Transition-metal Nitrosyl Compounds. Part IX.[1] The Preparation and Study of the Osmium Cation $[OsH_2(CO)(NO)L_2]^+$ (L = triphenyl- or tricyclohexyl-phosphine

By **Brian F. G. Johnson** * and **John A. Segal**, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The dihydrides $[OsH_2(CO)(NO)L_2]PF_6$ [L = PPh_3 (1) or $P(C_6H_{11})_3$ (2)] have been prepared from the reaction of $Os(CO)(NO)L_2Cl$ and $AgPF_6$ in the presence of H_2. ^1H N.m.r. data indicate that these compounds are stereochemically non-rigid and $\Delta G^{\ddagger}_{T_c}$ values of 48·5 ± 0·8 kJ mol^{-1} and 53·1 ± 0·8 kJ mol^{-1} have been determined for (1) and (2) respectively. On reaction with CO the dihydrides readily undergo H_2 displacement to give the salts $[Os(CO)_2(NO)L_2]PF_6$. Complex (1) reacts similarly with PPh_3 to give $[Os(CO)(NO)(PPh_3)_3]PF_6$ but complex (2) reacts with $P(C_6H_{11})_3$ to form the neutral complex $OsH(CO)(NO)\{P(C_6H_{11})_3\}_2$ by H$^+$ abstraction.

READY intramolecular rearrangement is not a feature commonly exhibited by six-co-ordinate molecules.[2,3] The pervading stability of one co-ordination polyhedron, the octahedron, tends to promote stereochemical rigidity. However, examples of polytopal rearrangements in six-co-ordinate complexes were reported recently by Muetterties and his co-authors.[4,5] These workers carried out extensive studies on a series of species of type *cis*- and *trans*-MH_2L_4 and *cis*-MH_2L_3X (M = Fe or Ru, L = tertiary phosphorus donor, and X = CO) and proposed a new physical model by which the observed rearrangements could occur.[6] Here we describe the preparation and study of the cationic complexes, $[OsH_2(CO)(NO)L_2]^+PF_6^-$ (*i.e.* of the type MH_2L_2XY), where L = PPh_3 or $P(C_6H_{11})_3$. These complexes have also been found to exhibit fluxional behaviour.

Preparation.—Addition of silver hexafluorophosphate in acetone to a solution of the neutral compound $Os(CO)(NO)L_2Cl$ [L = PPh_3 or $P(C_6H_{11})_3$] in dichloromethane leads to rapid precipitation of silver chloride. The resulting yellow solution, which is thought to contain the species $[Os(CO)NO(acetone)L_2]^+$ (or $[Os(CO)(NO)L_2]^+$), readily reacts with hydrogen to give the required cations. Although not unique this reaction represents one of the few instances where dihydrogen co-ordinates to a metal of the iron triad at ambient temperature and pressure.[7] These cations are best stored under a hydrogen atmosphere as they decompose slowly in air and also under nitrogen. Satisfactory microanalytical results have been obtained and are given in the Experimental section.

I.r. Studies.—The i.r. spectrum (2120—1770 cm^{-1}) of each dihydrido-complex shows a single very strong band in the region of 1800 cm^{-1} which can be assigned to the NO stretch. However, in the carbonyl region more than one absorption occurs (Figure 1 *a*, *c* and Table) and the observed band pattern cannot be readily interpreted in terms of simple ν(CO) and ν(OsH) absorptions.

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[1] Part VIII, B. F. G. Johnson and J. A. Segal, *J.C.S. Dalton*, 1973, 478.

[2] E. L. Muetterties, *Accounts Chem. Res.*, 1970, **3**, 266.

[3] P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1973, **95**, 75.

[4] F. N. Tebbe, P. Meakin, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1970, **92**, 1068.

[5] P. Meakin, L. J. Guggenberger, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, W. G. Peet, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1970, **92**, 3482.

[6] P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1971, **93**, 4701.

[7] For other recently reported systems see *e.g.* W. H. Knoth, *J. Amer. Chem. Soc.*, 1972, **94**, 104; P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 3143; P. Giannoccaro, M. Rossi, and A. Sacco, *Co-ordination Chem. Rev.*, 1972, **8**, 77; B. E. Cavit, K. R. Grundy, and W. R. Roper, *J.C.S. Chem. Comm.*, 1972, 60.

Resonance interaction between the carbonyl and metal hydride stretching modes has been verified by comparison of the i.r. spectra of the hydrides with those of the corresponding D_2 derivatives (see later) which show a single, more intense, ν(CO) band in each case (Figure 1 c, d). In addition, small shifts to higher frequency (*ca.* 15 cm^{-1}) were recorded for the ν(NO) absorptions of the deuterides implying that some interaction of this mode with the OsH stretching vibrations also occurs. These observations strongly suggest [8] a stereochemistry in which the hydride atoms lie *trans* to the CO and NO groups, hence a *cis*-hydride and *trans*-phosphine arrangement is proposed as shown in idealized form in Figure 2. Similar coupling of ν(NO) and ν(MH) has been observed recently by Wilson and Osborn [8] in the species $RuH(NO)L_3$ for which a stereochemistry with H *trans* to NO has been confirmed on the basis of spectroscopic and crystallographic studies.[9] No ν(OsD) absorptions were observed in the spectra of the D_2 complexes. These are probably very weak as has been observed in other similar complexes.[10] The simple form of the i.r. spectra of the deuterides eliminates the possibility that *trans*-forms of the cations exist as found previously in certain other MH_2L_4 derivatives.[3]

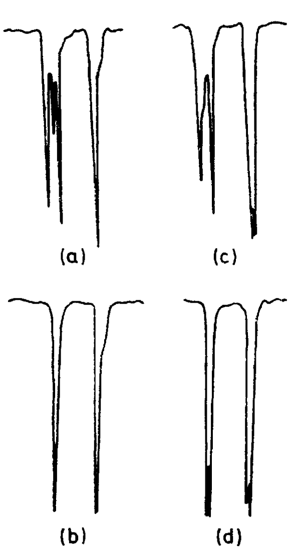

FIGURE 1 I.r. spectra (2150—1750 cm^{-1}, Nujol mulls) of (a) $[OsH_2(CO)NO(PPh_3)_2]PF_6$ and (b) $[OsD_2(CO)NO(PPh_3)_2]PF_6$; (c) $[OsH_2(CO)NO\{P(C_6H_{11})_3\}_2]PF_6$ and (d) $[OsD_2(CO)NO\{P(C_6H_{11})_3\}_2]PF_6$

I.r data (2150—1600 cm^{-1}) for the hydrido- and deuterido-complexes

Complex [a]	ν(CO)/ν(OsH)	ν(NO)	Solution or mull
$[OsH_2(CO)NO(PPh_3)_2]PF_6$	2120s, 2073m, 2048s	1809vs	Nujol
$[OsD_2(CO)NO(PPh_3)_2]PF_6$	2077vs	1823vs	Nujol
$[OsH_2(CO)NO\{P(C_6H_{11})_2\}_2]PF_6$	2097s, 2022s	1789vs, 1772vs	Nujol [b]
	2087s, 2029s	1790vs	CH_2Cl_2
$[OsD_2(CO)NO\{P(C_6H_{11})_3\}_2]PF_6$	2057s, 2043s	1805vs, 1789vs	Nujol [b]
	2058vs	1808vs	CH_2Cl_2
$OsH(CO)NO(PPh_3)_2$	1895vs	1630vs	Nujol
$OsH(CO)NO\{P(C_6H_{11})_3\}_2$ [c]	1880vs	1611vs	Nujol

[a] Absorptions at *ca.* 850 cm^{-1} characteristic of PF_6^- were seen for the ionic complexes. [b] Splitting seen in the solid state only. [c] Not isolated in an analytically pure state.

^{1}H *N.m.r. Studies*.—The room-temperature ^{1}H n.m.r. spectrum of $[OsH_2(CO)NO\{P(C_6H_{11})_3\}_2]PF_6$ in CD_2Cl_2 solution showed a broad resonance at τ *ca.* 16. When the compound was warmed to +45 °C this resonance sharpened to a well resolved 1 : 2 : 1 triplet centred at τ 15·74 * (J_{PH} 20 Hz). As the temperature was lowered the signal broadened and disappeared; two new resonances then began to emerge and finally sharpened to 1 : 2 : 1 triplets, each of the same intensity but half that of the higher temperature signal. At −60 °C their positions were τ 14·79 (J_{PH} = 18 Hz) and 17·10 (J_{PH} = 22 Hz) (see Figure 3). Similar results were obtained for $[OsH_2(CO)NO\{P(C_6H_5)_3\}_2]PF_6$. In this case the fully time-averaged spectrum was accessible at room temperature exhibiting a triplet centred at τ 13·77 (J_{PH} = 21 Hz). At −60 °C two signals at τ 13·27 (J_{PH} = 19 Hz) and 14·39 (J_{PH} = 23 Hz) were observed. In each system the higher field resonance in the non-exchange spectrum shows a larger ^{31}P coupling and, as expected, the fully time-averaged spectrum shows a J_{PH} value which is the mean of the two coupling constants measured at the low temperature limit. This latter observation rules out the possibility of an intermolecular exchange process. No H/H coupling was observed in the low-temperature spectra and $J_{HH'}$ must be very small. As seen from the data above some

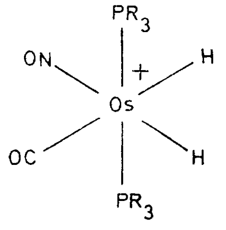

FIGURE 2 Probable structure of the $[OsH_2(CO)NO(PR_3)_2]^+$ cation

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* Spectra were measured relative to the CH_2Cl_2 resonance taking its position as τ 4·65.

[8] S. T. Wilson and J. A. Osborn, *J. Amer. Chem. Soc.*, 1971, **93**, 3068.

[9] C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 1972, **11**, 1094.

[10] J. P. Jesson in 'Transition Metal Hydrides,' ed. E. L. Muetterties, Marcel Dekker, New York, 1971, p. 87.

temperature dependence has been noted in the *mean* chemical shift of the hydride resonances.

The spectra of the cations were measured over a range of intermediate temperatures and the coalescence points (T_c) were determined; the peak separations ($\Delta\nu$) in the absence of exchange were also noted: for complex (1) $T_c = -28$ °C and $\Delta\nu = 112$ Hz; for complex (2) $T_c = +3$ °C and $\Delta\nu = 231$ Hz. Using the approximate relationship, $\Delta G^\ddagger_{T_c} = -RT_c \ln \pi\Delta\nu h/\sqrt{2}K_BT_c$ where K_B, h, and R have their usual significance, the activation energies $\Delta G^\ddagger_{T_c}$ were calculated. Values of $48{\cdot}5 \pm 0{\cdot}8$ and $53{\cdot}1 \pm 0{\cdot}8$ kJ mol^{-1} were found for (1) and (2) respectively. The observation of a higher barrier for the tricyclohexylphosphine complex is consistent with the larger cone angle of $P(C_6H_{11})_3$[11] and the larger donor properties of this phosphine which may lead to a stronger metal–hydride linkage.

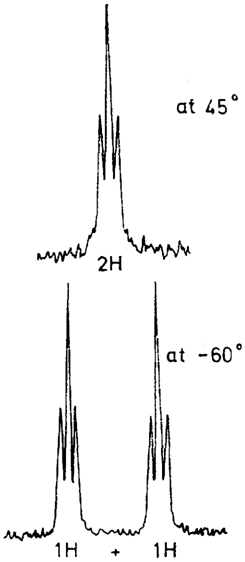

FIGURE 3 The limiting fast and slow exchange ^{1}H n.m.r. spectra (τ 14·5—17·5) of $[OsH_2(CO)NO\{P(C_6H_{11})_3\}_2]PF_6$

The low-temperature limit spectra of the dihydrides confirm the stereochemistry in Figure 2 but it is not possible to determine which resonance results from H *trans* to NO and which from H *trans* to CO. Intuitively one might expect H *trans* to NO to appear at lower field as NO is normally a stronger π-acceptor than CO; however results recently obtained by Norton and Dolcetti[12] in a study of $(CO)_3Re(\mu\text{-}OEt)_3Re(CO)_2NO$ show that in this species OEt *trans* to CO is actually the more deshielded. It is hoped that isotopic labelling experiments currently in progress may help to distinguish between the proton resonances and hence give an indication of the relative acceptor properties of NO and CO in these dihydrido-systems.

In their detailed mechanistic analysis of the intramolecular rearrangement process in the MH_2L_4 complexes, Muetterties and his co-workers[3,6] took into account the considerable distortion from octahedral geometry observed in these species. An *X*-ray diffraction study[13] of $FeH\{P(C_6H_5)(OC_2H_5)_2\}_4$ has shown an iron–phosphorus arrangement intermediate between octahedral and tetrahedral in the crystalline state. As a result the structure has been described as a tetrahedron with the hydrogens located at the centre of two faces. This result led to proposal of the 'tetrahedral jump' model in which the hydrogens move from one face to another *via* a tetrahedral edge. The process takes the system from the ground state through an edge transition state back to the ground-state arrangement. In the carbonyl–nitrosyl system however movement of a single hydrogen in this way cannot lead back to the ground-state geometry as no vacant face exists which is similar to either of the two ground-state faces. It would seem that the rearrangement cannot be visualised as occurring through a *single* hydride 'jump' and must involve movement of both protons in the basic equilibration process. In the absence of further information a simple positional interchange of the two hydrogens through the P–M–P plane seems attractive. It is possible that in these cationic derivatives there remains some interaction between the two H atoms. This suggestion is not without precedent as Mays and his co-workers[14] were led to a similar conclusion as a result of their work on the substitution reactions of $[Ir(CO)_2L_2H_2]^+$. Equilibration by rotation of H_2 could then occur in a fashion analogous to olefin rotation in $[Os(CO)NO(C_2H_4)\text{-}\{P(C_6H_5)_3\}_2]^+$.[15] However, the possibility that the interchange goes *via* a *trans*-intermediate cannot be excluded.

The origin of the barrier to H–H interconversion in the complexes H_2ML_4 remains a matter of dispute. Others have shown that, in general, the barrier increases (*a*) when one of the tertiary phosphine ligands L is replaced by a less bulky ligand such as CO[2,6] and (*b*) as the size of the central metal ion M increases.[3,6] This behaviour may be correlated with the extent of the distortion from an octahedral geometry imposed by either the ligand L or the metal. The greater the distortion the lower the barrier. The barriers in the nitrosyl cations are surprisingly low (see above). There is no simple explanation of this as undoubtedly a NO^+ group is smaller than a tertiary phosphine and the complex must show a closer proximity to an octahedral geometry than either the H_2ML_4 or $H_2M(CO)L_3$ species. On these grounds an increase in the barrier is expected.

In these arguments the relative donor and acceptor properties of the ligands employed (*i.e.* R_3P or CO) have been ignored since, with the limited information available at present, the contribution they make to the overall barrier cannot be determined. The effect of the positive charge on the osmium species has also been ignored. This is expected to lead to an increase in at least some

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[11] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2956.

[12] J. R. Norton and G. Dolcetti, *Inorg. Chem.*, 1973, **12**, 485.

[13] L. J. Guggenberger, D. D. Titus, M. T. Flood, R. E. Marsh, A. K. Orio, and H. B. Gray, *J. Amer. Chem. Soc.*, 1972, **94**, 1135.

[14] M. J. Mays, R. N. F. Simpson, and F. P. Stefanini, *J. Chem. Soc.* (*A*), 1970, 3000.

[15] B. F. G. Johnson and J. A. Segal, *J.C.S. Chem. Comm.*, 1972, 1313.

of the metal–ligand distances and consequently to a structure exhibiting a smaller distortion from an octahedral geometry than a related neutral species such as $MH_2(CO)_2L_2$. Hence, again, an increase in ΔG^* would be anticipated.

Chemical Studies.—A major feature in the chemistry of the cations is the readiness with which H_2 may be displaced. This behaviour is also observed in the related iridium species $[IrH_2(CO)_2L_2]^+$.[14,16] In an atmosphere of dry deuterium virtually complete H_2/D_2 exchange occurs in a period of about one day giving the species $[OsD_2(CO)(NO)L_2]PF_6$. The process was found to be quite reversible leading to quantitative recovery of the starting material.

$$[OsH_2(CO)(NO)L_2]PF_6 \underset{H_2}{\overset{D_2}{\rightleftharpoons}} [OsD_2(CO)(NO)L_2]PF_6$$

The hydrides are unstable in most nucleophilic solvents and generally decompose with gas evolution. With carbon monoxide the species $[Os(CO)_2(NO)L_2]PF_6$ are formed. In contrast, in the isoelectronic *neutral* compounds $MH_2(CO)_2(PPh_3)_2$ (M = Ru or Os) the H_2 molecule is not labile and in the species $MH_2(CO)_3PPh_3$ the CO is labile whereas the H_2 is not.[17] The PPh_3 dihydrido-cation also undergoes H_2 displacement by triphenylphosphine leading to the tris(triphenylphosphine) product $[Os(CO)NO(PPh_3)_3]PF_6$ but the analogous derivative $[Os(CO)NO\{P(C_6H_{11})_3\}_3]PF_6$ is not formed in this way presumably because of the larger spatial requirements of tricyclohexylphosphine. If excess of $P(C_6H_{11})_3$ is used then the dihydrido-cation undergoes deprotonation leading to the neutral hydride $OsH(CO)(NO)\{P(C_6H_{11})_3\}_2$. Similarly if ethanol is added to a THF solution of $[OsH_2(CO)NO(PPh_3)_2]PF_6$ then the brown neutral species $OsH(CO)NO(PPh_3)_2$ is precipitated; alternative preparations of this hydride have been given previously.[1,18] The $P(C_6H_{11})_3$ complex has not been isolated in a pure state because of its high air sensitivity. All attempts to protonate these neutral species to retrieve the dihydrido-cations have failed, a result which contrasts with that obtained in the iridium systems explored by Malatesta and his co-workers,[19] in which reversible protonation and deprotonation can be effected.

$$[OsH_2(CO)(NO)L_2]^+PF_6^- \rightleftharpoons OsH(CO)(NO)L_2 + H^+PF_6^-$$

$$IrH(CO)L_2 + H^+ClO_4^- \rightleftharpoons [IrH_2(CO)L_2]^+ClO_4^-$$

Since the neutral hydrides show no coupling of ν(OsH) to ν(CO) (Table) it is thought that they possess distorted trigonal bipyramidal geometries with H *trans* to NO as is found in the complex $RuH(NO)(PPh_3)_3$.[9]

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 grating instrument and ^1H n.m.r. spectra on a Varian Associates XL100 or HA100 spectrometer at 100 MHz. Microanalyses were determined by Mr. D. Flory of this laboratory. The neutral chlorides $Os(CO)(NO)L_2Cl$ [L = PPh_3 or $P(C_6H_{11})_3$], were prepared by previously reported methods.[1,20] All reactions were carried out under an atmosphere of dry oxygen-free nitrogen.

Dihydridocarbonylnitrosylbis(tricyclohexylphosphine)osmium(II) *Hexafluorophosphate.*—Silver hexafluorophosphate (0·044 g) in acetone (1 ml) was added to a solution of $Os(CO)NO[P(C_6H_{11})_3]_2Cl$ (0·15 g) in dichloromethane (20 ml). Silver chloride precipitated rapidly and, after the mixture had been shaken for a few seconds, was filtered off; the filtrate was collected in a flask cooled to −196°. The frozen solution was then allowed to warm to room temperature under an atmosphere of hydrogen and the solution was saturated with the gas. Careful addition of pentane led to precipitation of the product as a cream solid (0·125 g) which was filtered off, washed with pentane, and dried *in vacuo* (Found: C, 46·5; H, 7·0; N, 1·3; P, 9·6. $C_{37}H_{68}F_6NO_2OsP_3$ requires C, 46·5; H, 7·2; N, 1·5; P, 9·7%).

Dihydridocarbonylnitrosylbis(triphenylphosphine)osmium(II) *hexafluorophosphate* was obtained similarly (Found: C, 48·1; H, 3·4; N, 1·4; P, 9·9. $C_{37}H_{32}F_6NO_2P_3Os$ requires C, 48·3; H, 3·5; N, 1·5; P, 10·1%).

Dideuteridocarbonylnitrosylbis(tricyclohexylphosphine)osmium(II) *Hexafluorophosphate.*—$[OsH_2(CO)NO\{P(C_6H_{11})_3\}_2]PF_6$ (0·100 g) was placed in a 25-ml flask which was then evacuated and filled with D_2 gas. After being set aside for 1 day an i.r. spectrum of the mixture showed that complete deuterium exchange had taken place.

Dideuteridocarbonylnitrosylbis(triphenylphosphine)osmium(II) *hexafluorophosphate* was prepared similarly.

Displacement of H_2 *from* $[OsH_2(CO)NO\{P(C_6H_{11})_3\}_2]PF_6$.—Carbon monoxide was bubbled through a solution of the dihydride (0·050 g) in CH_2Cl_2 solution (6 ml). Comparison of the i.r. spectrum (in CH_2Cl_2 solution) with that of an authentic sample[1] indicated clean conversion into the dicarbonyl species $[Os(CO)_2NO\{P(C_6H_{11})_3\}_2]PF_6$. The complex was crystallized by the addition of pentane or ether.

Similar reactions of $[OsH_2(CO)NO(PPh_3)_2]PF_6$ with CO or PPh_3 led to $[Os(CO)_2NO(PPh_3)_2]PF_6$ or $[Os(CO)NO(PPh_3)_3]PF_6$.

Deprotonation of $[OsH_2(CO)NO(PPh_3)_2]PF_6$.—Ethanol was added to a stirred solution of the dihydride (0·050 g) in dry THF (2 ml). The brown product slowly precipitated and this was filtered off and dried *in vacuo* (yield 0·027 g). Comparison of i.r. data with that of an authentic sample[1] confirmed the formulation of the product as the neutral hydride.

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