Alkoxide-ion attack at the Nitrosyl Group of $[IrCl_3(NO)(PPh_3)_2]^+$ to give Alkyl Nitrite Complexes of Iridium(III)

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The cationic nitrosyls, $[IrCl_3(NO)L_2]^+$ ($L = PPh_3, AsPh_3$) react with alcohols to give neutral iridium(III) complexes containing bound alkyl nitrites, $IrCl_3(RONO)L_2$ (R = Me, Et, Pr). These reactions parallel the formation of complexes containing alkoxycarbonyl groups as ligands by alkoxide-ion attack on cationic carbonyl complexes. The nitrite complexes revert to the parent nitrosyls with acids and it is suggested that this reaction bears upon the mechanism of formation of nitrosyl complexes in the frequently used preparations which make use of alkyl nitrites, *N*-nitroso-reagents, nitrous acid, and NO^+ salts. New routes to the dinitrosyl cations, $[Ir(NO)_2L_2]^+$, and preparations of $Ir(NO)(AsPh_3)_3$, are also reported.

NUCLEOPHILIC attack at the carbon atom of a co-ordinated carbon monoxide molecule, particularly in cationic complexes, is a frequently observed reaction. Attack by alkoxide ion,[1] amines,[2] carbanions,[3] and azide ion [4] have all been reported. By comparison, nitrosyl complexes have rarely been observed to undergo reactions of this type, although the nitroprusside ion [5] and $[Ru(bipy)_2(NO)Cl]^{2+}$ (ref. 6) react with hydroxide ion forming nitro-complexes. Purposeful attempts by Brunner [7] to bring about reaction between alkoxide ion and the nitrosyl-cation, $[Mn(\pi\text{-}C_5H_5)(NO)(Ph_2PCH_2CH_2PPh_2)]^+$ have failed while the mixed carbonyl-nitrosyl species, $[Mn(\pi\text{-}C_5H_5)(NO)(CO)(PPh_3)]^+$ and $[Os(NO)(CO)_2(PPh_3)_2]^+$ (ref. 8) react at the carbonyl group in preference to the nitrosyl group. We now describe successful reactions of this type between $[IrCl_3(NO)L_2]^+$, $[L = PPh_3, AsPh_3]$, and methanol, ethanol, and propanol. Since the cations $[IrCl_3(NO)L_2]^+$ are prepared by chlorine oxidation of $[Ir(NO)_2L_2]^+$ we first describe the preparation of these dinitrosyl species.

Preparations of $[Ir(NO)_2L_2]^+$.—Three methods are

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[1] D. Ibekwe and K. A. Taylor, *J. Chem. Soc.* (*A*), 1970, 1, and references therein.

[2] R. J. Angelici and D. L. Denton, *Inorg. Chim. Acta*, 1968, **2**, 3.

[3] E. O. Fischer and A. Maasböl, *Angew. Chem. Internat. Edn.*, 1964, **3**, 580.

[4] W. Beck, H. Werner, H. Engelmann, and H. S. Smedal, *Chem. Ber.*, 1968, **101**, 2143.

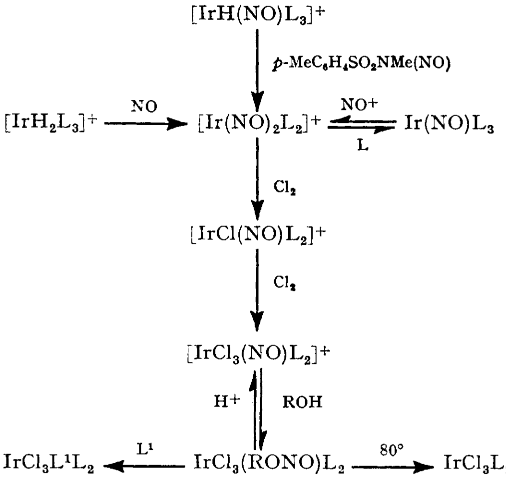
[5] J. H. Swinehart, *Co-ordination Chem. Rev.*, 1967, **2**, 385.

[6] T. J. Meyer, J. B. Godwin, and N. Winterton, *Chem. Comm.*, 1970, 872.

[7] H. Brunner, *Z. anorg. Chem.*, 1969, **368**, 120.

[8] B. F. G. Johnson and J. A. Segal, personal communication.

available for the preparation of these compounds (see Scheme and Table).



SCHEME $L = PPh_3, AsPh_3$. $L^1 = CO, NH_3, C_5H_5N$. $R = CH_3, C_2H_5$, n-C_3H_7. Anions, ClO_4, BF_4, or PF_6 are not shown.

(i) $[Ir(NO)_2(PPh_3)_2]ClO_4$ has been prepared by passing nitric oxide through ethanol solutions of $[IrH_2(PPh_3)_3]ClO_4$.[9] We have prepared $[Ir(NO)_2(AsPh_3)_2]ClO_4$ by the same method using $[IrH_2(AsPh_3)_3]ClO_4$.[10]

(ii) Nitrosonium tetrafluoroborate has been used to introduce a nitrosyl group into $IrCl(CO)(PPh_3)_2$.[11] We find reaction between $Ir(NO)L_3$ and nitrosonium tetrafluoroborate produces $[Ir(NO)_2L_2]BF_4$ in reasonable yield.

(iii) The preparation of $Ir(NO)(PPh_3)_3$ from an iridium hydride and N-methyl-N-nitrosotoluene-p-sulphonamide has been described.[12] Introduction of a second nitrosyl group can be achieved by first forming the hydride, $[IrH(NO)(PPh_3)_3]^+$ and further reaction with N-methyl-N-nitrosotoluene-p-sulphonamide. This reaction proceeds in very high yield (85%).

Chlorine Oxidation of $[Ir(NO)_2L_2]^+$ *and Subsequent Reactions with Alcohols.*—The addition of an equimolar quantity of chlorine to $[Ir(NO)_2L_2]^+$ produces the red, four co-ordinate nitrosyl cation $[IrCl(NO)L_2]^+$ (ref. 13). Addition of an excess of chlorine gives the brown, iridium(III) cation, $[IrCl_3(NO)L_2]^+$, which was characterised as the perchlorate salt. Solutions of this cation react immediately with alcohols forming the crystalline, non-electrolytes, $IrCl_3(RONO)L_2$ (see Scheme and Table). Since the iridium carbonyl cation, $IrCl_2(CO)_2(P(CH_3)_2Ph)_2^+$ (ref. 14) reacts with water to give a carboxylic acid group in $Ir(CO_2H)Cl_2(CO)(PMe_2Ph)_2$ we investigated the reaction of $[IrCl_3(NO)L_2]^+$ with water expecting to obtain a nitrous acid complex. However, although the solution turned orange, no nitrous acid complex could be isolated. Neither could any products be obtained from secondary and tertiary alcohols or with diethylamine.

Formulation of the orange compounds as alkyl nitrite complexes is based upon the following observations. Addition of perchloric acid regenerates the cationic nitrosyl group, substitution with carbon monoxide gives the known $IrCl_3(CO)(PPh_3)_2$,[15] similar replacement reactions with ammonia and pyridine give respectively $IrCl_3(NH_3)(PPh_3)_2$ and $IrCl_3(C_5H_5N)(PPh_3)_2$,[12] infrared absorption bands (see Table) are compatible with co-ordinated RONO, and the ^1H n.m.r. spectrum of the ethyl derivative shows a quartet (CH_2) and a triplet (CH_3) consistent with C_2H_5ONO, slightly upfield from free ethanol. The alkyl nitrite is lost upon heating in benzene solution with formation of brown crystals of $IrCl_3(PPh_3)_2$.[16]

TABLE

Physical data for iridium-nitrosyl and iridium-alkyl nitrite complexes

Compound	Colour	M.p. (°C)	I.r. bands [a] (cm^{-1})
$[Ir(NO)_2(PPh_3)_2]BF_4$	Black	189—192	1760s, 1705vs, ν(NO)
$[Ir(NO)_2(PPh_3)_2]PF_6$	Black	197—199	1760s, 1705vs, ν(NO)
$[Ir(NO)_2(AsPh_3)_2]ClO_4$	Black	192—194	1770s, 1710vs, ν(NO)
$[Ir(NO)_2(AsPh_3)_2]BF_4$	Black	173—174	1770s, 1710vs, ν(NO)
$Ir(NO)(AsPh_3)_3$	Orange	166—167	1620vs, ν(NO)
$[IrH(NO)(AsPh_3)_3]ClO_4$	Green	103—104	1720vs, ν(NO), 1095vs, 620s (ClO_4)
$IrCl_2(NO)(AsPh_3)_2$	Brown	220—221	1550vs, ν(NO)
$IrI_2(NO)(AsPh_3)_2$	Red-brown	236—239	1550vs, ν(NO)
$[IrCl_3(NO)(PPh_3)_2]ClO_4$	Brown	140—143	1945s, ν(NO), 345s,br, ν(IrCl)
$IrCl_3(CH_3ONO)(PPh_3)_2$	Orange	189—192	1550s, 1400m, 980sh, 970s, 880m (CH_3ONO), 325s,br, ν(IrCl)
$IrCl_3(C_2H_5ONO)(PPh_3)_2$	Orange	177—180	1550s, 1110w, 960s, 835m (C_2H_5ONO), 320s,br, ν(IrCl)
$IrCl_3(C_3H_7ONO)(PPh_3)_2$	Orange	169—173	1550s, 1095sh, 970s, 910w, 870m (C_3H_7ONO), 320s,br, ν(IrCl)
$IrCl_3(C_2H_5ONO)(AsPh_3)_2$	Orange	165—167	1535s, 1090w, 965s, 835m (C_2H_5ONO)

[a] Recorded as Nujol mulls.

The reversibility of the ligand reactions described here indicates that co-ordination of alkyl nitrite, N-nitroso-compounds, or nitrous acid, followed by loss of alkoxide ion, amide ion, or hydroxide ion respectively would be a path for preparing nitrosyl complexes. It seems likely that such a mechanism operates in the synthesis of molybdenum nitrosyls from n-pentyl

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[9] M. Angoletta and G. Caglio, *Gazzetta*, 1963, **93**, 1584.

[10] F. Canziani and F. Zingales, *Rend. Inst. Lombardo Sci. Lettere A*, 1962, **96**, 513 (*Chem. Abs.*, 1965, **62**, 11,401).

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

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

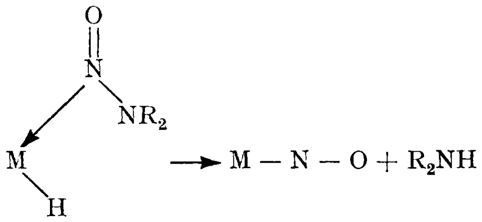
[13] C. A. Reed and W. R. Roper, *Chem. Comm.*, 1969, 1459.

[14] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 443.

[15] L. Vaska and S. S. Bath, *J. Amer. Chem. Soc.*, 1963, **85**, 3600.

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

nitrite,[17] and iridium [11] and ruthenium [18] nitrosyls from nitrosonium salts since the latter must form alkyl nitrites in alcohol solvents. The special effectiveness of metal hydrides in forming nitrosyl complexes with *N*-nitroso-reagents, *e.g.* $Ir(NO)(CO)(PPh_3)_2$ from $IrH(CO)(PPh_3)_3$,[12] could be due to elimination of amine as follows:



An obvious requirement for such a process is a labile co-ordination site on the metal to allow co-ordination of the *N*-nitroso-compound and this is in keeping with the experimental observations, *e.g.* $OsHCl(CO)(PPh_3)_3$ forms $OsCl(CO)(NO)(PPh_3)_2$ [19] with *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide while $OsHCl(CO)_2(PPh_3)_2$, which is comparatively inert, does not react.

$Ir(NO)(AsPh_3)_3$.—In order to characterise the triphenylarsine alkyl nitrite complexes described above it was necessary to have available $Ir(NO)(AsPh_3)_3$ and $Ir(NO)_2(AsPh_3)_2{}^+$. $Ir(NO)(PPh_3)_3$ is substitution inert with respect to triphenylarsine there being no exchange even after two days in xylene under reflux. In marked contrast, the cationic $Ir(NO)_2(PPh_3)_2{}^+$ exchanges readily with triphenylarsine and reacts further in ethanol to yield orange crystals of $Ir(NO)(AsPh_3)_3$. Like $Ir(NO)(PPh_3)_3$,[12] this compound is protonated by perchloric acid forming $[IrH(NO)(AsPh_3)_3]ClO_4$ and is oxidised by chlorine and iodine to $IrCl_2(NO)(AsPh_3)_2$ and $IrI_2(NO)(AsPh_3)_3$.

EXPERIMENTAL

I.r. spectra (4000—400 cm^{-1}) were measured on a Shimadzu IR 27 G 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. ^1H N.m.r. spectra were recorded on a Varian A60 spectrometer, and m.p.s were measured on a Reichert hot-stage apparatus. All reactions were carried out under oxygen-free nitrogen.

Dinitrosylbis(triphenylphosphine)iridium(-I) *Perchlorate, Tetrafluoroborate, and Hexafluorophosphate,* $[Ir(NO)_2(PPh_3)_2]Y$ ($Y = ClO_4$, BF_4, PF_6).—A suspension of $[IrH(NO)(PPh_3)_3]Y$ [12] (0·5 g) in ethyl acetate (60 ml) and acetone (7 ml) with *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (0·5 g) was heated under reflux for 5 min. On cooling, n-hexane (30 ml) was added and the purple-grey solid was filtered off. Recrystallisation was from dichloromethane–ethanol to give shiny black crystals (0·36 g, 85%) (Found: for $Y = BF_4$: C, 50·2; H, 3·95; N, 2·9. $C_{36}H_{30}BF_4IrN_2O_2P_2$ requires C, 50·05; H, 3·5; N, 3·25. Found for $Y = PF_6$: C, 47·65; H, 3·85; N, 2·85. $C_{36}H_{30}F_6IrN_2O_2P_3$ requires C, 46·9; H, 3·3; N, 3·05%).

Dinitrosylbis(triphenylarsine)iridium(-I) *Perchlorate,* $[Ir(NO)_2(AsPh_3)_2]ClO_4$.—Hydrated iridium trichloride (0·5 g) and triphenylarsine (2·5 g) were dissolved in warm ethanol (100 ml). Sodium borohydride (1 g) was added and the mixture was stirred for 3 h. The cream crystals were filtered off, recrystallized from benzene–ethanol, and identified as $IrH_3(AsPh_3)_3$ [10] from an i.r. spectrum [ν(IrH) 2100s] and a m.p. Perchloric acid (conc. 70% aqueous) was added dropwise to a dichloromethane–ethanol solution of $IrH_3(AsPh_3)_3$ (0·5 g) until no further hydrogen evolution was observed. n-Hexane (20 ml) was added and the solvents were slowly removed under reduced pressure. The white product was filtered off and recrystallised from dichloromethane–ethanol yielding colourless crystals of $[IrH_2(AsPh_3)_3]ClO_4$ [10] (0·46 g, 85%), [ν(IrH) 2210m, 2130m; δ(IrH) 875 w and 835 m, br] (Found: C, 52·2; H, 4·45; Cl, 3·3. $C_{54}H_{47}As_3ClIrO_4$ requires C, 53·5; H, 3·9; Cl, 2·95%). Nitric oxide was bubbled slowly through a warm (60—70°) ethanol solution (70 ml) of $[IrH_2(AsPh_3)_3]ClO_4$ (1 g) for 2 h. The solvent was partially removed at reduced pressure and n-hexane (30 ml) was added. The dark precipitate was filtered off and recrystallised from dichloromethane–ethanol to give shiny black crystals (0·5 g, 70%) (Found: C, 44·75; H, 3·35; N, 3·15. $C_{36}H_{30}As_2ClIrN_2O_6$ requires C, 44·85; H, 3·15; N, 2·9%).

Trichloronitrosylbis(triphenylphosphine)iridium(III) *Perchlorate,* $[IrCl_3(NO)(PPh_3)_2]ClO_4$.—A small excess of dry chlorine gas was bubbled through a dry dichloromethane solution (10 ml) of $[Ir(NO)_2(PPh_3)_2]ClO_4$ (100 mg). Dry n-pentane (40 ml) was added and the brown solid was filtered off (80 mg, 75%) (Found: C, 45·5; H, 3·45; N, 1·5. $C_{36}H_{30}Cl_4IrNO_4P_2$ requires C, 45·4; H, 3·15; N, 1·45%).

Trichloro(methyl nitrite)bis(triphenylphosphine)iridium (III), $IrCl_3(CH_3ONO)(PPh_3)_2$.—A small excess of dry chlorine was bubbled through a dichloromethane solution (20 ml) of $[Ir(NO)_2(PPh_3)_2]Y$ ($Y = ClO_4$, BF_4, PF_6) (100 mg). The solvent was partially removed under reduced pressure and dry methanol (20 ml) was added. On further reduction of solvent volume, orange crystals were deposited and these were recrystallised from dichloromethane–ethanol (80 mg, 80%) (Found: C, 50·65; H, 3·9; N, 1·3. $C_{37}H_{33}Cl_3IrNO_2P_2$ requires C, 50·25; H, 3·75; N, 1·6%).

Trichloro(ethyl nitrite)bis(triphenylphosphine)iridium(III), $IrCl_3(C_2H_5ONO)(PPh_3)_2$.—This compound was prepared as above using dry ethanol. ^1H N.m.r. in $CDCl_3$ (relative to tetramethylsilane τ 10): triplet at τ = 9·27 (*J* = 7 Hz) due to CH_3; quartet at τ = 7·02 (J = 7 Hz) due to $-CH_2-$; multiplets centred at τ = 2·7 and 2·1 due to PPh_3. The integral was found 2·9 : 2·30 required, 3 : 2 : 30 (Found: C, 51·35; H, 4·1; N, 1·25; P, 6·55. $C_{38}H_{35}Cl_3IrNO_2P_2$ requires C, 50·8; H, 3·95; N, 1·55; P, 6·9%).

Trichloro(n-propyl nitrite)bis(triphenylphosphine)iridium(III), $IrCl_3(C_3H_7ONO)(PPh_3)_2$.—This compound was prepared as above using dry n-propanol (Found: C, 51·4; H, 4·1; N, 1·5; P, 6·95. $C_{39}H_{37}Cl_3IrNO_2P_2$ requires C, 51·35; H, 4·1; N, 1·55; P, 6·8%).

Trichloro(ethyl nitrite)bis(triphenylarsine)iridium(III), $IrCl_3(C_2H_5ONO)(AsPh_3)_2$.—This compound was prepared as above by chlorination of $[Ir(NO)_2(AsPh_3)_2]ClO_4$ and treatment with dry ethanol (Found: C, 47·15; H, 4·0; N, 1·0. $C_{38}H_{35}As_2Cl_3IrNO_2$ requires C, 46·3; H, 3·6; N, 1·4%).

Reactions of $IrCl_3(C_2H_5ONO)(PPh_3)_2$.—(a) *With* CO *to form* $IrCl_3(CO)(PPh_3)_2$. A benzene solution of $IrCl_3$-

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[17] W. Hieber and H. Tengler, *Z. anorg. Chem.*, 1962, **318**, 136.

[18] C. G. Pierpont, D. G. van Derveer, W. Durland, and R. Eisenberg, *J. Amer. Chem. Soc.*, 1970, **92**, 4761.

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

$(C_2H_5ONO)(PPh_3)_2$ was heated to 60° under CO pressure (2 atm) for 30 min. On cooling, ethanol was added and on removal of solvents at reduced pressure light yellow crystals of $IrCl_3(CO)(PPh_3)_2$ were deposited. These were identified by comparison with an authentic sample prepared by chlorination of $IrCl(CO)(PPh_3)_2$. Other substitution reactions with ammonia and pyridine have been reported.[12]

(b) *Decomposition to* $IrCl_3(PPh_3)_2$. A benzene solution of $IrCl_3(EtONO)(PPh_3)_2$ was heated for 5 min on a water-bath and on cooling, yellow-brown crystals were deposited. These were difficult to recrystallise and purify but were found to have properties similar to those reported by Bennett[16] (Found: C, 50·3; H, 3·75. $C_{36}H_{30}Cl_3IrP_2$ requires C, 52·6; H, 3·7%).

(c) *Reversal with* $HClO_4$ *to* $[IrCl_3(NO)(PPh_3)_2]ClO_4$. Perchloric acid (1 drop, conc. 70% aqueous) was added to a dichloromethane–acetone solution of $IrCl_3(C_2H_5ONO)(PPh_3)_2$ (60 mg). n-Hexane was added and a brown oil separated. This was taken up into dichloromethane, dried with anhydrous Na_2SO_4, and on the addition of n-hexane a brown precipitate of $[IrCl_3(NO)(PPh_3)_2]ClO_4$ (identified by its i.r. spectrum) was deposited.

Nitrosyltris(triphenylarsine)iridium(-I), $Ir(NO)(AsPh_3)_3$.—(a) *From* $[Ir(NO)_2(AsPh_3)_2]ClO_4$. An ethanol solution (60 ml) of $[Ir(NO)_2(AsPh_3)_2]ClO_4$ (250 g) and triphenylarsine (400 mg) was heated under reflux for 12 h. The orange crystals were filtered off (200 mg, 70%) and were found to have an i.r. spectrum and m.p. identical to a sample prepared by method (b).

(b) *From* $[Ir(NO)_2(PPh_3)_2]ClO_4$. An ethanol solution (60 ml) of $[Ir(NO)_2(PPh_3)_2]ClO_4$ (0·3 g) and triphenylarsine (7 g) was heated under reflux in a nitrogen atmosphere for 12 h. The orange crystals were filtered off and recrystallised from benzene–ethanol (Found: C, 57·35; H, 4·15; N, 1·3. $C_{54}H_{45}A_{53}IrNO$ requires C, 56·8; H, 4·0; N, 1·25%).

Reactions of $Ir(NO)(AsPh_3)_3$.—(i) *With* $NOBF_4$. An ethanol solution of nitrosonium tetrafluoroborate (0·7 g) was added to a dichloromethane solution of $Ir(NO)(AsPh_3)_3$ (0·3 g). The solvents were reduced to a few ml under reduced pressure and n-hexane (50 ml) was added. On standing, black crystals of $[Ir(NO)_2(AsPh_3)_2]BF_4$ were deposited and these were recrystallised from dichloromethane–ethanol (Found: C, 46·45; H, 3·55; N, 2·85. $C_{36}H_{30}As_2BF_4IrN_2O_2$ requires C, 45·4; H, 3·2; N, 2·95%).

(ii) *With* $HClO_4$: *hydridonitrosyltris(triphenylarsine)iridium*(I) *perchlorate*. To a solution of $Ir(NO)(AsPh_3)_3$ (100 mg) in dichloromethane (20 ml) was added conc. (70%) perchloric acid (0·03 ml) followed by ethanol (5 ml) sufficient as to ensure homogeneity. The solvent volume was reduced to a few ml under reduced pressure and upon addition of n-hexane, green crystals appeared. These were washed with ethanol–n-hexane (1 : 2) (Found: C, 51·75; H, 3·95; N, 1·15. $C_{54}H_{46}As_3ClIrNO_5$ requires C, 52·25; H, 3·75; N, 1·15%).

(iii) *With* Cl_2: *dichloronitrosylbis(triphenylarsine)iridium*(I). A dilute chloroform solution of dry chlorine was added to a dichloromethane solution of $Ir(NO)(AsPh_3)_3$ (200 mg) until the solution just turned brown. The solvents were removed at reduced pressure and on the addition of ethanol brown crystals were deposited in good yield (Found: C, 48·1; H, 3·65; N, 1·55. $C_{36}H_{30}As_2Cl_2IrNO$ requires C, 47·75; H, 3·35; N, 1·55%).

(iv) *With* I_2: *di-iodonitrosylbis(triphenylarsine)iridium*(I). A solution of iodine (45 mg) in benzene was added to a benzene solution of $Ir(NO)(AsPh_3)_3$ (100 mg). Ethanol was added and on partial removal of solvents at reduced pressure, red-brown crystals of a 1 : 1 benzene solvate were deposited in good yield, m.p. 216—219°. An unsolvated product was obtained from dichloromethane–ethanol, m.p. 236—239° (Found for benzene solvate: C, 42·95; H, 3·15; N, 1·35. $C_{42}H_{36}As_2I_2IrNO$ requires C, 42·25; H, 3·1; N, 1·2%. Found for non-solvate: C, 39·75; H, 2·9; N, 1·35. $C_{36}H_{30}As_2I_2IrNO$ requires C, 39·71; H, 2·8; N, 1·3%).

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