Nonacarbonyldinitrosyltriosmium : Its Synthesis and Reactivity

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The title compound, $[Os_3(CO)_9(NO)_2]$, has been prepared by the reaction of NO with $[Os_3(CO)_{12}]$ in n-octane at 126 °C. Carbon-13 n.m.r. spectroscopy indicates that the structure is derived from that of $[Os_3(CO)_{12}]$ by the replacement of three CO ligands about one osmium by two terminally bound NO ligands. The stereodynamic behaviour of the molecule, as determined by [13]C n.m.r. spectroscopy over a range of temperature, has been interpreted in terms of a process involving terminal–bridging NO interchange of the type previously observed for certain CO-cluster compounds. On reaction with ligands L (= NH_3, $NEtH_2$, and CO) the formation of the unstable adducts $[Os_3(CO)_9(NO)_2L]$ is observed; with L = $P(OMe)_3$ or PPh_3 the substituted complexes $[Os_3(CO)_8(NO)_2\{P(OMe)_3\}]$ or $[Os_3(CO)_9(NO)_2(PPh_3)]$ are produced. A single-crystal analysis of the trimethyl phosphite compound confirms that two terminally bound NO ligands are present. For L = pyridine (py), $[Os_3(CO)_9(NO)_2]$ forms the dinitrosyl-bridged compound $[Os_3(CO)_9(\mu_2\text{-}NO)_2(py)]$, quantitatively. The factors which govern the course of these reactions are discussed.

METAL carbonyl clusters containing three or more metal atoms have been proposed as models for metal surfaces.[1] However, a problem often encountered with such clusters is the relative difficulty in carrying out certain simple reactions and it may be assumed that the carbonyl polyhedron surrounding the metal cluster effectively protects the metal unit from attack. The nitrosyl ligand, unlike the carbonyl ligand, can bind to a metal ion by alternately withdrawing or donating an electron pair thereby generating a vacant co-ordination position.[2] We have prepared the dinitrosyl cluster compound $[Os_3(CO)_9(NO)_2]$ in which activation of the metal ion is apparently achieved by the ability of the two NO ligands to modify their bonding modes.

Carbon monoxide mobility in cluster compounds is now a well established process.[3] At the present time, however, no study of a metal nitrosyl cluster has revealed a nitrosyl-exchange process of a similar type. The compound $[Os_2(CO)_9(NO)_2]$ executes an NO exchange process, which although solvent assisted, bears a close resemblance to the bridge–terminal CO site exchange so often observed in carbonyl clusters. A communication of some aspects of this work has been made.[4]

RESULTS AND DISCUSSION

Preparation and Structure.—The passage of nitrogen monoxide gas through a solution of $[Os_3(CO)_{12}]$ in n-octane at 126 °C produced the compound $[Os_3(CO)_9(NO)_2]$ (1) together with small amounts of the previously reported dinitrosyl cluster $[Os_3(CO)_{10}(\mu_2\text{-}NO)_2]$.[5] After separation on silica, compound (1) was obtained as dark red crystals from pentane and was characterised on the basis of analytical and spectroscopic data. On electron impact (80 eV) † the molecular ion $[Os_3(CO)_9(NO)_2]^+$ and ions formed by successive loss of either CO or NO were observed. The i.r. spectrum (Table) in cyclohexane exhibited nine bands in the CO stretching region and two strong nitrosyl bands at 1 731 and 1 705 cm⁻¹ indicating that the compound has low symmetry and that the NO ligands are terminally bound.

† Throughout this paper: 1 eV ≈ 1.60 × 10⁻¹⁹ J.

Attempts to produce a suitable crystal of (1) for X-ray analysis have, to date, been unsuccessful. However, the compound $[Os_3(CO)_8(NO)_2\{P(OMe)_3\}]$ (2), prepared from

Infrared spectra (cm⁻¹) of $[Os_3(CO)_9(NO)_2]$ and some of its derivatives

Compound [a]	ν(CO) and ν(NO)			
$[Os_3(CO)_9(NO)_2]$	2 117m	2 073vs	2 067s	2 033vs
	2 023s	2 019s	2 013m	2 003m
	1 991w	1 731s	1 705s	
b	2 072s	2 030vb		
		1 720(sh)	1 694s	
$[Os_3(CO)_{10}(NO)_2]$ [c]	2 069w	2 033m	2 020vs	1 966vs
$[Os_3(CO)_{10}(\mu_2\text{-}NO)_2]$	2 108w	2 068s	2 063s	2 054s
	2 025s	2 014w	2 008s	1 996m
	1 503m	1 484s		
$[Os_3(CO)_8(NO)_2\{P(OMe)_3\}]$	2 104m	2 056vs	2 021vs	2 006s
	1 993m	1 985m	1 705s	1 672s
$[Os_3(CO)_8(NO)_2(PPh_3)]$	2 100s	2 052vs	2 020vs	2 003s
	1 988w	1 971s	1 700m	1 671m
$[Os_3(CO)_9(\mu_2\text{-}NO)_2(py)]$ [d]	2 105w	2 100s	2 061vs	2 050m
	2 016vs	2 006vs	1 994m	1 974vs
	1 958s			
$[Os_3(CO)_9(\mu_2\text{-}NO)_2\{P(OMe)_3\}]$	2 100m	2 063vs	2 033m	2 019vs
	2 011s	2 001s	1 995s	1 979s
	1 470m	1 455m		
$[Os_3(CO)_9(\mu_2\text{-}NO)_2(PPh_3)]$	2 098m	2 063vs	2 022vs	2 011s
	2 001s	1 995m	1 981m	1 969m
	1 475m	1 457m		
$[Os_3(CO)_9(NO)_2(NEtH_2)]$	2 086m	2 068m	2 027vs	2 011s
	2 001vs	1 988s	1 973m	1 678m
	1 617w			

w = Weak, m = medium, v = very, s = strong, b = broad, sh = shoulder.

[a] Spectra in cyclohexane unless otherwise stated. [b] In toluene. [c] The spectrum of $[Os_3(CO)_9(NO)_2(NH_3)]$ has not been recorded. The compound is insoluble and could not be isolated without loss of NH_3. [d] Absorptions due to py occur in the same region as NO.

the reaction of (1) with $P(OMe)_3$ (see below), has been analysed by this method. The molecular structure of this compound is given in Figure 1. A full

description of this analysis will be given independently.[6] Compounds (1) and (2) are clearly related. From Figure 1 it is apparent that the molecular structure of (2) essentially consists of two $Os(CO)_4$ units and one $Os(NO)_2\{P(OMe)_3\}$ unit linked together by three direct Os–Os bonds. It is reasonable to conclude therefore that the structure of (1) is similar but with the $P(OMe)_3$ ligand replaced by CO.

This structure also appears to persist in solution. The [13]C n.m.r. spectra from -100 to 30 °C for enriched samples of (1) in CH_2Cl_2 or $CHFCl_2$ were recorded. Carbon-13 enriched samples were prepared by two methods. First, directly from ca. 60% [13]CO-enriched $[Os_3(CO)_{12}]$ by the reaction with NO as outlined above, and secondly from the reaction of (1) with [13]CO. The latter method was unsatisfactory and gave samples which exhibited anomalous intensity ratios. The spectrum reported earlier[4] was recorded for a sample enriched by this method.

Samples prepared by the first route gave reproducible spectra; at ca. 30 °C six signals at 182.7, 182.5, 173.7, 171.8, 171.4, and 170.4 p.p.m. of relative intensity $2:2:1:1:1:1$ were observed together with a signal at 178.0 p.p.m. whose intensity was not related simply to the other six signals. On decreasing the temperature no change in spectrum was observed apart from some signal broadening which may be associated with changes in the viscosity of the solvent, and at -100 °C (in $CHFCl_2$) essentially the same spectrum as that at 30 °C was observed. Carbon-13-enriched samples of the related compound $[Os_3(CO)_8(NO)_2\{P(OMe)_3\}]$, which were prepared from enriched samples of (1) by the re-
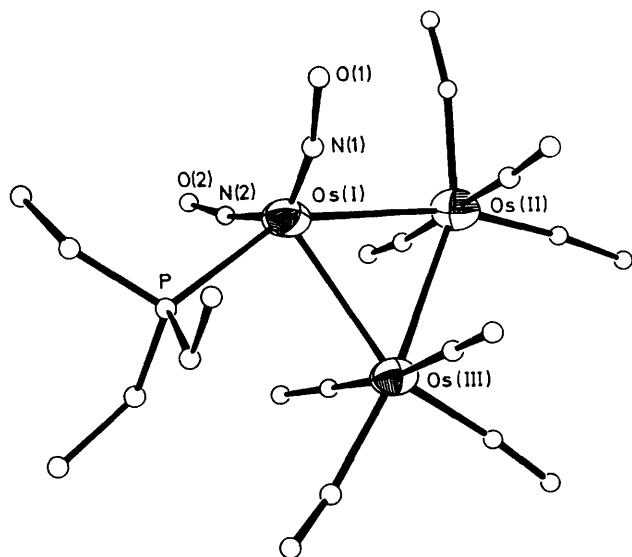

FIGURE 1 Molecular structure of $[Os_3(CO)_8(NO)_2\{P(OMe)_3\}]$

action with $P(OMe)_3$, exhibit related spectra. At ca. 30 °C six signals at 186.1, 184.2, 176.6, 174.1, 173.8, and 172.4 p.p.m. of intensity ratio $2:2:1:1:1:1$ were observed. This spectrum is consistent with the structure established crystallographically (Figure 1). Con-

sider Figure 2(b), a diagrammatic representation of the molecular structure of (2). Because of the plane of symmetry which passes through the three osmium atoms there are two sets of two equivalent CO ligands, a and b. These may be taken to give rise to the two signals at
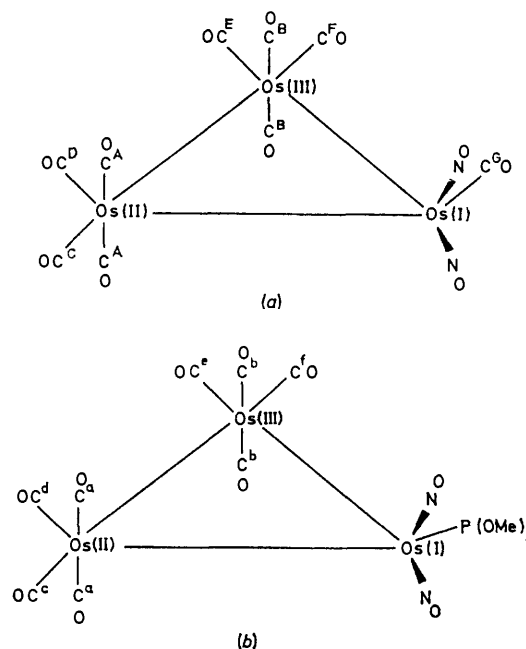

FIGURE 2 Representative structures of (a) $[Os_3(CO)_9(NO)_2]$ and (b) $[Os_3(CO)_8(NO)_2\{P(OMe)_3\}]$

186.1 and 184.2 p.p.m. each of intensity two, although an absolute assignment cannot be made. The remaining four signals may then be assigned to the four inequivalent CO groups c, d, e, and f. Returning to complex (1) [Figure 2(a)], similar assignments may be reasonably made. Signals at 182.7 and 182.5 p.p.m. each of intensity two may be associated with carbonyls A and B, signals at 173.7, 171.8, 171.4, and 170.4 p.p.m. with carbonyls C, D, E, and F (although again absolute assignments cannot be made) and, finally, the signal at 178.0 p.p.m., of anomalous intensity, to carbonyl G. This anomalous intensity may be readily explained. Carbonyl G is bound to osmium atom I which is also bonded to the two cis-NO ligands. The relaxation time of the [13]CO(C) nucleus may well be affected by the adjacent ^{15}N nuclei giving rise to the anomalous intensity observed.

The same low-temperature limiting [13]C n.m.r. spectrum is observed for solutions of (1) in toluene. Thus, at $\leqslant -15$ °C six resonances are observed at 185.7, 185.4, 176.5, 174.4, 173.9, and 172 9 p.p.m. of relative intensity $2:2:1:1:1:1$ together with a seventh signal of intensity ca. 0.8. However, as the temperature is increased additional signals appear and finally at 70 °C the original set of seven signals is replaced by four signals at 186.8, 186.0, 181.4, and 175.7 p.p.m. of relative intensity $1:4:1:3$. This change is reversible and on cooling to -15 °C the original spectrum is

regenerated. A tentative explanation of this solution may be given. Consider the reaction scheme outlined in Scheme 1. Since the ^{13}C n.m.r. spectra obtained over the temperature range −15 to 70 °C are consistent with a molecular interconversion rather than some dynamic
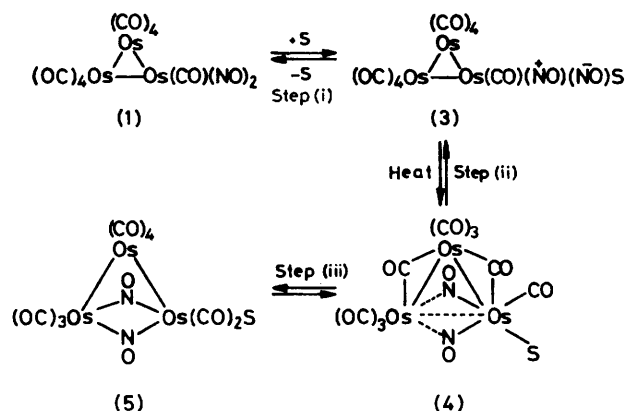
SCHEME 1 Possible reaction sequence for the interaction of solvent (S) with $[Os_3(CO)_9(NO)_2]$

exchange we make the following suggestions. (*a*) At ambient temperature, interaction with the solvent occurs to produce an unstable adduct $[Os_3(CO)_9(NO)_2S]$ (3). This interaction causes the NO ligands to adopt an alternative bonding mode in order to offset the additional electron density donated to the unique osmium atom by the solvent. Evidence for this interaction is provided by studies of the i.r. spectrum. In dichloromethane, compound (1) exhibits two strong NO bands at 1 731 and 1 705 cm^{-1}, and nine CO bands of variable intensity (see Table). In toluene, however, the spectrum is simpler, exhibiting one strong NO band at 1 694 cm^{-1} and a weak shoulder at 1 720 cm^{-1} and only two CO bands at 2 072 and 2 030 cm^{-1}. Although it may be argued that this change may, in some part, be associated with solvent-broadening effects, it must also indicate solvent inter-action with (1). (*b*) At higher temperatures conversion into the di-μ_2-NO system (5) [steps (ii) and (iii)] occurs. This conversion requires not only the formation of two NO bridges but also an intramolecular migration of CO groups. Allowing for CO equilibration about the $Os(CO)_4$ and $Os(CO)_3$ units with compound (5) the observed $4:3:1:1$ spectrum may thus be understood.

The idea of electron transfer *via* CO-bridge formation [step (ii)] is similar to that suggested by Karel and Norton[7] for the substitution reactions of $[Ir_4(CO)_{12}]$. The reversible NO-bridge formation [steps (ii) and (iii)] is clearly related to the bridge–terminal interchange suggested by Cotton[3] to account for CO fluxionality in carbonyls such as $[Fe_2(C_5H_5)_2(CO)_4]$, $[Fe_3(CO)_{12}]$, and $[Rh_4(CO)_{12}]$. Evidence in support of this overall mechanism is not easily obtained, but we believe that the reactions of $[Os_3(CO)_9(NO)_2]$ with donor ligands, such as CO, $P(OMe)_3$, PPh_3, NH_3, $NEtH_2$, and pyridine (py) provide additional evidence in favour of our proposal (see below).

Reactions of $[Os_3(CO)_9(NO)_2]$ *with Donor Ligands* L.—(*i*) L = NH$_3$ *or* NEtH$_2$. Ammonia reacts with (1) in dichloromethane at *ca.* 25 °C to produce a white solid which slowly separates out of the reaction solution. Attempts to isolate this solid either by the removal of solvent *in vacuo* or by filtration results in the loss of ammonia and the re-formation of (1). The i.r. spectrum of this compound has not been obtained. It is insoluble in dichloromethane and cannot be obtained as a pure solid.

Addition of NEtH$_2$ to a solution of (1) in dichloro-methane brings about a change in the i.r. spectrum. The two NO bands at 1 731 and 1 705 cm^{-1} disappear and two new less-intense bands appear at 1 678 and 1 617 cm^{-1}. Removal of NEtH$_2$ causes the spectrum to revert back to that originally observed. Attempts to isolate this compound led only to the re-formation of (1).

It would appear that the effect of these N-donor ligands is to modify the NO bonding modes and produce unstable adducts $[Os_3(CO)_9(NO)_2L]$. Clearly these adducts are similar to those proposed as the reaction intermediates (3) in Scheme 1.

(*ii*) L = CO. Under ambient conditions the reaction with CO is similar. As CO gas is passed through a solution of (1) in cyclohexane at *ca.* 25 °C the two NO bands at 1 731 and 1 705 cm^{-1} slowly decrease in intensity. The spectrum in the CO region also changes and after *ca.* 40 h a new spectrum, which exhibits four bands
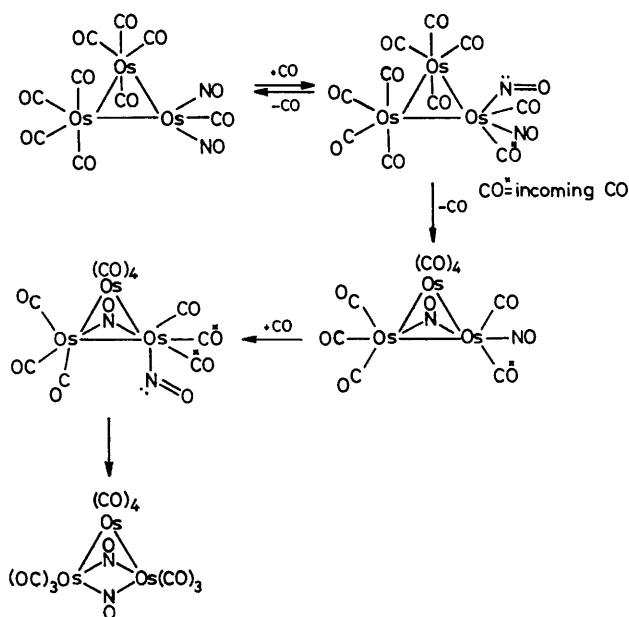
SCHEME 2 Possible mechanism for the reaction of CO with $[Os_3(CO)_9(NO)_2]$

in the CO region at 2 069s, 2 030m, 2 020vs, and 1 996vs cm^{-1}, is obtained. The reaction is reversible and on passing a rapid stream of nitrogen through the solution or by pumping off the CO the spectrum reverts back to that originally observed. At higher temperatures (*ca.*

80 °C) some conversion of (1) into the dinitrosyl-bridged complex $[Os_3(CO)_{10}(\mu_2\text{-}NO)_2]$ is observed. Again it would appear that at low temperatures an unstable adduct $[Os_3(CO)_{10}(NO)_2]$ is produced and at higher temperatures this undergoes conversion into the stable $[Os_3(CO)_{10}(\mu_2\text{-}NO)_2]$ in keeping with the ideas expressed in Scheme 1. An alternative mechanism can, however, be devised. This is given in Scheme 2. In this an intra-molecular CO migration is not required. Instead NO-bridge formation is considered to induce CO dissociation rather than migration.

(iii) L = py. Compound (1) reacts rapidly with pyridine to produce $[Os_3(CO)_9(\mu_2\text{-}NO)_2(py)]$ quantita-tively. At no stage in this reaction has evidence for the formation of an adduct of the type described above been found. The product possesses the structure shown in Figure 3, which is related to $[Os_3(CO)_{10}(\mu_2\text{-}NO)_2]$ but with
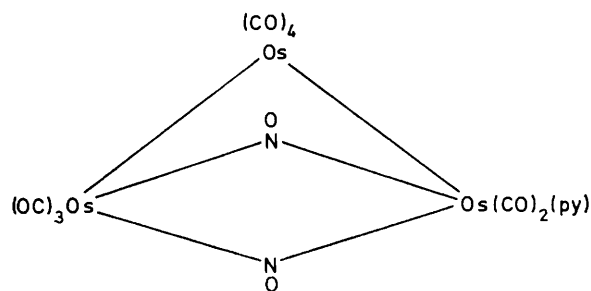

FIGURE 3 Probable structure of $[Os_3(CO)_9(\mu_2\text{-}NO)_2(py)]$

one terminal CO ligand replaced by pyridine. The formation of this compound is readily explained on the basis of Scheme 1 but less so in terms of Scheme 2 which would require the formation of a bis(pyridine) adduct. It seems reasonable, therefore, to assume that Scheme 1 is general and may be applied to account for the reactions of $[Os_3(CO)_9(NO)_2]$ with toluene, NH_3, $NEtH_2$, CO, or py.

(iv) L = $P(OMe)_3$ or PPh_3. The reaction of (1) with these ligands follows a different course. Here the replacement of the unique CO ligand by L occurs rapidly to produce $[Os_3(CO)_8(NO)_2\{P(OMe)_3\}]$ (2) or $[Os_3(CO)_8(NO)_2(PPh_3)]$ respectively. As discussed above, the molecular structure of compound (2) has been determined independently by single-crystal X-ray analysis (Figure 1) and in solution by ^{13}C n.m.r. spectro-scopy. On the basis of its i.r. spectrum (Table) the PPh_3 compound is considered to be isostructural with (2).

In these reactions we assume that the initial step corresponds to (i) in Scheme 1, i.e. the reaction proceeds by an associative step, to form the adduct $[Os_3(CO)_9\text{-}(NO)_2L]$ but which then loses a CO ligand to produce $[Os_3(CO)_8(NO)_2L]$ rather than undergo NO-bridge formation. The nonacarbonyl compounds $[Os_3(CO)_9\text{-}(\mu_2\text{-}NO)_2L]$ [L = $P(OMe)_3$ or PPh_3] may be produced from the reactions of CO with $[Os_3(CO)_8(NO)_2L]$ in boiling n-heptane. The effect of CO is presumably to generate the adduct $[Os_3(CO)_9(NO)_2L]$, which in the

presence of excess of CO prefers to generate NO bridges rather than undergo CO dissociation.

In summary, therefore, Scheme 1 seems to satisfy the ^{13}C n.m.r. spectra of (1) in toluene and the reactions which (1) undergoes with a variety of donor ligands. Whether the initial adduct undergoes CO dissociation to produce $[Os_3(CO)_8(NO)_2L]$ or NO-bridge formation to produce $[Os_3(CO)_9(\mu_2\text{-}NO)_2L]$ depends on the nature of the ligand, the better σ donors preferring the latter course. For CO, clearly Schemes 1 or 2 apply. In this connection it is interesting to recall that attempts to isotopically enrich compound (1) by simple ^{13}CO exchange leads to anomalous intensity ratios in the ^{13}C n.m.r. spectrum implying that stereospecific ^{13}CO incorporation occurs. Studies of this system are in hand as are mechanistic studies of the substitution reactions of compound (1).

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 421 IR spectrophotometer in KBr pellets, Nujol mulls, or solu-tions. Carbon-13 n.m.r. spectra were obtained on a Varian XL 100 FT for enriched samples (^{13}CO) and in the presence of $[Cr(pd)_3]$ (pd = pentane-2,4-dionate) as relaxation reagent. All the solvents were distilled under nitrogen before use and all reactions carried out under dry nitrogen gas.

Preparations.—$[Os_3(CO)_9(NO)_2]$ (1). In a typical re-action $[Os_3(CO)_{12}]$ (1.00 g, 1.1 mmol) was dissolved in boiling n-octane (250 cm³) and nitrogen monoxide passed through the solution for ca. 2 h. The solution was then flushed with nitrogen for 10 min and finally cooled to room temperature. Some residual solid was removed by filtr-ation and the filtrate evaporated to dryness to give red crystals, which were dissolved in hexane and chromato-graphed on thin silica plates. Three bands were observed. On elution with chloroform–cyclohexane (1 : 10), the first, yellow, band gave $[Os_3(CO)_{12}]$, the second, red, band $[Os_3(CO)_9(NO)_2]$ (0.01 g, 0.01 mmol, yield 1%) [Found: C, 12.2; N, 3.15%; M (mass spectrometry) 884. Calc. for $C_9N_2O_{11}OS_3$: C, 12.2; N, 3.15%; M 884.6], and the third, green, band $[Os_3(CO)_{10}(\mu_2\text{-}NO)_2]$.

$[Os_3(CO)_8(NO)_2L][L = P(OMe)_3$ or $PPh_3]$. In a typical reaction (1) (20 mg, 0.02 mmol) was dissolved in n-heptane (30 cm³) and excess of ligand L (0.4 mmol) added. The reaction solution was stirred under nitrogen for ca. 3 h and monitored by i.r. spectroscopy. When all the parent compound had reacted the solvent was removed by evapor-ation *in vacuo* and the solid residue dissolved in hexane. The resulting solution was chromatographed on thin silica plates. One band was observed. This was eluted with $CHCl_3$–C_6H_{12} (40% v/v), the solvent removed, and the residue crystallised from hexane to give red crystals of $[Os_3(CO)_8(NO)_2L]$ [L = $P(OMe)_3$], 15 mg (0.015 mmol, 68%) [Found: C, 13.6; H, 1.05; N, 2.75%; M (mass spectro-metry) 980. Calc.: C, 13.5; H, 0.90; N, 2.85%; M 980]; L = PPh_3, 20 mg (0.018 mmol, 80%) [Found: C, 27.8; H, 1.45; N, 2.50%; M (mass spectrometry) 1 118. Calc.: C, 27.9; H, 1.35; N, 2.50%; M 1118].

$[Os_3(CO)_9(NO)_2(py)]$.—Compound (1) (20 mg, 0.02 mmol) was dissolved in a solution of pyridine (0.04 mmol) in hexane (50 cm³) and the solution heated under reflux for ca. 5 h. The solvent was removed from the final green solution *in vacuo*, the product dissolved in chloroform, and

the solution chromatographed on thin silica plates. One band was observed which was eluted with chloroform–cyclohexane (4 : 10); the eluate was evaporated until green crystals began to separate. These were filtered off {Found: C, 17.6; H, 0.65; N, 4.35%; M (mass spectrometry) 963. Calc. for $[Os_3(CO)_9(NO)_2(py)]$: C, 17.5; H, 0.50; N, 4.35%; M 963}.

Reactions of $[Os_3(CO)_9(NO)_2]$.—(*i*) *With* CO. The compound (20 mg, 0.02 mmol) was dissolved in C_6H_{12} (30 cm³) to give a clear solution. Carbon monoxide was passed through the solution for *ca.* 40 h to produce a clear solution whose i.r. spectrum was different to that of the parent dinitrosyl (see above). Removal of solvent gave a quantitative yield of (1). In a separate experiment the same reaction was carried out at 81 °C. In this case high yields (*ca.* 80%) of $[Os_3(CO)_{10}(\mu_2\text{-NO})_2]$ (identified by its i.r. and mass spectra) were obtained.

(*ii*) *With* $NEtH_2$ (*or* NH_3). The ligand was added to a solution of (1) in C_6H_{12} and the i.r. spectrum monitored (see above). Removal of solvent gave quantitative amounts of (1).

Reaction of $[Os_3(CO)_8(NO)_2L][L = P(OMe)_3$ *or* $PPh_3]$ *with* CO.—The compound $[Os_3(CO)_8(NO)_2L]$ (20 mg, *ca.* 0.02 mmol) was dissolved in n-heptane and heated under reflux in the presence of a CO atmosphere for *ca.* 0.5 h.

The red solution changed to green and was chromatographed on thin silica plates. The one band observed was eluted with $CHCl_3$–C_6H_{12} (3 : 7). On removal of solvent, green crystals of $[Os_3(CO)_9(NO)_2L]$ were obtained (characterised by their mass spectra).

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