulting solid was recrystallised thrice from ethanol–diethyl ether, yielding very pale yellow *cis*-[Os(pdma)$_2$Cl(NO)]Cl$_2$·H$_2$O (0.20 g, 46%). The electronic spectrum of the product in ethanol showed only the tail of a strong band below 200 nm.

Reaction of cis-[Os(pdma)$_2$Cl(NO)]Cl$_2$·H$_2$O *with Hydroxide Ion.*—The complex *cis*-[Os(pdma)$_2$Cl(NO)]Cl$_2$·H$_2$O (0.03 g) was dissolved in Na[OH] (1 mol dm^{-3}, 1.0 cm^3) giving a dark yellow solution, which was filtered, leaving a very small quantity of a brown precipitate whose i.r. spectrum indicated a nitro-complex. To the filtrate was added solid NaI until precipitation of yellow *trans*-[Os(pdma)$_2$(NO)(OH)]I$_2$ was complete. The product was washed with water, ethanol, and diethyl ether and dried in air, yield 0.03 g (58%).

Reaction of trans-[Os(pdma)$_2$Cl(NO)]$^{2+}$ *with Phenylhydrazine: Chloro*[1-*oxo*-3-*phenyltriazene*(1 −)]*bis*[o-*phenylenebis*(*dimethylarsine*)]*osmium*, [Os(pdma)$_2$Cl(ONNNHPh)].—To *trans*-[Os(pdma)$_2$Cl(NO)]Br$_2$·H$_2$O (0.73 g), dissolved in ethanol (350 cm^3), was added phenylhydrazine (10 cm^3) dropwise. A pale yellow precipitate formed. The mixture was stirred for 1 h, then the precipitated [Os(pdma)$_2$Cl(ONNNHPh)] was removed by filtration, washed with water, ethanol, and diethyl ether, and dried in air, yield 0.24 g (35%). The yellow filtrate after removal of [Os(pdma)$_2$Cl(ONNNHPh)] was allowed to evaporate to a volume of *ca.* 20 cm^3 at room temperature. Addition of diethyl ether precipitated a mixture of [Os(pdma)$_2$Cl(N$_2$)]Br and [PhNHNH$_3$]Br. The mixture was separated by stirring with chloroform, filtering to remove insoluble [PhNHNH$_3$]Br, and adding diethyl ether to the filtrate to precipitate [Os(pdma)$_2$Cl(N$_2$)]Br. The product was recrystallised twice from chloroform–diethyl ether, yield 0.26 g (40%). Its physical and chemical properties were identical to those of *trans*-[Os(pdma)$_2$Cl(N$_2$)]Br obtained from [Os(pdma)$_2$Cl(N$_3$)] and HBr.

Reactions of [Os(pdma)$_2$Cl(ONNNHPh)].—*With hydrochloric acid.* A suspension of [Os(pdma)$_2$Cl(ONNNHPh)] (0.1 g) in concentrated HCl (70 cm^3) was stirred at room temperature for 3 d, forming a green solution and a pale yellow precipitate. The precipitate of *trans*-[Os(pdma)$_2$Cl(N$_2$)]Cl was removed by filtration and recrystallised from chloroform–diethyl ether; it was extremely difficult to decolourise the complex, the unknown green material (apparently some form of dye produced from the ligand) being strongly adsorbed on the solid. The i.r. and n.m.r. spectra, analysis, and conductivity were, however, identical to those of *trans*-[Os(pdma)$_2$Cl(N$_2$)]Cl obtained from [Os(pdma)$_2$Cl(N$_3$)] and HCl. Evaporation of the filtrate after removal of [Os(pdma)$_2$Cl(N$_2$)]Cl gave only starting material, contaminated with trace amounts of the green material.

With dioxygen in dimethylformamide or dimethyl sulphoxide. The complex (0.15 g) was dissolved in dmf (90 cm^3) or dmso (500 cm^3) in air. A yellow solution was formed within 15 min; this was evaporated to dryness at room temperature (dmf) or on a steam-bath (dmso). The crude product was dissolved in chloroform, filtered, and the filtrate again evaporated to dryness (room temperature).

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* The perchlorate and azide salts of [Os(pdma)$_2$Cl(NO)]$^{2+}$ were obtained using [Os(pdma)$_2$Cl(NO)]Cl$_2$·H$_2$O as starting material.

The solid was washed repeatedly with water, ethanol, and diethyl ether and dried in air. Yields of [Os(pdma)$_2$Cl(NO$_2$)]: from dmf, 0.077 g (68%); from dmso, 0.06 g, 45%. The product had physical and chemical properties identical to those of the same complex obtained by reaction of *trans*-[Os(pdma)$_2$Cl(NO)]$^{2+}$ with [OH]$^-$. The reaction in dmf was repeated after first vigorously purging the solvent with argon. After 8 d the yellow solution was evaporated and separated under argon. Yield of [Os(pdma)$_2$Cl(NO$_2$)], 0.01 g (7%). The remainder of the product was starting material.

With dioxygen in carbon tetrachloride or chloroform. A suspension of the complex (0.15 g) was stirred with a stream of O$_2$ passing through the appropriate solvent (100 cm^3 of CCl$_4$, 10 cm^3 of CHCl$_3$) for a few minutes (CHCl$_3$) or for 4 d (CCl$_4$). The yellow precipitate was removed by filtration. Recrystallisation of the precipitate from ethanol–diethyl ether gave [Os(pdma)$_2$Cl(NO$_2$)] as the ethanol-insoluble residue and *trans*-[Os(pdma)$_2$Cl(NO)]Cl$_2$ as the ethanol-soluble fraction. From the reaction in CHCl$_3$, *trans*-[Os(pdma)$_2$Cl(N$_2$)]Cl was obtained from the initial CHCl$_3$ filtrate. Yields in CHCl$_3$: *trans*-[Os(pdma)$_2$Cl(NO)]Cl$_2$, 0.06 g (41%), *trans*-[Os(pdma)$_2$Cl(N$_2$)]Cl, 0.028 g (21%). Yields in CCl$_4$: [Os(pdma)$_2$Cl(NO$_2$)], 0.017 g (13%), [Os(pdma)$_2$Cl(NO)]Cl$_2$, 0.062 g (44%), [Os(pdma)$_2$Cl(N$_2$)]Cl, trace. The three products had chemical and physical properties identical to those of the complexes produced by the other methods.

Reaction of trans-[Os(pdma)$_2$Cl(NO)]$^{2+}$ *and Hydroxylamine:* trans-*Hydroxonitrosylbis*[o-*phenylenebis*(*dimethylarsine*)]*osmium*, *trans*-[Os(pdma)$_2$(NO)(OH)]$^{2+}$.—Hydroxylamine hydrochloride (0.58 g) and *trans*-[Os(pdma)$_2$Cl(NO)]Cl$_2$·H$_2$O (0.58 g) were dissolved in the minimum quantity of water (75 cm^3). To the well stirred solution were added five pellets (*ca.* 0.5 g) of Na[OH]. Initially a yellow solution was obtained, which deposited a brown precipitate over 10 min. The mixture was filtered, the filtrate evaporated to dryness, the residue dissolved in ethanol, filtered, and diethyl ether added to the filtrate to precipitate *trans*-[Os(pdma)$_2$(NO)(OH)]Cl$_2$·H$_2$O. This was further purified by reprecipitation from aqueous Na[OH] (1 mol dm^{-3}) with KI. Yield of *trans*-[Os(pdma)$_2$(NO)(OH)]I$_2$, 0.26 g (39%). Attempted separation of the water- and ethanol-soluble fractions gave small quantities of starting material, a trace amount of *trans*-[Os(pdma)$_2$Cl(N$_2$)]$^+$, and another small amount of *trans*-[Os(pdma)$_2$(NO)(OH)]$^{2+}$. Other products could not be identified.

Microanalyses were by A. Bernhardt, West Germany. Electronic spectra were recorded on a Coleman–Hitachi EPS-3T instrument, i.r. spectra as Nujol mulls or in solution between KBr or CaF$_2$ plates on a Perkin-Elmer 467, and n.m.r. spectra on a Varian A60. Conductivity measurements over the concentration range 10^{-5}—5×10^{-4} mol dm^{-3} were made on a Beckman model RC-18A bridge.

We thank Professor Z. Valenta and Dr. C. A. Mansfield for helpful discussions, the National Research Council of Canada for support, Johnson, Matthey Limited for a very generous loan of osmium, and the Canadian International Development Agency for the award of a Commonwealth Scholarship (to E. M. R. K.).

[6/1965 *Received*, 22*nd October*, 1976]