$[IrCl(NO)(PPh_3)_2]^+$: a Nitrosyl Analogue of $IrCl(CO)(PPh_3)_2$

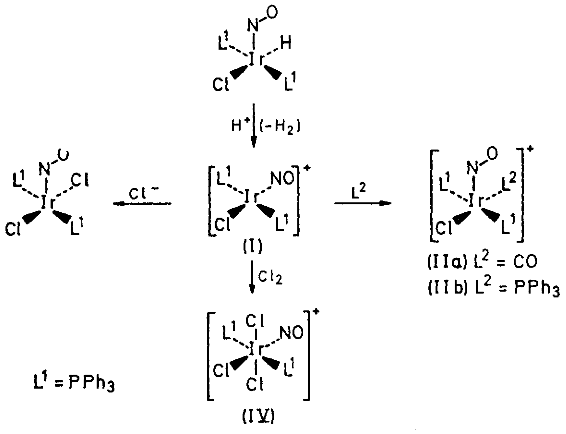
By C. A. REED and W. R. ROPER*

(*Department of Chemistry, University of Auckland, Auckland, New Zealand*)

Summary The synthesis and properties of the co-ordinatively unsaturated nitrosyl species, $[IrX(NO)(PPh_3)_2]^+$, (X = Cl, OH, OR) are described.

THE structure of the five-co-ordinate nitrosyl, $[IrCl(CO)(NO)(PPh_3)_2]^+$ has been determined.[1] From its method of preparation this is considered to be a nitrosonium ion adduct of $IrCl(CO)(PPh_3)_2$. However, it may also be regarded as a carbon monoxide adduct of the formally d^8, iridium(I) nitrosyl species, $[IrCl(NO)(PPh_3)_2]^+$. Such a species, which is isoelectronic with both $IrCl(CO)(PPh_3)_2$[2] and $[PtCl(CO)(PPh_3)_2]^+$,[3] is the subject of this communication.

The hydride, $IrHCl(NO)(PPh_3)_2$,[4] reacts with perchloric acid to eliminate hydrogen and form red crystals of $[IrCl(NO)(PPh_3)_2]ClO_4$, (I). Similar reactions occur with hexafluorophosphoric and tetrafluoroboric acids. As expected for a four-co-ordinate d^8 complex,[5] (I) undergoes addition reactions with various donor molecules to form five-co-ordinate cations, *e.g.* $[IrCl(CO)(NO)(PPh_3)_2]^+$ (IIa), and $[IrCl(NO)(PPh_3)_3]^+$ (IIb). With the bidentate phosphine ligand, $Ph_2PCH_2{\cdot}CH_2PPh_2$, the cation $[IrCl(NO)(PPh_3)(Ph_2PCH_2{\cdot}CH_2PPh_2)]^+$ (III) is formed. There is a drop of approx. 200 cm.$^{-1}$ in ν(NO) (see Table) during this co-ordination process, probably corresponding to a change from a linear Ir–N–O arrangement to a very bent Ir–N–O arrangement. ν(Ir–Cl), which is unusually high in (I) also decreases upon co-ordination of a neutral ligand. (I) is oxidised by Cl_2 to the octahedral nitrosyl, $[IrCl_3(NO)(PPh_3)_2]^+$, (IV). It also reacts immediately with co-ordinating anions to produce neutral five-co-ordinate



nitrosyls, *e.g.* with Cl^- to give $IrCl_2(NO)(PPh_3)_2$,[4] and this behaviour restricts other oxidative additions to (I) since many oxidants are potential sources of a co-ordinating anion. Furthermore, the presence of a positive charge on (I) reduces its reactivity. Thus, we find no interaction of (I) with oxygen, whereas the uncharged fragment, $RuCl(NO)(PPh_3)_2$, binds oxygen irreversibly.[6] Likewise $[PtCl(CO)(PPh_3)_2]^+$ shows reduced reactivity with respect to the isoelectronic $IrCl(CO)(PPh_3)_2$.[7]

Properties of iridium nitrosyl complexes[a]

		Colour	ν(NO) (cm.$^{-1}$)[b]	Other i.r. bands (cm.$^{-1}$)
(I)	$[IrCl(NO)(PPh_3)_2]^+$	red	**1890**	ν(Ir–Cl) 372, 365 (sh)
(IIa)	$[IrCl(CO)(NO)(PPh_3)_2]^+$	crimson	**1690**	ν(Ir–Cl) (CO) 320, ν(CO) 2060
(IIb)	$[IrCl(NO)(PPh_3)_3]^+$	green-brown	**1710**	ν(Ir–Cl) 265 (br)
(III)	$[IrCl(NO)(PPh_3)(Ph_2PCH_2{\cdot}CH_2PPh_2)]^+$	green-brown	**1640**	ν(Ir–Cl) 305 (br)
(IV)	$[IrCl_3(NO)(PPh_3)_2]^+$	brown	**1945**	
(V)	$[Ir(OH)(NO)(PPh_3)_2]^+$	orange	**1855**	ν(OH) 3545, ν(Ir–OH) 645
(VI)	$[Ir(OD)(NO)(PPh_3)_2]^+$	orange	**1855**	ν(OD) 2625, ν(Ir–OD) 635
(VII)	$[Ir(OEt)(NO)(PPh_3)_2]^+$	orange	**1855**	ν(Ir–OEt) 1050

[a] Good elemental analyses have been obtained for all of the above cations in association with at least one of the following anions, ClO_4^-, BF_4^-, PF_6^-, BPh_4^-. All the salts have molar conductivities in the range 22·8—27·1 ohm^{-1}cm.^{2}mole^{-1} measured in nitrobenzene at 25°. [b] All measured as Nujol mulls except (I) which was measured in $CHCl_3$ solution.

(I) is hydrolysed by water to give a four-co-ordinate hydroxy-species, $[(Ir(OH)(NO)(PPh_3)_2]^+$ (V) according to the following equation:

$$2[IrCl(NO)PPh_3)_2]^+ + H_2O = [Ir(OH)(NO)(PPh_3)_2]^+ + IrCl_2(NO)(PPh_3)_2 + H^+$$

(V) is also produced by the reaction of perchloric acid with $[IrH(NO)(PPh_3)_3]^+$[4] and we had previously formulated it as an aquo-species on the basis of elemental analysis of one derivative, the perchlorate. (V) has now been characterised as the perchlorate, hexafluorophosphate, tetrafluoroborate, and tetraphenylborate salts together with the corresponding deuteriated compounds containing $[Ir(OD)(NO)(PPh_3)_2]^+$ (VI). In alcohols (V) undergoes a reversible exchange reaction yielding alkoxy-derivatives, $[Ir(OR)(NO)(PPh_3)_2]^+$ (VII):

$$[Ir(OH)(NO)(PPh_3)_2]^+ + ROH \rightleftharpoons [Ir(OR)(NO)(PPh_3)_2]^+ + H_2O.$$

The unusual occurrence of hydroxy- and alkoxy-ligands in low oxidation state complexes such as (V), (VI), and (VII) must be associated both with the presence of a positive charge and with the high π-acidity of the NO ligand.

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[1] D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1968, **90**, 4486.

[2] L. Vaska and J. W. Diluzio, *J. Amer. Chem. Soc.*, 1962, **84**, 679.

[3] H. C. Clark, P. W. R. Corfield, K. R. Dixon, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1967, **89**, 3360.

[4] C. A. Reed and W. R. Roper, *Chem. Comm.*, 1969, 155.

[5] J. P. Collman and W. R. Roper, *Adv. Organometallic Chem.*, 1968, **7**, 53.

[6] K. R. Laing and W. R. Roper, *Chem. Comm.*, 1968, 1556.

[7] H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Amer. Chem. Soc.*, 1968, **90**, 2259.