Four- and Five-co-ordinate Nitrosyl Complexes of Iridium(I)

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$[IrCl(NO)(PPh_3)_2]^+$, the nitrosyl analogue of $IrCl(CO)(PPh_3)_2$ has been prepared by chlorination of $[Ir(NO)_2(PPh_3)_2]^+$ or by reaction of $IrHCl(NO)(PPh_3)_2$ with non-co-ordinating acids. Five-co-ordinate addition products are formed with the neutral ligands CO, PPh_3, $Ph_2PCH_2CH_2PPh_2$, $Ph_2PCH=CHPPh_2$, and $P(OPh)_3$ while the co-ordinating anions (X^-), NO_2^-, Cl^-, and HS^-, form $IrX_2(NO)(PPh_3)_2$. Hydrolysis of $[IrCl(NO)(PPh_3)_2]^+$ produces $[Ir(OH)(NO)(PPh_3)_2]^+$ and this same hydroxo-cation, together with triphenylphosphine oxide, results from the reaction of $[IrH(NO)(PPh_3)_3]^+$ with dioxygen. $[Ir(OH)(NO)(PPh_3)_2]^+$ forms $[Ir(OR)(NO)(PPh_3)_2]^+$ in alcohols, (R = Et or Pr^n) and these cations are returned to $[IrH(NO)(PPh_3)_3]^+$ by the action of hydrogen in the presence of triphenylphosphine. Another member of this four-co-ordinate, d^8, nitrosyl cation series, $[Ir(CH_3)(NO)(PPh_3)_2]^+$, was prepared from $Ir(CH_3)I(NO)(PPh_3)_2$ by reaction with silver ions. The tendency towards five-co-ordination within the series is compared.

MANY of the recent developments in metal nitrosyl chemistry have arisen from investigation of low-valent nitrosyl complexes of the platinum metals. These include non-linear M–N–O arrangements,[1] the co-ordination of dioxygen by nitrosyl derivatives[2] together with associated ligand oxidations,[3] and reactions occurring at the nitrosyl group including hydrogen transfer[4] and alkoxide ion attack.[5] Hodgson and Ibers[1] prepared the 18-electron, five-co-ordinate iridium(I) nitrosyl complex $[IrCl(CO)(NO)(PPh_3)_2]^+$, and we set out to isolate the 16-electron, four-co-ordinate $[IrCl(NO)(PPh_3)_2]^+$[6] which is formally derived from $IrCl(CO)(PPh_3)_2$ by replacement of CO by NO^+. This paper reports several preparative routes to $[IrCl(NO)(PPh_3)_2]^+$ and related cations, and details their chemical behaviour.

$[IrCl(NO)(PPh_3)_2]^+$.—Elimination of H_2 is one way of producing a co-ordinatively unsaturated compound. This can often be achieved by reacting a metal hydride with a non-co-ordinating acid, *e.g.*, $IrH_3(CO)(PPh_3)_2$ with $HClO_4$ evolves H_2 and gives $[IrH_2(CO)(PPh_3)_2]ClO_4$.[7] The nitrosyl hydride, $IrHCl(NO)(PPh_3)_2$, which is accessible from $[IrH(NO)(PPh_3)_3]^+$ by reaction with chloride,[8] presents itself as a likely precursor to $[IrCl(NO)(PPh_3)_2]^+$. We have found this reaction to proceed smoothly with perchloric, tetrafluoroboric, or hexafluorophosphoric acids.

$$IrHCl(NO)(PPh_3)_2 + HY \longrightarrow [IrCl(NO)(PPh_3)_2]Y + H_2$$
$$Y = ClO_4,\ BF_4,\ \text{or}\ PF_6$$

An alternative preparation is to add chlorine to $[Ir(NO)_2(PPh_3)_2]Y$[5] in strictly equivalent amount.

$$[Ir(NO)_2(PPh_3)_2]^+ \xrightarrow{Cl_2} [IrCl(NO)(PPh_3)_2]^+$$

Small quantities of $[IrCl(NO)(PPh_3)_2]^+$ also appeared in the prolonged reaction of $Ir(NO)(PPh_3)_3$[8] with aqueous HBF_4 in ethanol–dichloromethane. Chlorination of metal complexes with CCl_4,[9] $CHCl_3$,[10] and CH_2Cl_2[11] is known. A mechanism involving oxidative addition of CH_2Cl_2 to the d^8 $[IrH(NO)(PPh_3)_3]^+$ ion followed by reductive elimination of CH_3Cl is possible. Similar addition of CH_3I and elimination of CH_3Cl has been postulated to account for the formation of $RuI(CO)(NO)(PPh_3)_2$ from $RuCl(CO)(NO)(PPh_3)_2$ and CH_3I.[10]

Red dichloromethane solutions of $[IrCl(NO)(PPh_3)_2]ClO_4$ crystallise in two unsolvated forms having different nitrosyl stretching frequencies $\nu(NO) = 1900$ or 1870 cm^{-1} and different iridium–chlorine stretching frequencies $\nu(IrCl) = 372$ or 359 cm^{-1} respectively. Polymorphism is frequently observed in triphenylphosphine complexes, *e.g.* $Pt(CO)(PPh_3)_3$ crystallises in monoclinic or trigonal forms depending upon the mode of preparation,[12] $[IrH(NO)(PPh_3)_3]ClO_4$[8] and *trans*-$PtHCl(PPh_3)_2$[13] both crystallise in at least three different forms. The possibility of *cis* and *trans* isomers of $[IrCl(NO)(PPh_3)_2]ClO_4$ seems unlikely in view of the small differences in $\nu(NO)$ and $\nu(IrCl)$ and the fact that both forms have identical solution spectra: $\nu(NO) = 1890$ cm^{-1} in chloroform. The geometry, like $IrCl(CO)(PPh_3)_2$, must be planar with *trans* phosphines. An attempt to prepare $[IrCl(NO)(PPh_2CH_3)_2]^+$ by phosphine ligand exchange in order to confirm the *trans* phosphine arrangement by the virtual ^{31}P–^{31}P phenomenon[14] produced instead $[Ir(PPh_2CH_3)_4]^+$.[15] The iodide and triphenylarsine analogues of $[IrCl(NO)(PPh_3)_2]^+$ were prepared from $IrHI(NO)(PPh_3)_2$[8] and $[Ir(NO)_2(AsPh_3)_2]Y$[5] respectively, and have similar physical properties (see Table).

Five-co-ordinate Addition Products.—(a) *With neutral ligands*. As expected for a co-ordinatively unsaturated

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[1] D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 2345.

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

[3] K. R. Laing and W. R. Roper, *Chem. Comm.*, 1968, 1568.

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[5] C. A. Reed and W. R. Roper, *J.C.S. Dalton*, 1972, 1243.

[6] C. A. Reed and W. R. Roper, *Chem. Comm.*, 1969, 1459.

[7] L. Malatesta, G. Caglio, and M. Angoletta, *J. Chem. Soc.*, 1965, 6974.

[8] C. A. Reed and W. R. Roper, *J. Chem. Soc.* (*A*), 1970, 3054.

[9] W. J. Bland and R. D. W. Kemmitt, *J. Chem. Soc.* (*A*), 1968, 1278.

[10] K. R. Laing and W. R. Roper, *J. Chem. Soc.* (*A*), 1970, 2149.

[11] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1969, 2645.

[12] V. G. Albano, G. M. Basso Ricci, and P. L. Bellon, *Inorg. Chem.*, 1969, **8**, 2109.

[13] I. Collamati, A. Furlani, and G. Attioli, *J. Chem. Soc.* (*A*), 1970, 1694.

[14] J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 1963, 279.

[15] G. R. Clark, C. A. Reed, W. R. Roper, B. W. Skelton, and T. N. Waters, *Chem. Comm.*, 1971, 785.

d^8 complex, $[IrCl(NO)(PPh_3)_2]^+$ undergoes addition reactions with a variety of neutral donor molecules to form five-co-ordinate cations. Crystalline salts were isolated with carbon monoxide, triphenyl phosphite, *cis*-1,2-bis(diphenylphosphino)ethene (diphos), 1,2-bis(diphenylphosphino)ethane (dppe), and triphenylphosphine, the last being reversible (see Scheme). Neither triphenylarsine nor triphenylstibine add, and in view of the reversibility of triphenylphosphine addition this may be largely due to steric hindrance of the bulkier Group V donors. In other circumstances, for Rh^I [16] and Pt^{II},[17] it has been established that stibines favour five-co-ordination. The iodide, $[IrI(NO)(PPh_3)_2]^+$, does not add triphenylphosphine and this may also be due to the greater bulk of iodide compared with chloride. Carbon monoxide adds to give the known [18] $[IrI(CO)(NO)(PPh_3)_2]^+$.

Infrared data for iridium nitrosyl complexes [a]

Compound	Colour	ν(NO)	Other frequencies [b]
$[IrCl(NO)(PPh_3)_2]ClO_4$ (form 1)	Red	1870vs	ν(IrCl) 372m, 365sh; ν(IrN) 590m
$[IrCl(NO)(PPh_3)_2]ClO_4$ (form 2)	Red	1900vs	ν(IrCl) 359m, 350sh; ν(IrN) 595m
$[IrCl(NO)(PPh_3)_2]BF_4$ (form 1)	Red	1890vs	ν(IrN) 595m
$[IrCl(NO)(PPh_3)_2]BF_4$ (form 2)	Red	1870vs	ν(IrN) 590w
$[IrCl(NO)(PPh_3)_2]PF_6$	Red	1870vs	ν(IrCl) 372m, 365sh; ν(IrN) 590m
$[IrI(NO)(PPh_3)_2]ClO_4$	Brown	1875vs	
$[Ir(CH_3)(NO)(PPh_3)_2]ClO_4,0{\cdot}5CH_2Cl_2$	Crimson	1850vs	δCH_3 1270; ν(IrN) 570vw
$[Ir(OH)(NO)(PPh_3)_2]ClO_4$ [c]	Orange	1855vs	ν(OH) 3545m; ν[Ir(OH)] 645m
$[Ir(OD)(NO)(PPh_3)_2]ClO_4$	Orange	1855vs	ν(OD) 2645m; ν[Ir(OD)] 635m; ν(IrN) 590w
$[Ir(C_2H_5O)(NO)(PPh_3)_2]ClO_4$	Orange	1855vs	1050s($IrOC_2H_5$); 915w (C_2H_5O); ν(IrN) 565w
$[Ir(C_2H_5O)(NO)(PPh_3)_2]BF_4$	Orange	1855vs	915w (C_2H_5O); ν(IrN) 565vw
$[Ir(C_2H_5O)(NO)(PPh_3)_2]BPh_4$	Orange	1845vs	1050s ($IrOC_2H_5$); 915w (C_2H_5O); ν(IrN) 560vw
$[Ir(n\text{-}C_3H_7O)(NO)(PPh_3)_2]ClO_4$	Orange	1855vs	1065 ($IrOC_3H_7$); ν(IrN) 585w
$[Ir(SH)(NO)(PPh_3)_2]ClO_4$	Brown	1840vs	ν(SH) 2525w; ν(IrN) 575w
$[IrCl(NO)(AsPh_3)_2]ClO_4$	Red	1900vs	ν(IrN) 600m
$[IrI(NO)(AsPh_3)_2]ClO_4$	Brown	1830vs	
$[Ir(OH)(NO)(AsPh_3)_2]BF_4$	Orange	1860vs	ν(OH) 3545m; ν[Ir(OH)] 645m; ν(IrN) 590w
$[Ir(C_2H_5O)(NO)(AsPh_3)_2]ClO_4$	Orange	1860vs	1050s ($IrOC_2H_5$); 885vs (C_2H_5O)
$[IrCl(CO)(NO)(PPh_3)_2]ClO_4$	Crimson	1690s	ν(IrCl) 320m, 329sh; ν(CO) 2060s
$[IrCl(NO)(PPh_3)_3]ClO_4,CH_2Cl_2$	Green-brown	1710s,br	ν(IrCl) 265w,br
$[IrCl(NO)(P(OPh)_3)(PPh_3)_2]PF_6$	Green	1780s	1590s, 1200s, 1170s, 1150s, 1020m, 925m, 600m ($P(OPh)_3$)
$[IrCl(NO)(PPh_3)(Ph_2PCH{=}CHPPh_2)]ClO_4$	Green-brown	1650s	560s (P=P); [d] ν(IrCl) 305m,br
$[IrCl(NO)(PPh_3)(Ph_2PCH_2CH_2PPh_2)]ClO_4$	Green-brown	1640s	830m, 880w (P–P); [d] ν(IrCl) 305m,br
$[Ir(CH_3)(CO)(NO)(PPh_3)_2]ClO_4,0{\cdot}5CH_2Cl_2$	Red-brown	1655s	$\delta(CH_3)$ 1270w; ν(CO) 2055s
$[Ir(CH_3)(CO)(NO)(PPh_3)_2]ClO_4$	Yellow-brown	1680s	$\delta(CH_3)$ 1285vw; ν(CO) 2050s
$Ir(SH)_2(NO)(PPh_3)_2$	Brown	1510s	ν(SH) 2550vw; ν[Ir(SH)] 310s
$IrCl(NO_2)(NO)(PPh_3)_2$	Green-brown	1600vs	1400s, 1320s, 810s, 630m (NO_2)
$Ir(NO_2)_2(NO)(PPh_3)_2$	Green-brown	1630vs	1400s, 1320s, 810s, 630m (NO_2)

[a] Measured as Nujol mulls; in cm^{-1}. [b] ν(IrN) are tentative assignments only. [c] $[Ir(OH)(NO)(PPh_3)_2]BF_4$ and $[Ir(OH)(NO)(PPh_3)_2]PF_6$ have identical spectral properties except for differing anion absorptions. [d] P=P denotes *cis*-1,2-bis(diphenylphosphino)ethene and P–P, 1,2-bis(diphenylphosphino)ethane.

There is a drop of *ca.* 200 cm^{-1} in ν(NO) (see Table) during this co-ordination process which probably corresponds to a change from a linear Ir–N–O arrangement to a bent arrangement. This is certainly true for $[IrCl(CO)(NO)(PPh_3)_2]^+$, first prepared by NO^+ addition to $IrCl(CO)(PPh_3)_2$, where the Ir–N–O angle is 124°.[1] The iridium–halogen stretching frequency, unusually high in the four-co-ordinate cations, also decreases upon co-ordination of a fifth ligand (see Table). It is apparent that, when *trans* to nitrosyl in a square planar arrangement, chloride is strongly bonded to iridium, probably because of the effect of an extremely good π-acceptor (NO) [19] *trans* to a p_π donor (Cl). High metal–chlorine stretching frequencies have also been observed [20] for Cl *trans* to CO in $[PtCl_3(CO)]^-$.

(b) *With co-ordinating anions.* The kinetic lability of Cl^- in $[IrCl(NO)(PPh_3)_2]^+$ cannot be investigated owing to immediate reaction with co-ordinating nucleophiles to give neutral five-co-ordinate nitrosyls (see Scheme and Table). With chloride ions, the brown $IrCl_2(NO)(PPh_3)_2$ is produced. Nitrite ions yield green-brown $IrCl(NO_2)(NO)(PPh_3)_2$ which has been prepared previously by a different route [21] while an excess of nitrite converts $IrCl(NO_2)(NO)(PPh_3)_2$ to $Ir(NO_2)_2(NO)(PPh_3)_2$. Hydrogen sulphide gives brown $Ir(SH)_2(NO)(PPh_3)_2$ which has very low solubility in most organic solvents. A weak ν(S–H) absorption at 2550 cm^{-1} was detected in a concentrated Nujol mull. The weakness of sulphur–hydrogen stretching frequencies in organometallic mercapto-complexes may be due to broadening of already weak absorptions by hydrogen bonding; ν(S–H) could not be identified in $IrHCl(SH)(CO)(PPh_3)_2$ [22] or $PtH(SH)(PPh_3)_2$.[23] A strong band in the far i.r. spectrum at 310 cm^{-1} is assigned to ν(Ir–SH). Solutions of $Ir(SH)_2(NO)(PPh_3)_2$ when acidified with perchloric acid

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[16] R. Ugo, F. Bonati, and S. Cenini, *Inorg. Chim. Acta*, 1969, **3**, 220.

[17] A. D. Westland, *J. Chem. Soc.*, 1965, 3060.

[18] D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 1282.

[19] G. M. Bancroft, M. J. Mays, and B. E. Prater, *J. Chem. Soc.* (*A*), 1970, 956.

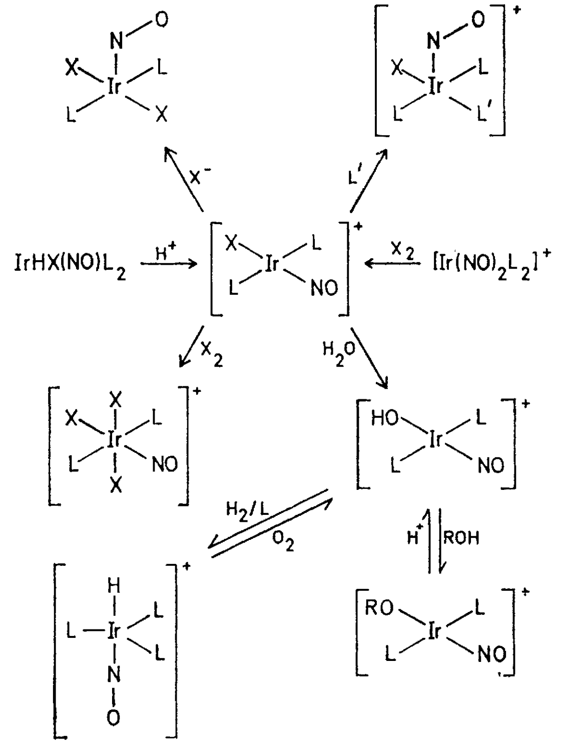
[20] R. J. Goodfellow, P. L. Goggin, and D. A. Duddell, *J. Chem. Soc.* (*A*), 1968, 504.

[21] M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, 1969, **91**, 6983.

[22] H. Singer and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2516.

[23] D. Morelli, A. Segre, R. Ugo, G. La Monica, S. Cenini, F. Conti, and F. Bonati, *Chem. Comm.*, 1967, 524.

liberated H_2S (detected by smell) and deposited small amounts of an impure brown solid whose i.r. spectrum showed $\nu(SH) = 2525$w and $\nu(NO) = 1840$s cm^{-1} consistent with the formation of $[Ir(SH)(NO)(PPh_3)_2]ClO_4$. A pure product could not be obtained.



SCHEME Reaction summary for $[IrX(NO)L_2]^+$
(X = Cl and sometimes I, Me, or SH; L = PPh_3 and sometimes $AsPh_3$). L′ = CO, PPh_3, and $P(OPh)_3$; R = Me, Et, or Pr^n; non-co-ordinating anions ClO_4^-, BF_4^-, or PF_6^- are omitted.

These five-co-ordinate iridium(I) complexes are probably isostructural with $IrCl_2(NO)(PPh_3)_2$, known[24] to have *trans* phosphines in a tetragonal pyramidal arrangement with a bent nitrosyl at the apex.

Oxidative Additions.—The behaviour with anions, described above, restricts oxidative additions to $[IrCl(NO)(PPh_3)_2]^+$ since many oxidants (*e.g.* HCl, RSO_2Cl, RCOCl, $HgCl_2$) are potential sources of a co-ordinating anion. Furthermore we have observed no interaction with dioxygen, sulphur dioxide, tetracyanoethylene, or diphenylacetylene. Hydrogen addition would not be expected since the preparation from $IrHCl(NO)(PPh_3)_2$ with $HClO_4$ involves reductive elimination of H_2. This reduced reactivity must be attributed both to the positive charge which must reside at least partially on the iridium atom and to the very efficient π-electron withdrawal by the nitrosyl group.[19] These effects are illustrated by comparison with the uncharged species $RuCl(NO)(PPh_3)_2$ and $IrCl(CO)(PPh_3)_2$ both of which bind dioxygen and sulphur dioxide. $[PtCl(CO)(PPh_3)_2]^+$ also shows reduced reactivity with respect to the isoelectronic $IrCl(CO)(PPh_3)_2$.[25] Chlorine does oxidise $[IrCl(NO)(PPh_3)_2]^+$ to brown $[IrCl_3(NO)(PPh_3)_2]^+$ and the reaction of this species with alcohols to give alkyl nitrite complexes of Ir^{III} has already been described.[5]

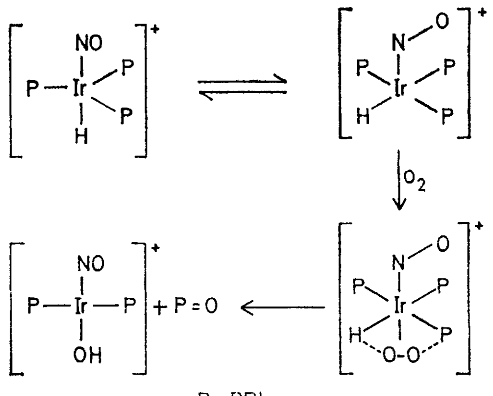
The Hydroxo-cation, $[Ir(OH)(NO)(PPh_3)_2]^+$.—$[IrCl(NO)(PPh_3)_2]^+$ is hydrolysed by water in aqueous ethanol to give a four-co-ordinate hydroxo-species, $[Ir(OH)(NO)(PPh_3)_2]^+$, according to the equation:

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

This cation also appeared, in high yield, in solutions of $[IrH(NO)(PPh_3)_3]^+$ (ref. 8) left to stand overnight, implicating dioxygen in the reaction. To test this, two identical dry dichloromethane solutions of $[IrH(NO)(PPh_3)_3]BF_4$ were enclosed in similar vessels, one under an oxygen-free nitrogen atmosphere and the other under dioxygen (2 atm). The latter solution changed colour to bright orange, characteristic of the hydroxo-species, within a few hours while the solution under nitrogen retained the dark brown colour characteristic of the hydride for 2 days. Reaction proceeded when dioxygen was introduced. The following stoicheiometry for the reaction was confirmed by the isolation of $[Ir(OH)(NO)(PPh_3)_2]BF_4$ (91% yield) and triphenylphosphine oxide (87% yield):

$$[IrH(NO)(PPh_3)_3]BF_4 + O_2 \longrightarrow [Ir(OH)(NO)(PPh_3)_2]BF_4 + OPPh_3$$

This novel ligand conversion of hydride to hydroxide probably proceeds *via* a dioxygen adduct of $[IrH(NO)(PPh_3)_3]^+$ which is unstable with respect to oxygen atom transfer to hydride and triphenylphosphine.



P = PPh$_3$

An alternative mechanism could involve a hydroperoxo-intermediate such as $[Ir(OOH)(NO)(PPh_3)_2]^+$ which upon solvolysis with traces of water in the solvent could yield the requisite cation together with hydrogen peroxide. The hydrogen peroxide could then be the agent for oxidation of the free triphenylphosphine. A hydroperoxo-intermediate, *trans*-$[Rh(OOH)(OH)(en)_2]^+$ has been detected in the reaction of *trans*-$[RhH(OH)$-

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[24] J. A. Ibers and D. M. P. Mingos, *Inorg. Chim.*, 1971, **10**, 1035.

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

$(en)_2]^+$ with dioxygen.[26] However, several factors favour the first mechanism. The reaction proceeds in dry non-protic media and an almost quantitative yield of triphenylphosphine oxide with no trace of its hydrogen peroxide adduct [27] point to the absence of hydrogen peroxide. Other dioxygen complexes are known to undergo numerous oxygen atom transfer reactions to adjacent anionic and neutral ligands.[3]

The physical properties of $[Ir(OH)(NO)(PPh_3)_2]^+$ confirm its formulation. The ^1H n.m.r. spectrum in $CDCl_3$ shows a singlet at τ 6·67 due to the hydroxylic proton which disappears on addition of D_2O. The integrated ratio with the phenyl protons, a multiplet at τ 2·3, was found to be the expected 1 : 30. An oxygen–hydrogen stretching frequency, $\nu(OH)$ appears strongly and sharply at **3454** cm^{-1} and on recrystallisation from ethanolic D_2O a $\nu(OD)$ band appears at **2625** cm^{-1}. A strong band at **645** cm^{-1} is assigned to $\nu(Ir–OH)$ and this decreases on deuteriation to **635** cm^{-1}. No expected region for $\nu(M–OH)$ is available owing to the paucity of platinum metal hydroxide complexes although for osmium complexes of the type $K_2[OsO_2(OH)_2X_2]$ the range is **500**—**530** cm^{-1} and a decrease of *ca.* **15** cm^{-1} is observed upon deuteriation.[28] Both the low oxidation state of $[Ir(OH)(NO)(PPh_3)_2]^+$ and the high $\nu(IrCl)$ found in $[Ir(Cl)(NO)(PPh_3)_2]^+$ are in keeping with a value of $\nu(Ir–OH)$ higher than this osmium range. The nitrosyl stretching frequency at **1855** cm^{-1} is consistent with a linear bonded NO^+ formulation and the geometry is probably planar with *trans* phosphine ligands.

The reactivity of $[Ir(OH)(NO)(PPh_3)_2]^+$ towards addition reactions is reduced when compared with $[IrCl(NO)(PPh_3)_2]^+$. There is no evidence for further co-ordination of triphenylphosphine. Uptake of CO is slow and is accompanied by further reaction leading to $[Ir(CO)_3(PPh_3)_2]^+$ presumably with elimination of HONO. Anions and H_2S give the neutral $IrX_2(NO)(PPh_3)_2$ species (X = Cl, Br, I, or SH).

Homogeneous Catalytic Hydrogenolysis of Dioxygen.—The preparation of $[Ir(OH)(NO)(PPh_3)_2]^+$ from interaction of the hydride $[IrH(NO)(PPh_3)_3]^+$ with dioxygen fulfils two of four steps on a pathway to homogeneous catalytic hydrogenolysis of dioxygen: (1) co-ordination of dioxygen to a hydride complex; (2) transfer of an oxygen atom to the hydride; (3) oxidative addition of hydrogen; and (4) loss of water with regeneration of the original hydride complex. Since $[Ir(OH)(NO)(PPh_3)_2]^+$ is not particularly activated towards oxidative addition it was not expected that it would undergo step (3). However, interaction takes place in the presence of triphenylphosphine and hydrogen (2 atm) and steps (3) and (4) are fulfilled according to the equation:

$$[Ir(OH)(NO)(PPh_3)_2]^+ + H_2 + PPh_3 \longrightarrow [IrH(NO)(PPh_3)_3]^+ + H_2O$$

Adding the formation step,

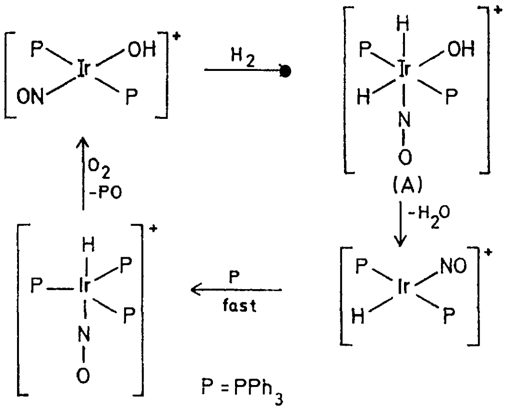
$$[IrH(NO)(PPh_3)_3]^+ + O_2 \longrightarrow [Ir(OH)(NO)(PPh_3)_2]^+ + OPPh_3$$

the overall cycle is

$$H_2 + O_2 + PPh_3 \longrightarrow H_2O + OPPh_3$$

thus providing a catalytic pathway for the combination of hydrogen and dioxygen accompanied by the oxidation of triphenylphosphine.

The mechanism proposed is as follows:



A probable intermediate resulting from the addition of hydrogen to $[Ir(OH)(NO)(PPh_3)_2]^+$ is the iridium(III) dihydride (A). Combination of adjacent H and OH fragments and their elimination as water could generate $[IrH(NO)(PPh_3)_2]^+$ which would rapidly co-ordinate further triphenylphosphine. A related reductive elimination of H_2 from $[IrH_2(CO)_2L_2]^+$ in the presence of L was found to have a rate independent of the incoming ligand, L.[29]

The Alkoxy-cations, $[Ir(OR)(NO)(PPh_3)_2]^+$.—Recrystallisation of $[Ir(OH)(NO)(PPh_3)_2]^+$ salts from dry ethanol gives orange crystals of similar appearance but whose i.r. spectra show the disappearance of $\nu(OH)$ and $\nu(Ir–OH)$ maxima and the appearance of a strong band at **1050** and a weak band at **915** cm^{-1}, consistent with hydroxide exchange for ethoxide. This formulation as $[Ir(OC_2H_5)(NO)(PPh_3)_2]^+$ was confirmed by elemental analysis and by the ^1H n.m.r. spectrum which showed a quartet at τ 6·62 due to $-CH_2-$ and a triplet at τ 9·99 due to $-CH_3$ with a correct integrated ratio. Addition of D_2O caused the disappearance of these signals and the appearance of a different quartet (CH_2) and triplet (CH_3) due to the presence of C_2H_5OD. A notable feature of the i.r. spectrum is the presence of a weak overtone of $\nu(NO)$ at **3700** cm^{-1}, approximately double the fundamental mode (**1855** cm^{-1}). The hydroxide-alkoxide

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[26] R. D. Gillard, B. H. Heaton, and D. H. Vaughan, *J. Chem. Soc.* (*A*), 1970, 3126.

[27] D. B. Copley, F. Fairbrother, J. F. Miller, and A. Thompson, *Proc. Chem. Soc.*, 1964, 300.

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

formation, also shown to proceed in dry n-propanol, is easily reversed by aqueous ethanolic acid.

$$[\mathrm{Ir(OH)(NO)L_2}]^+ \underset{\mathrm{H^+}}{\overset{\mathrm{ROH}}{\rightleftharpoons}} [\mathrm{Ir(OR)(NO)L_2}]^+$$

$$(\mathrm{R} = \mathrm{Et\ or\ Pr^n};\ \mathrm{L} = \mathrm{PPh_3\ or\ AsPh_3})$$

The cations could also be prepared from alcoholic suspensions of $IrCl_2(NO)(PPh_3)_2$ using two equivalents of $AgClO_4$ as a halide ion scavenger. The solvolysis of

$$\mathrm{IrCl_2(NO)(PPh_3)_2 + 2AgClO_4 + ROH \longrightarrow [Ir(OR)(NO)(PPh_3)_2]ClO_4 + 2AgCl + HClO_4}$$

$[IrCl(NO)(PPh_3)_2]^+$ in alcohols also yields 50% $[Ir(OR)(NO)(PPh_3)_2]^+$ according to the equation:

$$\mathrm{2[IrCl(NO)(PPh_3)_2]^+ + ROH \longrightarrow [Ir(OR)(NO)(PPh_3)_2]^+ + H^+ + IrCl_2(NO)(PPh_3)_2}$$

The reactions of $[Ir(OR)(NO)(PPh_3)_2]^+$ do not differ from those of $[Ir(OH)(NO)(PPh_3)_2]^+$. With hydrogen in the presence of triphenylphosphine, ethanol and $[IrH(NO)(PPh_3)_3]^+$ are produced.

In view of the Jørgensen 'symbiotic' effect,[30] the occurrence of 'hard' hydroxide and alkoxide ligands in low oxidation state phosphine complexes is unusual. The positive charge must contribute to this but more importantly these ligands are located *trans* to the highly π-acidic nitrosyl ligand. Hydroxide has also been found *trans* to carbon monoxide in $Ir(OH)(CO)(PPh_3)_2$ [15] and in $Ir(O_2S$-*p*-tolyl$)(CO)(PPh_3)_2$ the sulphinate ligand is O-bound.[31] Evidently groups of high π-acidity render the *trans* position more suitable for the bonding of hard bases. Other examples of hydroxide or alkoxide groups found in low oxidation state complexes are provided by the phosphinato-bridged platinum dimers [32] and by $Ru(OH)(CO)(NO)(PPh_3)_2$.[10]

Ethoxide complexes are often intermediates in the formation of hydrides by β-extraction of a hydrogen atom and elimination of acetaldehyde.[33] The present ethoxides do not show any tendency to form hydrides nor is the reverse reaction of $[IrH(NO)(PPh_3)_3]^+$ with acetaldehyde a route to $[Ir(OC_2H_5)(NO)(PPh_3)_2]^+$.

The Methyl Cation $[Ir(CH_3)(NO)(PPh_3)_2]^+$.—The deactivation towards oxidative addition observed in the cations discussed so far suggested that a less electronegative anionic group (X) would increase the reactivity of $[IrX(NO)(PPh_3)_2]^+$, counteracting to some extent the effect of the positive charge. Accordingly, one equivalent of $AgClO_4$ was added to $Ir(CH_3)I(NO)(PPh_3)_2$ [8] to prepare $[Ir(CH_3)(NO)(PPh_3)_2]^+$ in good yield.

$$\mathrm{Ir(CH_3)I(NO)(PPh_3)_2 + AgClO_4 \longrightarrow [Ir(CH_3)(NO)(PPh_3)_2]ClO_4 + AgI}$$

Like the chloride analogue, this methyl cation is deep red. A metal-bonded methyl group has a diagnostic i.r. symmetric bending mode (δCH_3) at 1270 cm^{-1}. This is *ca.* 150 cm^{-1} lower than in organic compounds and its assignment to the symmetric δCH_3 mode followed deuteriation studies by Adams.[34] An iridium–methyl stretching frequency, expected [35] as a weak band in the region 480—550 cm^{-1}, is probably obscured by the strong triphenylphosphine maxima in this region. A triplet at τ 9·32 in the ^1H n.m.r. spectrum had the expected integrated ratio of 3 : 30 with the phenyl protons, a multiplet at τ 2·4. The triplet must arise from coupling of the methyl protons with two equivalent phosphorus atoms confirming a *trans* square planar geometry. A similar coupling has been observed in *trans*-$[Pt(CH_3)(CO)(P(CH_3)_2Ph)_2]PF_6$.[36]

$[Ir(CH_3)(NO)(PPh_3)_2]^+$ reacts immediately with CO to form red-brown $[Ir(CH_3)(CO)(NO)(PPh_3)_2]^+$. A marked decrease in the chemical shift of the methyl resonance accompanies this addition. This drops from τ 9·32 to 7·77 (t) [J(HP) also decreases from 11·5 to 7·5 Hz] and must reflect a significant decrease in electron density on the iridium atom *via* π-backbonding to the carbonyl ligand and σ-acceptance by the bent nitrosyl group. A second crystalline form of $[Ir(CH_3)(CO)(NO)(PPh_3)_2]ClO_4$, yellow-brown in colour with the same solution i.r. spectrum but slightly different solid-state spectrum, crystallised slowly in low yield. There is no addition reaction with triphenylphosphine, a property which is attributed to the bulk of the methyl group being greater than that of chloride. Nor does $[Ir(CH_3)(NO)(PPh_3)_2]^+$ undergo oxidative addition reactions with O_2 or SO_2 and the less electronegative methyl group is therefore insufficient to overcome the deactivating effects of the positive charge and the nitrosyl ligand on the iridium atom.

Infrared Spectra.—Characteristic i.r. data for all the complexes prepared are listed in the Table. Shoulders on the low frequency side (by 7—9 cm^{-1}) of iridium–chlorine stretching frequencies are attributed to 24% natural abundance of ^{37}Cl. A comparison of the spectra of the isostructural cations $[IrX(NO)L_2]^+$ reveals a medium intensity band in the region 560—600 cm^{-1} which is absent in the five-co-ordinate products. This absorption is tentatively assigned to ν(IrN) although the possibility of its assignment to δ(IrNO) cannot be ruled out without recourse to Raman spectroscopy, a difficult proposition in view of the intense colour of these complexes. ^{15}N Substitution work by Griffith [37] has established the 600 cm^{-1} region for ruthenium and osmium nitrosyl stretching frequencies and a lower band (usually by *ca.* 50 cm^{-1}) is assigned to the bending mode (δMNO). Both bands are normally weak. For the iridium nitrosyl complexes prepared herein few assignments could be made since other ligand and anion bands obscure much of the 400—700 cm^{-1} region.

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CONCLUSION

The reactivity of $[IrCl(NO)(PPh_3)_2]^+$ contrasts interestingly with $IrCl(CO)(PPh_3)_2$. Whereas $IrCl(CO)(PPh_3)_2$ forms adducts with O_2, H_2, SO_2, it shows no tendency to co-ordinate further triphenylphosphine or other donor ligands. $[IrCl(NO)(PPh_3)_2]^+$ does not form stable adducts with O_2, H_2, SO_2, but it does co-ordinate triphenylphosphine, carbon monoxide, and other 2 electron donor ligands. The difference must be attributed to the positive charge and the effectiveness of the nitrosyl ligand as a π-acceptor. Variation of the anionic group (X) and the neutral ligands (L) in the series $[IrX(NO)L_2]^+$ for X = OH, OR, Cl, I, CH_3, and L = PPh_3 or $AsPh_3$ does not markedly change the reactivity, but steric factors seem to be important in determining whether five-co-ordinate complexes are formed.

EXPERIMENTAL

I.r. spectra (4000—400 cm^{-1}) were measured on a Shimadza IR27G spectrometer and (500—200 cm^{-1}) as petroleum jelly mulls between Polythene plates on a Grubb–Parsons DM4 spectrometer, calibrated with Polystyrene and water vapour respectively. M.p.s were measured on a Reichert hot-stage apparatus, conductivities with a Philips PR9501 meter, and ^1H n.m.r. spectra with a Varian A60 or T60. All reactions involving heating under reflux were carried out in a nitrogen atmosphere (<10 p.p.m. oxygen) but subsequent work-ups, unless otherwise specified, were done in open conditions.

Chloronitrosylbis(triphenylphosphine)iridium(I) *Perchlorate, Tetrafluoroborate, and Hexafluorophosphate* $[IrCl(NO)(PPh_3)_2]Y$ (Y = ClO_4, BF_4, and PF_6).—(a) *Perchlorate. Method* 1. To a solution of $IrHCl(NO)(PPh_3)_2$ (200 mg) in dichloromethane was added aqueous perchloric acid (70%, 0·2 ml) followed by sufficient ethanol to ensure homogeneity. The solvents were stripped under reduced pressure to a few ml and n-hexane (50 ml) was added. On standing overnight red crystals were deposited and these were washed with ethanol–n-hexane (1 : 4) (135 mg, 60%). This product was usually found to be the form having ν(NO) = 1870 cm^{-1}, m.p. 216—218°. However, on recrystallisation from dichloromethane–n-hexane a different crystalline form having ν(NO) = 1900 cm^{-1}, m.p. 208—209°, was sometimes obtained. Both forms gave identical solution i.r. spectra (CH_2Cl_2) having ν(NO) = 1890 cm^{-1} [Found for low ν(NO) form: C, 49·3; H, 3·7; N, 1·65; P, 7·2. Found for high ν(NO) form: C, 49·15; H, 3·65; N, 1·65. $C_{36}H_{30}Cl_2IrNO_5P_2$ requires C, 49·05; H, 3·45; N, 1·6; P, 7·05%].

Method 2. Chlorine, freshly dissolved in dichloromethane, was added carefully to a dilute dichloromethane solution of $[Ir(NO)_2(PPh_3)_2]ClO_4$ [5] (100 mg) until the brown solution just turned red. The volume of the solution was reduced under reduced pressure and passed down a short silica gel column with dichloromethane as eluant. Crystallisation was effected with cyclohexane containing 2% ethanol to yield red crystals identical to those prepared by method 1 (85 mg, 75%). The triphenylarsine analogue was prepared similarly from $[Ir(NO)_2(AsPh_3)_2]ClO_4$ [5] and its i.r. spectrum (Table) was found to be similar to the triphenylphosphine analogue.

(b) *Tetrafluoroborates.* $[IrCl(NO)(PPh_3)_2]BF_4$ was prepared in two crystalline forms ν(NO) = 1870 cm^{-1}, m.p. 203—205° and ν(NO) = 1890 cm^{-1}, m.p., 114—117°, by method 1 above using tetrafluoroboric acid (conc. 40% aqueous) [Found for high ν(NO) form: C, 49·4; H, 3·4; N, 1·45. Found for low ν(NO) form: C, 49·55; H, 3·5; N, 1·3. $C_{36}H_{30}BClF_4IrNOP_2$ requires C, 49·75; H, 3·5; N, 1·6%].

(c) *Hexafluorophosphate.* This was prepared from $[Ir(NO)_2(PPh_3)_2]PF_6$ [5] by method 2. M.p. 211—213°. Λ_M = 24·5 Ω^{-1} cm^2 mol^{-1} in nitrobenzene at 25° (10^{-3}M) (Found: C, 46·7; H, 3·6; N, 1·4; P, 10·15. $C_{36}H_{30}ClF_6IrNOP_3$ requires C, 46·65; H, 3·25; N, 1·5; P, 10·0%).

Iodonitrosylbis(triphenylphosphine)iridium(I) *Perchlorate* $[IrI(NO)(PPh_3)_2]ClO_4$.—A dichloromethane solution of $IrHI(NO)(PPh_3)_2$ [8] (100 mg) and aqueous perchloric acid (70%, 0·1 ml) was stirred vigorously for 1 h. The solution was dried with sodium sulphate (anhyd.) followed by molecular sieves. The addition of n-hexane precipitated the brown product (85 mg, 75%). M.p. 136—140°. The triphenylarsine analogue was prepared similarly and its i.r. spectrum (Table) found to be similar (Found: C, 45·25; H, 3·65; N, 0·95. $C_{36}H_{30}ClIIrNO_5P_2$ requires C, 44·45; H, 3·1; N, 1·45%).

Methylnitrosylbis(triphenylphosphine)iridium(I) *Perchlorate* $[Ir(CH_3)(NO)(PPh_3)_2]ClO_4$.—Silver perchlorate (48 mg) in acetone was added to a dichloromethane solution of $IrCH_3I(NO)(PPh_3)_2$ [8] (200 mg) and the solvents removed at reduced pressure. The product was extracted into dichloromethane, filtered, and passed down a short silica gel column eluting with dichloromethane–acetone (20 : 1). Crystallisation was effected with cyclohexane containing 2% ethanol to give crimson crystals of a 0·5 dichloromethane solvate (155 mg, 80%). M.p. 146—148°. ^1H N.m.r. ($CDCl_3$) shows τ 9·32 [t, CH_3, J (HP) = 11·5 Hz], τ 4·70 (s, CH_2Cl_2) and τ 2·4 (m, Ph). Integrated ratio found 2·9 : 1·1 : 30; required 3 : 1 : 30 (Found: C, 49·2; H, 4·0; N, 1·7. $C_{37}H_{33}ClIrNO_5P_2,0{\cdot}5CH_2Cl_2$ requires C, 49·85; H, 3·8; N, 1·5%).

Hydroxonitrosylbis(triphenylphosphine)iridium(I) *Perchlorate, Tetrafluoroborate, and Hexafluorophosphate* $[Ir(OH)(NO)(PPh_3)_2]Y$ (Y = ClO_4, BF_4, and PF_6).—A dichloromethane solution of $[IrH(NO)(PPh_3)_3]Y$ (100 mg) (Y = ClO_4, BF_4, or PF_6) was stirred under oxygen (2 atm) until orange (3 h). Aqueous (95%) ethanol containing a few drops of acid (HY) was added and on stripping the solvents at reduced pressure orange crystals were deposited (70 mg, 90%). M.p. 191—193° (ClO_4), 168—169° (BF_4), and 190—192° (PF_6). ^1H N.m.r. ($CDCl_3$) shows τ 6·68 (s, OH) and τ 2·3 (m, Ph). Integrated ratio found 1·1 : 30; required 1 : 30 (Found for the perchlorate: C, 50·55; H, 4·15; N, 1·55. $C_{36}H_{31}ClIrNO_6P_2$ requires C, 50·1; H, 3·6; N, 1·65. Found for the tetrafluoroborate: C, 50·75; H, 3·7; N, 1·75; P, 7·15. $C_{36}H_{31}BF_4IrNO_2P_2$ requires C, 50·85; H, 3·7; N, 1·65; P, 7·3. Found for the hexafluorophosphate: C, 47·7; H, 3·7; N, 1·6. $C_{36}H_{31}F_6IrNO_2P_3$ requires C, 47·6; H, 3·45; N, 1·55%).

Hydroxonitrosylbis(triphenylarsine)iridium(I) *Tetrafluoroborate* $[Ir(OH)(NO)(AsPh_3)_2]BF_4$.—This was prepared as above from $[IrH(NO)(AsPh_3)_3]BF_4$ [5] as orange crystals. M.p. 163—165° (Found: C, 46·9; H, 3·9; N, 1·65. $C_{36}H_{31}As_2BF_4IrNO_2$ requires C, 46·05; H, 3·35; N, 1·5%).

Ethoxonitrosylbis(triphenylphosphine)iridium(I) *Perchlorate, Tetrafluoroborate, and Tetraphenylborate* $[Ir(C_2H_5O)(NO)(PPh_3)_2]Y$ (Y = ClO_4, BF_4, and BPh_4).—A dichloromethane–dry ethanol solution of $[Ir(OH)(NO)(PPh_3)_2]Y$ (Y = ClO_4 or BF_4) was evaporated to a few ml on a water-bath. n-Hexane was added to give an almost quantitative yield of the orange ethoxide. M.p. 156—158° (ClO_4) and 154—156° (BF_4). ^1H N.m.r. ($CDCl_3$) shows τ 9·99 [t, CH_3,

J (HH) = 6·5 Hz], τ 6·62 [q, CH_2, J (HH) = 7 Hz], and τ 2·3 (m, Ph). Integrated ratio found 2·9 : 2 : 30; required 3 : 2 : 30. The triphenylarsine analogue was prepared similarly and found to have a similar i.r. spectrum (Table). The tetraphenylborate salt was prepared by recrystallising the perchlorate from ethanol containing an excess of sodium tetraphenylborate. M.p. 136—138° (Found for the perchlorate: C, 50·9; H, 4·15; N, 1·75. $C_{38}H_{35}ClIrNO_6P_2$ requires C, 51·2; H, 3·95; N, 1·55. Found for the tetrafluoroborate: C, 51·95; H, 4·1; N, 1·5; P, 7·05. $C_{38}H_{35}BF_4IrNO_2P_2$ requires C, 51·95; H, 4·0; N, 1·6; P, 7·05. Found for the tetraphenylborate: C, 67·05; H, 4·9; N, 1·15. $C_{62}H_{55}BIrNO_2P_2$ requires C, 67·05; H, 4·95; N, 1·25%).

n-Propoxonitrosylbis(triphenylphosphine)iridium(I) *Perchlorate* $[Ir(n\text{-}C_3H_7O)(NO)(PPh_3)_2]ClO_4$.—This was prepared as above from $[Ir(OH)(NO)(PPh_3)_2]ClO_4$ and dry n-propanol. M.p. 160—162° (Found: C, 52·05; H, 4·35; N, 1·35. $C_{39}H_{37}ClIrNO_6P_2$ requires C, 51·75; H, 4·1; N, 1·55%).

Addition Reactions of $[IrCl(NO)(PPh_3)_2]^+$.—(a) *Carbon monoxide to form chlorocarbonylnitrosylbis(triphenylphosphine)iridium*(I) *perchlorate* $[IrCl(CO)(NO)(PPh_3)_2]ClO_4$. A stream of carbon monoxide was passed briefly through a dichloromethane solution of $[IrCl(NO)(PPh_3)_2]ClO_4$ (200 mg) until the red solution turned purple. Methanol was added, and on reduction of the solvent volume at reduced pressure crimson crystals were deposited (190 mg, 90%). M.p. 193—196° (Found: C, 49·05; H, 3·55; N, 1·45. $C_{37}H_{30}Cl_2IrNO_6P_2$ requires C, 48·85; H, 3·3; N, 1·55%).

(b) *Triphenylphosphine to form chloronitrosyltris(triphenylphosphine)iridium*(I) *perchlorate* $[IrCl(NO)(PPh_3)_3]ClO_4$. Triphenylphosphine (100 mg) was added to a dichloromethane solution of $[IrCl(NO)(PPh_3)_2]ClO_4$ (100 mg) followed by ethanol–n-hexane (1 : 20) to give green-brown needles of a 1 : 1 dichloromethane solvate (115 mg, 90%). M.p. 128—131°. The reversibility of this addition was established by passing a dichloromethane solution of $[IrCl(NO)(PPh_3)_3]ClO_4$ down a short silica gel column. The appearance of a red slower moving band indicated partial dissociation (*ca.* 30%) to $[IrCl(NO)(PPh_3)_2]ClO_4$ which was crystallised with n-hexane and its i.r. spectrum compared with that of an authentic sample (Found: C, 53·95; H, 4·45; N, 1·3. $C_{55}H_{47}Cl_4IrNO_5P_3$ requires C, 53·75; H, 3·85; N, 1·15%).

(c) *Triphenyl phosphite to form chloronitrosyl(triphenyl phosphite)bis(triphenylphosphine)iridium*(I) *hexafluorophosphate* $[IrCl(NO)(P(OPh)_3)(PPh_3)_2]PF_6$. A dilute dichloromethane solution of triphenyl phosphite was added dropwise to a dichloromethane solution of $[IrCl(NO)(PPh_3)_2]PF_6$ (100 mg) until the red colour just turned green. n-Hexane was added to precipitate the light green product (100 mg, 80%). M.p. 120—122° (Found: C, 52·25; H, 4·2; N, 0·8. $C_{54}H_{45}ClF_6IrNO_4P_4$ requires C, 52·4; H, 3·65; N, 1·15%).

(d) cis-1,2-*Bis(diphenylphosphino)ethene to form chloronitrosyl(triphenylphosphine)*[cis-1,2-*bis(diphenylphosphino)ethene*]*iridium*(I) *perchlorate* $[IrCl(NO)(PPh_3)(Ph_2PCH{=}CHPPh_2)]ClO_4$. *cis*-1,2-Bis(diphenylphosphino)ethene (60 mg) was added to a dichloromethane solution of $[IrCl(NO)(PPh_3)_2]ClO_4$ (100 mg) followed by ethanol. On reduction of the solvent volume at reduced pressure, green-brown needles were deposited (105 mg, 90%). M.p. 206—209° (Found: C, 51·85; H, 4·15; N, 1·2. $C_{44}H_{37}Cl_2IrNO_5P_3$ requires C, 51·5; H, 3·65; N, 1·35%).

(e) 1,2-*Bis(diphenylphosphino)ethane to form chloronitrosyl(triphenylphosphine)*[1,2-*bis(diphenylphosphino)ethane*]*iridium*(I) *perchlorate* $[IrCl(NO)(PPh_3)(Ph_2PCH_2CH_2PPh_2)]ClO_4$. This was prepared as above using 1,2-bis(diphenylphosphino)ethane giving green-brown needles. M.p. 229—230° (Found: C, 51·8; H, 4·15; N, 1·35. $C_{44}H_{39}Cl_2IrNO_5P_3$ requires C, 51·4; H, 3·85; N, 1·35%).

Methylcarbonylnitrosylbis(triphenylphosphine)iridium(I) *Perchlorate* $[Ir(CH_3)(CO)(NO)(PPh_3)_2]ClO_4$.—This was prepared as above for the chloride analogue using $[Ir(CH_3)(CO)(NO)(PPh_3)_2]ClO_4$ and a brief stream of carbon monoxide. Red-brown crystals of a $0·5CH_2Cl_2$ solvate were obtained in good yield. M.p. 142—145°. ^1H N.m.r. ($CDCl_3$) shows τ 7·77 [t, CH_3, J(HP) = 7·5 Hz], τ 4·70 (s, CH_2Cl_2), and τ 2·4 (m, Ph). Integrated ratio found 2·9 : 0·8 : 30; required 3 : 1 : 30 (Found: C, 49·95; H, 3·75; N, 1·3. $C_{38}H_{33}ClIrNO_6P_2,0·5CH_2Cl_2$ requires C, 49·6; H, 3·7; N, 1·5%).

Dimercaptonitrosylbis(triphenylphosphine)iridium(I) $Ir(SH)_2(NO)(PPh_3)_2$.—A stream of hydrogen sulphide was passed briefly through an acetone solution of $[Ir(OH)(NO)(PPh_3)_2]ClO_4$ (100 mg). Ethanol was added to deposit shiny brown crystals (85 mg, 90%). M.p. 190—192°. The addition of perchloric acid to a dichloromethane–ethanol solution of $Ir(SH)_2(NO)(PPh_3)_2$ gave off H_2S (smell) and deposited small amounts of a brown crystalline material identified by its i.r. spectrum (Table) to contain $[Ir(SH)(NO)(PPh_3)_2]ClO_4$ (Found: C, 53·45; H, 4·15; N, 1·55; P, 7·75; S, 8·35. $C_{36}H_{32}IrNOP_2S_2$ requires C, 53·2; H, 3·95; N, 1·7; P, 7·6; S, 7·9%).

Dinitronitrosylbis(triphenylphosphine)iridium(I) $Ir(NO_2)_2(NO)(PPh_3)_2$.—An aqueous ethanol solution of sodium nitrite (300 mg) was added to a dichloromethane solution of $[IrCl(NO)(PPh_3)_2]ClO_4$ (100 mg). The solvents were removed at reduced pressure and the product extracted into dichloromethane. Crystallisation of green-brown crystals was effected by addition of ethanol (55 mg, 60%). M.p. 165—166°. The use of one mole of sodium nitrite gave a green-brown product whose i.r. spectrum was identical to that reported by Bennett [21] for $IrCl(NO_2)(NO)(PPh_3)_2$ (Found: C, 51·7; H, 3·75; N, 4·4. $C_{36}H_{30}IrN_3O_5P_2$ requires C, 51·55; H, 3·6; N, 5·0%).

Reaction of Hydrogen with $[Ir(OH)(NO)(PPh_3)_2]^+$.—A dichloromethane solution of $[Ir(OH)(NO)(PPh_3)_2]BF_4$ (100 mg) and triphenylphosphine (50 mg) was stirred under a hydrogen atmosphere (2 atm) for 16 h. The orange solution gradually turned dark brown and brown crystals of $[IrH(NO)(PPh_3)_3]BF_4$ were isolated. The i.r. spectrum was found to be identical to an authentic sample.

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