Reactions of Organic Isocyanates and *tert*-Butyl Isocyanide with Manganese(II) Alkyls and Trimesitylchromium†

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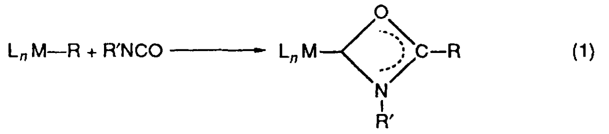
The dialkylmanganese compounds $[Mn(CH_2Bu^t)_2]_4$ and $[Mn(CH_2CMe_2Ph)_2]_2$ react with organic isocyanates to give chelating amido products that can be verified by hydrolysis to the amides. For Me_3SiNCO the products of reaction with $[Mn(CH_2Bu^t)_2]_4$ with 2 and 4 equivalents have been shown by X-ray crystallography to be, respectively, $Mn_3(CH_2Bu^t)_2[\mu\text{-}OC(CH_2Bu^t)N(SiMe_3)]_2(\mu\text{-}CH_2Bu^t)_2$ and $Mn_4(CH_2Bu^t)_2(\mu_3\text{-}NCO)_2[\mu\text{-}OC(CH_2Bu^t)N(SiMe_3)]_4$. In the triangular, and quite unsymmetrical trinuclear species each manganese has a distorted four-co-ordinate geometry. Two manganese atoms are chelated by the amide ligands (Mn–O 2.208, 2.276 Å; Mn–N 2.149, 2.184 Å) the oxygen of which then bridge to a neighbouring metal atom. Two of the manganese atoms carry one terminal alkyl (Mn–C 2.122 and 2.154 Å) and one edge of the Mn_3 triangle is bridged by one symmetrical (Mn–C 2.309 and 2.311 Å) and one unsymmetrical (Mn–C 2.184 and 2.646 Å) bridging alkyl. The tetranuclear species is centrosymmetric. One of the unique Mn atoms carries a terminal alkyl (Mn–C 2.092 Å) and is further co-ordinated by two bridging amide oxygens (Mn–O 2.070 and 2.073 Å) and one triply bridging cyanate nitrogen (Mn–N 2.282 Å). The other independent manganese is chelated by two amides with Mn–O 2.308 and 2.359 Å, Mn–N 2.146 and 2.176 Å and its six-co-ordination is completed by bonds to both triply bridging cyanate groups with Mn–N 2.298 and 2.138 Å. The reaction of $Cr(mes)_3(thf)$ (mes = 2,4,6-$Me_3C_6H_2$, thf = tetrahydrofuran) with BuNCO gives $Cr[OC(mes)NBu^t]_3$. Similar interactions using Bu^tNC lead to $Mn[Bu^tCH_2C{=}NBu^t]_2(PMe_3)$ and $Cr[(mes)C{=}NBu^t]_3$.

Reactions of transition-metal alkyls and aryls with heterocumulene type ligands (*e.g.* CO_2 and $R_2C{=}C{=}O$ have been well studied[1] but those with organic isocyanates have received somewhat less attention.[2] Metal–carbon σ bonds were shown[3] to react as in equation (1) to give chelate amido compounds



(1)

but the insertion products have been structurally characterised in only a few cases.[3] Some recent studies involve insertions into $MoO_2(mes)_2$[4] (mes = $C_6H_2Me_3$-2,4,6) and $U(cp)_3(CHPMe_2Ph)$ (cp = η-C_5H_5);[5] for the latter the structure of the product with PhNCO was determined. Unpublished work quoted in a paper on isocyanide insertions into $V(mes)_3(thf)$ (thf = tetrahydrofuran)[6] indicates insertion also of $C_6H_{11}NCO$, the product hydrolysing to $(C_6H_{11})HNC(O)(mes)$.

Reactions of manganese dialkyls and chromium trimesityl with isocyanates and with Bu^tNC are now described.

Results and Discussion

Manganese Compounds.—The dimeric or polymeric manganese dialkyls[7a] including $[Mn(CH_2Bu^t)_2]_4$ and $[Mn(CH_2CMe_2Ph)_2]_2$ have been shown to undergo a variety of reactions with Lewis bases[7a,b] and compounds with acidic hydrogen atoms.[7c] We now show that isocyanates react readily. When hydrocarbon solutions of $[Mn(CH_2Bu^t)_2]_4$ and $[Mn(CH_2CMe_2Ph)_2]_2$ are treated with isocyanates, RNCO (R = Pr^i, Bu^t, CH_2Ph, C_6H_{11}, Ph, 2,6-$Me_2C_6H_3$ or $SiMe_3$), in a 1:2 ratio (Mn:RNCO) the pale brown solutions of the alkyls are decolourised and colourless crystals can be isolated. Only those from Me_3SiNCO and the neopentyl are of X-ray quality, due to twinning or disorder problems. The compounds are all paramagnetic so NMR spectra are not useful and analytical data and IR spectra are inadequate to formulate the species. However, hydrolysis gives the corresponding amides RC(O)NHR′ identified by comparison with authentic samples *via* mass and IR spectra.[8] Hydrolysis of the reaction product of PhNCO and $LiMnMe_3$ also gives amide.[9]

For the reaction of 2 equivalents of Me_3SiNCO and $[Mn(CH_2Bu^t)_2]_4$ we were able to obtain X-ray-quality crystals that were thermally stable (m.p. 177 °C) but very air and water sensitive, hydrolysis leading to $Bu^tCH_2C(O)NH(SiMe_3)$. A diagram of the trinuclear compound $Mn_3(CH_2Bu^t)_2[\mu\text{-}OC(CH_2Bu^t)N(SiMe_3)]_2(\mu\text{-}CH_2Bu^t)_2$ **1** is shown in Fig. 1; selected bond lengths and angles are in Table 1.

The molecule contains a scalene triangle of manganese atoms, each of which is four-co-ordinate but with a different combination of ligands. Atoms Mn(1) and Mn(2) each carry one terminal neopentyl ligand; Mn(1) is then chelated by one of the amide ligands, the oxygen of which also bridges over to Mn(2). The Mn(2)–Mn(3) edge of the Mn_3 triangle is then bridged, symmetrically by one neopentyl (Mn–C 2.309, 2.311 Å) and asymmetrically by another [Mn(2)–C(30) 2.646, Mn(3)–C(30) 2.184 Å]. This latter feature is reminiscent of the structure of the linear tetrameric $[Mn(CH_2Bu^t)_2]_4$ itself.[10] Atom Mn(3) is then also chelated by a second amide, the oxygen of which bridges over to Mn(1) to complete its four-co-ordination. The Mn–O distances in the chelate rings, 2.208, 2.276 Å, are larger than the bridging Mn–O distances, 2.086, 2.127 Å. The Mn–N distances are slightly different at 2.149 and 2.184 Å. Bond lengths and angles in the amido functions indicate their bonding

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

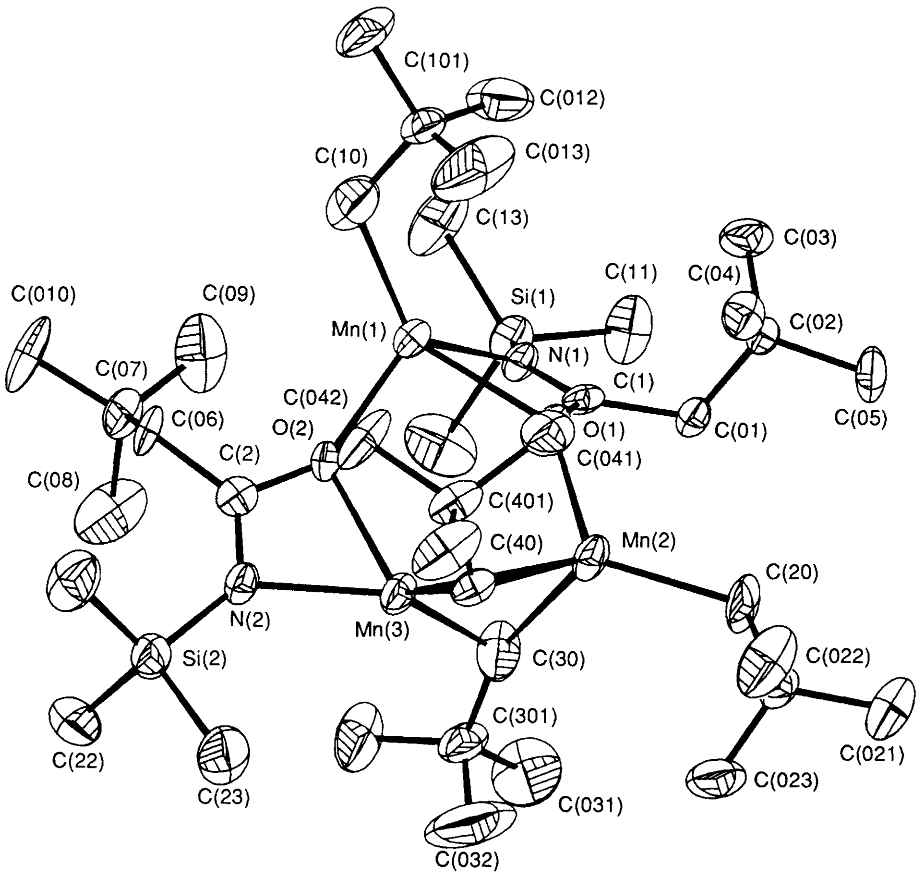
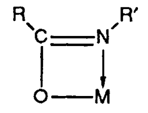


Fig. 1 The structure of $Mn_3(CH_2Bu^t)_2[\mu\text{-}OC(CH_2Bu^t)N(SiMe_3)]_2(\mu\text{-}CH_2Bu^t)_2$

Table 1 Selected bond lengths (Å) and angles (°) for $Mn_3(CH_2Bu^t)_2[\mu\text{-}OC(CH_2Bu^t)N(SiMe_3)]_2(\mu\text{-}CH_2Bu^t)_2$

O(1)–Mn(1)	2.276(11)	N(1)–Mn(1)	2.184(10)
O(2)–Mn(1)	2.086(8)	C(10)–Mn(1)	2.122(15)
O(1)–Mn(2)	2.127(10)	C(20)–Mn(2)	2.154(17)
C(30)–Mn(2)	2.646(16)	C(40)–Mn(2)	2.309(11)
O(2)–Mn(3)	2.208(11)	N(2)–Mn(3)	2.149(12)
C(30)–Mn(3)	2.184(14)	C(40)–Mn(3)	2.311(14)
Mn(3)–Mn(2)	2.702(6)	C(1)–O(1)	1.353(13)
C(1)–N(1)	1.265(19)	C(2)–O(2)	1.326(13)
C(2)–N(2)	1.311(17)		
N(1)–Mn(1)–O(1)	60.6(4)	O(2)–Mn(1)–O(1)	93.0(4)
O(2)–Mn(1)–N(1)	109.1(4)	C(10)–Mn(1)–O(1)	133.9(4)
C(10)–Mn(1)–N(1)	128.8(5)	C(10)–Mn(1)–O(2)	116.8(5)
C(20)–Mn(2)–O(1)	120.7(5)	C(30)–Mn(2)–O(1)	85.9(5)
C(30)–Mn(2)–C(20)	110.0(6)	C(40)–Mn(2)–O(1)	108.0(5)
C(40)–Mn(2)–C(20)	125.0(6)	C(40)–Mn(2)–C(30)	96.6(5)
N(2)–Mn(3)–O(2)	60.8(4)	C(30)–Mn(3)–O(2)	107.7(6)
C(30)–Mn(3)–N(2)	133.1(5)	C(40)–Mn(3)–O(2)	120.7(4)
C(40)–Mn(3)–N(2)	113.1(5)	C(40)–Mn(3)–C(30)	111.1(6)
Mn(2)–O(1)–Mn(1)	137.2(3)	Mn(3)–O(2)–Mn(1)	114.3(5)
Mn(3)–C(30)–Mn(2)	67.2(4)	C(301)–C(30)–Mn(2)	152.5(12)
C(301)–C(30)–Mn(3)	113.9(9)	Mn(3)–C(40)–Mn(2)	71.6(4)
C(401)–C(40)–Mn(2)	116.1(7)	C(401)–C(40)–Mn(3)	123.7(10)
C(1)–O(1)–Mn(1)	86.5(8)	C(1)–O(1)–Mn(2)	125.1(8)
C(1)–N(1)–Mn(1)	92.7(8)	Si(1)–N(1)–Mn(1)	130.5(6)
Si(1)–N(1)–C(1)	136.7(8)	N(1)–C(1)–O(1)	118.7(12)
C(01)–C(1)–O(1)	113.8(12)	C(01)–C(1)–N(1)	127.4(10)
C(2)–O(2)–Mn(1)	146.4(7)	C(2)–O(2)–Mn(3)	91.2(8)
C(2)–N(2)–Mn(3)	94.3(8)	Si(2)–N(2)–Mn(3)	133.7(6)
Si(2)–N(2)–C(2)	131.6(9)	O(2)–C(2)–Mn(3)	58.1(7)
N(2)–C(2)–Mn(3)	55.5(8)	N(2)–C(2)–O(2)	113.6(13)
C(06)–C(2)–O(2)	117.1(11)	C(06)–C(2)–N(2)	129.2(11)
C(101)–C(10)–Mn(1)	119.8(10)	C(201)–C(20)–Mn(2)	125.3(9)



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in the imidate form I, most likely supported by the further bridging of the oxygen atoms.

It will be noted that Me_3SiNCO has not inserted into all the available Mn–C bonds; similar incomplete insertion of RNCO, where only one of the M–C groups react, has been observed for $MoO_2(mes)_2$[4] and $Zr(cp)_2Me_2$.[11] In the latter case steric factors were proposed to mitigate against co-ordination of a second $C_6H_{11}NCO$ ligand, thus preventing its insertion. Steric arguments in the present case may also be relevant in spite of the low co-ordination number of manganese(II), since both types of alkyl groups, neopentyl and trimethylsilyl, are bulky.

When an excess of Me_3SiNCO is used, a different compound $Mn_4(CH_2Bu^t)_2(\mu_3\text{-}NCO)_2[\mu\text{-}OC(CH_2Bu^t)N(SiMe_3)]_4$ **2** is obtained. A diagram of this molecule is shown in Fig. 2; some bond lengths and angles are given in Table 2. The presence of the NCO groups in the molecule was first suggested by the appearance of a strong band in the IR spectrum of 2166 cm^{-1}.

The centrosymmetric tetranuclear species comprises a planar, approximately square array of Mn atoms. Two of these, Mn(1) and its symmetry relative Mn(1′), carry a terminal neopentyl group. The four amide groups present bond in a fashion analogous to that found in the trinuclear species described above, chelating to one Mn and oxygen bridging along the Mn_4 square edge to another. The arrangement of these ligands is not cyclic, however, since the chelation of the two independent ligands occurs at one manganese atom, Mn(2). Atom Mn(1) is then co-ordinated on each side by bridging oxygens of the

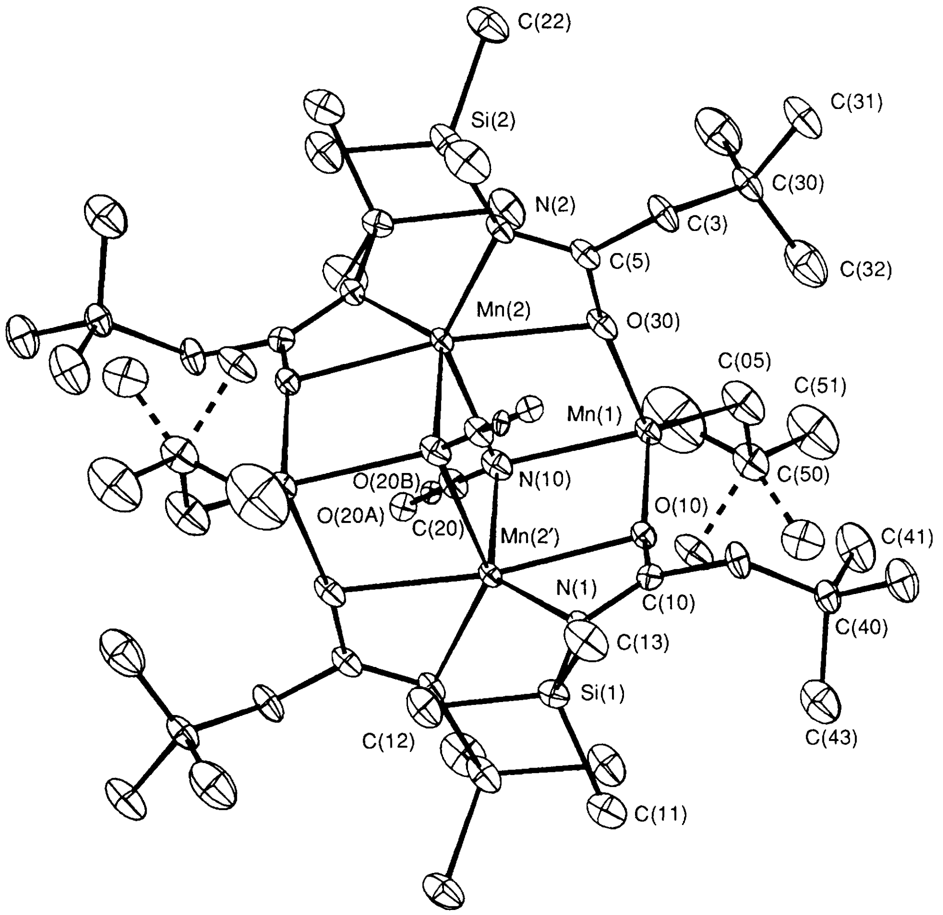
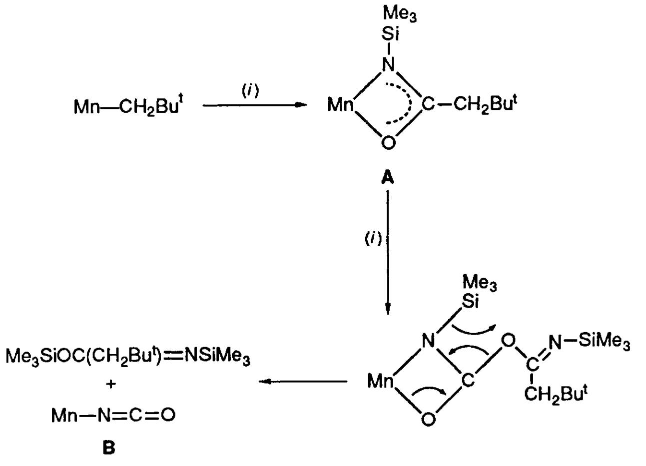


Fig. 2 The structure of $Mn_4(CH_2Bu^t)_2(\mu_3\text{-}NCO)_2[\mu\text{-}OC(CH_2Bu^t)N(SiMe_3)]_4$



Scheme 1 Possible mechanism for cleavage of the Si–N bond in Me_3SiNCO and initial formation of an MnNCO group by second insertion of Me_3SiNCO into the Mn–O bond of **A**. (*i*) Me_3SiNCO

amide functions. The molecule is then completed by the two triply bridging cyanates, one on each side of the Mn_4 square. The bridging is symmetrical and involves bonds to Mn(1), Mn(2) and Mn(2′) on one side, and Mn(1), Mn(2) and Mn(2′) on the other; Mn(1) and Mn(1′) are thus four-co-ordinate and Mn(2) and Mn(2′) six-co-ordinate. Both geometries are highly distorted, mainly as a result of the restrictions imposed by the chelate/bridging of the amides.

The co-ordination of the NCO ligand as *N*-bonded was confirmed by switching the O/N atoms in the refinement. The chosen arrangement gave the best combination of thermal parameters, although the situation is complicated by excessive vibration of the terminal atom of the three, the O atom, which is disordered over two close, but resolvable sites.

Since compound **2** has six neopentyl groups, four $SiMe_3$ and six NCO moieties, eight of each of these units would be expected had complete insertion of Me_3SiNCO into the available Mn–C bonds in the starting material occurred. As two unreacted CH_2Bu^t groups remain on Mn(1) and Mn(1′) in **2**, we can infer the loss of two $SiMe_3$ and two CH_2Bu^t groups in the synthesis reaction. The mechanism proposed in Scheme 1 can account for this loss by assuming second insertion of Me_3SiNCO into the Mn–O–C bond of the amido group first formed. There are numerous precedents for insertion of RNCO into alkoxide, MOR, groups;[12] also the product of a 'second' insertion of RNCO into the η^2-iminoacyl formed by insertion of RNC into $V(mes)_3(thf)$ has been structurally characterised.[6] The affinity for oxygen of the Me_3Si group could lead to a transfer from N to O atoms with the elimination of $(Me_3Si)N{=}C(CH_2Bu^t)(OSiMe_3)$; we have not identified this product unambiguously however.

The reaction of the bis(neopentyl)manganese with 2 equivalents per Mn atom of Bu^tNC and of PMe_3 in Et_2O gave a compound analysing correctly for $Mn[Bu^tCH_2C{=}NBu^t]_2(PMe_3)$ **3** but the mass, IR and EPR data were not informative. X-Ray-quality crystals could not be obtained nor could any product be obtained if the PMe_3 was omitted.

Chromium.—The reaction of $V(mes)_3(thf)$ with $C_6H_{11}NCO$ has been mentioned in ref. 6. The reaction of 3 equivalents of Bu^tNCO with $Cr(mes)_3(thf)$[13] leads similarly to insertion and formation of $Cr[OC(mes)NBu^t]_3$ **4** as green, paramagnetic, air and moisture sensitive crystals; none was of X-ray quality. Hydrolysis produces $(mes)C(O)NHBu^t$. The mass spectrum shows the parent ion of **3**. The IR spectra shows bands at 1613 and 1541 cm^{-1} that can be assigned as C–N and C–O stretches of the η^2-amido group respectively. The structure is evidently octahedral with three chelate, *O,N*-bonded OC(mes)NBu^t groups.

The reaction of Cr(mes)$_3$(thf) with 3 equivalents of Bu^{t}NC led to a green crystalline material but an unstable air-sensitive side product made purification difficult. If 1 equivalent of PMe$_3$ was added this difficulty was avoided, no PMe$_3$ appearing in the product Cr[(mes)C=NBu^t]$_3$ **5**.

Table 2 Selected bond lengths (Å) and angles (°) for Mn$_4$(CH$_2$Bu^t)$_2$(μ_3-NCO)$_2$[μ-OC(CH$_2$Bu^t)N(SiMe$_3$)]$_4$ *

O(10)–Mn(1)	2.073(6)	N(10)–Mn(1)	2.282(7)
O(30)–Mn(1)	2.070(6)	C(05)–Mn(1)	2.092(9)
O(10–Mn(2)	2.308(6)	N(10)–Mn(2)	2.298(7)
N(2)–Mn(2)	2.146(7)	N(1)–Mn(2)	2.176(7)
Mn(2)–O(30)	2.359(6)	Mn(2a)–N(10)	2.138(7)
C(5)–O(30)	1.306(7)	C(10)–O(10)	1.309(8)
C(20)–N(10)	1.225(9)	C(10)–N(1)	1.264(8)
O(20A)–C(20)	1.174(15)	O(20B)–C(20)	1.204(20)
Mn(2)–Mn(1)	3.393(4)	Mn(2)–Mn(2a)	3.484(4)
N(10)–Mn(1)–O(10)	84.1(3)	O(30)–Mn(1)–O(10)	97.7(3)
O(30)–Mn(1)–N(10)	85.4(3)	C(05)–Mn(1)–O(10)	130.1(3)
C(05)–Mn(1)–N(10)	123.5(4)	C(05)–Mn(1)–O(30)	122.8(4)
N(10)–Mn(2)–O(10)	78.7(3)	N(2)–Mn(2)–O(10)	126.1(3)
N(2)–Mn(2)–N(10)	99.7(3)	N(1)–Mn(2)–O(10)	58.5(3)
N(1)–Mn(2)–N(10)	136.4(2)	N(1)–Mn(2)–N(2)	111.7(3)
O(10)–Mn(2)–N(10a)	97.2(4)	N(10)–Mn(2)–N(10a)	82.0(3)
N(2)–Mn(2)–N(10a)	136.3(2)	N(1)–Mn(2)–N(10a)	94.8(3)
O(10)–Mn(2)–O(30)	170.0(4)	N(10)–Mn(2)–O(30)	91.9(3)
N(10a)–Mn(2)–O(30)	78.4(3)	N(2)–Mn(2)–O(30)	58.0(3)
N(1)–Mn(2)–O(30)	130.1(2)	Mn(2)–O(10)–Mn(1)	101.4(3)
C(10)–O(10)–Mn(1)	161.0(4)	C(10)–O(10)–Mn(2)	88.2(5)
Mn(2)–N(10)–Mn(1)	95.6(3)	C(20)–N(10)–Mn(1)	129.6(6)
C(20)–N(10)–Mn(2)	116.2(5)	Mn(2)–N(10)–Mn(2a)	98.0(3)
C(20)–N(10)–Mn(2a)	115.7(3)	Si(2)–N(2)–Mn(2)	130.7(3)
Si(1)–N(1)–Mn(2)	129.4(4)	C(10)–N(1)–Mn(2)	95.5(5)
C(5)–O(30)–Mn(1)	172.4(4)	Mn(1)–O(30)–Mn(2a)	100.5(3)
C(5)–O(30)–Mn(2a)	87.0(5)	C(3)–C(5)–O(30)	116.9(7)
N(2)–C(5)–O(30)	117.0(9)	C(50)–C(05)–Mn(1)	128.3(7)
N(1)–C(10)–O(10)	117.1(7)	C(4)–C(10)–O(10)	115.3(7)
C(4)–C(10)–N(1)	127.5(8)	C(40)–C(4)–C(10)	120.3(7)
O(20A)–C(20)–N(10)	168.0(10)	O(20B)–C(20)–N(10)	166.1(11)
O(20B)–C(20)–O(20A)	25.9(10)		

* Key to symmetry operations relating designated atoms to reference atoms at *x*, *y*, *z*: (a) $-x$, $1.0 - y$, $-z$.

Experimental

The general methods and instruments used have been described.[13] Microanalysis by Pascher, Remagen. Commercial chemicals were from Aldrich. Solvents were purified by standard methods and all operations were carried out under nitrogen or argon. Infrared spectra were recorded in KBr discs, mass spectra by electron impact (EI) and EPR X-band spectra were in toluene at 77 and 293 K.

The dialkyls [Mn(CH$_2$CMe$_2$Ph)$_2$]$_2$ and [Mn(CH$_2$Bu^t)$_2$]$_4$ were prepared as before[7a] and Cr(mes)$_3$(thf) by Stolze's method.[14] Interactions of hexane solutions of these alkyls with isocyanates other than Me$_3$SiNCO gave colourless products that gave the amides on hydrolysis as noted in the text.

Mn$_3$(CH$_2$Bu^t)$_2$[μ-OC(CH$_2$Bu^t)N(SiMe$_3$)]$_2$(μ-CH$_2$Bu^t)$_2$ **1**.—To a stirred solution of [Mn(CH$_2$Bu^t)$_2$]$_4$ (0.2 g, 1.02 mmol) in hexane (30 cm^3) at -78 °C was added 2 equivalents of Me$_3$SiNCO per Mn atom (0.27 cm^3) and the mixture allowed to warm to room temperature with stirring for 12 h. Removal of volatiles under vacuum and extraction of the residue with hexane (2 × 25 cm^3) followed by filtration and cooling of the solution at -20 °C gave colourless, very air-sensitive, X-ray-quality crystals. Yield: 0.11 g, 40%. M.p. 135–139 °C [Found (Calc.): C, 55.3 (55.5); H, 10.5 (10.2); N, 3.4 (3.4)%]. A further crop of crystals could be obtained after concentration and cooling. The compound is paramagnetic and gives only broad NMR lines while the EPR spectrum has a broad signal, $g \approx 2$. IR: 1646m(sh) and 1529s(br) cm^{-1}.

Mn$_4$(CH$_2$Bu^t)$_2$(μ_3-NCO)$_2$[μ-OC(CH$_2$Bu^t)N(SiMe$_3$)]$_4$ **2**.—Similarly but using 4 equivalents of Me$_3$SiNCO per Mn atom, extraction with hexane (2 × 30 cm^3), concentration (to 10 cm^3) and cooling gave X-ray-quality air-sensitive pale brown crystals. Yield: 0.13 g, 29%. M.p. 176–177 °C. Further crops can be obtained on concentration and cooling [Found (Calc.): C, 48.4 (48.1); H, 8.6 (8.7); N, 7.1 (6.9)%]. IR: 2166s (NCO), 1641m(sh) and 1532s(br) cm^{-1}. The EPR spectrum gave $g \approx 2$ as for **1**.

Mn[Bu^{t}CH$_2$C=NBu^t]$_2$(PMe$_3$) **3**.—To a stirred solution of [Mn(CH$_2$Bu^t)$_2$]$_4$ (0.2 g, 1.02 mmol) in toluene (30 cm^3) at -78 °C was added 2 equivalents per Mn atom of Bu^{t}NC (0.2 cm^3) and of PMe$_3$ (0.2 cm^3) and the mixture allowed to warm with stirring (24 h). Removal of volatiles under vacuum left a dark brown solid which was extracted with hexane (2 × 30 cm^3), filtered, concentrated (to 10 cm^3) and cooled (-20 °C)

Table 3 Crystal data, details of intensity measurements and crystal refinement

Formula	C$_{38}$H$_{86}$Mn$_3$N$_2$O$_2$Si$_2$	[C$_{24}$H$_{52}$Mn$_2$N$_4$O$_3$Si$_2$]$_2$
M	824.10	1 165.47
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	19.169(3)	11.288(1)
b/Å	11.997(2)	12.644(3)
c/Å	23.399(3)	14.027(3)
α/°	90	113.01(1)
β/°	110.46(1)	107.50(1)
γ/°	90	91.80(1)
U/Å^3	5 041.62	1 731.95
Z	4	1
D_c/g cm^{-3}	1.086	1.117
F(000)	1788	624
μ/cm^{-1}	7.84	7.89
Total no. of reflections	15 507	7 307
No. of unique reflections	7 719	4 553
No. of observed reflections [$F_o > 3\sigma(F_o)$]	2 996	3 094
No. of refined parameters	501	369
Weighting scheme paramater *g* in $w = 1/[\sigma^2(F) + gF^2]$	0.004	0
Final *R*	0.0458	0.0634
Final *R*	0.0476	0.0688

Table 4 Fractional atomic coordinates (× 10^4) for $Mn_3(CH_2Bu^t)_2[\mu\text{-}OC(CH_2Bu^t)N(SiMe_3)]_2(\mu\text{-}CH_2Bu^t)_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mn(1)	2315(1)	1604(1)	724(1)	C(010)	−659(9)	1921(12)	224(7)
Mn(2)	3499(1)	2322(2)	−388(1)	C(30)	2612(8)	4076(10)	−566(7)
Mn(3)	2000(1)	2509(2)	−817(1)	C(301)	2212(7)	5063(10)	−931(5)
O(1)	3292(4)	2101(5)	441(3)	C(40)	2682(6)	1198(8)	−1120(4)
N(1)	3001(6)	3031(7)	1163(4)	C(401)	2698(7)	−63(9)	−962(5)
C(1)	3469(7)	2844(9)	904(5)	C(011)	2396(8)	−1590(11)	1775(7)
O(2)	1530(4)	2114(6)	−103(3)	C(012)	3237(9)	47(13)	2020(7)
N(2)	840(5)	2090(7)	−1081(4)	C(013)	3089(10)	−1091(14)	1137(8)
C(2)	863(7)	1937(8)	−520(5)	C(021)	5588(8)	3293(12)	−765(7)
C(10)	2053(7)	159(10)	1132(6)	C(022)	4845(9)	1653(11)	−1146(7)
C(101)	2685(7)	−605(10)	1528(5)	C(023)	4248(8)	3460(12)	−1444(6)
C(20)	4583(8)	2826(13)	−377(6)	C(11)	2188(9)	5037(11)	1159(7)
C(201)	4820(7)	2851(9)	−911(5)	C(12)	2449(8)	3300(12)	2137(6)
Si(1)	2866(2)	4036(3)	1646(2)	C(13)	3678(7)	4852(10)	2138(5)
C(01)	4256(6)	3317(9)	1077(5)	C(21)	−283(8)	457(11)	−1807(6)
C(02)	4903(6)	2537(10)	1480(5)	C(22)	−571(8)	2980(13)	−1959(7)
C(03)	4846(7)	2440(11)	2115(5)	C(23)	613(9)	1917(15)	−2370(6)
C(04)	4876(6)	1374(9)	1214(5)	C(031)	2602(9)	6136(11)	−724(9)
C(05)	5624(7)	3075(11)	1521(6)	C(032)	1428(8)	5141(12)	−995(8)
Si(2)	128(2)	1870(4)	−1788(2)	C(033)	2168(12)	4900(18)	−1578(8)
C(06)	259(7)	1533(9)	−297(5)	C(041)	2059(8)	−418(10)	−760(6)
C(07)	−7(7)	2414(10)	83(5)	C(042)	3431(8)	−345(10)	−450(6)
C(08)	−245(10)	3461(12)	−264(8)	C(043)	2650(9)	−729(9)	−1524(6)
C(09)	596(8)	2672(14)	679(7)				

Table 5 Fractional atomic coordinates (× 10^4) for $Mn_4(CH_2Bu^t)_2(\mu_3\text{-}NCO)[\mu\text{-}OC(CH_2Bu^t)N(SiMe_3)]_4$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mn(1)	848(1)	3989(1)	1588(1)	C(51)	−407(18)	−2117(15)	3327(13)
Mn(2)	−12(1)	6307(1)	1061(1)	C(52)	−1280(21)	2408(19)	1953(16)
O(10)	1476(6)	5768(5)	2247(4)	C(53)	−1181(21)	3912(18)	2973(16)
N(10)	−770(7)	4353(6)	382(5)	C(53A)	114(26)	3948(23)	3926(19)
N(2)	−1651(7)	7008(6)	1326(5)	C(3)	3596(11)	2979(10)	101(9)
Si(2)	−2118(3)	7440(3)	2468(2)	C(30)	3915(11)	2284(10)	728(9)
C(21)	−763(12)	7436(12)	3584(8)	C(31)	5111(13)	1879(12)	758(11)
C(22)	−3494(13)	6445(11)	2232(10)	C(32)	2925(16)	1182(13)	126(12)
C(23)	−2457(13)	8942(11)	2892(9)	C(33)	3927(16)	2823(13)	1830(10)
N(1)	1719(7)	7493(6)	2238(5)	C(10)	2197(9)	6765(8)	2585(6)
Si(1)	2255(3)	8897(3)	2447(2)	C(4)	3539(10)	6881(9)	3303(7)
C(11)	2197(13)	9970(10)	3740(9)	C(40)	−3816(11)	6898(9)	4438(7)
C(12)	1123(13)	9124(11)	1336(9)	C(41)	5188(13)	−7085(12)	5018(9)
C(13)	3877(13)	9115(12)	2356(11)	C(42)	3298(15)	5811(12)	4419(10)
O(30)	1626(7)	3489(6)	350(5)	C43)	3295(14)	7820(12)	5089(9)
C(5)	2224(10)	3117(8)	−353(8)	C(20)	−1909(11)	4083(9)	130(8)
C(05)	591(14)	2928(12)	2364(11)	O(20A)	−3014(17)	3968(14)	−192(13)
C(50)	−286(13)	2933(10)	2893(8)	O(20B)	−2953(26)	3671(20)	−3(19)

* Partial occupancies: C(53) 0.5075, (C53A) 0.4925, O(20A) 0.6061 and O(20B) 0.3939.

to give a brown crystalline solid. Yield: 0.05 g (11%) [Found (Calc.): C, 63.0 (62.9); H, 11.0 (11.2)%].

$Cr[OC(mes)NBu^t]_3$ **4**.—To a stirred solution of $Cr(mes)_3(thf)$ (0.25 g, 0.52 mmol) at −78 °C were added 3 equivalents of Bu^tNCO (0.18 cm^3). On warming to room temperature the colour changed from deep blue to deep green. After removal of solvent and extraction of the residue with hexane (3 × 10 cm^3), filtration, concentration (to 10 cm^3) and cooling (−20 °C) gave green crystals. Yield: 0.26, 71%. M.p. 160 °C (decomp.) [Found (Calc.): C, 70.2 (70.4); H, 9.1 (8.5); N, 5.5 (5.2)%]. Mass spectrum (EI): *m*/*z* 706; 691 (*M* − CH_3). IR: 1613m(sh) and 1541s cm^{-1}. EPR: $g \approx 2$ (77 K).

$Cr[(mes)C{=}NBu^t]_3$ **5**.—To a stirred solution of $Cr(mes)_3(thf)$ (0.2 g, 0.42 mmol) in tetrahydrofuran (30 cm^3) at −78 °C were added 3 equivalents of Bu^tNC (0.14 cm^3) and PMe_3 (0.1 cm^3) and the mixture allowed to warm to room temperature. After 2 h the volatiles were removed and the green residue extracted with hexane (2 × 25 cm^3). Concentration (to 30 cm^3) and cooling (−20 °C) gave dark green crystals. Yield: 48%. M.p. 84–87 °C [Found (Calc.): C, 76.7 (76.6); H, 9.3 (9.2); N, 6.4 (6.4)%]. IR: 1629m and 1595s [ν(C=N)]. EPR: $g_x = 5.5$, $g_y = 2.1$ and $g_z = 2.0$.

X-Ray Crystallography.—Crystals of both compounds were sealed under argon in thin-walled glass capillaries. Cell dimensions and intensity data were obtained using a FAST TV area diffractometer as outlined previously.[15] The structures were solved by direct methods, developed *via* Fourier difference syntheses and refined *via* full-matrix least squares. All atoms were refined anisotropically and hydrogens were included in idealised positions. Absorption corrections were applied using the DIFABS procedure.[16] Crystal data and experimental details are collected in Table 3. Final fractional atomic coordinates are given in Tables 4 and 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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