Transition-metal Nitrosyl Compounds. Part 12.[1] Bis- and Tris-(tertiary phosphine)nitrosylnickel(II) Hexafluorophosphate Complexes

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The nickel nitrosyl cations $[Ni(NO)L_n]^+$ (L = PPh_3, n = 2 or 3; L = $PMePh_2$, n = 3) have been prepared from the reaction of $[Ni(CO)_2L_2]$ with $NOPF_6$ in C_6H_6–MeOH or from the reaction of $[NiCl_2L_2]$ with $Na[NO_2]$ and L in the presence of CO. Some reactions of $[Ni(NO)(PPh_3)_3]^+$ with the nucleophiles $[OMe]^-$, X^- (X = Cl, Br, or I), $[S_2CNR_2]^-$, $Ph_2P[CH_2]_2PPh_2$, and $PMePh_2$ have been examined. A ^{31}P n.m.r. study reveals that the complex $[Ni(NO)(PPh_3)_3][PF_6]$ probably exists in two isomeric forms, one of symmetry C_{3v} and the other of C_{2v}.

It has been suggested that the complexes $[Rh(NO)(PPh_3)_3]$ and $[Ir(NO)(PPh_3)_3]$, which are known to function as hydrogenation catalysts, undergo phosphine dissociation. Evidence for such dissociation has been provided from osmometric molecular-weight determination for which values of 300 (calc.: 920) and 800 (1009) were found for $[Rh(NO)(PPh_3)_3]$ and $[Ir(NO)(PPh_3)_3]$ respectively.[2] The suggestion has also been made that the catalytic activity of these species may be associated with their ability to undergo an intramolecular redox process of the type $M^{n+}(NO^+) \rightleftharpoons M^{(n+2)+}(NO^-)$.[3] This process would involve a simultaneous change in the M–N–O bond angle from *ca.* 180 to 120° and a change in the geometry of the complexes from C_{3v} to C_{2v}. A relatively recent study of $[Co(NO)(PPh_3)_3]$ and $[Rh(NO)(PPh_3)_3]$ revealed that phosphine exchange probably occurs *via* a dissociative process.[4]

We report the preparation of the complex cation $[Ni(NO)(PPh_3)_3]^+$, which is isoelectronic with $[Co(NO)(PPh_3)_3]$, and also the co-ordinatively unsaturated species $[Ni(NO)(PPh_3)_2]^+$. The cation $[Ni(NO)(PPh_3)_3]^+$ undergoes phosphine exchange but the mechanism of this exchange is complex and appears to embrace both the mechanisms outlined above.

RESULTS AND DISCUSSION

Preparation of the Complexes $[Ni(NO)L_n][PF_6]$.—(*i*) *From the reaction of* $[Ni(CO)_2L_2]$ *with* $NOPF_6$.[5] On treatment of $[Ni(CO)_2L_2]$ with $NOPF_6$ in benzene–methanol at *ca.* 20 °C, carbon monoxide was evolved and the colourless solution became blue. Addition of diethyl ether to this blue solution resulted in precipitation of a blue solid. After crystallisation from CH_2Cl_2–EtOH–C_6H_{12} the salts $[Ni(NO)L_3][PF_6]$ [L = PPh_3 (1a) or $PMePh_2$ (1b)] were obtained as dark blue needles. Although moderate yields of the salts were obtained by this method, yields were considerably increased when the reaction was carried out in the presence of a large excess of phosphine. When the reaction of $[Ni(CO)_2(PPh_3)_2]$ and $NOPF_6$ took place in benzene a second product, $[Ni(CO)(NO)(PPh_3)_2][PF_6]$, was also formed. This red-brown salt is unstable and readily evolves CO to produce $[Ni(NO)(PPh_3)_2][PF_6]$ (2), the co-ordinatively unsaturated salt. This carbonyl complex is very unstable and has been characterised on the basis of its i.r. spectrum which has ν(CO) at 2 080 and ν(NO) at 1 735 cm^{-1}.

These observations lead to the mechanism in equations (1)—(4). We have shown that the carbonyl nitrosyl complex readily evolves CO to produce the co-ordinatively unsaturated species $[Ni(NO)(PPh_3)_2]^+$ [equation (2)].

$$[Ni(CO)_2L_2] + NOPF_6 \longrightarrow [Ni(CO)(NO)L_2][PF_6] + CO \quad (1)$$

$$[Ni(CO)(NO)L_2][PF_6] \longrightarrow [Ni(NO)L_2][PF_6] + CO \quad (2)$$

$$[Ni(CO)_2L_2] \rightleftharpoons [Ni(CO)_2L] + L \quad (3)$$

$$[Ni(NO)L_2][PF_6] + L \rightleftharpoons [Ni(NO)L_3][PF_6] \quad (4)$$

This has been shown to react rapidly with free PPh_3 to produce $[Ni(NO)(PPh_3)_3]^+$ [step (4)]. Phosphine exchange of co-ordinatively saturated carbonylphosphine complexes usually proceeds by a dissociative path [step (3)].[6] Finally, by monitoring the reaction conditions carefully both $[Ni(NO)(PPh_3)_3][PF_6]$ and $[Ni(NO)(PPh_3)_2][PF_6]$ may be isolated from the reaction. Attempts to recrystallise $[Ni(NO)(PPh_3)_3][PF_6]$ from benzene–methanol led to the formation of a mixture of $[Ni(NO)(PPh_3)_3][PF_6]$ and $[Ni(NO)(PPh_3)_2][PF_6]$. Recrystallisation must be carried out in the presence of free PPh_3.

(*ii*) *From the reaction of* $[NiCl_2L_2]$ *with* $Na[NO_2]$ *and* L *in the presence of* CO. It is now established that the reduction of M–NO_2 or M–NO_3 compounds by CO provides a convenient route to many NO systems.[7] The complex $[NiCl_2(PMePh_2)_2]$ reacted with $Na[NO_2]$, $Na[PF_6]$, and $PMePh_2$ in the presence of CO at *ca.* 56 °C and 1 atm* to produce $[Ni(NO)(PMePh_2)_3][PF_6]$ in good yield. This reaction probably occurs as in equations (5)—(8). Nitronickel(II) complexes are known to react with CO to produce nitrosylnickel(0) complexes [step (6)].[8] This reaction probably proceeds first by addition of CO to produce the five-co-ordinate species $[Ni(CO)Cl(NO_2)(PMePh_2)]$ followed by an intramolecular oxygen transfer

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* Throughout this paper: 1 atm = 101 325 Pa.

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to form the nitrosyl complex and CO_2. The complex $[NiCl(NO)(PMePh_2)_2]$ reacts with $Na[PF_6]$ to produce $[Ni(NO)(PMePh_2)_2][PF_6]$ and NaCl [related to step (7)], and finally the co-ordinatively unsaturated complex

$$[NiCl_2(PMePh_2)_2] + Na[NO_2] \longrightarrow [NiCl(NO_2)(PMePh_2)_2] + NaCl \quad (5)$$

$$[NiCl(NO_2)(PMePh_2)_2] + CO \longrightarrow [NiCl(NO)(PMePh_2)_2] + CO_2 \quad (6)$$

$$[NiCl(NO)(PMePh_2)_2] + Na[PF_6] \longrightarrow [Ni(NO)(PMePh_2)_2][PF_6] + NaCl \quad (7)$$

$$[Ni(NO)(PMePh_2)_2][PF_6] + PMePh_2 \longrightarrow [Ni(NO)(PMePh_2)_3][PF_6] \quad (8)$$

$[Ni(NO)(PMePh_2)_2][PF_6]$ is reasonably expected to combine with $PMePh_2$ to produce the required product [step (8)].

In contrast, under identical conditions, the reaction with $[NiCl_2(PPh_3)_2]$ produced $[NiCl(NO)(PPh_3)_2]$ as the sole product. This may be a result of the ease with which complex (1a) undergoes PPh_3 dissociation [equations (9) and (10)]. Treatment of $[NiBr(NO)(PPh_3)_2]$ with

$$[Ni(NO)(PPh_3)_3]^+ \rightleftharpoons [Ni(NO)(PPh_3)_2]^+ + PPh_3 \quad (9)$$

$$[Ni(NO)(PPh_3)_2]^+ + X^- \rightleftharpoons [Ni(NO)(PPh_3)_2X] \quad (10)$$

$Ag[PF_6]$, however, readily gave $[Ni(NO)(PPh_3)_2][PF_6]$.

Characterisation and Reactivity of Complexes (1a) *and* (1b).—The two salts were readily characterised on the basis of their i.r. spectra, analytical data, and conductivity values in nitrobenzene. Both exhibited a strong NO stretching vibration in their i.r. spectra in the 1 750—1 800 cm^{-1} region which, allowing for the fact that the complexes have a 1+ charge, probably indicates that the NO ligand is present formally as $[NO]^+$ and that the complexes are best formulated as pseudo-tetrahedral (C_{3v}) derivatives of Ni^0 possessing a similar geometry to their cobalt counterparts. In keeping with this view, ν(NO) for $[Co(NO)(PPh_3)_3]$ occurs *ca.* 50 cm^{-1} lower than for $[Ni(NO)(PPh_3)_3]$. The values of ν(NO) for (1a) (1 783 cm^{-1}) and (1b) (1 780 cm^{-1}) are remarkably similar, particularly in view of the fact that (1a) easily loses a phosphine ligand whereas (1b) apparently does not. For the bis(triphenylphosphine) salt $[Ni(NO)(PPh_3)_2][PF_6]$, the NO stretching vibration appears at 1 755 cm^{-1}.

The ^{31}P n.m.r. spectrum of (1a) in $CDCl_3$ at 30 °C showed a resonance at *ca.* —38.9 p.p.m. (relative to free PPh_3). No resonance was detectable at the chemical shift of free PPh_3. The ^{31}P n.m.r. spectrum of a freshly crystallised sample of (1a) in CD_2Cl_2 at 30 °C consisted of two resonances at —42.4 and —38.9 p.p.m. Addition of free PPh_3 to the solution at 30 °C caused the signal at —42.4 p.p.m. to disappear. The addition of excess of PPh_3 (up to 8 mol dm^{-3}) did not cause the spectrum to change further, apart from the emergence of a sharp signal due to free PPh_3. The i.r. spectrum of the same sample in CH_2Cl_2 showed a weak absorption at 1 755 cm^{-1}. This weak band disappeared when an excess of PPh_3 was added to the solution. The ^{31}P resonance at —42.4 p.p.m. and i.r. band at 1 755 cm^{-1} are reasonably assigned to the co-ordinatively unsaturated species $[Ni(NO)(PPh_3)_2][PF_6]$. The ^{31}P n.m.r. spectrum of solutions of (1a) in CD_2Cl_2 showed an unexpected feature at low temperatures. As reported above, at *ca.* 30 °C the spectrum of this solution exhibits one signal at —38.9 p.p.m.; as the solution was cooled to —85 °C two new signals of relative intensity 2 : 1 appeared at —69.5 and —46.7 p.p.m.

These ^{31}P spectra indicate that the three triphenylphosphine ligands are equivalent, consistent with the proposed C_{3v} geometry for salt (1a). No evidence for dissociated phosphine was found from the ^{31}P n.m.r. spectra, although the co-ordinatively unsaturated species is readily isolable (see above). The observation that the mixture of salts (1a) and (2) exhibit independent resonances in the ^{31}P n.m.r. spectrum at 30 °C indicates that the dissociation (9) is slow on the n.m.r. time scale. At —85 °C a new isomer or complex was detectable. Since there is no evidence for the elimination of $NOPF_6$ (see below), and the new signals had intensity values in the ratio *ca.* 2 : 1, it is reasonable to assume that the new species is the square planar (C_{2v}) form of (1a). At —85 °C exchange of phosphine was detectable since the signals due to the proposed square-planar form of (1a) broadened on the addition of free phosphine. Substitution reactions of nitrosyl complexes often occur by an associative mechanism. Such reactions occur if an intramolecular redox process is energetically accessible, *i.e.* for the interconversion $M^{n+}(NO^+) \rightleftharpoons M^{(n+2)+}(NO^-)$ which corresponds to a change in the M–N–O bond angle from *ca.* 180 to 120°. Co-ordinatively unsaturated complexes $[NiX_2L_2]$ all exchange phosphine by an associative path and in some cases five-co-ordinate $[MX_2L_3]$ complexes may be isolated.[9,10] Here a mechanism involving two isomeric forms of $[Ni(NO)(PPh_3)_3]^+$ must be involved: one of C_{3v} geometry which is co-ordinatively saturated and undergoes slow PPh_3 dissociation, and one of C_{2v} geometry which is co-ordinatively unsaturated and undergoes fast phosphine exchange *via* an S_N2 mechanism.

$$\begin{tikzcd}
{[Ni^0(NO^+)(PPh_3)_3]^+ \; (C_{3v})} \arrow[r, leftrightarrow, "slow", "(a)"'] \arrow[d, leftrightarrow, "slow"', "(b)"] & {[Ni(NO)(PPh_3)_2]^+ + PPh_3} \\
{PPh_3 + [Ni^{II}(NO^-)(PPh_3)_3]^+ \; (C_{2v})} \arrow[r, leftrightarrow, "fast", "(c)"'] & {[Ni^{II}(NO^-)(PPh_3)_4]^+}
\end{tikzcd}$$

The chemistry of $[Ni(NO)(PPh_3)_3]^+$ contrasts with that of $[Co(NO)(PPh_3)_3]$ and $[Rh(NO)(PPh_3)_3]$. For the complexes of Co and Rh, no evidence for phosphine dissociation to produce $[M(NO)(PPh_3)_2]$ as an isolable species has been reported, although both undergo phosphine exchange by what appears to be a dissociative process and it has been suggested that $[Rh(NO)(PPh_3)_2]$

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is the intermediate species rather than the solvent (S) adduct [$Rh(NO)(PPh_3)_2(S)$].[4]

The existence of two isomeric forms of (1a) is not unreasonable. Isolable isomeric nitrosyl complexes of [$CoCl_2(NO)(PPh_3)_2$], which differ in the bonding mode of the NO ligand, have been described.[11] An activation energy for the process $C_{3v} \rightleftharpoons C_{2v}$ is difficult to estimate but, for example, the complexes [NiX_2L_2] form both tetrahedral (C_{3v}) and planar (C_{2v}) forms. At present we are attempting the preparation of other [$NiXL_3$]$^+$ complexes. In an attempt to provide additional evidence for the C_{2v} isomer at low temperatures the i.r. spectrum of (1a) in CH_2Cl_2 was examined over the range −50 to 20 °C. No substantial change was observed and no new bands in the 1 500—1 800 cm^{-1} region appeared. The fact that we do not see an NO vibration which may be associated with the second isomeric species does not rule out the isomerisation step. Bands due to [NO]$^-$ are often broad and weak and if the isomer was present in only small concentrations (*ca.* 5% at −85 °C from ^{31}P n.m.r. studies) detection would be difficult.

It has been argued that the tendency of [$Co(NO)(PPh_3)_3$] to undergo phosphine dissociation is brought about by the bulkiness of the triphenylphosphine. This seems to be the case with [$Ni(NO)(PPh_3)_3$]$^+$ since the strongly electron-withdrawing [NO]$^+$ ligand might be expected to increase the acidity of the metal centre and the complex [$Ni(NO)(PMePh_2)_2$][PF_6] containing the less bulky $PMePh_2$ ligand cannot be isolated. The complex [$Ni(NO)(PMePh_2)_3$][PF_6] (1b) does not appear to undergo $PMePh_2$ dissociation under similar conditions. The i.r. spectrum showed no evidence of an NO band at *ca.* 1 755 cm^{-1} and, in contrast to the complex (1a), (1b) may be obtained in an analytically pure state after recrystallisation from CH_2Cl_2–EtOH–C_6H_{12}.

On reaction of (1a) with PMe_2Ph phosphine exchange occurred to produce [$Ni(NO)(PMe_2Ph)_3$][PF_6]. The reaction may be conveniently monitored at 30 °C by ^1H n.m.r. studies. In none of the experiments reported here was evidence for the loss of [NO]$^+$ observed (from i.r. spectrum in the 2 200—2 300 cm^{-1} region). Dissociation of [NO]$^+$ from the cationic complex [$Ir(NO)_2(PPh_3)_2$]$^+$ has been noted during the reactions with $AsPh_3$.[12]

$$[Ni(NO)L_n]^+ \rightleftharpoons [NiL_n] + [NO]^+ \qquad (11)$$

Some Reactions of [$Ni(NO)(PPh_3)_3$][PF_6].—Complex (1a) underwent phosphine ligand-exchange reactions with $PMePh_2$ and $Ph_2P[CH_2]_2PPh_2$ (dppe) to yield [$Ni(NO)(PMePh_2)_n(PPh_3)_{3-n}$][$PF_6$] ($n$ = 1—3) and [$Ni(NO)(PPh_3)(dppe)$][PF_6] respectively. Reaction with X$^-$ (X = Cl, Br, or I) yielded the known complexes [$NiX(NO)(PPh_3)_2$]. In these reactions attack occurs, as expected, on the metal. The reaction of [OMe]$^-$ also produced the mononitrosyl species [$Ni(NO)(OMe)(PPh_3)_2$]. Attack does not occur on the co-ordinated [NO]$^+$ group and these reactions probably occur *via* the prior dissociation of PPh_3.

Addition of Na[S_2CNR_2] (R = Me or Et) in methanol to [$Ni(NO)(PPh_3)_3$][PF_6] produced the neutral complexes [$Ni(NO)(PPh_3)(S_2CNR_2)$], although in the case of Na[S_2CNMe_2] the major product was [$Ni(S_2CNMe_2)_2$]. These dithiocarbamato-complexes showed a single strong NO band in the i.r. spectrum and are best formulated as pseudo-tetrahedral derivatives of the [Ni(NO)]$^+$ unit. The ^1H n.m.r. spectrum of [$Ni(NO)(PPh_3)(S_2CNEt_2)$] showed a sharp methyl triplet which broadened on cooling to −55 °C. We were unable to obtain a temperature-limiting spectrum and so it is therefore difficult to decide whether or not this signal broadening is due to some exchange phenomenon. Broadening could occur by a number of processes and this behaviour was not investigated further.

EXPERIMENTAL

The complexes [$Ni(CO)_2L_2$] (L = PPh_3 or $PMePh_2$) were prepared by the reaction of 2 mol of L with [$Ni(CO)_4$] in diethyl ether;[13] [$NiCl_2L_2$] was prepared by the methods of Venanzi.[14]

Reactions.—[$Ni(CO)_2(PPh_3)_2$] *with* $NOPF_6$ *in benzene and methanol.* The compound $NOPF_6$ (0.34, 2 mmol) was added to a solution of [$Ni(CO)_2(PPh_3)_2$] (0.68 g, 1 mmol) in benzene (30 cm^3) and methanol (10 cm^3) at room temperature. The colourless solution became deep blue with evolution of CO, was stirred vigorously for 3.5 h, and then taken to dryness and washed with benzene and diethyl ether. The residue was dissolved in dichloromethane and diethyl ether was added to precipitate a mixture of [$Ni(NO)(PPh_3)_3$][PF_6] and [$Ni(NO)(PPh_3)_2$][PF_6]. Fractional crystallisation was effected from dichloromethane–ethanol–hexane at −20 °C and deep blue *crystals* of [$Ni(NO)(PPh_3)_3$][PF_6] (1a) (0.38 g, 40%) were obtained. Reaction of [$Ni(CO)_2(PMePh_2)_2$] with $NOPF_6$ in benzene–methanol was carried out in a similar fashion, except no fractional crystallisation was necessary.

[$Ni(CO)_2(PPh_3)_2$] *with* $NOPF_6$ *in benzene.* The compound $NOPF_6$ (0.34 g, 2 mmol) was added to a solution of [$Ni(CO)_2(PPh_3)_2$] (0.68 g, 1 mmol) in benzene (40 cm^3) at room temperature and stirred vigorously for 3 h. Red-brown [$Ni(CO)(NO)(PPh_3)_2$][PF_6] together with a small amount of (1a) came out of solution and was separated by filtration and washed with diethyl ether.

[$Ni(CO)(NO)(PPh_3)_2$][PF_6] *with* (*a*) $CHCl_3$ *and* (*b*) PPh_3. (*a*) The complex [$Ni(CO)(NO)(PPh_3)_2$][PF_6] (0.1 g, 0.1 mmol) was dissolved in chloroform (15 cm^3) and the solution was stirred at room temperature for 4 h. The solution was taken to dryness and the crude [$Ni(NO)(PPh_3)_2Cl$] thus obtained was recrystallised from diethyl ether to give royal blue crystals, yield 0.05 g (77%).

(*b*) Triphenylphosphine (0.1 g, 0.4 mmol) was added to a solution of [$Ni(CO)(NO)(PPh_3)_2$][PF_6] (0.1 g, 0.1 mmol) in dichloromethane (5 cm^3). The solution was stirred at 20 °C for 1 h and the evolved gas was identified as CO on the basis of its i.r. spectrum. Diethyl ether was added to the solution to give deep blue crystals of (1a) (0.08 g, 78%).

[$NiCl_2(PMePh_2)_2$] *with* Na[NO_2], $PMePh_2$, *and* CO. Sodium nitrite (0.1 g, 1.5 mmol), Na[PF_6] (0.3 g, 2 mmol),

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and $PMePh_2$ (0.4 g, 2 mmol) were added to a refluxing solution of $[NiCl_2(PMePh_2)_2]$ (0.8 g, 1.5 mmol) in acetone (40 cm^3) and water (5 cm^3). Carbon monoxide was passed through the solution for 3 h and after filtration the solution was taken to dryness *in vacuo*. The crude $[Ni(NO)(PMePh_2)_3][PF_6]$ (1b) thus obtained was recrystallised from dichloromethane–hexane to give deep purple *crystals*, yield 0.6 g (50%).

$[NiCl_2(PPh_3)_2]$ *with* $Na[NO_2]$, $Na[PF_6]$, PPh_3, *and* CO. Sodium nitrite (0.1 g, 1.5 mmol), $Na[PF_6]$ (0.3 g, 2 mmol), and PPh_3 (0.4 g, 2 mmol) were added to a refluxing solution of $[NiCl_2(PPh_3)_2]$ (0.8 g, 1.2 mmol) in acetone (40 cm^3) and water (5 cm^3). Carbon monoxide was passed through the solution for 3 h and after filtration the solution was taken to dryness. The crude $[NiCl(NO)(PPh_3)_2]$ thus obtained was recrystallised from diethyl ether to give royal blue crystals, yield 0.5 g (75%).

Reactions of (1a).—*With* $PMePh_2$. Methyldiphenylphosphine (0.1 g, 0.5 mmol) was added to a solution of (1a) (0.1 g, 0.1 mmol) in dichloromethane. The colour of the solution turned from deep blue to deep purple within 2 min, and after taking the solution to dryness (1b) (0.07 g, 84%) was recrystallised from dichloromethane–hexane. Reaction of (1a) with dppe was carried out similarly.

With $CHCl_3$. The complex (0.1 g, 0.1 mmol) was dissolved in chloroform (15 cm^3) and the solution was heated under reflux for 6 h. The solution was then taken to dryness and royal blue crystals of $[NiCl(NO)(PPh_3)_2]$ (0.06 g, 92%) were obtained by recrystallisation from diethyl ether.

With $[NEt_4]I$. Tetraethylammonium iodide (0.2 g, 1.7 mmol) was added to a refluxing solution of (1a) (0.4 g, 0.4 mmol) in tetrahydrofuran (thf). After 2 h the solution was filtered, taken to dryness, and the crude $[NiI(NO)(PPh_3)_2]$ thus formed was recrystallised from diethyl ether to give royal blue crystals, yield 0.25 g (75%). Reactions of (1a) with $[NEt_4]Br$ and $[NEt_4]Cl$ were carried out similarly.

Reaction of $[NiBr(NO)(PPh_3)_2]$ *with* $Ag[PF_6]$ *and* $PMePh_2$.—Silver(I) hexafluorophosphate (0.02 g, 0.1 mmol) was added to a solution of $[NiBr(NO)(PPh_3)_2]$ (0.1 g, 0.15 mmol) in thf (10 cm^3). The solution was stirred for 10 min at room temperature and then filtered. Methyldiphenylphosphine (0.1 g, 0.5 mmol) was added to the filtrate and the solution was taken to dryness. The (1b) thus obtained was recrystallised from dichloromethane–hexane to give deep purple crystals, yield 0.07 g (60%).

With Na(OMe). Sodium methoxide (0.01 g, 0.2 mmol) was added to a solution of (1a) (0.1 g, 0.1 mmol) in methanol (20 cm^3). The solution was stirred for 24 h at 20 °C and then taken to dryness. The complex $[Ni(NO)(OMe)(PPh_3)_2]$ thus obtained was recrystallised from diethyl ether to give deep blue crystals, yield 0.06 g (90%).

With $Na[S_2CNEt_2]$. Sodium diethyldithiocarbamate (0.1 g, 0.6 mmol) was added to a solution of (1a) (0.25 g, 0.2 mmol) in methanol (20 cm^3). The solution was stirred for 30 min at room temperature and the precipitate of $[Ni(NO)(PPh_3)(S_2CNEt_2)]$ was separated by filtration. Recrystallisation was effected from diethyl ether to give blue-black crystals, yield 0.1 g (95%).

Reaction of (1a) with $Na[S_2CNMe_2]$ was carried out similarly. The ether-soluble fraction of the precipitate was identified as $[Ni(NO)(PPh_3)(S_2CNMe_2)]$ on the basis of its i.r. spectrum. The rest of the precipitate was washed with diethyl ether and dichloromethane to give pure green-yellow $[Ni(S_2CNMe_2)_2]$.

With Na(pd). Sodium pentane-2,4-dionate (0.015 g, 1 mmol) was added to a solution of (1a) (0.9 g, 1 mmol) in methanol (20 cm^3). The solution was stirred for 30 min and then filtered. The filtrate was taken to a minimum volume to give a deep blue oil whose i.r. spectrum showed the presence of $[Ni(NO)(pd)(PPh_3)]$.

Infrared spectra were recorded on a Perkin-Elmer 257 grating instrument. Phosphorus-31 n.m.r. spectra were obtained in 12-mm (outside diameter) tubes, using the Fourier-transform technique at 40.5 M Hz, on a Varian XL 100 spectrometer. All the spectra employed white-noise proton decoupling. Microanalysis were by Mr. D. Flory of this laboratory. Conductivities were measured with a Philips conductivity bridge. These data are recorded in Tables 1 and 2.

TABLE 1

Infrared data (cm^{-1}) for the mononitrosyl complexes of nickel

Complex	ν(NO)	ν(CO)	Medium
$[Ni(NO)(PPh_3)_3][PF_6]$	1 790		Nujol
	1 785		CH_2Cl_2
$[Ni(NO)(PMePh_2)_3][PF_6]$	1 785		Nujol
	1 780		CH_2Cl_2
$[Ni(NO)(PPh_3)(dppe)][PF_6]$	1 800		CH_2Cl_2
$[Ni(NO)(PPh_3)_2][PF_6]$	1 755		CH_2Cl_2
$[Ni(CO)(NO)(PPh_3)_2][PF_6]$	1 795	2 080	Nujol
$[NiCl(NO)(PPh_3)_2]$	1 730		Nujol
$[NiBr(NO)(PPh_3)_2]$	1 730		Nujol
$[NiI(NO)(PPh_3)_2]$	1 740		Nujol
$[Ni(NO)(PPh_3)(S_2CNEt_2)]$ [a]	1 730		Nujol
	1 735		CH_2Cl_2
$[Ni(NO)(pd)(PPh_3)]$ [b]	1 735		CH_2Cl_2
$[Ni(NO)(OMe)(PPh_3)_2]$	1 710		Nujol
$[Ni(NO)(PPh_3)(S_2CNMe_2)]$ [a]	1 735		Nujol

[a] ν(CN) at 1 511 cm^{-1} in CH_2Cl_2. [b] ν(pd) at 1 580 cm^{-1}.

TABLE 2

Microanalytical data (%) for the mononitrosyl complexes of nickel

	Found			Calc.		
Complex	C	H	N	C	H	N
$[Ni(NO)(PPh_3)_3][PF_6]$ [a]	63.2	4.1	1.3	63.5	4.4	1.4
$[Ni(NO)(PMePh_2)_3][PF_6]$ [b]	56.3	4.7	1.5	56.1	4.7	1.7
$[Ni(NO)(PPh_3)(dppe)][PF_6]$	59.1	4.7	1.4	59.1	4.4	1.5
$[NiCl(NO)(PPh_3)_2]$	66.8	4.8	2.0	66.6	4.7	2.2
$[NiBr(NO)(PPh_3)_2]$	62.4	4.5	2.0	62.4	4.4	2.0
$[NiI(NO)(PPh_3)_2]$	58.4	4.0	1.7	58.4	4.1	1.9
$[Ni(NO)(OMe)(PPh_3)_2]$	68.6	5.1	2.1	68.9	5.2	2.2
$[Ni(NO)(PPh_3)(S_2CNEt_2)]$	55.3	4.9	5.6	55.3	5.0	5.7
$[Ni(S_2CNMe_2)_2]$	24.3	4.2	9.4	24.1	4.1	9.4

[a] Λ (in 10^{-3} mol dm^{-3} nitrobenzene solution) = 19.2 S cm^2 mol^{-1}. [b] Λ = 19.6 S cm^2 mol^{-1}. [c] Λ = 19.8 S cm^2 mol^{-1}.

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