In memory of S. M. Nelson

The Co-ordination of Small Molecules by Manganese(II) Phosphine Complexes. Part 10.[1] The Reversible Binding of Nitric Oxide by $[MnX_2(PR_3)]$ ($X = Cl, Br, I$; $R_3 = Pr^n{}_3, Bu^n{}_3, PhMe_2, PhEt_2$) in the Solid State and in Tetrahydrofuran Solution. The Effect of the Nature of the Halogen and the Phosphine on Stability and Reversibility

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The complexes $[MnX_2(PR_3)]$ ($X = Cl, Br$, or I; $PR_3 = PPr^n{}_3, PBu^n{}_3, PPhMe_2$, or $PPhEt_2$) have been shown to react with nitric oxide (NO) both in the solid state and in tetrahydrofuran (thf) solution. For X = Cl or Br, the reaction is reversible and $[MnX_2(PR_3)(NO)]$ species are formed. For X = I the reaction is irreversible even at low temperatures, the phosphine ligand being oxidised. For the reversible reaction in the solid state the complexes have ν(NO) *ca.* 1 600 cm^{-1}; the magnetic moment and e.s.r. data indicate that the $[MnX_2(PR_3)(NO)]$ species have four unpaired electrons and are formulated as $Mn^{III}-NO^-$ moieties. In thf solution the formation of 1 : 1 Mn : NO adducts has been confirmed by quantitative gas absorption measurements. These adducts are also highly coloured and NO-binding isotherms have been constructed. Cycling experiments have shown the adducts to be more stable at lower temperatures. The decomposition product has been studied with phosphine oxides being formed both in solid-state and solution decomposition. It is postulated that NO oxidation of the PR_3 ligand occurs at higher temperature.

Complexes of the type $[MnX_2(PR_3)]$ ($X = Cl, Br, I$, or NCS; R = alkyl or aryl) have been shown to bind reversibly a number of small molecules, namely dioxygen,[2,3] carbon monoxide,[4,5] carbon dioxide,[5] ethylene,[1,6] and to bind irreversibly sulphur dioxide,[7,8] carbon disulphide[9,10] and tetracyanoethylene.[11]

There has been continuous interest in the co-ordination of nitric oxide to transition metal complexes,[12] and there are a number of examples of manganese complexes which will bind nitric oxide (NO). For example, some manganese porphyrin complexes which reversibly bind dioxygen[6,13–17] also bind nitric oxide[18–21] and, in certain cases, the binding is reversible.[22] The reactivity of the manganese porphyrin complexes towards dioxygen and nitric oxide, together with an already demonstrated wide-ranging affinity for small molecules of the $[MnX_2(PR_3)]$ complexes, prompted this study into the reaction of nitric oxide with the $[MnX_2(PR_3)]$ complexes. No systems as simple as the $[MnX_2(PR_3)]$ complexes have been reported to bind nitric oxide reversibly. A preliminary account of this work has appeared.[23]

Results and Discussion

The reactions of a range of $[MnX_2(PR_3)]$ ($X = Cl, Br$, or I; $R_3 = Pr^n{}_3, Bu^n{}_3, PhMe_2$, or $PhEt_2$) with nitric oxide have been studied both in the solid state and in tetrahydrofuran (thf) solution. This solvent was chosen because of the relatively high solubility of the complexes which, in turn, facilitated accurate gas absorption measurements using a gas burette.

Solid-state Studies.—Upon contact with nitric oxide at room temperature the off-white $[MnX_2(PR_3)]$ complexes become vividly coloured (X = Cl, deep red-purple; X = Br, deep blue; X = I, brown). Upon exposure to a vacuum the chloro and bromo complexes lost their colour, but the iodo complexes remained brown even when left under vacuum for 24 h.

Below 0 °C the nitric oxide adducts are stable indefinitely (the i.r. and e.s.r. spectra showed no changes even after several weeks of storage), and at these temperatures it was possible to monitor changes in mass and magnetic properties as samples of $[MnX_2(PR_3)]$ were exposed to NO, Table 1. It can be seen that the Mn:NO ratio is, in each case, very close to 1:1, and the magnetic moments of the adducts have been calculated based on the formulation $[MnX_2(PR_3)(NO)]$. Although there may be some small error in the calculated μ_{eff}, the adducts can be said to be high spin and almost certainly having four unpaired electrons per molecule. The e.s.r. spectral properties are consistent with this, as they indicate the presence of species with an even number of electrons.

The $[MnX_2(PR_3)]$ complexes exhibit solid-state e.s.r. spectra which consist of a broad band in the $g = 2$ region, with no fine structure being observed even at liquid-nitrogen temperatures.[2,7] This signal gradually loses intensity as NO is absorbed, eventually leading to complete signal loss as $[MnX_2(PR_3)(NO)]$ is totally formed. Upon pumping off the NO the original signal returns. The e.s.r.-silent $[MnX_2(PR_3)(NO)]$ complexes are thus high-spin d^4 manganese(III), $S = 2$ species; the majority of such species produce zero-field splittings and are e.s.r. silent.

The $[MnX_2(PR_3)(NO)]$ complexes exhibit a strong i.r. absorption in the 1 600 cm^{-1} region, assignable to ν(NO); this band is absent in the spectra of the $[MnX_2(PR_3)]$ complexes. The large shift in the ν(NO) frequency from that of free NO gas (1 840 cm^{-1}) proves that NO is chemically bonded to the manganese.

The ν(NO) frequency appears to be both halide and phosphine dependent. Table 1 shows that for the same phosphine

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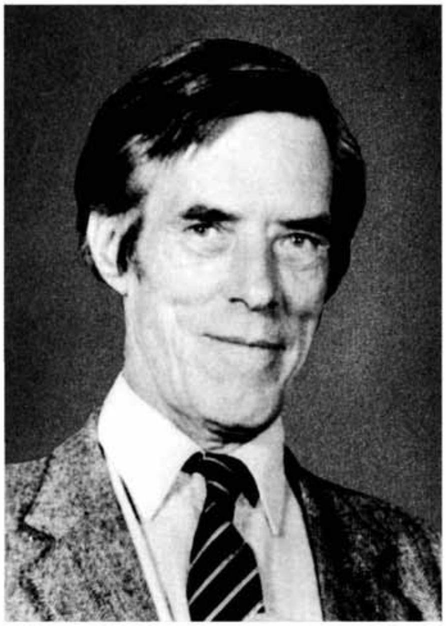

S. M. Nelson
1928—1985

T. A. Stephenson
1940—1986

S. M. Nelson Memorial Lecture presented by D. E. Fenton at the 11th International Symposium on Macrocyclic Chemistry, Florence, 1—4 September 1986 (*Pure Appl. Chem.*, 1986, **58**, 1437).

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Table 1. Characteristics of the NO reaction with [MnX$_2$(PR$_3$)] in the solid state

Complex	Amount[a] (mol × 10^{-3})	NO absorbed (mol × 10^{-3})	Mn:NO	$\mu_{eff.}$[b]	ν(NO)/ cm^{-1}
[MnCl$_2$(PPr$^n_3$)]	2.14	1.93	1:0.90	4.90	1 610
[MnCl$_2$(PPhMe$_2$)]	3.16	3.00	1:0.95	4.85	1 605
[MnCl$_2$(PPhEt$_2$)]	2.60	2.42	1:0.93	4.85	1 607
[MnBr$_2$(PPr$^n_3$)]	2.94	2.59	1:0.88	5.05	1 600
[MnBr$_2$(PPhMe$_2$)]	3.00	2.73	1:0.91	5.00	1 595
[MnBr$_2$(PPhEt$_2$)]	3.27	2.78	1:0.85	5.25	1 598

[a] For example, 0.6250 g [MnCl$_2$(PPr$^n_3$)] absorbed 0.0579 g NO. [b] Calculation of $\mu_{eff.}$ based on the formulation [MnX$_2$(PR$_3$)(NO)].

ligand the bromo complex absorbs 10 cm^{-1} lower than the chloro complex (additionally, dialkylphenylphosphine complexes absorb at slightly lower frequencies than do the trialkylphosphine complexes). There thus appears to be more back π-bonding in the bromo than the chloro analogues. This might arise from differences in electronegativities, and thus two chloro ligands would be expected to compete more effectively with nitric oxide than would two bromo ligands for electron density on the manganese atom.

As stated above, the [MnX$_2$(PR$_3$)(NO)] complexes are not stable for long periods at room temperature and decompose irreversibly forming brown materials. In an attempt to clarify the mechanism of decomposition a sample of [MnBr$_2$(PPhMe$_2$)(NO)] was stored for several days at room temperature. The i.r. spectrum of the resulting brown powder exhibited ν(P=O) at 1 140 cm^{-1}* and a broad e.s.r. band in the $g = 2$ region indicated the presence of manganese(II). Extraction of this material with hot toluene led to the isolation of [MnBr$_2$(PPhMe$_2$O)] (Found: C, 25.9; H, 3.0; Br, 43.0. Calc. for C$_8$H$_{11}$Br$_2$MnOP: C, 26.0; H, 3.0; Br, 43.3%). Only a small quantity of brown oily material remained after extraction. From these results it would appear that the decomposition reaction involves oxidation of the tertiary phosphine ligand, although the actual mechanism is unclear.

Solution Studies.—The quantity of NO absorbed by 100 cm^3 thf was measured at various temperatures using a gas burette. The amount of NO absorbed by 100 cm^3 of thf solutions of the [MnX$_2$(PR$_3$)] complexes was then recorded for various concentrations. The results obtained at −78 °C are presented in Table 2 and Figure 1. As can be seen, the intercept for each plot lies within the range (1.41—1.46) × 10^{-3} mol NO per 100 cm^3 thf. These values correspond very closely to the independently measured value of 1.43 × 10^{-3} mol NO per 100 cm^3 thf at −78 °C, Figure 1. Subtraction of the blank value from the value for the solution absorption gives the quantity absorbed by each complex. Each complex was found to absorb almost exactly 100 mol% NO per mol [MnX$_2$(PR$_3$)] at each concentration studied within the solubility limits of the complex. The slope of each concentration plot (Table 2, Figure 1) provides additional evidence for the stoicheiometry of the reactions, indicating a 1:1 Mn:NO interaction.

The number of successive absorption/desorption cycles that each solution of the [MnX$_2$(PR$_3$)] complexes could undergo was also determined. After a gas burette measurement of NO uptake by a 100 cm^3 of a solution of a [MnX$_2$(PR$_3$)] complex, the solution was degassed and the NO uptake experiment repeated. The [MnX$_2$(PR$_3$)] species was regenerated by purging solutions with dry argon for several minutes or by applying a vacuum. The uptakes were repeated until the sample solution no longer absorbed any NO over and above the blank value. Each complex was studied at three temperatures: −78, 0, and 25 °C. A large number of complexes was studied, and Figure 2 illustrates the results obtained for the [MnX$_2$(PBu$^n_3$)] (X = Cl, Br, or I) complexes. From these and similar graphs[11] some general points have emerged. (*i*) As the temperature increases the number of cycles reaching 100% uptake, *i.e.*, complete formation of [MnX$_2$(PR$_3$)(NO)] from [MnX$_2$(PR$_3$)], decreases and the rate of decomposition of the [MnX$_2$(PR$_3$)] complex increases. (*ii*) All the [MnX$_2$(PR$_3$)] (X = Cl or Br) complexes undergo at least two cycles at room temperature before decomposition occurs, and more cycles as the temperature is decreased. (*iii*) The [MnI$_2$(PR$_3$)] complexes only fully react with NO to form [MnI$_2$(PR$_3$)(NO)] at −78 °C, and even at this temperature decomposition is rapid. (*iv*) The stability of the system below appears to be halide dependent, Cl > Br > I, but the nature of the phosphine has little effect.

Table 2. Data from plots of NO uptake at −78 °C, as a function of complex concentration.

Complex	Slope/ cm^3	10^3 (Intercept)/ cm^3
[MnCl$_2$(PPr$^n_3$)]	0.96	1.43
[MnCl$_2$(PBu$^n_3$)]	0.92	1.44
[MnCl$_2$(PPhMe$_2$)]	0.89	1.43
[MnCl$_2$(PPhEt$_2$)]	0.95	1.41
[MnBr$_2$(PPr$^n_3$)]	0.89	1.42
[MnBr$_2$(PBu$^n_3$)]	0.92	1.45
[MnBr$_2$(PPhMe$_2$)]	0.90	1.46
[MnBr$_2$(PPhEt$_2$)]	0.91	1.46
[MnI$_2$(PPr$^n_3$)]	0.94	1.44
[MnI$_2$(PBu$^n_3$]	0.95	1.43

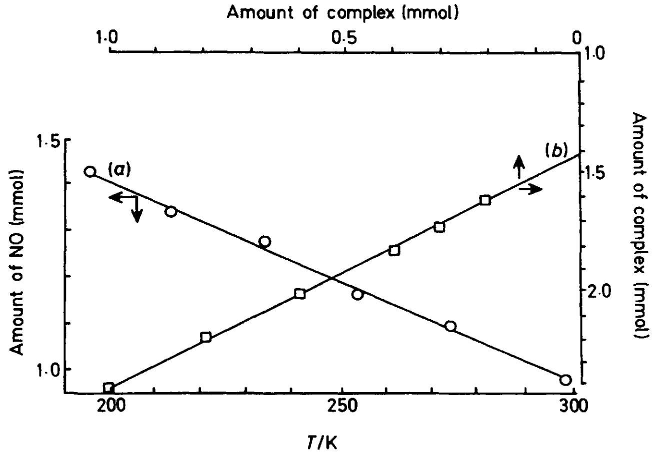

Figure 1. (*a*) Amount of NO absorbed by 100 cm^3 thf at different temperatures. (*b*) Plot of NO absorbed *versus* concentration of [MnI$_2$(PPr$^n_3$)] (in 100 cm^3 thf) at −78 °C

$$[\mathrm{MnX_2(PR_3)}] \underset{-\mathrm{NO}}{\overset{+\mathrm{NO}}{\rightleftharpoons}} [\mathrm{MnX_2(PR_3)(NO)}]$$

Structures of the Complexes in Solution.—On the basis of their e.s.r. spectra[3] in thf the [MnX$_2$(PR$_3$)] species have been formulated as six-co-ordinate monomers, (**I**). As in the solid state, these solutions colour deeply as the [MnX$_2$(PR$_3$)(NO)]

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* An independently synthesised sample of [MnBr$_2$(PPhMe$_2$O)] also exhibited ν(P=O) at 1 140 cm^{-1}.

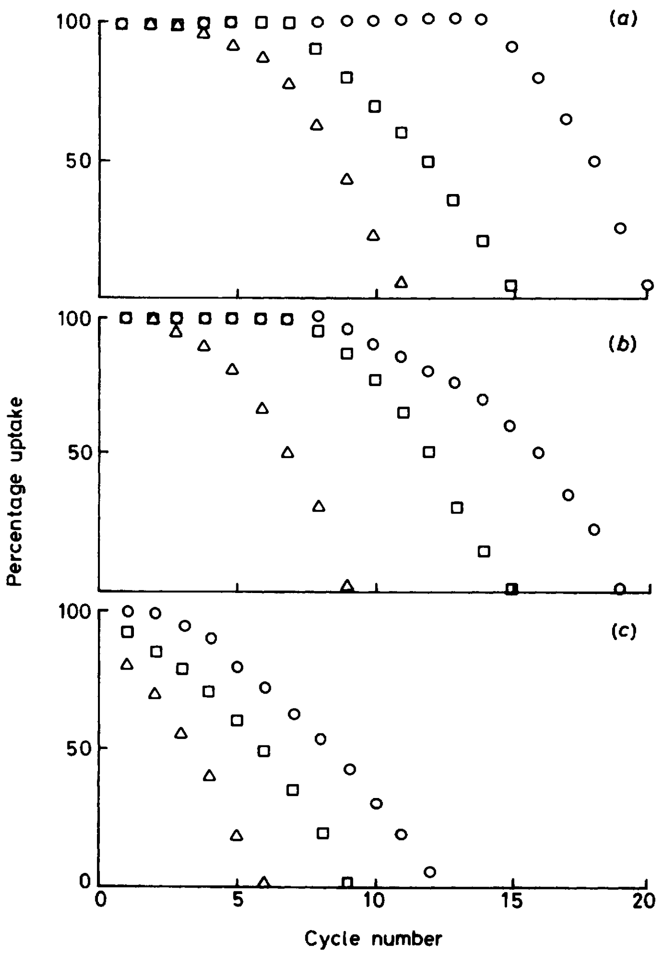
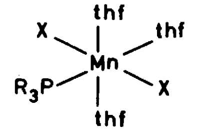


Figure 2. Plot of percentage uptake of NO over a range of absorption/desorption cycles for the complexes $[MnX_2(PBu^n{}_3)]$ [X = Cl (*a*), Br (*b*), or I (*c*)] at −78 (○), 0 (□), and 25 °C (△)



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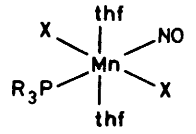

(II)

species form. Similarly, absorption of NO led to a diminution in the e.s.r. spectra of the $[MnX_2(PR_3)]$ compounds until, after 1:1 reaction to form $[MnX_2(PR_3)(NO)]$ is complete, no e.s.r. signals are observed.

We have suggested that reaction of the complexes in thf solution with dioxygen involves replacement of a co-ordinated thf molecule by the O_2 ligand.[3] Reaction with nitric oxide can reasonably be assumed to be similar to reaction with O_2, *i.e.*, thf replacement by NO. Since tertiary phosphine ligands are *trans* labilising and it seems reasonable that the thf *trans* to PR_3 is the likely substitution site, structure (**II**).

The lack of e.s.r. spectra for the $[MnX_2(PR_3)(NO)]$ species clearly indicates an even-electron species in solution. Moreover, for all solutions studied, no ^{31}P n.m.r. spectrum could be recorded; this presumably arises from paramagnetic broadening and implies a high-spin configuration for the manganese atom. This can be rationalised in terms of a manganese(III)–NO^- (formally d^4) species, and using the criteria of Enemark and Feltham,[12] whereby complexes are classified according to the number of *d*-type electrons present, these complexes can be classified as $\{MNO\}^5$ species.

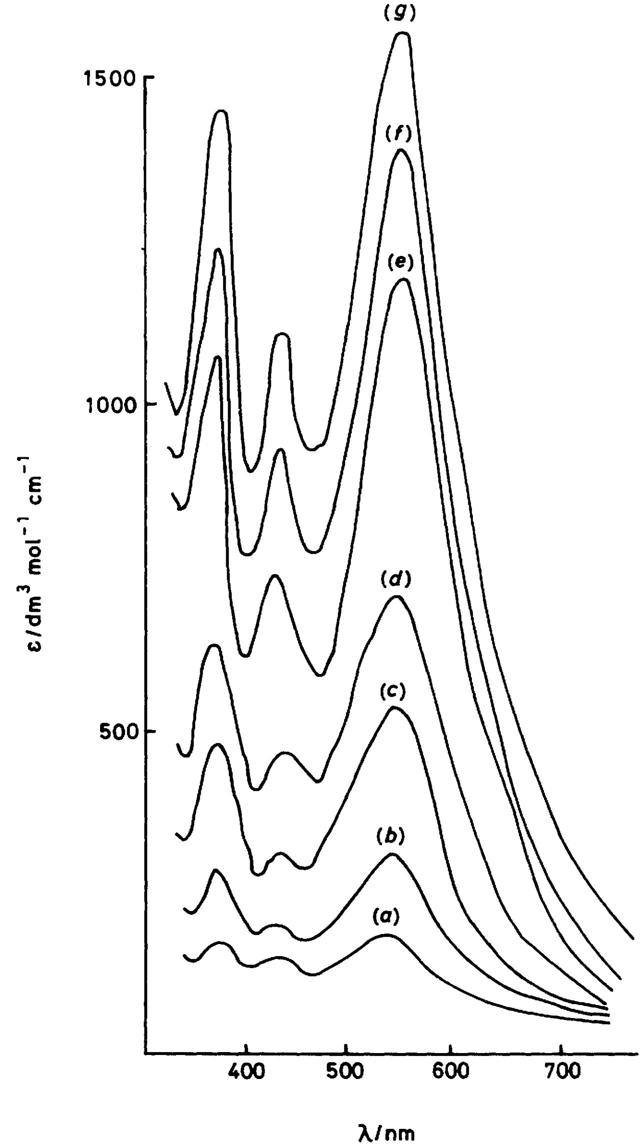

Figure 3. Variation of electronic spectrum of $[MnCl_2(PPhMe_2)]$ with the pressure of nitric oxide in thf at 25 °C: *p*(NO) = 5 (*a*), 10 (*b*) 20 (*c*), 30 (*d*), 50 (*e*), 80 (*f*), and 100 Torr (*g*)

Solution Isotherms and Equilibrium Data.—The electronic spectra of the $[MnX_2(PR_3)(NO)]$ (X = Cl or Br; R_3 = $Pr^n{}_3$, $Bu^n{}_3$, $PhMe_2$, or $PhEt_2$) complexes were recorded but, because of their instability with respect to decomposition, the iodo analogues could not be studied.

The spectra are characterised by three intense bands in the visible region: 535, 410, 385 nm (chloro complexes) and 550, 395, and 370 nm (bromo complexes); see Figure 3. The high molar absorption coefficients tend to suggest that these bands are charge transfer in origin. Since the absorption coefficients of these bands are directly related to the concentration of $[MnX_2(PR_3)(NO)]$ species in solution, it has been possible to construct nitric oxide binding curves (isotherms) by measuring $\lambda_{max.}$ as a function of *p*(NO). Typical spectra are illustrated in Figure 3, and two isotherms are plotted in Figure 4.

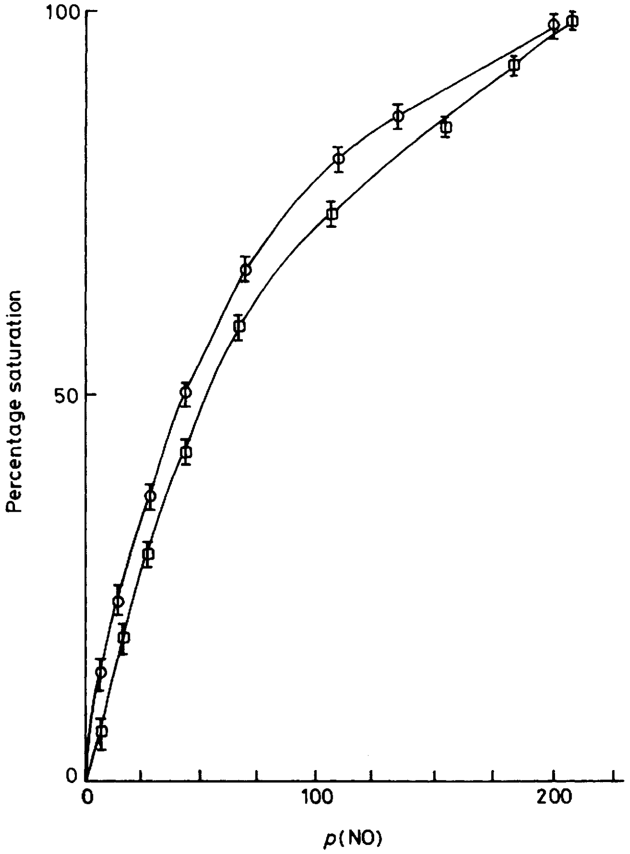

Figure 4. Nitric oxide binding curves (isotherms) for $[MnCl_2(PPhR_2)]$ complexes in thf at 25 °C: R = Me (○) or Et (□)

As is shown in Figure 2, the $[MnX_2(PR_3)(NO)]$ complexes are more stable at low temperatures, and as in the solid state, they decompose on long exposure to NO. In thf solution the decomposition products exhibit e.s.r. spectra consistent with high-spin manganese(II) species. Identical e.s.r. spectra were generated by mixing MnX_2 salts with 1 mol equiv. of the corresponding PR_3O ligand in thf. These experiments clearly demonstrate that the decomposition product from solution is essentially the same as that observed in the solid state, namely a 1:1 $[MnX_2(PR_3O)]$ complex.

Although we do not fully understand the mechanism of decomposition, it is clear that oxidation of the phosphine ligand is involved at some stage in the reaction pathway. Since NO is known to be thermally unstable and can function as an oxidising agent it is not surprising that lack of functionality of the $[MnX_2(PR_3)]$ species is due to formation of $[MnX_2(PR_3O)]$.

Experimental

Solvents were dried as previously described and the $[MnX_2(PR_3)]$ complexes were synthesised by published methods. Two methods were employed to prepare solutions of the complexes. The first method involved weighing the pre-analysed solid $[MnX_2(PR_3)]$ compound into a dry flask under argon and then adding the freshly distilled solvent by means of a syringe to give the solution of required concentration. The second method involved the *in situ* generation of the $[MnX_2(PR_3)]$ complex in thf and the use of this solution directly without isolating the solid compound. This may be illustrated for $[MnI_2(PBu^n{}_3)]$. A round-bottom flask (250 cm^3), equipped with a side arm with a ground glass tap and a magnetic stirrer bar, was flame-dried and then charged with dry MnI_2 (0.31 g, 1.0 mmol) and flushed with argon. Freshly distilled anhydrous thf (100 cm^3) was then added *via* a syringe followed by $PBu^n{}_3$ (0.25 cm^3, 1.0 mmol). The mixture was then stirred under argon for 3 d at room temperature. The resulting solution could then be used or diluted with freshly distilled thf to the required concentration.

Gas Uptake Measurements.—The quantitative absorption of nitric oxide was studied as previously described for dioxygen.[2]

Solution Isotherms.—(*i*) *Room-temperature measurements.* A u.v. cell, fitted with a bulb stopper and a side inlet, and a syringe were dried in an oven at 130 °C for 2 h prior to transfer to an argon-filled dry-box. A sample of the solution (stored in a 250 cm^3 flask in the dry-box) was put into the cell whilst in the dry-box. The cell was then removed and a spectrum of the stock solution recorded after which the cell was connected to the vacuum line and evacuated. The gas under study (NO) was then admitted to the line, the pressure being measured using a manometer and the overall pressure then returned to atmospheric by the addition of dry argon. This gas mixture was then introduced to the cell and the solution in the cell stirred magnetically for 20 min to ensure complete equilibration.

The cell was then sealed, removed from the vacuum line and placed in the spectrophotometer. After the spectrum had been recorded the cell was removed from the machine, emptied, cleaned, dried and replaced in the dry-box for another sample of solution to be run at a different partial pressure of gas. 100% saturation was judged to be when any further increase in partial pressure caused no increase in $\lambda_{max.}$ [maximum test pressure was 760 Torr (*ca.* 10^5 Pa) of gas under study].

(*ii*) *Low-temperature measurements.* A specially constructed u.v. cell was cleaned and oven-dried prior to use. Samples of the solution under study were loaded as described in section (*i*). The cell was placed in the cryostat unit within the spectrophotometer and allowed to reach thermal equilibrium. The cell was then connected to a vacuum line and the inert gas above the solution removed. A gaseous mixture containing the gas under study at the required partial pressure was made up as previously described and introduced to the cell. The mixture was left connected to the vacuum line and the spectrum of the solution was then run at intervals (10 min) until no further increase in $\lambda_{max.}$ was observed, which was taken to mean that the reaction was at equilibrium. The cell was then removed from the spectrophotometer, cleaned, dried and reloaded and the process repeated at a different partial pressure of the gas under study.

Electron Spin Resonance Spectra.—These were obtained on a Varian E9 spectrometer using the dual cavity mode and were referenced to strong pitch. The spectra were run at *X*-band frequency and were recorded as single derivatives of the resonance signal. Specially built e.s.r. tubes with a ground glass joint and a ground glass tap were used in this study. The samples were loaded in a dry-box and the tube was then attached to a vacuum line and the required atmosphere introduced into it above the sample.

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