Transition-metal Nitrosyl Compounds. Part 13.[1] Some Reactions of Dinitrosylbis(triphenylphosphine)-cobalt, -rhodium, and -iridium Cations †

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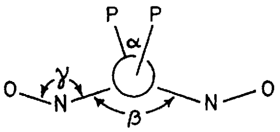
The dinitrosyl cations $[M(NO)_2(PPh_3)_2]^+$ (M = Co, Rh, or Ir) have been prepared and some of their reactions examined. A ^{31}P n.m.r. study of the cations of Rh and Ir suggests that phosphine exchange is primarily *via* an associative process; evidence is also presented to suggest that exchange with the Co proceeds *via* a predominantly dissociative mechanism. Reaction of $[Rh(NO)_2(PPh_3)_2]^+$ or $[Ir(NO)_2(PPh_3)_2]^+$ with tertiary phosphines (L′) gives $[M(NO)(PPh_3)_3]$ and $[NO]^+$ when L′ = PPh_3 but $[ML'_4]^+$ when L′ = a less bulky phosphine. In contrast, $[Co(NO)_2(PPh_3)_2][PF_6]$ gives $[Co(NO)_2L'_2][PF_6]$. A rationale which accounts for this variation in reactivity is offered. The salt $[Co(NO)_2(PPh_3)_2][PF_6]$ reacts with Cl^-, Br^-, or I^- (X^-) to provide $[Co(NO)_2(PPh_3)X]$; $[Ir(NO)_2(PPh_3)_2][PF_6]$ reacts with HCl to form $[Ir(NO)(PPh_3)_2Cl_2]$. Reaction of $[Ir(NO)_2(PPh_3)_2][PF_6]$ with 2,2′-bipyridyl produces $[Ir(NO)(PPh_3)_2(bipy)]^{2+}$ and N_2O. Reduction of $[M(NO)_2(PPh_3)_2]^+$ by $Na[BH_4]$ in tetrahydrofuran and in the presence of PPh_3 produces $[M(NO)(PPh_3)_3]$ and ammonia.

We report an investigation into the reactions of the three complex cations $[M(NO)_2(PPh_3)_2]^+$ (M = Co, Rh, and Ir) with tertiary phosphines (L′) and halide ions (X^-). This work has established that the chemistry of these three salts is remarkably different, the cobalt salt reacting with both L′ and X^- with retention of the two NO ligands, whereas reaction of the other two salts produces N_2O and some oxidised species, *e.g.* PPh_3O. An attempt to rationalise this change in behaviour in terms of the ground-state geometry of the salts and their tendency to undergo or resist phosphine dissociation is also made. Brief details of some aspects of this work have appeared elsewhere.[2] The structures of the three cationic complexes have been determined previously by single-crystal *X*-ray analysis [3] and are shown in Table 1. These structures have been discussed in some detail in several accounts [4] which have placed emphasis on the observed M–N–O bond angles. Some reactions of the cations with tetrahydroborate, hydrazine, and bipyridyl are also reported.

TABLE 1

Structure of $[M(NO)_2(PPh_3)_2]^{n+}$ species (M = Co, Rh, or Ir, $n = 1$; M = Fe, Ru, or Os, $n = 0$)

	Bond/Å		Angle/°		
M	M–N	N–O	P–M–P(α)	N–M–N(β)	M–N–O(γ)
Fe	1.650 (7)	1.190 (10)	111.9(1)	123.8(4)	178.2(7)
Ru	1.762 (6)	1.190 (7)	103.85(6)	139.2(3)	177.7(6)
	1.776 (6)	1.194 (7)			170.6(5)
Ru	1.748 (2)	1.215 (18)	105.5(2)	139.9(8)	174.7(17)
	1.688(20)	1.229(18)			168.0(16)
Os	1.771 (6)	1.195 (8)	103.51(6)	139.1(3)	178.7(7)
	1.776 (7)	1.211 (7)			174.0(6)
Co	1.663 (5)	1.157 (5)	106.7	132.4	170.9
	1.664 (5)	1.156 (5)			171.2
Rh	1.818 (4)	1.158 (6)	155.88(5)	157.5(3)	158.9(4)
Ir	1.771 (12)	1.213 (13)	116.3(2)	154.2(7)	163.5(10)



RESULTS AND DISCUSSION

Preparation of $[M(NO)_2L_2]^+$ *Derivatives* (M = Co, Rh, *or* Ir).—$[Co(NO)_2L_2][PF_6]$ (1). The carbonyl nitrosyl complexes $[Co(NO)(CO)L_2]$ [L = PPh_3 or $P(OPh)_3$] reacted with $[NO][PF_6]$ in benzene–methanol to produce the black salts $[Co(NO)_2L_2][PF_6]$ [L = PPh_3 (1a), or $P(OPh)_3$ (1b)]. Salt (1a) underwent phosphine exchange with L′ {L′ = $\frac{1}{2}Ph_2P[CH_2]_2PPh_2$ ($\frac{1}{2}$ dppe), $PPhMe_2$, PPh_2Me, $PPhEt_2$, or PPh_2Et} to give the salts $[Co(NO)_2L'_2][PF_6]$ in quantitative yields. The complex $[Co(NO)(CO)_2(PPh_3)]$ also reacted with $[NO][PF_6]$ to produce $[Co(NO)_2(CO)(PPh_3)][PF_6]$. The expected complex $[Co(NO)_2(CO)_2(PPh_3)][PF_6]$, which is presumably formed as an intermediate in this reaction, was not observed. This reaction presumably proceeds *via* a sequence similar to that discussed in Part 12 of this series [5] for the reactions of $[Ni(CO)_2(PPh_3)_2]$ with $[NO][PF_6]$ to give $[Ni(NO)(PPh_3)_3][PF_6]$.

$[Rh(NO)_2(PPh_3)_2][PF_6]$ (2). Osborn and Schrock [6] showed that the cations $[Rh(diene)L_2]^+$ [diene = cycloocta-1,5-diene or norbornadiene (nbd); L = tertiary phosphine or arsine] serve as useful precursor materials for a range of cationic rhodium complexes. We found that $[Rh(nbd)(PPh_3)_2][PF_6]$ reacted with NO at 25 °C and atmospheric pressure to produce $[Rh(NO)_2(PPh_3)_2][PF_6]$ (2) in good yield. Unlike the cobalt analogue (1), salt (2) did not undergo simple substitution reactions with other tertiary phosphines L′ (see above), but reacted to produce the tetrakis(tertiary phosphine) cations $[ML'_4][PF_6]$, N_2O, phosphine oxide, and phosphine.

$[Ir(NO)_2(PPh_3)_2][PF_6]$ (3). A number of routes to this salt have been reported; [7] in this work we have developed two alternative methods. The first route [equation

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† No reprints available.

[1] For preceding part see ref. 5.

[2] S. Bhaduri, N. Connelly, and B. F. G. Johnson, *J. Organometallic Chem.*, 1972, **40**, C36.

[3] J. A. Kaduk and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 3072 and refs. therein.

[4] B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 2610; J. Reed and R. Eisenberg, *Science*, 1974, **184**, 568; B. L. Haymore and J. A. Ibers, *J. Amer. Chem. Soc.*, 1974, **96**, 3325.

[5] S. Bhaduri, B. F. G. Johnson, and T. W. Matheson, *J.C.S. Dalton*, 1977, 561.

[6] J. Osborn and R. Shrock, *J. Amer. Chem. Soc.*, 1971, **93**, 2397.

[7] See, for example, C. A. Reed and W. R. Roper, *J.C.S. Dalton*, 1972, 1243 and refs. therein.

(1)] probably occurs *via* the sequence (2)—(4). First, the nitro-complex $[Ir(CO)(NO_2)(PPh_3)_2]$ is formed.

$$[Ir(CO)Cl(PPh_3)_2] \xrightarrow[CO, 150\ ^\circ C, 1\ atm]{Na[NO_2]} [Ir(NO)(CO)(PPh_3)_2] \xrightarrow{[NO][PF_6]} [Ir(NO)_2(PPh_3)_2][PF_6] \quad (1)$$

$$[Ir(CO)Cl(PPh_3)_2] + Na[NO_2] \longrightarrow [Ir(CO)(NO_2)(PPh_3)_2] + NaCl \quad (2)$$

$$[Ir(CO)(NO_2)(PPh_3)_2] + CO \rightleftharpoons [Ir(CO)_2(NO_2)(PPh_3)_2] \quad (3)$$

$$[Ir(CO)_2(NO_2)(PPh_3)_2] \longrightarrow [Ir(NO)(CO)(PPh_3)_2] + CO_2 \quad (4)$$

Nitro-complexes of nickel [8] and palladium and platinum [9] are known to react with CO to produce nitrosyl complexes, and the reaction of $[Ir(CO)(NO_2)(PPh_3)_2]$ probably proceeds initially by addition of CO to produce the five-co-ordinate 18-electron species $[Ir(CO)_2(NO_2)(PPh_3)_2]$ and then by an intramolecular oxygen transfer to form $[Ir(NO)(CO)(PPh_3)_2]$ and CO_2. This would involve an intramolecular redox process of the type formally $Ir^{I}{-}NO_2 \longrightarrow Ir^{-I}{-}NO$ and a concomitant change in geometry from trigonal bipyramidal to quasi-tetrahedral (C_{2v}). The nitrosyl carbonyl $[Ir(NO)(CO)(PPh_3)_2]$ may then be treated with $[NO][PF_6]$ in benzene–methanol to produce $[Ir(NO)_2(PPh_3)_2][PF_6]$. This product was usually contaminated with some $[IrH(NO)(PPh_3)_3][PF_6]$ which is almost certainly formed from the small amounts of HPF_6 present in the reaction. Separation of these two components is not necessary since this mixture reacts with mnts * to give pure $[Ir(NO)_2(PPh_3)_2][PF_6]$.

A second route to $[Ir(NO)_2(PPh_3)_2][PF_6]$ requires the prior formation of $[Ir(CO)_3(PPh_3)_2][PF_6]$; this is achieved by the reaction of $[Ir(CO)Cl(PPh_3)_2]$ with carbon monoxide in the presence of $Na[PF_6]$.[10] Treatment of $[Ir(CO)_3(PPh_3)_2][PF_6]$ in acetone with NO at 50 °C gave good yields of complex (3).

$$[Ir(CO)_3(PPh_3)_2][PF_6] \xrightarrow{NO} [Ir(NO)_2(PPh_3)_2][PF_6] \quad (5)$$

Some Reactions of the Cations $[M(NO)_2(PPh_3)_2][PF_6]$.—In this section are described some of the reactions of complexes (1a), (2), and (3). The structures of these three salts have been established and are shown, together with salient bond angles and bond distances, in Table 1. Some of the reactions observed may be correlated with the observed structures (1a), (2), and (3) (see below).

(*a*) *With tertiary phosphines.* $[Co(NO)_2(PPh_3)_2][PF_6]$. As briefly mentioned above, $[Co(NO)_2(PPh_3)_2][PF_6]$ readily undergoes phosphine exchange. Thus reaction of an excess of the appropriate phosphine (L′) with complex (1a) in CH_2Cl_2 at *ca.* 20 °C led to the formation of $[Co(NO)_2L'_2][PF_6]$ ($L' = PPh_2Me$, $PPhMe_2$, PPh_2Et, $PPhEt_2$, or $\frac{1}{2}$dppe). The nature of the reaction product does not appear to vary with the incoming ligand L′ and, in contrast to the behaviour reported for $[Ir(NO)_2(PPh_3)_2][PF_6]$ (see below), no evidence for the dissociation of $[NO]^+$ has been found in the reaction with PPh_3.

$$PPh_3 + [Co(NO)_2(PPh_3)_2][PF_6] \not\rightleftharpoons [Co(NO)(PPh_3)_3] + [NO][PF_6] \quad (6)$$

$[Rh(NO)_2(PPh_3)_2][PF_6]$. The reactions of salt (2) with the same range of tertiary phosphines (L′) are dramatically different. The products obtained depend on the nature of L′ and, unlike the cobalt system, in no reaction has the simple substitution (7) been observed.

$$[M(NO)_2(PPh_3)_2][PF_6] + 2L' \rightleftharpoons [M(NO)_2L'_2][PF_6] + 2PPh_3 \quad (7)$$

In general, the reactions were rapid (complete in a matter of minutes) and yielded the tetrakis(phosphine) salts $[ML'_4][PF_6]$, *e.g.* as in equation (8). Triphenylphosphine oxide, triphenylphosphine, and N_2O were the other products of these reactions and the evolution of N_2O was quantitative. The reactions with trialkylphosphines, *e.g.* PBu^n_3 or PEt_3, were virtually instantaneous. The iridium analogue $[Ir(NO)_2(PPh_3)_2][PF_6]$ (3) reacted similarly but in this case the reactions were comparatively slow (although still complete in minutes). Reaction with PPh_3 was different from those observed with L′ and gave $[NO][PF_6]$ and $[Ir(NO)(PPh_3)_3]$. This reaction, which is much slower than with L′ {as is the reaction with $AsPh_3$ to produce $[Ir(NO)(AsPh_3)_3]$} was first reported by Reed and Roper.[7] We monitored this reaction by i.r. spectroscopy at *ca.* 25 °C and found that as the reaction proceeds the two NO bands at 1 783 and 1 735 cm^{-1} diminish in intensity and are replaced by bands at 2 230 and 1 630 cm^{-1}. These bands may be assigned to the N–O stretching vibration of $[NO]^+$ and $[Ir(NO)(PPh_3)_3]$ respectively. No other products were observed.

$$[Rh(NO)_2(PPh_3)_2][PF_6] + 2dppe \longrightarrow [Rh(dppe)_2][PF_6] + PPh_3 + PPh_3O + N_2O \quad (8)$$

Phosphorus-31 *N.M.R. Spectra of Complexes* (1a), (2), *and* (3).—The ^{31}P n.m.r. spectrum of $[Co(NO)_2(PPh_3)_2][PF_6]$ in CD_2Cl_2 at 30 °C consisted of an extremely broad resonance (width at half-height, 140 Hz) at *ca.* 58 p.p.m. No signal was detectable at the resonance of free PPh_3. This observation tends to imply that phosphine dissociation is occurring; however, no great reliance should be placed on these data since intermediate relaxation rates of quadrupolar nuclei (^{59}Co, $\frac{7}{2}$) broaden resonances coupled to the quadrupolar nucleus. More detailed mechanistic studies of these exchange reactions are currently in progress.

The ^{31}P n.m.r. spectrum of $[Rh(NO)_2(PPh_3)_2][PF_6]$ in

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* mnts = *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide.

[8] G. Booth and J. Chatt, *J. Chem. Soc.*, 1962, 2099.

[9] S. Bhaduri, B. F. G. Johnson, C. J. Savory, J. N. Segal, and R. H. Walters, *J.C.S. Chem. Comm.*, 1974, 809.

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

CD_2Cl_2 at 30 °C consisted of a sharp doublet centred at *ca.* −47.6 p.p.m. [^1J(Rh–P) 114 Hz]. No signal was detectable at the resonance of free PPh_3 and these data suggest that phosphine dissociation is not occurring. The ^{31}P n.m.r. spectrum of $[Ir(NO)_2(PPh_3)_2][PF_6]$ at room temperature was similar, consisting of a sharp singlet at −45.3 p.p.m. Again there is no evidence for dissociated phosphine. The single phosphorus resonance observed for salts (2) and (3) is consistent with the C_{2v} structure observed in the solid.

Studies by Basolo and other workers[11] have shown that substitution reactions of nitrosyl complexes usually follow a (predominantly) S_N2 path in contrast to the dissociative (S_N1) path commonly observed for the substitution reactions of metal carbonyls. This S_N2 path is considered to involve the intramolecular redox process which formally corresponds to $M^{n+}(NO^+) \rightleftharpoons M^{(n+2)+}-(NO^-)$, with a simultaneous decrease in the MNO bond angle from *ca.* 180 to *ca.* 120°. It may also involve a change in the ligand geometry about the metal. The ^{31}P n.m.r. spectra indicate that, for salts (2) and (3), phosphine dissociation either does not occur or is at least slow on the n.m.r. time scale. Although we were unable to examine phosphine exchange in $[Co(NO)_2(PPh_3)_2][PF_6]$ by ^{31}P n.m.r. because of signal broadening, we were able to examine the exchange with the isoelectronic species $[Fe(NO)_2(PPh_3)_2]$. Both the iron and cobalt species exhibit basically similar reactions with tertiary phosphines or carbon monoxide.

Thus, whereas the complexes $[M(NO)_2(PPh_3)_2][PF_6]$ (M = Rh or Ir) and $[M(NO)_2(PPh_3)_2]$ (M = Ru or Os) react with CO to liberate N_2O and CO_2 [equation (9);

$$[M(NO)_2(PPh_3)_2]^{n+} + 4CO \longrightarrow [M(CO)_3(PPh_3)_2]^{n+} + N_2O + CO_2 \quad (9)$$

M = Rh or Ir, n = 1; M = Ru or Os, n = 0], $[Co(NO)_2(PPh_3)_2]^+$ and $[Fe(NO)_2(PPh_3)_2]$ do not. The iron dinitrosyl, for example, undergoes the simple substitution reactions (10) and (11).

$$[Fe(NO)_2(PPh_3)_2] + CO \longrightarrow [Fe(NO)_2(PPh_3)(CO)] + PPh_3 \quad (10)$$

$$[Fe(NO)_2(PPh_3)(CO)] + CO \longrightarrow [Fe(NO)_2(CO)_2] + PPh_3 \quad (11)$$

At 40 °C in toluene, the ^{31}P n.m.r. spectrum of $[Fe(NO)_2(PPh_3)_2]$ consisted of a single peak at 56.3 p.p.m. relative to H_3PO_4. No change was observed on cooling to −60 °C. The spectrum of the same complex (0.2 mol dm^{-3}) in the presence of added PPh_3 (0.4 mol dm^{-3}) showed little change. The singlet resonance remained at *ca.* 56.3 p.p.m. and no signal appeared at the chemical shift of free PPh_3. Phosphine dissociation is, therefore, rapid on the n.m.r. time scale.

$$[Fe(NO)_2(PPh_3)_2] \rightleftharpoons [Fe(NO)_2(PPh_3)] + PPh_3 \quad (12)$$

The ^{31}P n.m.r. spectrum of $[Ru(NO)_2(PPh_3)_2]$ at 40 °C in toluene showed no dissociated phosphine and a single sharp phosphine resonance was observed at 66.0 p.p.m. (downfield from H_3PO_4). The ^{31}P spectrum of $[Ru(NO)_2(PPh_3)_2]$ in the presence of excess of PPh_3 (0.08 mol dm^{-3}) was a superimposition of the spectra of the two components. No line broadening of the free PPh_3 resonance was observed implying that exchange is slow at these concentrations.

As discussed above, phosphine exchange of co-ordinatively saturated phosphine nitrosyl complexes usually proceeds by an associative path with the retention of the M–NO link. However, it appears from these studies that $[Fe(NO)_2(PPh_3)_2]$, and possibly $[Co(NO)_2(PPh_3)_2]^+$, undergoes phosphine exchange by a predominantly dissociative path. The corresponding complexes of Rh, Ir, Ru, and Os apparently do not; for these it is not unreasonable to assume, and ^{31}P n.m.r. spectra to some extent support this, that reaction with incoming phosphine proceeds *via* an associative step. This difference in the reaction mechanism offers a plausible explanation for the major differences shown in their reactivity towards tertiary phosphines. Since the sterically demanding phosphine PPh_3 will maximise ligand dissociation, reaction *via* a dissociative path will be favoured for the smaller metal ions Co and Fe, but less so for the larger ions Rh, Ir, Ru, and Os. There is another factor to consider. The structures of both $[Fe(NO)_2(PPh_3)_2]$ and $[Co(NO)_2(PPh_3)_2]^+$ approximate to an *idealised* tetrahedral (C_{2v}) arrangement of the four ligands with the bond angles P–M–P, P–M–N, and N–M–N approaching 108° (Table 1). In contrast, the analogues of Rh, Ir, Ru, and Os show a significant distortion towards a *trans*-planar (D_{2h}) arrangement. The iron and cobalt systems may reasonably be regarded as *co-ordinatively saturated* complexes (18-electron) and therefore favour exchange *via* a dissociative path. In contrast, the complexes of Ru, Os, Rh, and Ir are (at least to some extent) co-ordinatively unsaturated (16-electron).

Consider the reaction sequence given in Scheme 1.

$$[M(NO)_2(PPh_3)_2]^{n+} \rightleftharpoons [M(NO)_2(PPh_3)_2]^{n+} \quad (i)$$

quasi-tetrahedral (C_{2v}), co-ordinatively saturated (18-electron) — planar (D_{2h}) co-ordinatively unsaturated (16-electron)

$$[M(NO)_2(PPh_3)_2]^{n+} \overset{L'}{\rightleftharpoons} [M(NO)_2(PPh_3)_2L']^{n+} \quad (ii)$$

$$[M(NO)_2(PPh_3)_2L']^{n+} \longrightarrow [M(PPh_3)L']^{n+} + PPh_3O + N_2O \quad (iii)$$

$$[M(PPh_3)L']^{n+} + 2L' \rightleftharpoons [M(PPh_3)L'_3]^{n+} \quad (iv)$$

$$[M(PPh_3)L'_3]^{n+} \overset{L'}{\rightleftharpoons} [ML_4]^{n+} + PPh_3 \quad (v)$$

SCHEME 1

In step (*i*) the isomerisation of quasi-tetrahedral (C_{2v}) to planar (D_{2h}) occurs. Since the complex $[Rh(NO)_2(PPh_3)_2]^+$ shows some tendency towards the D_{2h} arrangement in its ground-state geometry whereas the cobalt analogue does not, it is reasonable to assume that the activation energy for the process $C_{2v} \rightleftharpoons D_{2h}$ will be less for the heavier metals. The other important step in this sequence is (iii), the production of N_2O by an intramolecular oxygen transfer; this will be discussed in greater detail in a subsequent paper concerned with the

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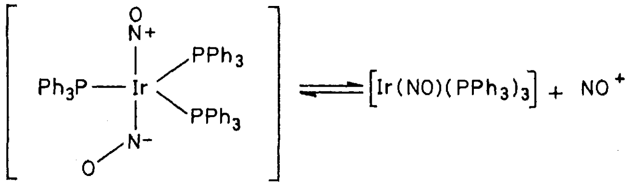
[11] F. Basolo, *Chem. in Britain*, 1969, **5**, 505 and refs. therein.

conversion of CO into CO_2 using the dinitrosyls as catalysts. A preliminary account of this work has already been published.[12]

In a previous paper in this series[5] we observed isomerisation of $[Ni(NO)(PPh_3)_3]^+$ (quasi-tetrahedral) to $[Ni(NO)(PPh_3)_3]^+$ (planar) which is slow on the n.m.r. (^{31}P) time scale. Significantly, the former cation easily lost PPh_3, whereas the latter appeared to undergo PPh_3 exchange by a non-dissociative mechanism. The similarity between these two sets of observations is apparent. An associative mechanism for phosphine exchange is, therefore, sterically and energetically less accessible to $[Fe(NO)_2(PPh_3)_2]$ and $[Co(NO)_2(PPh_3)_2]^+$ than their analogues of Ru, Os, Rh, and Ir. These data on the phosphine-exchange reactions of $[M(NO)_2(PPh_3)_2]^{n+}$ ($M = Ru$ or Os, $n = 0$; $M = Rh$ or Ir, $n = 1$) thus provide good evidence for the ability of NO to function as an electron sink and may be taken as evidence for linear–bent nitrosyl tautomerism.

There remains the question of why the iridium cation loses $[NO]^+$ on reaction with PPh_3 and $AsPh_3$ but reacts with PBu^n_3 and PEt_3, for example, to produce $[IrL'_4]^+$. This difference in reactivity probably depends on the ease of formation of the proposed five-co-ordinate intermediate $[M(NO)_2(PPh_3)_3][PF_6]$ (see above). The formation of this intermediate is expected to involve the intramolecular redox process $M^{n+}(NO^+) \rightleftharpoons M^{(n+2)+}\text{-}(NO^-)$ and the five-co-ordinate intermediate may be formulated, therefore, as $[M(NO^+)(NO^-)(PPh_3)_3]$, which is an 18-electron co-ordinatively saturated species. The bulkiness of PPh_3 is likely to determine the geometry of this intermediate. The complex $[Ru(CO)_3(PPh_3)_2]$, which bears an obvious similarity to the proposed intermediate, has a trigonal-bipyramidal structure[13] with the two CO ligands *trans*. Since $[NO]^-$ is potentially a strongly *trans*-directing ligand, loss of $[NO]^+$ from $[Ir(NO)_2(PPh_3)_3]^+$ is not unexpected.



The difference in basicity of the metal ion in $[Os(NO)_2(PPh_3)_3]$ and $[Ir(NO)_2(PPh_3)_3]^+$ would account for the preference of the osmium system to lose PPh_3. For other, less bulky, phosphines, it is possible that in the five-co-ordinate intermediate the two NO ligands are arranged in a *cis* position and, as formally $[NO]^+$ and $[NO]^-$ couple to form an N_2O_2 ligand, which, being strongly oxidising, leads to the formation of PR_3O and N_2O.

Reactions with Halide Ion.—Addition of $[NEt_4]X$ ($X = Cl$, Br, or I) to $[Co(NO)_2(PPh_3)_2][PF_6]$ in CH_2Cl_2 led to the formation of the neutral complexes $[Co(NO)_2(PPh_3)X]$. These are stable in an inert atmosphere but in the presence of O_2, especially in solution, undergo oxidation to give nitro- and nitrato-species. The cation $[Co(NO)_2(dppe)]^+$ reacted with $[NEt_4]I$ to produce $[Co(NO)_2(dppe)I]$. The structure of this complex is uncertain but only two possibilities need be considered. In the first there is five-fold co-ordination about the cobalt, the dppe ligand is chelating, and one NO ligand is *formally* present as $[NO]^-$. In the second, the arrangement is similar to that found for other $[Co(NO)_2(L)X]$ systems; dppe acts as a unidentate ligand with both NO ligands present as (*formally*) $[NO]^+$ giving rise to a basically tetrahedral arrangement about the Co atom. The complex $[Co(NO)_2(dppe)I]$ was prepared initially with the idea that it would undergo fluxional behaviour corresponding to interchange between these two proposed forms. Unfortunately, because of the broadening brought about in the ^{31}P n.m.r. by the quadrupolar ^{59}Co nucleus we were unable to fully explore this possibility.

Treatment of this complex with *small amounts* of O_2 brought about *partial* oxidation of the dppe ligand and the formation of $[Co(NO)_2\{Ph_2P(CH_2)_2P(O)Ph_2\}]I$. This oxidation probably takes place *via* steps (13)—(15). The

$$[Co(NO)_2\{Ph_2P(CH_2)_2PPh_2\}I] \rightleftharpoons [Co(NO)_2\{Ph_2P(CH_2)_2P'Ph_2\}I] \quad (13)$$

(P′ = unbound P atom)

$$[Co(NO)_2\{Ph_2P(CH_2)_2P'Ph_2\}I] + O_2 \longrightarrow [Co(NO)_2(O_2)\{Ph_2P(CH_2)_2P'Ph_2\}I] \quad (14)$$

$$[Co(NO)_2(O_2)\{Ph_2P(CH_2)_2P'Ph_2\}I] \longrightarrow [Co(NO)_2\{Ph_2P(CH_2)_2P'(O)Ph_2\}I] + \tfrac{1}{2}O_2 \quad (15)$$

reaction probably proceeds first by the partial dissociation of dppe to produce a reaction intermediate which contains one bound and one unbound P atom (P′). The vacant co-ordination site created by this process is then filled by incoming O_2; this is followed in turn by oxygen transfer to the unbound P atom.

A single-crystal *X*-ray analysis of $[Co(NO)_2\{Ph_2P(CH_2)_2P(O)Ph_2\}I]$ has shown[13] that the complex exists in two molecular forms, one containing two Co–N–O units of intermediate geometry with a Co–N–O bond angle of *ca.* 150° and the other containing one distinctly bent (Co–N–O *ca.* 166°) Co–N–O linkage. It was suggested that, unlike the five-co-ordinate mononitrosyl complexes $[Co(NO)Cl_2(PR_3)_2]$ which exist in two isomeric forms,[14] the difference in configuration of the two sets of NO ligands arises from intermolecular packing forces and does not necessitate a change in geometry about the cobalt atom.

An investigation of the i.r. spectrum of the complex in the solid (Nujol) and in solution (CH_2Cl_2) does not clearly indicate the presence of two isomeric forms. Certainly, in solution only one form appears to be present. Two bands, both broad, were observed at 1 834 and 1 776

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[12] B. F. G. Johnson, A. Khair, G. G. Savory, and R. H. Walters, *J.C.S. Chem. Comm.*, 1974, 744.

[13] S. Bhaduri, J. S. Field, and P. J. Wheatley, *J.C.S. Dalton*, 1974, 74.

[14] C. P. Brock, J. P. Collman, G. Dolcetti, P. H. Farnham, J. A. Ibers, J. F. Lester, and C. A. Reed, *Inorg. Chem.*, 1973, **12**, 1304.

$\mathrm{cm^{-1}}$; none was found in the 1 500—1 700 $\mathrm{cm^{-1}}$ region. In a Nujol mull the spectrum was more complex. Four bands were observed at 1 840s, 1 825(sh), 1 780s, and 1 755(sh) $\mathrm{cm^{-1}}$. Intramolecular dipole interactions of the type found from the *X*-ray analysis would be expected to influence the N–O stretching frequencies and lead to the more complicated spectrum observed. Such interactions are not expected in solution where only one isomer, presumably that containing two linear NO groups, is expected. There is no clear indication of co-ordinated $[\mathrm{NO}]^-$ in any of these spectra.

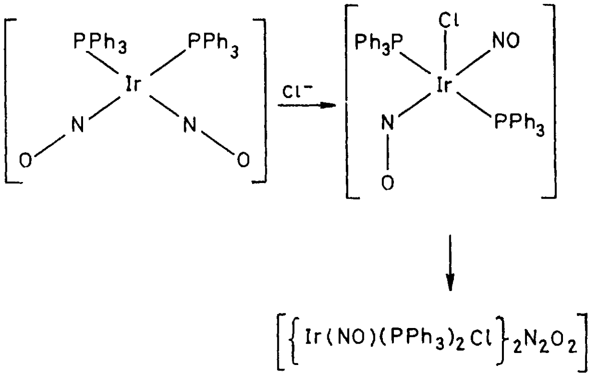
$[\mathrm{Ir(NO)_2(PPh_3)_2}][\mathrm{PF_6}]$. It has been shown previously[15] that treatment of salt (3) with iodide ion leads to a mixture of $[\mathrm{Ir(NO)_2(PPh_3)_2I}]$ and $[\mathrm{Ir(NO)(PPh_3)_2I_2}]$.[7] We found that the iridium salt (3) readily reacts with Cl^- to produce $[\mathrm{Ir(NO)Cl_2(PPh_3)_2}]$ as the sole product. Our original intention was to produce $[\mathrm{Ir(NO)_2Cl(PPh_3)}]$ but this complex was difficult to isolate and readily reacted further to yield the mononitrosyl complex. We have carried out a more detailed investigation of the reaction of (3) with HCl.[7] Dinitrogen monoxide is evolved and the only organometallic product we were able to characterise was $[\mathrm{Ir(NO)Cl_2(PPh_3)_2}]$. We believe that this reaction proceeds *via* the formation of a bridged hyponitrite complex [equations (16)—(18)]. The first step involves the addition of Cl^-

$$[\mathrm{Ir(NO)_2(PPh_3)_2}]^+ + \mathrm{Cl}^- \longrightarrow [\mathrm{Ir(NO)_2(PPh_3)_2Cl}] \qquad (16)$$

$$2[\mathrm{Ir(NO)_2(PPh_3)_2Cl}] \longrightarrow [\{\mathrm{Ir(NO)(PPh_3)_2Cl}\}_2\mathrm{N_2O_2}] \qquad (17)$$

$$[\{\mathrm{Ir(NO)(PPh_3)_2Cl}\}_2\mathrm{N_2O_2}] + \mathrm{HCl} \longrightarrow [\mathrm{Ir(NO)(PPh_3)_2Cl_2}] + \mathrm{N_2O} + \mathrm{H_2O} \qquad (18)$$

to yield the 20-electron system $[\mathrm{Ir(NO)_2(PPh_3)_2Cl}]$. This five-co-ordinate complex will contain *formally* an $[\mathrm{NO}]^+$ and $[\mathrm{NO}]^-$ ligand. The coupling of two such NO systems to produce dimeric bridged hyponitrite species is now a common feature of nitrosyl chemistry[16] [step (17)] and in general hyponitrite complexes react with H^+ to liberate $\mathrm{N_2O}$ [step (18)]. There are two points worthy of comment at this stage. First, the question might reasonably be asked why $[\mathrm{Ir(NO)_2(PPh_3)_2Cl}]$ undergoes a bimolecular coupling reaction [step (17)] whereas in the reactions of $[\mathrm{Ir(NO)_2(PPh_3)_2}]^+$ with L′ an intramolecular coupling is postulated? This difference we believe is, in part, associated with the rigidity of the five-co-ordinate intermediate dinitrosyl complexes, and in part with the difference in charge. Thus, in order for an intramolecular coupling to occur the two NO groups in the intermediate $[\mathrm{Ir(NO)_2(PPh_3)_2Cl}]$ must be in a *cis* orientation. *X*-Ray analysis of $[\mathrm{Ir(NO)_2(PPh_3)_2}]^+$ clearly shows that the two NO ligands are tending towards a planar *trans* arrangement and, if the Cl^- ligand is assumed to approach from above the plane (*e.g.* see Scheme 2) and produce a square-pyramidal intermediate, the NO ligand will occupy a *trans* position in the basal plane. Coupling cannot occur therefore until isomerisation has taken place and this process has been found to be slow for a number of nitrosyl species, *e.g.* $[\mathrm{Co(NO)Cl_2(PPh_3)_2}]$,[14] $[\mathrm{Ru(NO)_2(PPh_3)_2Cl}]$,[17] and $[\mathrm{Mo(NO)_2(NCMe)_3}]^{2+}$.[12] Thus, the bimolecular reaction to produce the bridged $\mathrm{N_2O_2}$ complex is preferred. In the case of the charged species, a bimolecular reaction is clearly less favoured. The ease of isomerisation of the five-co-ordinate intermediate will also depend on the size of the incoming substrate and the rate of reaction of $[\mathrm{Ir(NO)_2(PPh_3)_2}]^+$ showed a marked dependence on the bulkiness of L′ (see above).



SCHEME 2 Reaction of $[\mathrm{Ir(NO)_2(PPh_3)_2}]^+$ with HCl

Secondly, why does $[\mathrm{NO}]^-$ coupling occur at all? If we accept the suggestion (see above) that coupling only occurs when an $[\mathrm{NO}]^+/[\mathrm{NO}]^-$ (or so-called '20-electron') system is produced then any of the five-co-ordinate intermediates suggested for the interaction between $[\mathrm{Rh(NO)_2(PPh_3)_2}]^+$ or $[\mathrm{Ir(NO)_2(PPh_3)_2}]^+$ and either L′ or Cl^- should undergo $[\mathrm{NO}]^-$ coupling. Since $[\mathrm{Co(NO)_2(PPh_3)_2}]^+$ and $[\mathrm{Fe(NO)_2(PPh_3)_2}]$ undergo reactions with L′ or Cl^- (with the cobalt complex) by primarily a phosphine-dissociation step the intermediate produced will be an 18-electron system and is not expected to undergo a coupling reaction of either description.

Conclusions. The reactions of $[\mathrm{M(NO)_2(PPh_3)_2}][\mathrm{PF_6}]$ (M = Co, Rh, or Ir) with tertiary phosphines or chloride ion fall into three classes.

(1) For M = Co, reaction with either L′ or Cl^- occurs *via* phosphine dissociation and the formation of the unsaturated (16-electron) $[\mathrm{Co(NO)_2(PPh_3)}]^+$ intermediate.

(2) For M = Rh or Ir, reactions with L′ occur *via* an associative path with the formation of a '20-electron' intermediate which may be regarded *formally* as a derivative of $[\mathrm{NO}]^+$ and $[\mathrm{NO}]^-$. This leads to coupling of the two nitrosyl ligands and formation of $\mathrm{N_2O}$ and LO if L = $\mathrm{PEt_3}$, $\mathrm{PBu_3}$, or $\frac{1}{2}$ dppe but to the production of $[\mathrm{NO}]^+$ and $[\mathrm{M(NO)(PPh_3)_3}]$ if L = $\mathrm{PPh_3}$.

(3) For M = Rh or Ir, reaction with HCl produces $[\mathrm{M(NO)(PPh_3)_2Cl_2}]$, $\mathrm{N_2O}$, and water. This reaction also proceeds *via* a '20-electron' intermediate but in this case coupling occurs *via* a bimolecular reaction.

These reactions may be correlated with the ease of

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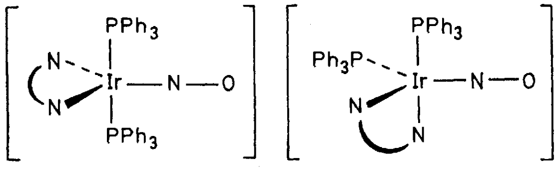
[15] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 1970, **9**, 1105.

[16] For a recent review see N. G. Connelly, *Inorg. Chim. Acta Rev.*, 1972, **6**, 47.

[17] J. P. Collman, P. Farnham, and G. Dolcetti, *J. Amer. Chem. Soc.*, 1971, **93**, 1788.

phosphine dissociation, the ground-state geometries shown by the three cations, and finally the high barrier to polytopal rearrangement shown by the five-co-ordinate intermediates.

The cation $[Ir(NO)_2(PPh_3)_2]^+$ reacts with 2,2′-bipyridyl (bipy) with evolution of N_2O to give small amounts of $[Ir(NO)(PPh_3)_2(bipy)]^{2+}$. Although this reaction corresponds to the simple replacement of nitrogen monoxide as $[NO]^-$ (*formally*) by bipy, the precise nature of this reaction, which is not quantitative, has not been established. Almost certainly some form of hyponitrite complex is involved. The complex $[Ir(NO)(OH)(PPh_3)_2][PF_6]$ is also formed and it appears that small amounts of water are necessary for the reaction to take place. The cation $[Ir(NO)(PPh_3)_2(bipy)]^{2+}$ has ν(NO) at 1 790 cm^{-1} which suggests that the NO is present (*formally*) as $[NO]^+$ and that the M–N–O linkage is linear. Two possible geometries for this dication are shown. The dication $[Rh(NO)(dppe)_2]^{2+}$, which bears a close relation to the bipy salt, has been reported previously and is thought to possess a trigonal-bipyramidal structure with NO in the equatorial plane.



(a) (b)

Reactions involving Attack at Co-ordinated NO.—The cations $[M(NO)_2(PPh_3)_2]^+$ are expected to undergo attack by nucleophilic reagents. We observed that the reactions of the cations with $Na[BH_4]$ or N_2H_4 in tetrahydrofuran (thf) and in the presence of PPh_3 led to the formation of $[M(NO)(PPh_3)_3]$. In the reaction with $Na[BH_4]$ the evolution of ammonia was also observed indicating that attack of H^- on one of the co-ordinated NO ligands is occurring.

TABLE 2

Microanalytical and conductivity data for the dinitrosyl complexes and the complexes obtained from the dinitrosyl species

	Analysis (%)								
	Found			Calc.			$\bar{\nu}(NO)/cm^{-1}$		Λ [a] $/S\ cm^2\ mol^{-1}$
Complex	C	H	N	C	H	N			
$[Co(NO)_2(PPh_3)_2][PF_6]$	54.7	3.6	3.5	54.8	3.8	3.5	1 840, 1 850	1 785, 1 795 [b]	19.10
$[Co(NO)_2(PPh_2Me)_2][PF_6]$	46.8	4.0	4.2	47.0	3.9	4.2	1 840	1 780	19.65
$[Co(NO)_2\{P(OPh)_3\}_2][PF_6]$	48.5	3.3	3.0	48.9	3.4	3.2	1 845	1 790	20.25
$[Co(NO)_2(dppe)][PF_6]$	47.1	3.7	4.2	47.1	3.7	4.2	1 860	1 805	19.80
$[Rh(NO)_2(PPh_3)_2][PF_6]$ [c]	51.9	3.7	3.8	51.9	3.6	3.7	1 768m, 1 788m	1 714s, 1 742s [d]	21.29
$[Ir(NO)_2(PPh_3)_2][PF_6]$	46.8	3.3	2.8	47.0	3.3	3.1	1 765m	1 700s	20.92
$[Co(NO)_2(PPh_3)I]$ [e]	42.7	3.1	5.4	42.5	2.9	5.4	1 823	1 769 [f]	
$[Co(NO)_2(PPh_3)Br]$ [e]	46.6	3.1	5.9	46.9	3.3	6.1	1 826	1 762 [f]	
$[Co(NO)_2\{Ph_2P(CH_2)_2P(O)Ph_2\}I]$ [e]	47.4	3.7	3.9	47.3	3.7	4.2	1 834b	1 776b [d]	
$[Co(NO)(PPh_3)_3]$	73.9	5.1	1.6	74.0	5.2	1.6		1 635	
$[Rh(NO)(PPh_3)_3]$	70.2	4.9	1.3	70.5	4.9	1.5		1 611	
$[Ir(NO)(PPh_3)_3]$	64.7	4.6	1.2	64.3	4.5	1.4		1 600	
$[Ir(NO)(CO)(PPh_3)_2]$	57.4	3.8	1.8	57.3	3.9	1.8		1 600	
$[Ir(NO)(PPh_3)_2(bipy)][PF_6]_2$	46.1	3.2	3.3	46.3	3.2	3.5		1 790	46.1

[a] Molar conductivities measured in 10^{-3} mol dm^{-3} nitrobenzene solution. [b] In CH_2Cl_2. [c] For $[Rh(^{15}NO)_2(PPh_3)_2][PF_6]$, ν(NO) at 1 758 and 1 715s cm^{-1}. [d] All the spectra were recorded for Nujol mulls unless stated otherwise. [e] Λ 0—5 S cm^2 mol^{-1}. [f] In C_6H_{12}.

EXPERIMENTAL

All the reactions were carried out under dry oxygen-free nitrogen unless stated otherwise, and conventional methods for the handling of air- and moisture-sensitive materials were employed throughout. All the solvents were dried and degassed before use.

Octacarbonyldicobalt was purchased from Alpha Inc. (U.S.A.) and hydrated rhodium and iridium trichloride were kindly supplied on loan by Johnson, Matthey Ltd. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer. Conductivities were measured for 10^{-3} mol dm^{-3} solutions at 25 °C in a standard conductivity cell using a Philips GM 4249 conductivity bridge. Hydrogen-1 and ^{31}P n.m.r. spectra were recorded on a Varian Associates XL 100 spectrometer. Carbon, hydrogen, and nitrogen microanalytical results were by Microanalytical Developments of the Cambridge University Chemical Laboratory and are recorded in Table 2.

The precursor complexes, $[Co(NO)(CO)L_2]$, were obtained using previously reported methods.[18] The complexes $[Rh(nbd)L_2][PF_6]$ were prepared by the reaction of $[\{Rh(nbd)Cl\}_2]$ with L in the presence of sodium hexafluorophosphate.[6] The salt $[Ir(CO)_3(PPh_3)_2][PF_6]$ was obtained by the method of Mays *et al.*[10] In reactions where free NO was used the gas was purified by passing it through a U tube cooled to −78 °C and then through potassium hydroxide pellets.

Dinitrosylbis(triphenylphosphine)cobalt Hexafluorophosphate.—Nitrosonium hexafluorophosphate (0.45 g) was added to a well stirred solution of $[Co(NO)(CO)(PPh_3)_2]$ (1 g) in dry benzene (40 cm^3)–methanol (10 cm^3). The solution changed colour from deep red to greenish black and a black crystalline solid was precipitated. After 2 h the solution was reduced in volume and the greenish black precipitate was collected by filtration. After washing with diethyl ether, the solid was recrystallised from dichloromethane–ethanol to give black crystals (0.9 g). The other cations of this type, L = $P(OPh)_3$, PPh_2Me, or ½dppe, were prepared in good yield from the corresponding $[Co(NO)(CO)L_2]$ complexes.

[18] J. P. Candlin and W. H. Janes, *J. Chem. Soc.* (*C*), 1968, 1856; F. Basolo and S. G. Clarkson, *Inorg. Chem.*, 1973, **12**, 1528.

Dinitrosylbis(triphenylphosphine)rhodium Hexafluorophosphate.—The salt $[Rh(nbd)(PPh_3)_2][PF_6]$ (0.5 g) was dissolved in dry dichloromethane (4 cm^3). An atmosphere of NO was then introduced and the solution was stirred vigorously for 30 min when the solution changed colour from red to black. Addition of methanol yielded a black precipitate, $[Rh(NO)_2(PPh_3)_2][PF_6]$, which was collected by filtration (0.4 g). Recrystallisation was from dichloromethane–methanol. An analogous procedure using ^{15}NO in place of ^{14}NO yielded $[Rh(^{15}NO)_2(PPh_3)_2][PF_6]$.

Carbonylnitrosylbis(triphenylphosphine)iridium(−I).—Sodium nitrite (0.13 g) was dissolved in water (2 cm^3) and the aqueous solution was added to a solution of *trans*-$[Ir(CO)Cl(PPh_3)_2]$ (1 g) in refluxing dimethylformamide (30 cm^3). Carbon monoxide was bubbled through the solution for 1.5 h. The solution was cooled to room temperature and ethanol (50 cm^3) was added. Addition of more water (15 cm^3) caused precipitation of orange microcrystals of $[Ir(NO)(CO)(PPh_3)_2]$ (0.8 g, 80%) which were recrystallised from benzene–ethanol.

Reactions.—*Nitrosonium hexafluorophosphate with* $[Ir(NO)(CO)(PPh_3)_2]$. Nitrosonium hexafluorophosphate (0.7 g) was added to a well stirred solution of $[Ir(NO)(CO)(PPh_3)_2]$ (1.7 g) in dry benzene (60 cm^3)–anhydrous methanol (10 cm^3). The solution changed colour from deep orange to greenish black and black crystals were precipitated. After 4.5 h the solution was filtered and the precipitate collected. An i.r. spectrum of the crude product suggested the presence of $[IrH(NO)(PPh_3)_3][PF_6]$ together with $[Ir(NO)_2(PPh_3)_2][PF_6]$. This mixture (1.6 g) was heated under reflux with *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (1.4 g) in an ethyl acetate (180 cm^3) – acetone (20 cm^3) solution for 20 min. After cooling the solution to room temperature, hexane (30 cm^3) was added to give black microcrystals of $[Ir(NO)_2(PPh_3)_2][PF_6]$ (1.4 g).

$[Ir(CO)_3(PPh_3)_2][PF_6]$ *with* NO. Pure NO was bubbled through a refluxing solution of $[Ir(CO)_3(PPh_3)_2][PF_6]$ (1 g) in acetone (70 cm^3). The colourless solution rapidly became orange and then slowly deep reddish black. After 6 h the flow of NO was stopped and nitrogen was passed through the solution for 10 min. The solution was then taken to dryness and the crude $[Ir(NO)_2(PPh_3)_2][PF_6]$ thus obtained was recrystallised from dichloromethane–ethanol to give shiny black microcrystals, yield 0.85 g.

$[Co(NO)_2(PPh_3)_2][PF_6]$ with dppe. 1,2-Bis(diphenylphosphino)ethane (0.15 g) was added to a dichloromethane (20 cm^3) solution of $[Co(NO)_2(PPh_3)_2][PF_6]$ (0.2 g). The colour of the solution immediately turned from greenish black to deep red. After reducing the volume of the solution, diethyl ether was added to give an orange precipitate of $[Co(NO)_2(dppe)][PF_6]$ (0.85 g). Recrystallisation was from dichloromethane–ethanol. Reactions of $[Co(NO)_2(PPh_3)_2][PF_6]$ with other phosphines, L′ (see above), were carried out similarly.

$[Co(NO)_2(PPh_3)_2][PF_6]$ *with* $[NEt_4]X$ (X = Cl, Br, *or* I). The ammonium salt was added to a solution of $[Co(NO)_2(PPh_3)_2][PF_6]$ (0.7 g) in thf. The solution was heated under reflux for 2 h and then filtered. The filtrate was taken to dryness and the crude $[Co(NO)_2(PPh_3)X]$ thus obtained was recrystallised from hot hexane to give deep brown crystals, yield 0.45 g. Reaction of the cation $[Co(NO)_2(dppe)][PF_6]$ and $[NEt_4]I$ was carried out similarly.

$[Ir(NO)_2(PPh_3)_2][PF_6]$ *with* PPh_3. Triphenylphosphine (0.3 g) was added to a solution of $[Ir(NO)_2(PPh_3)_2][PF_6]$ (0.1 g) in dichloromethane (7 cm^3). The solution was stirred for 1 h and then, using a PPh_3 solution of the same concentration as reference, a solution i.r. spectrum was recorded. The presence of $[NO][PF_6]$ was inferred from the band at 2 230 cm^{-1}. The solution was then stirred for 24 h and after taking it to dryness the small amount of $[Ir(NO)(PPh_3)_3]$ thus formed was extracted with benzene. Reaction of $[Ir(NO)_2(PPh_3)_2][PF_6]$ with $AsPh_3$ was studied similarly.

$[Ir(NO)_2(PPh_3)_2][PF_6]$ *with 2,2′-bipyridyl.* 2,2′-Bipyridyl (0.15 g) was added to a solution of $[Ir(NO)_2(PPh_3)_2][PF_6]$ (0.3 g) in dichloromethane (4 cm^3) and the solution was stirred at room temperature for 8 h. Evolution of N_2O was confirmed by i.r. spectroscopy (see above) and the white precipitate of $[Ir(NO)(PPh_3)_2(bipy)][PF_6]_2$ (0.1 g) was collected by filtration. The filtrate was taken to dryness and an i.r. spectrum of the residue in a Nujol mull showed bands (see Table 2) which can be attributed to $[Ir(NO)(OH)(PPh_3)_2][PF_6]$.

$[Ir(NO)_2(PPh_3)_2][PF_6]$ *with* HCl. Hydrochloric acid (0.01 g) was added to a solution of $[Ir(NO)_2(PPh_3)_2][PF_6]$ (0.1 g) in acetone (5 cm^3). The solution was stirred for 10 min and the yellow-brown precipitate of $[Ir(NO)(PPh_3)_2Cl_2]$ (0.068 g) was collected by filtration. The evolved gas was identified by i.r. spectroscopy as N_2O.

$[Co(NO)_2(PPh_3)_2][PF_6]$ *with* $Na[BH_4]$. Addition of $Na[BH_4]$ (0.3 g) in thf (15 cm^3) to $[Co(NO)_2(PPh_3)_2][PF_6]$ (0.5 g) resulted in evolution of a gas and a colour change in the solution from greenish black to brown. After 4 h the solution was taken to dryness *in vacuo* and washed with diethyl ether to yield $[Co(NO)(PPh_3)_3]$ (0.2 g). Recrystallisation from benzene–methanol gave purple crystals. The evolved gas turned red litmus blue, produced white fumes with concentrated HCl, and gave a positive test with Nessler's reagent: all indicative of ammonia. The i.r. spectrum of the gas showed bands due to thf and an additional band at 970 cm^{-1} which can be attributed to ammonia. Reactions of $Na[BH_4]$ with $[M(NO)_2(PPh_3)_2][PF_6]$ (M = Rh or Ir) were carried out similarly.

$[Co(NO)_2(dppe)][PF_6]$ *with* $Na[BH_4]$. The procedure here was similar to the previous preparation, except that the reaction was carried out in refluxing thf for 4 h, and crystallisation of $[Co(NO)_2(dppe)(thf)]$ was effected from diethyl ether to give pink crystals.

$[Co(NO)_2(dppe)][PF_6]$ *with* $Na[BH_4]$ *in the presence of* PPh_3. Triphenylphosphine (0.1 g) and $Na[BH_4]$ (0.12 g) were added to a refluxing solution of $[Co(NO)_2(dppe)][PF_6]$ (0.25 g) in thf (50 cm^3). After 4 h the solution was taken to dryness and $[Co(NO)(dppe)(PPh_3)]$ (0.12 g) was recrystallised from diethyl ether.

$[Co(NO)_2(PPh_3)_2][PF_6]$ *with hydrazine.* The salt $[Co(NO)_2(PPh_3)_2][PF_6]$ (0.08 g) was placed in a flask and hydrazine hydrate (0.5 cm^3) in methanol (2 cm^3) was added. After stirring the suspension for 24 h, $[Co(NO)(PPh_3)_3]$ (0.05 g) was separated by filtration and recrystallised from benzene–ethanol as purple crystals. Reactions of $[M(NO)_2(PPh_3)_2][PF_6]$ (M = Rh or Ir) were carried out similarly except that these were complete in a much shorter time (30 min).

$[Ir(NO)_2(PPh_3)_2][PF_6]$ *with* $PhNHNH_2$. The cation $[Ir(NO)_2(PPh_3)_2]^+$ (0.1 g) was heated under reflux with $PhNHNH_2$ (0.35 g) in methanol (20 cm^3) for 2 h. The orange precipitate of $[Ir(NO)(PPh_3)_3]$ (0.06 g) was separated by filtration and recrystallised from benzene–ethanol.

[6/1960 *Received, 20th October,* 1976]