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The Coordination of Small Molecules by Manganese(II) Phosphine Complexes. Part 13*. The Synthesis and Characterisation of some Novel Manganese(II) Complexes of Tertiary Butylisocyanide, $MnX_2(CNBu^t)$ (X = Cl, Br, I, NCS), and their Reaction with Tri(n-butyl)phosphine and Molecular Oxygen

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Abstract

Novel tertiary butylisocyanide complexes of manganese(II) with unusual stoichiometry, $MnX_2(CNBu^t)$ (X = Cl, Br, I, NCS), have been prepared and characterised by magnetic susceptibility measurements and infrared and electron spin resonance spectroscopy. For X = Cl, Br, I the complexes have been assigned a polymeric structure similar to that found for $MnI_2(PPhMe_2)$, whilst $Mn(NCS)_2(CNBu^t)$ is probably dimeric as the infrared spectrum exhibits bands assignable to both bridging and terminal thiocyanate groups. The $MnX_2(CNBu^t)$ show no ability to reversibly bind dioxygen, but in solution in tetrahydrofuran PBu_3^n displaces the isocyanide ligand and for X = Cl, Br, I these solutions absorb dioxygen in a 1:1 Mn:O_2 ratio.

Introduction

We have reported our investigations of manganese(II) phosphine complexes, $MnX_2(PR_3)$ (X = Cl, Br, I, NCS), which can reversibly coordinate small molecules such as dioxygen [1–4], carbon monoxide [5], nitric oxide [6], and ethylene [7] and irreversibly coordinate carbon disulphide [8], sulphur dioxide [9] and tetracyanoethylene [10].

We have extended these studies to manganese(II) complexes containing ligands other than tertiary phosphines. For example, we have shown that the $Mn(OPPh_3)_4I_2$ complex can undergo an insertion reaction with sulphur dioxide to form $[Mn(OPPh_3)_4(OSOI)_2]$, and half of the sulphur dioxide may be desorbed by heating [11]. We now wish to report our studies of manganese(II)/isocyanide complexes.

The isocyanide ligand in transition metal complexes can be formally regarded as an analogue of the CO ligand. Manganese(II) complexes of isocyanides of general formula $[Mn(CNR)_6]X_2$ (R = Ph, Et, Bu^t, $CH{=}CH_2$) have previously been prepared by nitric acid oxidation of the corresponding manganese(I) complex, followed by precipitation with a suitable counterion (e.g. $CdBr_4^{2-}$, PF_6^-, NO_3^-) [12–15]. All of these complexes have the low-spin (t_{2g}^5) ground state and not the high-spin ($t_2^3e_g^2$) configuration, which is more usual for manganese(II) complexes. Cyclic voltammetry of $[Mn(CNR)_6]^{z+}$ (z = 1, 2) species result in complexes of manganese in the 0, +1, +2, and +3 oxidation states [15–18]. A number of other manganese(I) complexes are known, e.g. $Mn_2(CO)_{10-n}(CNR)_n$ (n = 1–3), $Mn_2(CO)_7(CNR)\{P(OPh)_3\}_2$ and $Mn_2(CO)_n(diphos)(CNR)$ (n = 4, 5), formed by the reaction of RNC with $Mn_2(CO)_{10}$ [19, 20], $R'Mn(CO)_5$ [21], $Mn_2(CO)_8\{P(OPh)_3\}_2$ [19] or $Mn_2(CO)_5(diphos)$ [22, 23]. In the case of manganese(I) complexes ν(CN) of the isocyanide ligand decreases in energy upon coordination, indicating $d\pi-\pi_{CN}^*$ bonding in the complexes, whereas for manganese(II) the ν(CN) increases on coordination [15, 24].

It can thus be seen that manganese(II) complexes of isocyanides are rare, but those which are known are of the $[Mn(CNR)_6]^{2+}$ type. Here we wish to report some novel $[MnX_2(CNBu^t)]$ (X = Cl, Br, I, NCS) complexes and our observations of their reaction with PBu_3^n and molecular oxygen.

Results and Discussion

The method used to prepare the $MnX_2(CNBu^t)$ complexes is essentially the same as that used to prepare the analogous $MnX_2(PR_3)$ complexes (see 'Experimental'). It thus differs greatly from the methods used to prepare the $[Mn(CNR)_6]^{2+}$ complexes inasmuch as the method reported here is a direct one-step process employing anhydrous condi-

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*For Parts 11 and 12, see refs. 1 and 2, respectively.

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TABLE I. Some Physical and Analytical (%)[a] Data for the Manganese(II) Complexes

Complex	Colour	Melting point (°C)	μ_{eff} (μ_B)	C	H	N	X	Mn
$MnCl_2(CNBu^t)$	White	>280	6.0	30.3(28.7)	4.3(4.9)		35.3(33.9)	26.5(26.3)
$MnBr_2(CNBu^t)$	White	>280	5.6	21.2(20.1)	3.3(3.0)		52.7(53.7)	17.9(18.5)
$MnI_2(CNBu^t)$	yellow	126(d)	5.1	15.0(15.3)	2.9(2.3)	3.5(3.6)	62.2(64.8)	15.0(14.0)
$Mn(NCS)_2(CNBu^t)$	pale green	>280	6.0	32.8(33.1)	3.7(3.5)	16.4(16.5)		21.2(21.6)

[a] Found(calc.).

TABLE II. Some Significant Infrared Bands for the Manganese(II) Complexes (cm^{-1})

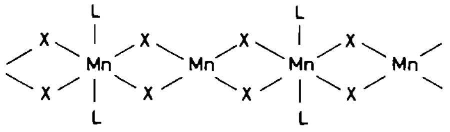
Compound	ν(CN)	ν(Mn–C)	ν(Mn–X–Mn)	Other
$MnCl_2(CNBu^t)$	2220(s)	213(sh)	234(sh)	
$MnBr_2(CNBu^t)$	2105(s)	213(m)	188(br)	
$MnI_2(CNBu^t)$	2179(s)	212(m)	120(br)	
$Mn(NCS)_2CNBu^t)$	2200(s)	214(sh)		2120(s)[a] 2098(s)[a] 264(s)[b]

[a] ν(CN) of NCS group. [b] ν(Mn–N).

tions, whereas the latter require the pre-preparation of the manganese(I) complex followed by subsequent oxidation [12, 13]. Some physical properties and analytical data for the complexes are listed in Table I.

Some significant infrared spectral bands of the complexes as mulls are listed in Table II. A strong ν(CN) band due to the isocyanide ligand is present in the 2220–2179 cm^{-1} region, which may be compared to ν(CN) in the free ligand at 2122 cm^{-1}. Isocyanide ligands are capable of acting as either good σ-donors or π-acceptors [15, 24] and, in general, $CNBu^t$ behaves as a π-acceptor in zerovalent complexes, ν(CN) decreases on coordination and as a σ-donor, ν(CN) increases in energy on coordination, towards metals in higher oxidation states. It is clearly acting as a σ-donor ligand in these $MnX_2(CNBu^t)$ complexes. The magnitude of the shift to higher energy, Cl(78 cm^{-1}) > Br(60 cm^{-1}) > I(57 cm^{-1}), is in accord with the electronegativity of the coordinated halogen, causing an overall shift in electron density away from the $CNBu^t$ ligand towards the halide, $X \leftarrow Mn \leftarrow CNBu^t$.

For the $MnX_2(CNBu^t)$ (X = Cl, Br, I) complexes only one ν(Mn–X) band, assignable to bridging Mn–X–Mn moieties, Table II, is observable, and it is tempting, in the absence of terminal ν(Mn–X) bands, to assign the complexes the structure found for the analogous $MnI_2(PPhMe_2)$ (**I**) [25]. For $Mn(NCS)_2(CNBu^t)$, however, there are two ν(CN) bands assignable to thiocyanate at 2120 and 2097 cm^{-1}. Using accepted criteria [26], these can be assigned to bridging and terminal thiocyanate, respectively, suggesting a dimeric structure **II**. All of the complexes exhibit an infrared band between 214–212 cm^{-1}, tentatively assigned to ν(Mn–C).



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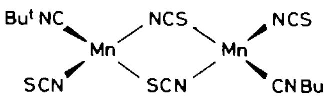


II

The room temperature magnetic moments are listed in Table I. The values, 6.0–5.1 μ_B, are, for the most part, consistent with a degree of spin-pairing via Mn–X–Mn bridges and appear to mirror the magnetic behaviour of the analogous phosphine complexes. They also differ fundamentally from the low-spin hexakis(isocyanide)manganese(II) complexes [12]. The variable room temperature magnetic susceptibility measurements for $MnBr_2(CNBu^t)$ show, Fig. 1, that this complex obeys the Curie–Weiss law with θ = 28 K, suggesting antiferromagnetism, Fig. 1.

The room temperature X-band powder ESR spectra of the $MnX_2(CNBu^t)$ show only single intense peaks at g = 2, providing no unambiguous structural information. However, the complexes dissolved in tetrahydrofuran (THF) and the X-band spectra at 93 K, Figs. 2–5, did yield some relevant structural data.

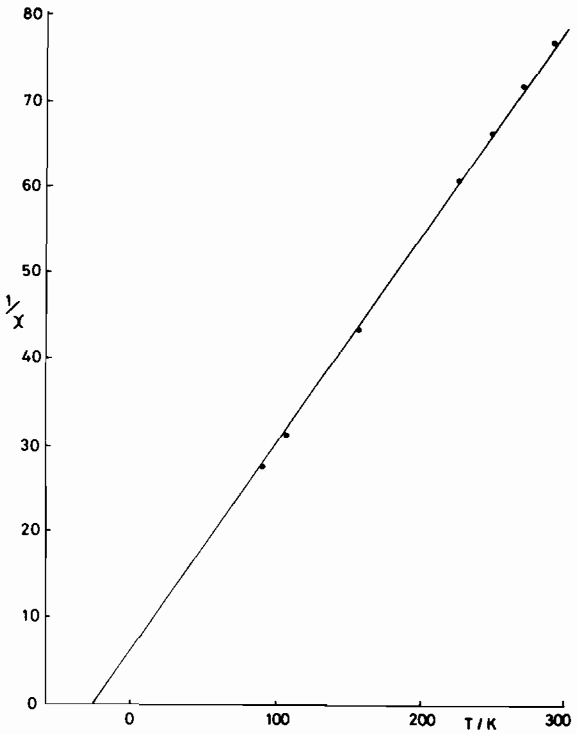


Fig. 1. Graph of reciprocal magnetic susceptibility *vs.* temperature for $MnBr_2(CNBu^t)$.

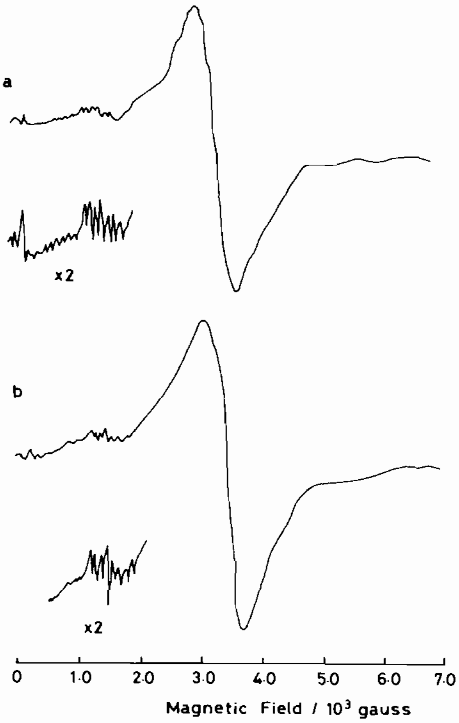


Fig. 2. X-band ESR spectra of (a) $MnCl_2(CNBu^t)$ and (b) $MnCl_2(PPhBu_2{}^i)$ in frozen THF, 93 K.

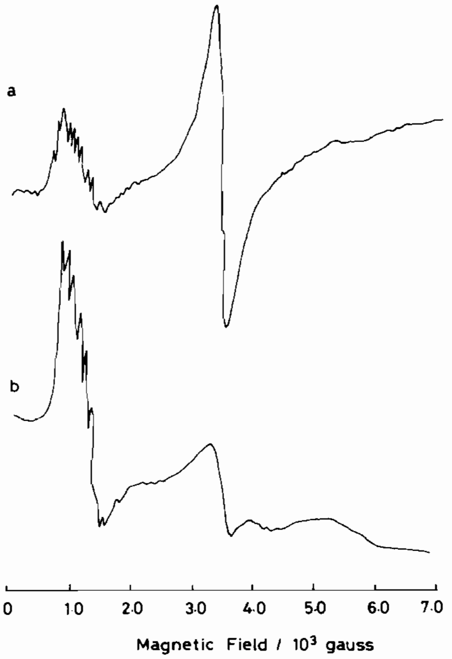


Fig. 3. X-band ESR spectra of (a) $MnBr(CNBu^t)$ and (b) $MnBr_2(PPhBu_2{}^i)$ in frozen THF, 93 K.

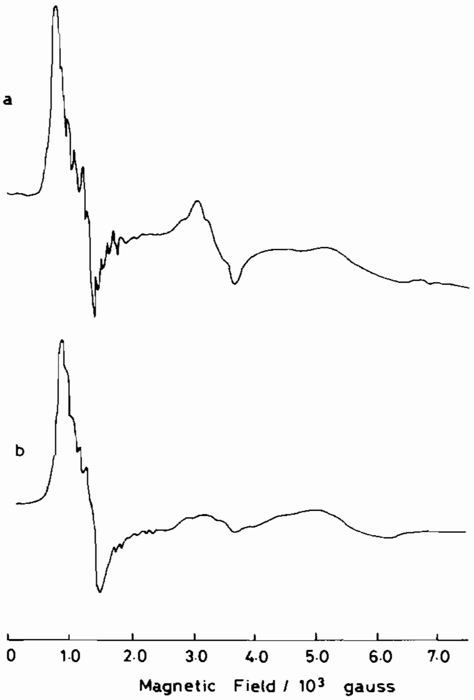


Fig. 4. X-band ESR spectra of (a) $MnI_2(CNBu^t)$ and (b) $MnI_2(PPhBu_2{}^i)$ in frozen THF, 93 K.

For the $MnX_2(CNBu^t)$ ($X = Br, I$), Figs. 3 and 4, peaks at $g = 6$ and $g = 2$ suggest axial symmetry and structure **III** would seem likely in tetrahydrofuran solution. Whilst the ESR spectra of the MnX_2-

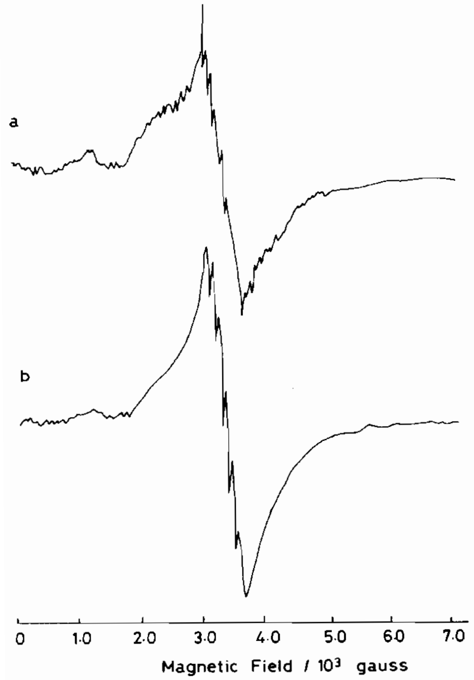
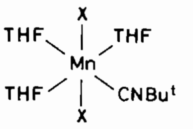


Fig. 5. X-band ESR spectra of (a) $Mn(NCS)_2(CNBu^t)$ and (b) $Mn(NCS)\{P(C_5H_{11})_3\}$ in frozen THF, 93 K.



III

$(CNBu^t)$ (X = Cl, NCS) are more complex, Figs. 2 and 5, they are also indicative of axial symmetry. Further evidence for structure **III** is available from the solution infrared spectrum which exhibits only a single band at 2097 cm^{-1} assignable to terminal Mn–NCS moieties.

Whilst the stoichiometry and magnetic and ESR properties of the $MnX_2(CNBu^t)$ complexes mirror those of the $MnX_2(PR_3)$ complexes no activity towards the reversible coordination of dioxygen has been observed in the former. Figures 2–5 contain a comparison of the ESR spectra of the two types of complexes (for X = Cl, I, NCS) and it can be seen that there are strong similarities in THF solution. The exception is the bromide, for, whilst $MnBr_2(CNBu^t)$ does exhibit peaks at $g = 2$ and $g = 6$, Fig. 3, the $g = 6$ peak is of a different character from that of, for example, $MnBr_2(PPhBu_2^i)$.

Phosphine/Isocyanide Exchange Reactions

Although no activity towards dioxygen binding was observed for the $MnX_2(CNBu^t)$ complexes, tetrahydrofuran solutions of some $MnX_2(CNBu^t)$ complexes became active on addition of a stoichiometric (1:1) quantity of PBu_3^n, Table III. All measurements were made at 193 K using our standard gas burette apparatus [3].

The data given in Table III indicate that all the halide complexes, $MnX_2(CNBu^t)$ (X = Cl, Br, I), on addition of PBu_3^n (1:1), are active towards dioxygen coordination. The pseudohalide thiocyanate complex does not, however, form an active complex with PBu_3^n in tetrahydrofuran. This is consistent with data from observations of $Mn(NCS)_2(PBu_3^n)$ in THF solution [27].

On exposure of THF solutions of a 1:1 mixture of $MnX_2(CNBu^t)$ (X = Cl, Br, I) and PBu_3^n at 0 °C to an atmosphere of dry dioxygen a rapid and vivid colour change occurs. The visible spectra of the $MnCl_2(CNBu^t)/PBu_3^n/O_2$ and $MnBr_2/PBu_3^n)O_2$ systems exhibited absorption bands at 529 and 395 nm (X = Cl) and 574 and 418 nm (X = Br), the spectra being identical to those found for $MnX_2(PBu_3^n)(O_2)$ (X = Cl, Br) complexes in tetrahydrofuran [28]. The infrared spectra of these solutions exhibit bands at *ca.* 2120 cm^{-1}, assignable to free $CNBu^t$. The reactions may thus be expressed

$$MnX_2(CNBu^t) + PBu_3^n \xrightarrow[0\ ^\circ C]{O_2} MnX_2(PBu_3^n)(O_2) + CNBu^t$$

The $MnI_2(CNBu^t)/PBu_3^n$ system also undergoes a vivid colour change in THF at 195 K when exposed to dioxygen. On warming to room temperature,

TABLE III. Dioxygen Uptake for the $MnX_2(CNBu^t)/PBu_3^n$ System[a]

Complex	Concentration ($\times 10^{-3}$ mol dm^{-3})	Total O_2 uptake (cm^3)	Less blank (cm^3)	$Mn:O_2$ ratio
$MnCl_2(CNBu^t)/PBu_3^n$	4.44	32.0	10.0	1.01
$MnBr_2(CNBu^t)/PBu_3^n$	6.19	35.2	13.2	0.95
$MnI_2(CNBu^t)/PBu_3^n$	9.14	42.6	20.6	1.01
$Mn(NCS)_2(CNBu^t)/PBu_3^n$	6.23	22.4	0	0

[a] 100 cm^3 aliquots; blank THF absorbs 22.0 cm^3 dioxygen at 193 K.

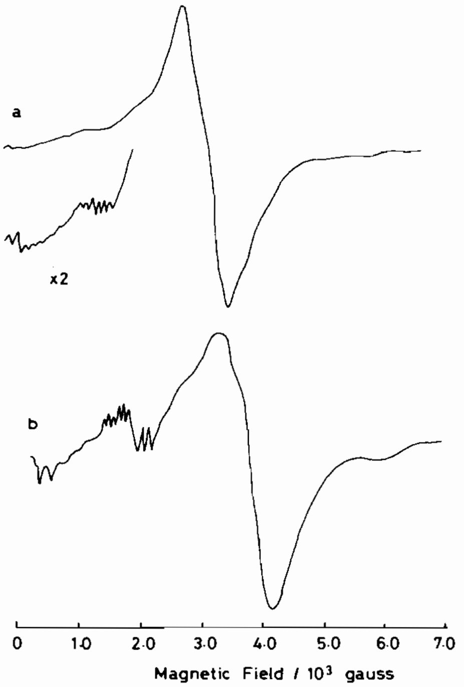


Fig. 6. X-band ESR spectra of (a) $MnCl_2(CNBu^t) + PBu_3^n$ and (b) $MnCl_2(PBu_3^n)$ in frozen THF, 93 K.

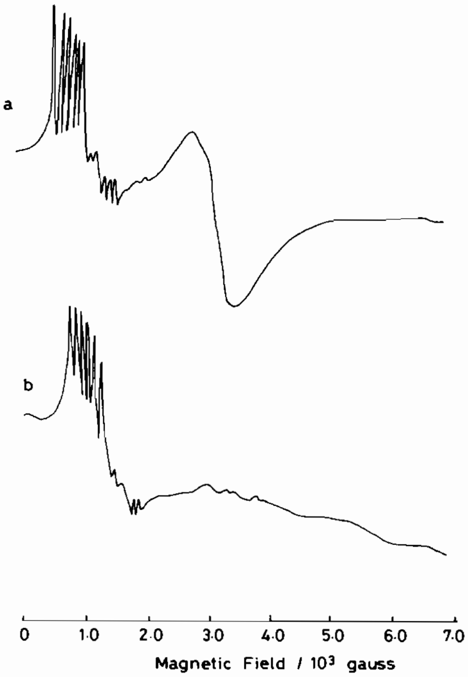


Fig. 7. X-band ESR spectra of (a) $MnBr_2(CNBu^t) + PBu_3^n$ and (b) $MnBr_2(PBu_3^n)$ in frozen THF, 93 K.

however, the green colour rapidly dispersed, consistent with observations on the $MnI_2(PBu_3^n)/O_2$ system [28].

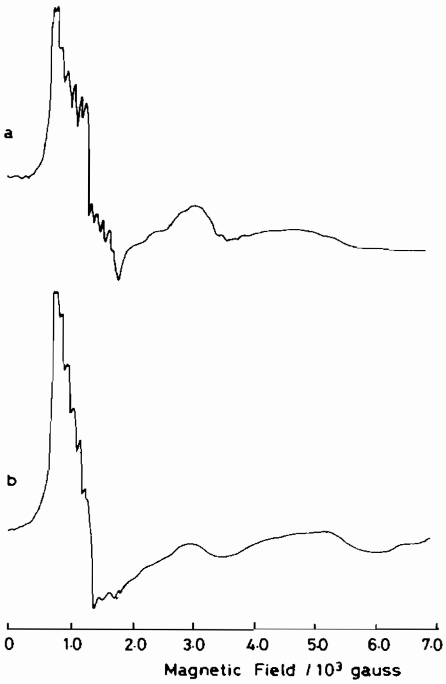


Fig. 8. X-band ESR spectra of (a) $MnI_2(CNBu^t) + PBu_3^n$ and (b) $MnI_2(PBu_3^n)$ in frozen THF, 93 K.

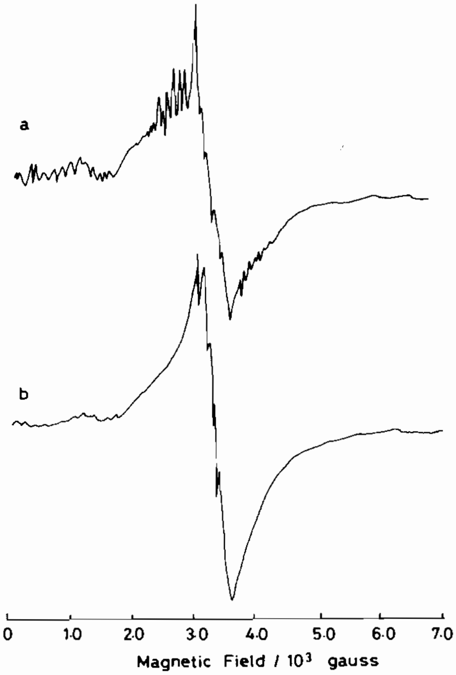


Fig. 9. X-band ESR spectra of (a) $Mn(NCS)_2(CNBu^t) + PBu_3^n$ and (b) $Mn(NCS)_2\{P(C_5H_{11})_3\}$ in frozen THF, 93 K.

Further evidence for a ligand-exchange process taking place on addition of PBu_3^n to $MnX_2(CNBu^t)$ comes from ESR spectra which show subtle differences between the $MnX_2(CNBu^t)$ and the $MnX_2(CNBu^t)/PR_3$ systems, Figs. 6–9.

Experimental

Anhydrous manganese(II) salts were prepared as previously reported [29]. Physical measurements were performed as published earlier [30]. Gas uptakes were carried out as described in ref. 3.

Preparation of $MnX_2(CNBu^t)$ *Complexes*

The method was the same for each complex and will be exemplified for $Mn(NCS)_2(CNBu^t)$ here: anhydrous manganese(II) thiocyanate (1.02 g, 6.0 mmol) was added to freshly distilled dry toluene (70 cm^3) in a 250 cm^3 side-arm flask which had previously been flame dried *in vacuo*. Tertiary butylisocyanide (0.67 cm^3) (Fluka Chemicals) was added and the mixture stirred for 72 h. The resulting yellow–white complex was filtered using a Schlenk apparatus and dried *in vacuo*.

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