The Reversible Co-ordination of Nitric Oxide by the Manganese(II) Phosphine Complexes, $MnX_2(PR_3)$, in the Solid State and in Tetrahydrofuran Solution

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The $MnX_2(PR_3)$ ($X = Cl, Br, I$; $R_3 = Pr^n{}_3, Bu^n{}_3, PhMe_2, PhEt_2$) complexes bind nitric oxide to form $MnX_2(PR_3)(NO)$ in the solid state and in tetrahydrofuran; the reaction is reversible, and the affinity for NO is both halide and phosphine dependent.

Complexes of type MnX_2L ($X = Cl, Br, I, NCS$; L = tertiary phosphine) have been shown to bind a number of small molecules in the solid state or in solution, *e.g.* dioxygen,[1,2] carbon monoxide,[3,4] and ethylene.[5,6] Although certain manganese porphyrin systems can bind nitric oxide,[7—9] sometimes reversibly,[10] no simple systems such as $MnX_2(PR_3)$ have been reported to do so. We here report the reversible co-ordination of nitric oxide by some $MnX_2(PR_3)$ complexes ($X = Cl, Br, I$; $R_3 = Pr^n{}_3, Bu^n{}_3, PhMe_2, PhEt_2$) in the solid state and in tetrahydrofuran (THF) solution.

Upon contact with nitric oxide the off-white $MnX_2(PR_3)$ complexes colour vividly (X = Cl, deep red–purple; X = Br, deep blue; X = I, brown). Below 0 °C it is possible to monitor weight changes as NO is absorbed and this corresponds to a 1:1 complex $MnX_2(PR_3)(NO)$. The complexes are indefinitely stable below 0 °C, and for X = Cl, Br the NO may be removed by applying a vacuum. At room temperature the $MnX_2(PR_3)(NO)$ complexes undergo a very slow decomposition [for example $MnBr_2(PPhMe_2)(NO)$ stored at room temperature for several days exhibited a gradual loss of $\nu(NO)$ and a gain in $\nu(P{=}O)$; work-up of the material gave, as a major product, $MnBr_2(OPPhMe_2)$].

Magnetic susceptibility measurements at room temperature give magnetic moments for the $MnX_2(PR_3)(NO)$ complexes in the range 4.85—5.25 μ_B, indicative of four unpaired electrons. The broad e.s.r. signal of the $MnX_2(PR_3)$ compounds ($g = 2$) gradually loses intensity as NO is absorbed, eventually leading to complete signal loss. Upon pumping off the NO the original signal returns. Both these data are consistent with an even number of electrons for the $MnX_2(PR_3)(NO)$ complexes. The majority of manganese(III), $S = 2$, complexes produce zero field splittings and are e.s.r. silent.

The $MnX_2(PR_3)(NO)$ complexes exhibit an i.r. band in the 1595—1607 cm^{-1} range, which is not present in the $MnX_2(PR_3)$ complexes, assignable to $\nu(NO)$. This large shift from that of free nitric oxide, $\nu(NO)$ at 1840 cm^{-1}, proves that NO is chemically bonded in these complexes, and is consistent with the magnetic changes reported above.

In THF solution at −78 °C all complexes absorb nitric oxide in a 1:1 Mn:NO ratio as measured by gas burette measurements. For example Figure 1 shows a plot of NO absorbed *vs.* concentration of $MnI_2(PBu^n{}_3)$ in solution. The slope is 0.94 and the intercept is equivalent to that amount of NO absorbed by 100 cm^3 of THF, which was checked by a blank measurement.

It is possible to desorb the NO by purging the $MnX_2(PR_3)(NO)$ solutions with dry argon for several minutes. At −78 °C up to 15 complete cycles (100% absorption, 100% desorption) could be obtained for the chloro and bromo complexes, but usually only 2 for the iodo species. All systems were less stable at 0 and 25 °C.

The THF solutions of $MnBr_2(PR_3)(NO)$ did not exhibit any e.s.r. spectra and no ^{31}P n.m.r. spectra could be recorded. This presumably arises from paramagnetic broadening and implies a high spin configuration for the manganese atom.

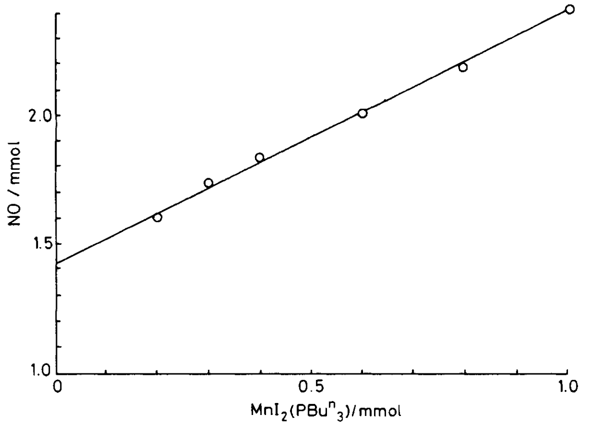

Figure 1. Plot of NO (mmol) absorbed *vs.* $MnI_2(PBu^n{}_3)$ (mmol) at −78 °C in THF.

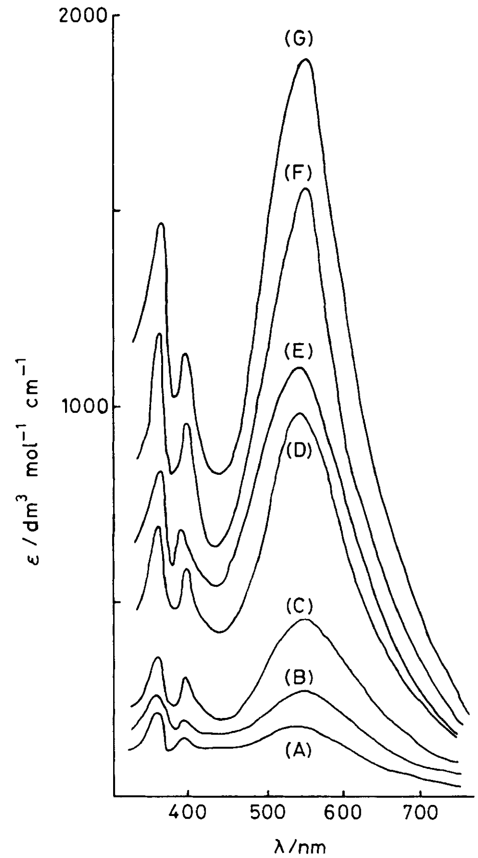

Figure 2. Variation of electronic spectrum with p_{NO} for $MnBr_2(PPhEt_2)$ in THF at 25 °C [(A) 6; (B) 11; (C) 20; (D) 60; (E) 78; (F) 120; (G) 154 Torr].

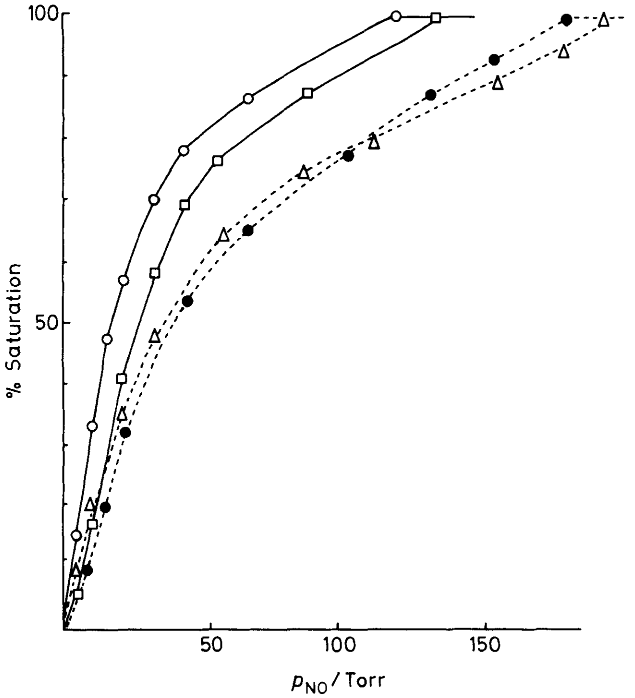

Figure 3. Solution isotherms for $MnX_2(PR_3)$ complexes in THF at 25 °C; $MnCl_2(PPr^n_3)$ (○), $MnBr_2(PPr^n_3)$ (□), $MnCl_2(PPhEt_2)$ (△), $MnBr_2(PPhEt_2)$ (●).

This can be rationalised in terms of a manganese(III)-NO^- (formally d^4) species, and using the criteria of Enemark and Feltham,[11] whereby the complex is classified according to the number of d-type electrons present, these complexes can be classified as $[MNO]^6$ species.

In THF the visible electronic spectra of the $MnX_2(PR_3)(NO)$ complexes exhibit intense bands at 535, 410, 385 nm ($X = Cl$) and 550, 395, 370 nm ($X = Br$) (the iodo complexes were too unstable to be studied at room temperature). Since there is a linear relationship between the intensity of the visible absorption bands and the amount of NO absorbed, Figure 2, it was possible to construct nitric oxide binding curves similar to the well known isotherms established for dioxygen systems.[2] Figure 3 illustrates well how these are a function of both the nature of the phosphine and the halide. The affinity for NO of the $MnX_2(PR_3)$ complexes is generally greater for $X = Cl$ than for $X = Br$, and as determined by equilibrium constants lies in the order $PPr^n_3 > PBu^n_3 > PPhMe_2$ *ca.* $= PPhEt_2$ (for $X = Cl$) and $PPhEt_2 > PPhMe_2 > PPr^n_3 > PBu^n_3$ (for $X = Br$); K_{NO} lay in the range 4.0—6.5 ($\times 10^3$) for the bromo complexes and 14.5—21.3 ($\times 10^3$) for the chloro complexes at 25 °C. It is not clear why changing the halogen from chloride to bromide inverts the order of dependence of affinity for NO on the nature of the phosphine ligand (Figure 3); it is presumably connected with the electronegativity of the two halogens.

There is controversy surrounding this area of chemistry. Green, Mingos, and co-workers' results[12] differ from our own observations regarding the preparation and reversible binding of dioxygen by these $MnX_2(PR_3)$ complexes. The results reported here give further evidence of the versatile nature of the $MnX_2(PR_3)$ compounds.

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