The Geometry of Nitrosyl Ligands. Preparation, Reactions, and *X*-Ray Structure Determination of $[Os(NO)(CO)_2(PPh_3)_2]^+$

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Summary $OsH(CO)(NO)(PPh_3)_2$ eliminates H_2 when treated with acids HY (Y = ClO_4, BF_4, or PF_6) in the presence of CO, forming $[Os(NO)(CO)_2(PPh_3)_2]Y$; one carbonyl group is easily displaced from this cation by other ligands and an *X*-ray structure determination of $[Os(NO)(CO)_2(PPh_3)_2]ClO_4,CH_2Cl_2$ reveals trigonal bipyramidal geometry with a linear nitrosyl group.

FIVE co-ordinate nitrosyl complexes of the platinum metals have been found to adopt either of two geometries: trigonal bipyramidal with a linear nitrosyl group, or tetragonal pyramidal with a bent nitrosyl group at the apex $[IrH(NO)(PPh_3)_3]^+$ (ref. 1) and $RuH(NO)(PPh_3)_3$[2] are examples of trigonal bipyramidal geometry while $[IrCl(CO)(NO)(PPh_3)_2]^+$ (ref. 3), $IrCl_2(NO)(PPh_3)_2$,[4] $Ir(CH_3)I(NO)(PPh_3)_2$,[5] and $[Os(OH)(NO)_2(PPh_3)_2]^+$ (ref. 6) exemplify the bent arrangement. To investigate further which of the geometries is preferred in a given situation we have prepared $[Os(NO)(CO)_2(PPh_3)_2]^+$ and studied its reactions and structure.

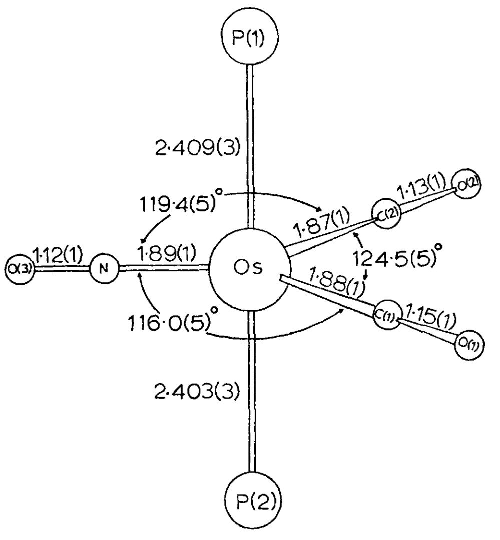

TABLE. *I.r. data for osmium complexes*[a]

	$\nu(CO)cm^{-1}$	$\nu(NO)cm^{-1}$	$\nu(CN)cm^{-1}$
$OsH(CO)(NO)(PPh_3)_2$	1895(vs)	1620(vs)	
$[Os(CO)_2(NO)(PPh_3)_2]^+$	2055(w), 2000(vs)	1750(vs)	
$[Os(CO)(NO)(PPh_3)_3]^+$	1950(s)	1705(vs)	
$[Os(CO)(NO)(PPh_2Me)_3]^+$	1960(s)	1700(vs)	
$[Os(CO)(NO)(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)(PPh_3)]^+$	1960(s)	1700(vs)	
$[Os(CO)(NO)(RNC)(PPh_3)_2]^+$	1960(s)	1700(vs)	2150(m)
$[Os(NO_2)(CO)(RNC)_2(PPh_3)_2]^{+b}$	2050(s)		2200(m), 2160(s)

[a] Satisfactory elemental analyses have been obtained for all compounds reported; the cations were in association with ClO_4, BF_4, or PF_6. [b] $\nu(NO)$, 1380s, 1310m; $\delta(NO_2)$, 815sh.

Reduction of $OsCl(CO)(NO)(PPh_3)_2$[7] with $NaBH_4$ produces red $OsH(CO)(NO)(PPh_3)_2$ (see Table for i.r. data) [^1H n.m.r. in C_6H_6 τ, 14·6; triplet, J(P–H) 25 Hz]. This hydride loses H_2 when treated with non-co-ordinating acids in the presence of CO, forming $[Os(NO)(CO)_2(PPh_3)_2]^+$. In marked contrast to the substitution-inert $Os(CO)_3(PPh_3)_2$,[8] one carbonyl group is easily displaced from $[Os(NO)(CO)_2(PPh_3)_2]^+$ by PPh_3, PPh_2Me, $Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2$, and RNC (R = *p*-tolyl) (see Table). When an excess of isocyanide is used, and in the presence of O_2, an interesting ligandoxidation reaction occurs producing $[Os(NO_2(CO)(CNR)_2(PPh_3)_2]^+$. Co-ordinating anions react rapidly with $[Os(NO)(CO)_2(PPh_3)_2]^+$ forming both $OsX(CO)(NO)(PPh_3)_2$ and $OsX_2(CO)_2(PPh_3)_2$ but similar reactions with $[Os(NO)(CO)(PPh_3)_3]^+$ produce exclusively $OsX(CO)(NO)(PPh_3)_2$.

Orange crystals of $[Os(CO)_2(NO)(PPh_3)_2]ClO_4$ crystallise from dichloromethane solutions with one molecule of solvent per molecule of complex. The crystals are monoclinic; $a = 17{\cdot}031(2)$, $b = 13{\cdot}951(1)$, $c = 17{\cdot}270(1)$ Å, $\beta = 104{\cdot}33(1)°$, space group $P2_1/n, Z = 4$. Intensity data were collected on a Hilger and Watts automatic four-circle diffractometer with Cu-K_α X-radiation.

All non-hydrogen atoms were located using Patterson and Fourier methods. As there was no initial crystallographic way of distinguishing NO from CO, least-squares refinement was commenced assuming all three were carbonyl groups. When anisotropic thermal parameters were introduced the thermal ellipse of one "carbon" atom distorted to an unacceptable extent. This atom was therefore assigned nitrogen scattering factors and subsequent refinement has resulted in much more satisfactory amplitudes of vibration. At present, the conventional R-factor is 0·054 for 4281 observed reflections.

The structure is shown in the Figure. In view of the bent nitrosyl groups in the closely related cations $[IrCl(CO)(NO)(PPh_3)_2]^+$ (ref. 3) and $[Os(OH)(NO)_2(PPh_3)_2]^+$ (ref. 6) it is surprising to find that the geometry of $[Os(CO)_2(NO)(PPh_3)_2]^+$ is trigonal bipyramidal. The osmium atom is coplanar with the NO and CO groups, while the PPh_3 ligands occupy the axial sites. This arrangement is similar to those found for $Os(CO)_3(PPh_3)_2$[9] and $Mn(NO)(CO)_2PPh_3)_2$.[10] The osmium nitrosyl and osmium carbonyl linkages are approximately linear, the Os–N–O and Os–C–O angles being 177 ± 1°.

It is also surprising to find a rather long Os–NO distance (1·89 ± 0·01 Å) since linear nitrosyl groups have usually been associated with shorter M–NO lengths. In this connection it may be significant that $[Os(NO)(CO)_2(PPh_3)_2]^+$ is oxidised by chlorine with loss of NO to $OsCl_2(CO)_2(PPh_3)_2$.

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