Synthesis and Reactivity of Manganese(II) Dialkylamido Complexes. Crystal and Molecular Structure of $[Mn_3(\mu\text{-}NEt_2)_6(\mu\text{-}Cl)_2\{Li(thf)_2\}_2]\cdot C_7H_{16}$ (thf = tetrahydrofuran) and $[Mn_2(\mu\text{-}NPr^i_2)_2(NPr^i_2)_2]$†

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By reaction of $MnCl_2$ with $LiNR_2$ (R = Me, Et or Pr^i) the corresponding dialkylamido complexes were prepared. The compounds $[Mn_3(\mu\text{-}NEt_2)_6(\mu\text{-}Cl)_2\{Li(thf)_2\}_2]$ **1** (thf = tetrahydrofuran), $[Mn_2(\mu\text{-}NPr^i_2)_2(NPr^i_2)_2]$ **2** and $[Mn_2(NMe_2)_4(LiCl)]$ **3** were isolated, and the molecular and crystal structures of **1** and **2** determined by single-crystal X-ray diffraction methods. Crystal data: **1**, monoclinic, space group *C*2/*c*, *a* = 18.81(1), *b* = 20.45(2), *c* = 18.15(2) Å, β = 113.31(8)°, *R* = 0.063; **2**, monoclinic, space group $P2_1/c$, *a* = 9.361(2), *b* = 9.724(2), *c* = 16.883(2) Å, β = 100.91(1)°, *R* = 0.046. The pentanuclear compound **1** consists of a trinuclear $Mn_3(NEt_2)_6Cl_2$ core, built up by edge-sharing of the three co-ordination tetrahedra, which are connected by four bridging diethylamido ligands, and terminally bonded to the $Li(thf)_2$ moieties *via* chloride and amido bridges. The homoleptic compound **2** contains two three-co-ordinated manganese atoms, joined by two bridging dialkylamido groups, with an overall planar arrangement of the Mn_2N_4 skeleton. Both **1** and **2** react with CO_2 to give the expected dialkylcarbamato complexes. The reactions of **1**–**3** with CO result in reductive carbonylation to $[Mn(CO)_5]^-$. The compounds also catalyse the selective carbonylation of secondary amines to dialkylformamides, a 87% yield of $Et_2NC(O)H$ being obtained from $NHEt_2$ and CO at atmospheric pressure, in 24 h, in the presence of **1**, at room temperature.

During our studies on transition-metal dialkylcarbamato complexes[1] we became interested in homoleptic manganese(II) dialkylcarbamato complexes[1h] and, before discovering the possibility to use manganocene $[Mn(\eta^5\text{-}C_5H_5)_2]$ as starting material,[1h,i] had planned to prepare them by formal CO_2 insertion into the metal–nitrogen bond of manganese dialkylamides.[2] However, dialkylamido complexes of manganese were totally unknown. A literature survey indicated that stable manganese amides had been obtained only with special amido groups, characterized by low nucleophilicity and steric hindrance and by the absence of β-hydrogen atoms, *i.e.* $N(SiMe_3)_2$[3] and $N(C_6H_2Me_3\text{-}2,4,6)[B(C_6H_2Me_3\text{-}2,4,6)_2]$.[4] Previous attempts to prepare diethylamido derivatives from $MnCl_2$ and $LiNEt_2$ did not give definite products.[5] As far as the middle and late transition elements are concerned, our knowledge of metal–nitrogen bonds is still limited,[6] and this contrasts with the idea that catalytic functionalization of amines may involve formation of such bonds,[6b] and with the growing opinion that the design of catalytic cycles may be aided by a detailed knowledge of the metal–nitrogen bond.[7] The synthesis of homoleptic metal dialkylamido complexes $M(NR_2)_n$ for elements of groups higher than 6 (chromium) has been considered only in recent years. Reported examples include $[FeL_2(NPh_2)_2]$,[8] $[Co_2(NPh_2)_4]$,[9] $[Ni_2(NPh_2)_4]$[9] and $[Cu_4(NR_2)_4]$,[10] while no derivatives of this kind are known for heavier congeners in the same groups, and, moreover, no detailed information about the chemistry of these systems is available.

We here report the synthesis of some manganese(II) dialkylamido complexes (alkyl = Me, Et or Pr^i), together with the X-ray crystal and molecular structure of two of them, and discuss their reactivity towards carbon dioxide and monoxide. Some of these compounds are catalytic precursors for the carbonylation of secondary amines to dialkylformamides. A preliminary communication of the structure of the diethylamido derivative has appeared.[11]

Results and Discussion

Synthesis and Structure.—The straightforward metathetical reaction of metal salts with lithium amides[6a] proved to be successful, provided the appropriate experimental conditions were used to isolate the products, see equations (1)–(3). The

$$3\,MnCl_2 + 6\,LiNEt_2 \xrightarrow{thf} \underset{\mathbf{1}}{[Mn_3(\mu\text{-}NEt_2)_6(\mu\text{-}Cl)_2\{Li(thf)_2\}_2]} + 4\,LiCl \quad (1)$$

$$2\,MnCl_2 + 4\,LiNPr^i_2 \longrightarrow \underset{\mathbf{2}}{[Mn_2(\mu\text{-}NPr^i_2)_2(NPr^i_2)_2]} + 4\,LiCl \quad (2)$$

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† Di-μ-chloro-1:2-κ²*Cl*; 4,5-κ²*Cl*-hexakis(μ-diethylamido)-1:2κ²*N*; 2:3κ⁴*N*;3,4κ⁴*N*;4:5κ²*N*-tetrakis(tetrahydrofuran)-1κ²*O*,5κ²*O*-1,5-dilithiumtrimanganese–heptane (1/1) and bis(μ-diisopropylamido)-κ²*N*-bis[(diisopropylamido-κ*N*)manganese].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI unit employed: atm = 101325 Pa.

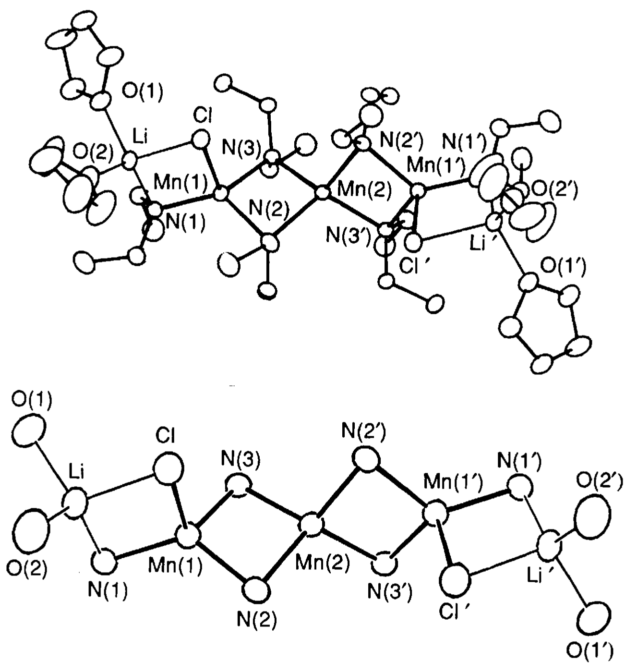

Fig. 1 A view (upper) of the pentanuclear complex $[Mn_3(\mu\text{-}NEt_2)_6(\mu\text{-}Cl)_2\{Li(thf)_2\}_2]\cdot C_7H_{16}$ **1**. Primed atoms are related to unprimed ones by a two-fold crystallographic axis ($2 - x, y, \frac{3}{2} - z$). In the lower view, the carbon chains have been omitted for clarity

$$2\,MnCl_2 + 4\,LiNMe_2 \longrightarrow \underset{\mathbf{3}}{[Mn_2(NMe_2)_4(LiCl)]} + 3\,LiCl \quad (3)$$

reactions were performed at room temperature. The products gave correct elemental analyses, and their IR spectra (see Experimental section) exhibited the expected absorptions due to the metal–amido moieties.[12] The composition of compounds **1**–**3** was a consequence of the synthetic method, of the solvent used and of their solubility properties. Reaction (1) was carried out in a heptane–tetrahydrofuran (thf) medium (2:1 v/v), and the complex $[Mn_3(\mu\text{-}NEt_2)_6(\mu\text{-}Cl)_2\{Li(thf)_2\}_2]$ **1** was obtained in 54% yield by cooling the filtered solution at about −30 °C. Use of larger heptane:thf volume ratios did not result in the separation of more lithium chloride than required by the stoichiometry of equation (1), and recrystallization of the final product did not change its halogen content. The isopropyl derivative $[Mn_2(\mu\text{-}NPr^i{}_2)_2(NPr^i{}_2)_2]$ **2** is well soluble in heptane, and could be obtained free from chloride; the metathetical reaction (2) did not occur in pure heptane, and it was therefore carried out in a 10:1 mixture of heptane and thf. The reaction of $MnCl_2$ and $LiNMe_2$ in neat thf, finally, led to a very sparingly soluble amido complex of formula $[Mn_2(NMe_2)_4(LiCl)]$ **3**. Crystallization of **3** was not possible, due to its low solubility in common organic solvents, and the presence of manganese-bonded dimethylamido groups was established on the basis of its IR spectrum, which shows the same absorptions [1220m (CH_3 deformation), 1125s (CH_3 rocking or NC_2 asymmetric stretching), 1050m (CH_3 rocking or NC_2 asymmetric stretching) and 910s cm^{-1} (NC_2 symmetric stretching)] observed for other $M(NMe_2)_n$ complexes.[12] On the basis of the established connectivities of compounds **1** and **2** (see below), co-ordination of the chloride to manganese appears to be likely while the very low solubility of **3** may be explained by an ionic formulation of the type $Li^+[Mn_2(NMe_2)_4Cl]^-$.

Table 1 Selected interatomic distances (Å) in $[Mn_3(\mu\text{-}NEt_2)_6(\mu\text{-}Cl)_2\{Li(thf)_2\}_2]\cdot C_7H_{16}$ **1**

Mn(1)$\cdots$Mn(2)	2.917(2)	Li–O(1)	1.98(2)
Mn(1)–Cl	2.444(2)	Li–O(2)	1.99(2)
Mn(1)–N(1)	2.06(1)	Li–N(1)	2.07(2)
Mn(1)–N(2)	2.089(7)	N(1)–C(11)	1.47(2)
Mn(1)–N(3)	2.16(1)	N(1)–C(13)	1.44(2)
Mn(2)–N(2)	2.20(1)	N(2)–C(21)	1.48(2)
Mn(2)–N(2′)	2.20(1)	N(2)–C(23)	1.47(2)
Mn(2)–N(3)	2.152(8)	N(3)–C(31)	1.47(1)
Mn(2)–N(3′)	2.152(8)	N(3)–C(33)	1.47(2)
Cl–Li	2.38(2)	N(2)$\cdots$N(3)	3.12(1)

Numbers in parentheses in all crystallographic tables are estimated standard deviations in the least significant digit.

Table 2 Selected bond angles (°) in $[Mn_3(\mu\text{-}NEt_2)_6(\mu\text{-}Cl)_2\{Li(thf)_2\}_2]\cdot C_7H_{16}$ **1**

Cl–Mn(1)–N(1)	97.3(3)	Mn(1)–Mn(2)–Mn(1′)	160.0(1)
Cl–Mn(1)–N(2)	104.3(3)	Mn(1)–N(1)–C(11)	119.0(8)
Cl–Mn(1)–N(3)	106.1(3)	Mn(1)–N(1)–C(13)	116.5(7)
N(1)–Mn(1)–N(2)	126.2(4)	Mn(1)–N(1)–Li	89.2(7)
N(1)–Mn(1)–N(3)	125.7(4)	C(11)–N(1)–C(13)	111(1)
N(2)–Mn(1)–N(3)	94.6(3)	C(11)–N(1)–Li	108.4(8)
N(2)–Mn(2)–N(2′)	122.4(3)	C(13)–N(1)–Li	110(1)
N(2)–Mn(2)–N(3)	91.5(3)	Mn(1)–N(2)–C(21)	116.2(7)
N(2)–Mn(2)–N(3′)	112.6(3)	Mn(1)–N(2)–C(23)	117.3(6)
N(2′)–Mn(2)–N(3)	112.6(3)	C(21)–N(2)–C(23)	108.4(9)
N(2′)–Mn(2)–N(3′)	91.5(3)	Mn(2)–N(2)–C(21)	116.4(7)
N(3)–Mn(2)–N(3′)	129.5(3)	Mn(1)–N(2)–Mn(2)	85.6(3)
Mn(1)–Cl–Li	73.8(5)	Mn(2)–N(2)–C(23)	111.6(8)
Cl–Li–O(1)	106.8(9)	Mn(1)–N(3)–Mn(2)	85.3(3)
Cl–Li–O(2)	103.6(9)	Mn(1)–N(3)–C(31)	110.2(7)
Cl–Li–N(1)	99.3(7)	Mn(1)–N(3)–C(33)	113.0(8)
O(1)–Li–O(2)	102.1(8)	Mn(2)–N(3)–C(31)	116.0(7)
O(1)–Li–N(1)	121(1)	Mn(2)–N(3)–C(33)	119.1(6)
O(2)–Li–N(1)	122(5)	C(31)–N(3)–C(33)	110.6(9)

With the aim of obtaining a chloride-free derivative, we treated $LiNMe_2$ with manganocene, equation (4). Lithium

$$[Mn(\eta^5\text{-}C_5H_5)_2] + 2\,LiNMe_2 \xrightarrow{\text{thf}} 2\,Li(\eta^5\text{-}C_5H_5) + Mn(NMe_2)_2 \quad (4)$$

cyclopentadienide was recovered almost quantitatively from the filtered solution, but the sparingly soluble manganese complex was too unstable to be isolated. It was stabilized by reaction with 1,2-bis(diphenylphosphino)ethane (dppe, see Experimental section); however, although the IR bands due to the metal–amido group were present and comparable with those displayed by **3**, thus suggesting the presence of $Mn-NMe_2$ groups in both compounds, complete characterization of the dppe adduct failed. While **3** is a flesh coloured solid [as usual for high-spin manganese(II) compounds],[13] both **1** and **2** are orange-red. The extreme sensitivity to air of our amido complexes, both in solution and in the solid state, together with the fact that manganese(III) derivatives are usually highly coloured,[13] may suggest the presence of trace amounts of an oxidized impurity.

Both the fact that **1**–**3** are the first reported dialkylamido complexes of manganese, and their complex formulation, justified a deeper investigation of their structure; thus, complexes **1** and **2**, which gave suitable crystals, were studied by X-ray diffraction methods.

Compound **1** crystallizes in discrete pentanuclear units, with one molecule of lattice heptane. A view of the complex is shown in Fig. 1, together with the numbering scheme used, while selected interatomic distances and bond angles are in Tables 1 and 2, respectively. The molecule consists of two equivalent halves, related by a crystallographically imposed two-fold axis of rotation passing through the central manganese atom, the overall molecular symmetry being C_2. The structure can be best described as built up by a trinuclear core $Mn_3(NEt_2)_6Cl_2$, with two bridging diethylamido groups and two bridging chlorides co-ordinated to two terminal $Li(thf)_2$ moieties. Each manganese atom lies at the centre of a distorted tetrahedron, with angles ranging from 91.5(2) [N(2)–Mn(2)–N(3)] to 129.5(3)°

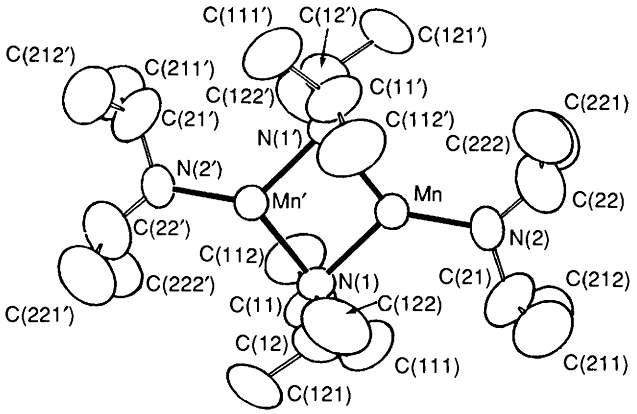

Fig. 2 Molecular structure of $[Mn_2(\mu\text{-}NPr^i{}_2)_2(NPr^i{}_2)_2]$ **2**. Primed atoms are related to unprimed ones by an inversion centre

Table 3 Selected interatomic distances (Å) in $[Mn_2(\mu\text{-}NPr^i{}_2)_2(NPr^i{}_2)_2]$ **2**

Mn(1)···Mn(1′)	2.844(1)	C(11)–C(111)	1.54(1)
Mn(1)–N(1)	2.140(5)	C(11)–C(112)	1.42(1)
Mn(1)–N(1′)	2.138(5)	C(12)–C(121)	1.52(1)
Mn(1)–N(2)	1.925(6)	C(12)–C(122)	1.45(1)
N(1)···N(1′)	3.195(7)	C(21)–C(211)	1.47(1)
N(1)–C(11)	1.49(1)	C(21)–C(212)	1.53(1)
N(1)–C(12)	1.47(1)	C(22)–C(221)	1.52(1)
N(2)–C(21)	1.51(2)	C(22)–C(222)	1.51(2)
N(2)–C(22)	1.40(2)		

Table 4 Interatomic angles (°) in $[Mn_2(\mu\text{-}NPr^i{}_2)_2(NPr^i{}_2)_2]$ **2**

Mn(1′)–Mn(1)–N(2)	172.2(2)	N(1)–C(11)–C(112)	114.9(7)
N(1)–Mn(1)–N(1′)	96.6(2)	C(111)–C(11)–C(112)	110.2(8)
N(1)–Mn(1)–N(2)	126.5(2)	N(1)–C(12)–C(121)	115.7(7)
N(1′)–Mn(1)–N(2)	136.2(2)	N(1)–C(12)–C(122)	112.7(7)
Mn(1)–N(1)–Mn(1′)	83.4(2)	C(121)–C(12)–C(122)	110.7(7)
Mn(1)–N(1)–C(11)	116.2(4)	N(2)–C(21)–C(211)	115.0(8)
Mn(1)–N(1)–C(12)	114.5(5)	N(2)–C(21)–C(212)	113.4(7)
C(11)–N(1)–C(12)	109.7(5)	C(211)–C(21)–C(212)	113.9(8)
Mn(1)–N(2)–C(21)	117.1(4)	N(2)–C(22)–C(221)	116.7(9)
Mn(1)–N(2)–C(22)	130.2(6)	N(2)–C(22)–C(222)	114.3(7)
C(21)–N(2)–C(22)	112.6(7)	C(221)–C(22)–C(222)	108.9(9)
N(1)–C(11)–C(111)	114.2(6)		

Table 5 Comparison of metal–nitrogen bond distances (Å) in structurally related manganese(II) amido complexes

Complex	Mn–N$_T$[a]	Mn–N$_B$[a]	Ref.
$[Mn_3(\mu\text{-}NEt_2)_6(\mu\text{-}Cl)_2\{Li(thf)_2\}_2]$	2.06(1)	2.089(7) 2.16(1) 2.20(1) 2.152(8)	*b*
$[Mn_2(\mu\text{-}NPr^i{}_2)_2(NPr^i{}_2)_2]$	1.925(6)	2.140(5) 2.138(5)	*b*
$[Mn_2\{\mu\text{-}N(SiMe_3)_2\}_2\{N(SiMe_3)_2\}_2]$	1.999(3)[c] 1.997(3)[c]	2.174(3)[c] 2.170(3)[c]	3*b*
$[Mn\{N(SiMe_3)_2\}_2(thf)]$	1.99(2)		3*c*
$[Mn\{N(SiMe_3)_2\}_2]$	1.95(2)[d]		3*a*

[a] T = Terminal, B = bridging. [b] This work. [c] Structure determined at 140 K. [d] Structure determined in the gas phase.

[N(3)–Mn(2)–N(3′)]; the trimeric core is obtained by edge sharing of the three tetrahedra through four bridging diethylamido groups. The chain is completed by two tetrahedrally co-ordinated lithium atoms, whose geometrical parameters are very similar to those reported for some analogous lithium compounds,[14] the presence of metal-bonded LiCl being apparently a common feature of transition-metal amido or alkoxo complexes.[15] The quasi-linear Mn_3 unit [Mn(1′)–Mn(2)–Mn(1) is 160.0(1)°] can be compared with that observed in the trimeric mesitylmanganese(II) complex $[Mn_3(C_6H_2Me_3\text{-}2,4,6)_6]$,[16] while a unique example in amido complexes is provided by $[Be_3(\mu\text{-}NMe_2)_4(NMe_2)_2]$.[17] In the latter case, chain termination was suggested to be caused by the steric requirements of the four groups in the NMe_2 bridges, preventing a correct alignment for polymer formation. In our case no such effect is believed to operate, due to the longer M–N distance and the lower steric hindrance of the ethyl groups; thus, chain termination may be ascribed to the presence of the lithium-bearing chlorine atoms. The angles around the nitrogen atoms [ranging from 108.4(4) to 119.1(3)°] are consistent with a nearly regular tetrahedral geometry, the only exception being the smaller angles inside the Mn–N–Mn and Mn–N–Li bridges [85.3(3), 85.6(3) and 89.2(7)°, respectively]. Homoleptic metal dialkylamido complexes, when the oxidation number of the metal is lower than four, may be co-ordinatively unsaturated, and thus prone to decomposition pathways such as valence disproportionation[18] or β-hydrogen abstraction.[6b,19] Adopting NR_2-bridged structures or co-ordination of additional neutral ligands may be ways to stabilize the system. The presence of lithium chloride in the structure of **1** presumably has the effect of stabilizing the system by maintaining the co-ordination number of four around each manganese atom.

An interesting question thus arose with regard to the behaviour of the bis(isopropyl)amido group of compound **2**, less sterically demanding than the bis(trimethylsilyl)amido group in $[Mn_2\{N(SiMe_3)_2\}_4]$.[3b,c] The molecular structure of compound **2** was shown to consist of discrete dinuclear units (see Fig. 2), having the same connectivity as that in $[Mn_2\{N(SiMe_3)_2\}_4]$.[3b,c] Tables 3 and 4 contain selected interatomic distances and bond angles, respectively. The stabilization of three-co-ordinated manganese by the $NPr^i{}_2$ ligand is noteworthy, since the availability of β-hydrogen atoms in the alkyl chains is usually regarded as prerequisite for thermally accessible decomposition pathways. Although this can be a useful rule, its generality appears to have been overemphasized, as suggested also by the isolation of a monomeric chromium(III) amido complex with the $NPr^i{}_2$ ligand.[20a] Also, a dimeric chromium(II) diisopropylamide, $[Cr_2(NPr^i{}_2)_4]$, has recently been isolated and characterized.[20b]

The dimer is characterized by a nearly planar arrangement of the Mn_2N_4 backbone, with a virtual D_{2h} molecular symmetry. The two manganese atoms, related through a crystallographic inversion centre, are joined by two bridging diisopropylamido groups, and terminally bonded to the remaining $NPr^i{}_2$ ligands. The co-ordination geometry around each manganese atom is distorted trigonal planar with angles of 96.2(2), 126.5(2) and 136.2(2)°, respectively. The terminal nitrogen atom has a regular trigonal-planar co-ordination, with angles of 117.1(4), 130.2(6) and 112.6(7)°, respectively; the bridging nitrogen has a highly distorted tetrahedral geometry, with angles of 109.7(5) (C–N–C), 114.5(5) and 116.2(4) (Mn–N–C) and 83.4(2)° (Mn–N–Mn), respectively. The Mn–$NPr^i{}_2$ bond distances are similar to those reported for the previously discussed NEt_2 derivative, and a comparison with the known amido complexes of manganese is provided in Table 5.

In $[Mn_2(NPr^i{}_2)_4]$ both Mn–N$_T$ (N$_T$ = terminal amide) and Mn–N$_B$ (N$_B$ = bridging amide) distances are considerably shorter than those of the corresponding silyl derivative, studied at a lower temperature.[3b,c] Although the correlation between bond distance and bond strength is a debatable matter, the comparison could suggest that the generally observed easier accessibility of the trimethylsilyl derivatives may be related to kinetic inertness rather than to a thermodynamic stabilization of the M–N bond. Generally, M–NR_2 bonds are believed to be weaker, with respect to M–C or M–OR bonds, as suggested, for middle and late transition metals, by the few available thermodynamic data.[7,20c–e]

The metal–metal distances are 2.917(2) and 2.844(1) Å in the μ-NEt_2 and in the μ-NPr^i_2 complexes **1** and **2**, respectively. These values seem to exclude a direct interaction within the metallic centres, and can be compared with the values of 2.811(1) and 2.851(3) Å found in the μ-$N(SiMe_3)_2$[3b] and $[Mn_3(C_6H_2Me_3\text{-}2,4,6)_6]$[16] complexes, respectively. A remarkable feature of compounds **1** and **2** is, however, their high degree of magnetic coupling. The measured magnetic moments for the μ-NEt_2 and the μ-NPr^i_2 complexes are 6.47 and 3.68, respectively. These values correspond to average magnetic moments per manganese atom of 3.74 and 2.60 respectively, considerably reduced with respect to the high-spin value of 5.91 found for $[Mn\{N(SiMe_3)_2\}_2(thf)]$.[3c] Similar antiferromagnetic coupling has been observed for $[Mn_2\{N(SiMe_3)_2\}_4]$ (μ_{eff} = 3.34)[3b] and for some other amido-bridged metal complexes.[9]

Reactivity.—Both the NEt_2 and NPr^i_2 dialkylamido complexes show the expected reactivity towards CO_2. A thf solution of **2** readily adsorbed CO_2 at room temperature, and after evaporation of the solvent the carbamato complex $[\{Mn(O_2CNPr^i_2)_2\}_n]$ could be isolated, see equation (5). It is

$$\frac{n}{2}[Mn_2(NPr^i_2)_4] + nCO_2 \longrightarrow [\{Mn(O_2CNPr^i_2)_2\}_n] \quad (5)$$

to be noted that this compound could not be obtained from $MnCl_2$.[1h] In the case of compound **1**, retention of LiCl was observed in the product [equation (6)]. Attempts to purify the

$$[Mn_3(\mu\text{-}NEt_2)_6(\mu\text{-}Cl)_2\{Li(thf)_2\}_2] \xrightarrow{CO_2} [Mn_3(O_2CNEt_2)_6(LiCl)_2] \quad (6)$$

mixed chlorocarbamato complex, or to substitute the halide ligands with carbamato groups, were unsuccessful. The molecular complexity of this product is not known; on the other hand, its low solubility may suggest a polynuclear μ-Cl,μ-O_2CNEt_2 structure. Some suggestions about this structure come from the known[1h] connectivity of $[Mn_6(O_2CNEt_2)_{12}]$: the hexanuclear structure, which contains four five- and two six-co-ordinated manganese(II) centres, is held together by bridging diethylcarbamato ligands. In the present case, the five-co-ordinated manganese centres may be saturated by chlorides, leading to an ionic structure of the type $4Li^+$ $[Mn_6(O_2CNEt_2)_{12}Cl_4]^{4-}$.

Although several unsaturated molecules, other than CO_2, can insert into the metal–nitrogen bond,[6a] migratory insertion of CO in transition-metal amides is quite rare. The known examples include dialkylamido complexes of Th,[21] U,[21] Mo,[22] W,[23] Rh[24] and Pt,[25] and in the first three cases the corresponding carbamoyl complexes have been structurally characterized. Carbamoyl compounds from alkali-metal amido derivatives,[26] are, on the contrary, commonly encountered, and synthetic applications of the easily accessible dialkylcarbamoyllithium derivatives have been considered.[27] A similar chemistry has also been discovered for lithium cuprates(I) $Li[Cu(NR_2)_2]$ reacting with CO under mild conditions to give $Li(Cu(OCNR_2)_2]$.[28] It is noteworthy that the corresponding amides of copper(I) $CuNR_2$ are unreactive towards CO.[28b]

High-spin manganese(II) is rather unique among its 3d congeners, owing to its d^5 electron configuration and the absence of crystal-field stabilization. In this respect, its chemistry resembles that of the corresponding Group 2 and 12 cations, *i.e.* those of d^0 and d^{10} electronic configurations.[13] We therefore wondered whether the Mn–NR_2 bond could exhibit a reactivity similar to that of lithium amides, and therefore we treated our complexes with carbon monoxide.

Tetrahydrofuran solutions of **1**, **2** or **3** were exposed to CO at atmospheric pressure, and the course of the reaction was monitored by IR spectroscopy: a similar behaviour was observed in each case, but only a weak absorption could be detected around 1610 cm^{-1}, presumably due to a dialkylcarbamoyl derivative, to be compared with the carbonylation of lithium diethylamide.* A band was formed initially around 1680 cm^{-1}, attributed to the corresponding dialkylformamides $HC(O)NR_2$ by comparison with pure samples (the presence of the formamides was confirmed by mass spectra of the reaction mixtures). This was followed by the appearance of metal–carbonyl bands at 2045w, 1965s, 1940ms, 1910s, 1895w and 1860m cm^{-1} for **3**, 2045w, 1965s, 1940ms, 1910m, 1900(sh) and 1860s cm^{-1} for **1** and 1960w, 1930w, 1895ms and 1860s cm^{-1} for **2**. The intensity of the absorption around 1680 cm^{-1} gradually decreased, as did the intensity of the bands above 1900 cm^{-1}. After some days only the bands at 1895 and 1860 cm^{-1}, due to the $[Mn(CO)_5]^-$ anion, were present. No attempt at product isolation was made. The IR spectra suggest the formation of intermediate carbonyl complexes of manganese, which on the basis of their ν_{CO} values, can be tentatively suggested to be manganese(I) derivatives. A comparison can be made† with the compounds $[Mn(CO)_3(NHBu^n{}_2)_2(CONHBu^n)]$[29a] ($\nu_{CO}$ 2030 and 1955 cm^{-1}) and $[Mn(CO)_4(NH_2Et)(CONHEt)]$[29b] [$\nu_{CO}$ (pentane) 2076w, 1985s and 1938 cm^{-1}].

Manganese-catalysed Carbonylation of Secondary Amines.—Once it had been established that carbonylation of the manganese(II) dialkylamido complexes did not produce significant amounts of the corresponding dialkylcarbamoyl complexes, and that infrared reduction to the $[Mn(CO)_5]^-$ anion was taking place, the question remained as to what was the corresponding oxidation product and how the dialkylformamides (responsible for the IR absorption at 1680 cm^{-1}) had been formed in the initial stages of the carbonylation reaction.

The possible role of lithium in compound **1** was considered first. Lithium amides[31] have been reported to catalyse the carbonylation of secondary amines to dialkylformamides, and at 200 atm CO and 150 °C a 70% conversion of $HNEt_2$ into the corresponding formamide was obtained in the presence of LiPh or LiBu as catalyst.

We therefore decided to run some reactions of secondary amines with CO in the presence of one of the compounds **1**–**3**. The unexpected outcome of these experiments was the ability to promote catalytic carbonylation reactions. In the presence of compound **1** or **2**, thf solutions of dialkylamines are selectively carbonylated to dialkylformamides, at room temperature and at atmospheric pressure of CO [equation (7)]. The results are

$$NHR_2 + CO \xrightarrow{[Mn]} HC(O)NR_2 \quad (7)$$

collected in Table 6; no evidence for the formation of other carbonylated products could be obtained. Compound **2** showed a lower activity than **1**; yields of dialkylformamides are moderate ($HNMe_2$) to good ($HNEt_2$), and monoalkylamines were found to be totally unreactive.

Some indirect evidence was gathered about the possible nature of the catalyst. First, the presence of lithium in the catalytic cycle was found not to be essential. Our reaction was not greatly affected by the lithium-complexing agent 12-crown-

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* In agreement with the literature,[26] we found that thf solutions of $LiNEt_2$ absorb CO at room temperature and at atmospheric pressure, the resulting diethylcarbamoyl derivative being distinctly evidenced by a strong carbonyl stretching vibration at 1625 cm^{-1}.

† The room-temperature reaction of $[Mn(CO)_4(NH_2Bu^n)(CONHBu^n)]$ with CO gives $[Mn_2(CO)_{10}]$.[29b] Also, the routine preparation of $[Mn_2(CO)_{10}]$ from $Mn(O_2CMe)_2$ and AlR_3 in ethers[30] may possibly proceed by a concerted reductive elimination of a manganese–alkyl intermediate and carbonylation of the metallic fragment.

Table 6 Catalytic carbonylation of amines to formamides in the presence of manganese(II) amido complexes[a]

Complex	Amine	Reaction time/h	Conversion (%)	Mol product per mol of Mn
1	NHEt$_2$	24	87	39
1[b]	NHEt$_2$	96	73	31
1[c]	NHEt$_2$	24	70	28
1[b,d]	NHEt$_2$	24	0	0
1	NHMe$_2$	24	60	33
1	NHPr$^i_2$	24	20	8
1[b]	NH$_2$Pr^n	24	0	0
1	NH$_2$(C$_6$H$_{11}$)	24	0	0
2	NHEt$_2$	70	83	38
2	NHPr$^i_2$	70	10	4
2	NH$_2$(C$_6$H$_{11}$)	70	0	0

[a] Solvent thf, molar ratio amine:manganese = 50:1, manganese concentration about 10^{-2} mol dm^{-3}, room temperature, 1 atm CO, spectroscopic yields. [b] Preformed solutions, directly obtained from MnCl$_2$ and LiNEt$_2$, were used, without isolation of the amido complex. [c] The complexing agent 12-crown-4 (3.4 mol per mol of Li) was added before the admission of CO. [d] Lithium bromide (13 mol per mol of Mn) was added before the admission of CO. This salt is soluble in thf; MnCl$_2$ also is soluble in thf in the presence of excess of LiBr.

4[*] (1,4,7,10-tetraoxacyclododecane) and the catalytic effect obtained with the lithium-free **2** indicates that manganese alone is the active centre.[†] By contrast, the catalytic activity was suppressed by addition of an excess of LiBr. This salt possibly has the effect of saturating the co-ordination sphere of the metal cation, presumably forming the $[Mn(NR_2)^2Br_2]^{2-}$ anion. Reaction with CO$_2$ of the final mixtures from the catalytic reactions, using **1** as catalyst precursor, led to the manganese carbamato complex of equation (6), thus suggesting that at least part of the manganese was still present as a dialkylamido complex.

Catalytic carbonylation of amines is an established reaction,[34] also used industrially,[35] and the products range from formamides to ureas or oxalamides. Our reaction presents, however, some novel features. Two main types of catalyst have been reported for the carbonylation of amines: basic catalysts, such as lithium amides[29] or alkali-metal alkoxides,[31,36] and metal carbonyls or their precursors;[34,37] high temperatures and/or high pressures are normally used. Transition metal-based catalysts are believed to operate by nucleophilic attack of amine[‡] on co-ordinated carbon monoxide.[34] In the present case, no evidence is available for the formation of manganese(II) carbonyl species and, to the best of our knowledge, no example of such compounds has been reported other than some unstable derivatives with tertiary phosphine ligands.[39] The presence of manganese(I) carbonyl species was, on the other hand, suggested in the catalytic carbonylation of primary amines to dialkylureas in the presence of [Mn$_2$(CO)$_{10}$];[30,40] it is indeed a striking contrast that in that case dialkylamines were unreactive, whereas the opposite is true in the present case.[§] We propose that the present catalysis could be explained by an ionic mechanism, with carbon monoxide being attacked by the strongly nucleophilic anion R$_2$N$^-$, thus implying that the Mn–NR$_2$ system has a reactivity similar to that of LiNR$_2$.[26,31] The ionic character of the actinide–amide bond has been suggested to have an important role in the CO insertion reactions of these Th and U complexes.[21]

It is interesting to compare the manganese-catalysed carbonylation of secondary amines to dialkylformamides, see equation (7), and the carbonylation of manganese(II) dialkylamides to give [Mn(CO)$_5$]$^-$ eventually. In the former process, manganese(II) dialkylamides are treated with CO in the presence of free amine in large excess, and this situation appears to be convenient to avoid reductive carbonylation of the transition metal. In the latter process, free amine is absent. Reduction to [Mn(CO)$_5$]$^-$ requires the oxidation of one of the reagents. A possible candidate is CO itself giving dialkylurea co-ordinated to Mn^{2+}, but we could not find any evidence for the presence of urea in our reaction mixtures (see Experimental section). A second possibility is an oxidation process involving the alkyl chains on nitrogen. This hypothesis is in agreement with the mechanism proposed for the decomposition of the unstable cobalt(II) diethylamido complexes to metallic cobalt;[¶] the oxidation of the dialkylamido group should lead to double-bond formation and to free amine. Assuming a similar mechanism in our system, the carbonylation of this amine would account for the noticeable amount of dialkylformamide observed after exposure of the manganese(II) dialkylamido complexes to CO (see Experimental section).

Conclusion

We have demonstrated that dialkylamido complexes of manganese(II) can be prepared, and have structurally characterized two of them. We have also shown that these complexes can be used for catalytic purposes; they are the first reported transition-metal catalytic precursors for the efficient carbonylation of amines under ambient conditions.

Experimental

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified argon, and solvents were carefully dried prior to use. Both CO and CO$_2$ were purchased as high-purity gases and used as such. Metal dichlorides were dehydrated by refluxing the commercial salt with thionyl chloride for several hours, followed by careful washing with heptane and drying. Dimethylamine was vacuum transferred in a Schlenk tube over molecular sieves and stored at about −30 °C, while NHEt$_2$, NHPr$^i_2$, NH$_2$Pr and NH$_2$(C$_6$H$_{11}$) were distilled from sodium or sodium–potassium alloy and kept over sodium sand. Manganocene was prepared by a published procedure.[41] The complexing agent 12-crown-4 was a Fluka product, dried over molecular sieves prior to use. The lithium derivatives LiNR$_2$ were obtained as colourless, pyrophoric solids after dropping a LiMe (R = Pr^i) or LiBu (R = Me or Et) solution over the amine at about −80 °C, followed by evaporation of the solvent and excess of amine and prolonged drying under reduced pressure. The manganese was determined by ethylenediaminetetraacetate titration, while chloride was analysed by the Volhard method, and thf was determined in acidic aqueous solution by gas chromatography using a Carbowax 20 M column with Bu^{n}OH as internal standard and a Dani 8400 gas chromatograph. Carbon dioxide in the dialkylcarbamato complexes was determined by gas-volumetric measurement after decomposition with 20% aqueous H$_2$SO$_4$. Infrared spectra were measured with a Perkin-Elmer 283

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[*] This crown ether has been shown to be effective in separating the lithium cation from organometallic anions such as [EPh$_2$]$^-$ (E = P or As).[32] Dioxane-bonded sodium atoms have been found to participate in a covalent As–Na–As bonding mode in [{Na(AsPh$_2$)(C$_4$H$_8$O$_2$)}$_n$].[33]

[†] The LiNEt$_2$–HNEt$_2$–CO–thf system was found to have a modest catalytic activity, and a 10% yield of HC(O)NEt$_2$ was obtained over a comparable reaction time (24 h), corresponding to 6 mol of CO per mol of lithium.

[‡] A similar mechanism has been postulated also for the palladium-catalysed double carbonylation of amines.[38]

[§] This is hardly surprising since we are dealing with two completely different processes, the catalytic carbonylation of primary amines to dialkylureas involving a redox process with dihydrogen formation.[30]

[¶] By repeating this experiment[5] under a CO atmosphere, we isolated the [Co(CO)$_4$]$^-$ anion in 55% yield, in place of metallic cobalt.

analyser. Magnetic susceptibilities were measured in the solid state using a Faraday balance.

Synthesis of [$Mn_3(\mu\text{-}NEt_2)_6(\mu\text{-}Cl)_2\{Li(thf)_2\}_2]\cdot C_7H_{16}$, **1**·$C_7H_{16}$.—Anhydrous $MnCl_2$ (2.209 g, 17.6 mmol) was suspended in a mixture of heptane (50 cm^3) and thf (25 cm^3), and $LiNEt_2$ (2.728 g, 34.5 mmol) was added. An exothermic reaction took place, the mixture was stirred at room temperature for 15 h, and the formation of a colourless solid and of an orange solution was observed. The solid was filtered off and identified as LiCl (55% yield) by chloride analysis. After cooling to about −30 °C, orange crystals slowly separated from the filtered solution; they were collected by filtration and briefly dried in a stream of argon (3.415 g, 54% yield) (Found: Cl, 6.6; Mn, 15.4; thf, 25.0. $C_{47}H_{108}Cl_2Li_2Mn_3N_6O_4$ requires Cl, 6.6; Mn, 15.4; thf, 26.9%). IR (Nujol mull): 2980–2840vs, 2680w, 1460s, 1380s, 1360s, 1335(sh), 1300w, 1280w, 1170m, 1140s, 1100s, 1070(sh), 1045s, 1030(sh), 990s, 910(sh), 895m, 840ms, 790m, 660w, 535m, 515m and 425w cm^{-1}. Magnetic susceptibility at 293 K: $\chi_M{}^{corr} = 17\,849 \times 10^{-6}$ cgs units ($\chi_{SI} = \chi_{cgs} \times 4\pi \times 10^{-6}$) (diamagnetic correction = -745×10^{-6} cgs units), corresponding to $\mu_{eff} = 6.47$; $\chi_{Mn}{}^{corr}$ is 5950×10^{-6} cgs units corresponding to μ_{eff} 3.74. The product is extremely sensitive to air and moisture, both in the solid state and in solution.

In a separate experiment the reaction was performed in neat thf and a clear orange solution was obtained; heptane was then added dropwise: formation of a colourless precipitate was observed, which continued until the added heptane reached a 2:1 (v/v) ratio with respect to thf. No further precipitate was formed by adding more heptane.

X-Ray Data Collection and Structure Solution of [$Mn_3(\mu\text{-}NEt_2)_6(\mu\text{-}Cl)_2\{Li(thf)_2\}_2]\cdot C_7H_{16}$.—The crystals are very sensitive to loss of lattice heptane, and some problems encountered in the structure determination probably stem from this fact. Among several crystals, removed from the solvent and sealed as fast as possible under argon in glass capillaries, one of approximate dimensions 0.3 × 0.3 × 0.5 mm proved to be the best. Even in this case the standard deviations of the lattice constants were quite high and the diffraction intensity at higher θ angles was poor.

Crystal data. $C_{47}H_{108}Cl_2Li_2Mn_3N_6O_4$, M = 1071.1, monoclinic, space group $C2/c$ (no. 15 in ref. 42), a = 18.81(1), b = 20.45(2), c = 18.15(2) Å, β = 113.31(8)° (by least-squares refinement of 25 reflections), graphite-monochromatized Mo-Kα radiation (λ = 0.7107 Å), U = 6411(20) $Å^3$, Z = 4, D_c = 1.109 g cm^{-3}, μ(Mo-Kα) = 7.055 cm^{-1}, $F(000)$ = 2316.

Data collection and processing. CAD4 diffractometer, ω scan with scan range $3 < \theta < 23°$; 293 K; 6270 reflections measured; 2216 having $I > 3\sigma(I)$ were retained as observed, and 1850 symmetrically independent observations remained after merging.

Structure analysis and refinement. The structure was solved by direct methods,[43] which gave the approximate positions for the Mn and Li atoms, the chlorine and part of the ligands. One manganese atom occupies a special positon 4*e* in space group no. 15, and the resulting molecule shows point symmetry $C2$. After refinement[43a,b] of this partial structure a Fourier difference synthesis revealed all non-hydrogen atoms with acceptable geometry except those of the lattice heptane. Full-matrix refinement at this stage gave an agreement factor R = 0.140 with isotropic and 0.099 with anisotropic thermal parameters.

While the thf groups co-ordinated to Li could be located with quite high thermal parameters for the corresponding atoms but with acceptable geometry, no complete localization of the lattice heptane could be achieved. The presence of about one molecule of heptane per trimer was known from analytical data; on the other hand, the 18 $Å^3$ rule[44] suggested a content of over 40 atoms in the asymmetric unit. This indicates that the remaining solvent shows considerable disorder. After anisotropic refinement of the [$\{Mn_{1.5}Cl(NEt_2)_3Li(thf)_2\}_2$] moiety, a Fourier difference map showed four relatively high peaks (about 1.5 e $Å^{-3}$), one of them being in the $\bar{1}$ position. Owing to the low quality of the crystal and the relatively small number of observations, we refined these peaks isotropically as carbon atoms of a heptane molecule and did not try more sophisticated models for the disorder. We are aware of the fact that the resulting geometry causes unrealistic bond angles and distances within the lattice heptane.

We used the original data set and applied an empirical absorption correction.[45] The agreement factor at this stage of refinement was 0.078. Hydrogen atoms were calculated for the ethyl groups (C–H 0.95 Å) and included in structure-factor calculations. In the final refinement a correction for secondary extinction (applied on F_c)[46] was made, giving R = 0.063, R' = 0.078 [$w = 1/\sigma^2(I)$], with 1850 observations for 272 parameters. Atomic coordinates are in Table 7.

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

Synthesis of [$Mn_2(NPr^i{}_2)_4$] **2**.—Manganese dichloride (2.137 g, 17.0 mmol) was suspended in a mixture of heptane (50 cm^3) and thf (5 cm^3). The presence of a small amount of thf was found to be necessary for the reaction to take place, although it has no substantial effect on the relative solubility of the reactants and products. Then, $LiNPr^i{}_2$ (3.530 g, 33.0 mmol) was added, and the mixture stirred at room temperature for 24 h. The colourless solid thus formed was removed by filtration (LiCl, 92% yield), and the red-orange solution evaporated to dryness in order to remove all the thf. The solid residue was taken up in heptane (50 cm^3), and the resulting red solution filtered and cooled to about −30 °C for 24 h. Orange-pink crystals were thus obtained, collected by filtration and dried under reduced pressure (1.159 g, 27% yield) (Found: Cl, 0; Mn, 23.0. $C_{24}H_{56}Mn_2N_4$ requires Cl, 0; Mn, 21.5%). IR spectrum (Nujol mull): 2980–2850vs, 2600w, 1460s, 1380s, 1360(sh), 1350(sh), 1340(sh), 1330(sh), 1310mw, 1160s, 1140s, 1110m, 1000w, 980m, 930ms, 900m, 830w, 805m, 780m, 590m, 575(sh), 560(sh), 500w, 450w, 425w, 400w and 330w cm^{-1}. Magnetic susceptibility at 291 K: $\chi_M{}^{corr} = 5816 \times 10^{-6}$ cgs units (diamagnetic correction -360.4×10^{-6} cgs units), corresponding to $\mu_{eff} = 3.68$; $\chi_{Mn}{}^{corr} = 2908 \times 10^{-6}$ cgs units, corresponding to $\mu_{eff} = 2.60$. The product is pyrophoric and, when stored at room temperature, decomposes slowly to a black tar. It can be, otherwise, safely stored under argon at about −30 °C for months.

X-Ray Data Collection and Structure Solution of [$Mn_2(\mu\text{-}NPr^i{}_2)_2(NPr^i{}_2)_2$].—Owing to the extreme sensitivity of this compound to air, conventional Schlenk or vacuum-handling techniques were not suitable; crystal manipulations could successfully be carried out in a glove-box equipped with forced argon circulation and continuous oxygen monitoring. A crystal was chosen and sealed in a glass capillary for X-ray data collection.

Crystal data. $C_{24}H_{56}Mn_2N_4$, M = 510.6, monoclinic, space group $P2_1/c$ (no. 14 in ref. 42), a = 9.361(2), b = 9.724(2), c = 16.883(2) Å, β = 100.91(1)° (by least-squares fit of 20 reflections in the range θ 17–31°), graphite-monochromatized Cu-Kα radiation (λ = 1.541 Å), U = 1509.0 $Å^3$, Z = 2, D_c = 1.124 g cm^{-3}, crystal dimensions 0.5 × 0.35 × 0.25 mm, μ(Cu-Kα) = 69.5 cm^{-1}, $F(000)$ = 556.

Data collection and processing. CAD4 diffractometer, ω scan technique, with $6 < \theta < 52$, 293 K. 2423 Reflections were measured, and after Lorentz and polarization corrections, 1394 having $I > 3\sigma(I)$ were retained as observed, which were corrected for absorption[45] and merged to give 1030 independent reflections.

Structure analysis and refinement. The manganese atom was located from a Patterson map, and successive Fourier difference syntheses revealed all the remaining non-hydrogen atoms. Re-

Table 7 Fractional atomic coordinates of $[Mn_3(\mu\text{-}NEt_2)_6(\mu\text{-}Cl)_2\{Li(thf)_2\}_2]\cdot C_7H_{16}$, **1**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mn(1)	0.834 6(1)	0.077 05(9)	0.698 7(1)
Mn(2)	1.000	0.052 3(1)	0.750
Cl	0.813 0(2)	0.171 3(2)	0.609 6(2)
O(1)	0.625 6(5)	0.119 4(5)	0.488 0(5)
O(2)	0.642 2(6)	0.222 4(5)	0.618 2(6)
N(1)	0.722 0(5)	0.065 9(5)	0.687 5(5)
N(2)	0.928 8(5)	0.104 2(4)	0.802 7(5)
N(3)	0.899 2(5)	0.007 4(4)	0.660 7(5)
C(11)	0.680 0(7)	0.006 0(7)	0.650 8(7)
C(12)	0.696 2(9)	−0.053 5(8)	0.707 4(9)
C(13)	0.705 6(7)	0.085 4(8)	0.755 1(8)
C(14)	0.620 2(9)	0.094(1)	0.738(1)
C(21)	0.929 9(6)	0.077 7(7)	0.879 1(6)
C(22)	0.913 3(7)	0.005 9(7)	0.873 7(7)
C(23)	0.948 3(7)	0.174 3(7)	0.813 9(7)
C(24)	0.893 3(9)	0.216 7(8)	0.832(1)
C(31)	0.887 1(7)	0.019 5(7)	0.576 6(6)
C(32)	0.804 4(7)	0.007 3(8)	0.515 2(7)
C(33)	0.880 8(7)	−0.060 9(6)	0.671 7(7)
C(34)	0.925 9(8)	−0.112 3(7)	0.647 6(9)
C(41)	0.566 0(9)	0.073 9(9)	0.448 9(9)
C(42)	0.540(1)	0.084(1)	0.362 2(9)
C(43)	0.587(1)	0.137(1)	0.349 0(9)
C(44)	0.642(1)	0.154 4(9)	0.424 1(9)
C(51)	0.582(1)	0.257(1)	0.565(2)
C(52)	0.591(2)	0.323 7(9)	0.575(1)
C(53)	0.652(2)	0.329(1)	0.647(2)
C(54)	0.679(1)	0.269(1)	0.676(1)
C(91)	0.391(2)	0.139(2)	0.536(2)
C(92)	0.345(2)	0.181(2)	0.527(3)
C(93)	0.296(2)	0.214(2)	0.505(2)
C(94)	0.250	0.250	0.500
Li	0.689(1)	0.139(1)	0.602(1)

Table 8 Fractional atomic coordinates of $[Mn_2(\mu\text{-}NPr^i{}_2)_2(NPr^i{}_2)_2]$ **2**.

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mn(1)	0.119 3(1)	0.092 4(1)	0.006 20(6)
N(1)	−0.040 2(5)	0.027 3(5)	−0.094 9(3)
N(2)	0.262 1(6)	0.234 8(6)	0.006 6(4)
C(11)	0.012 9(9)	−0.061 6(8)	−0.154 8(5)
C(12)	−0.130 0(9)	0.138 6(8)	−0.136 7(5)
C(21)	0.255 6(9)	0.315 7(9)	−0.070 6(5)
C(22)	0.375 4(9)	0.278(1)	0.067 9(6)
C(111)	0.115(1)	0.011(1)	−0.202 6(5)
C(112)	0.074(1)	−0.189 0(9)	−0.123 9(5)
C(121)	−0.267(1)	0.094(1)	−0.194 6(6)
C(122)	−0.164(1)	0.244(1)	−0.081 7(7)
C(211)	0.210(1)	0.460(1)	−0.066 8(6)
C(212)	0.389(1)	0.296(1)	−0.108 9(6)
C(221)	0.500(1)	0.178(1)	0.092 5(7)
C(222)	0.326(1)	0.329(1)	−0.142 9(6)

finement with anisotropic thermal parameters for all the non-hydrogen atoms converged to $R = 0.063$. At this stage the 28 hydrogen atoms were included with a riding model, and in the last refinement cycles a correction for secondary extinction[46] was applied. A final electron-density map did not show any peaks higher than 0.28 e Å^{-3}, and the refinement converged to $R = 0.046$, $R' = 0.05$ [$w = 1/\sigma^2(I)$], with 1030 reflections for 137 parameters. Atomic coordinates are in Table 8.

Reaction between $MnCl_2$ *and* $LiNMe_2$. *Synthesis of* $[Mn_2(NMe_2)_4(LiCl)]$ **3**.—A suspension of anhydrous $MnCl_2$ (0.526 g, 4.18 mmol) in thf (256 cm^3) was treated at room temperature with $LiNMe_2$ (0.409 g, 8.02 mmol). In an exothermic reaction, the manganese halide dissolved completely in a few minutes, forming a clear orange solution. Soon after a flesh-coloured solid began to precipitate. This was collected by filtration and dried under reduced pressure (346 mg). Analytical data suggested the $[Mn_2(NMe_2)_4(LiCl)]$ formulation (Found: Cl, 9.9; Mn, 34.6; Mn/Cl, 2.3. $C_8H_{24}ClLiMn_2N_4$ require Cl, 10.8; Mn, 33.4%; Mn/Cl, 2.0). The infrared spectrum of this solid (Nujol mull) showed absorptions at 1220m, 1125s, 1050m, 910vs and 470w cm^{-1}.

Reaction between $[Mn(\eta^5\text{-}C_5H_5)_2]$ *and* $LiNMe_2$.—To a thf solution (50 cm^3) of $LiNMe_2$ (0.515 g, 10.1 mmol) was added manganocene (0.940 g, 5.10 mmol). An immediate reaction took place, with formation of a clear pink solid. After 1 h the solution was filtered. Evaporation to dryness of the slightly yellow filtered solution gave $Li(\eta^5\text{-}C_5H_5)$ (0.596 g, 82% yield), identified by comparison of its IR spectrum with that of an authentic sample. The isolated pink solid was unstable towards solvent loss, and decomposition to a brown powder was observed after a short treatment under reduced pressure. It was therefore shaken with a thf solution of 1,2-bis(diphenylphosphino)ethane (dppe) (40 cm^3, 0.25 mol dm^{-3}) and filtered again. The resulting dark pink solid was stable under reduced pressure and was dried. Reproducible analytical data could not be obtained, but its IR spectrum (Nujol) showed, in addition to those due to dppe, absorptions very close to those of the product obtained from $MnCl_2$ and $LiNMe_2$ (1220m, 1130vs, 1045m, 910vs and 400vw cm^{-1}).

Reaction of $[Mn_3(\mu\text{-}NEt_2)_6(\mu\text{-}Cl)_2\{Li(thf)_2\}_2]\cdot C_7H_{16}$ *with* CO_2.—Compound **1** (0.235 g) was dissolved in thf (10 cm^3), and the resulting orange solution exposed to CO_2 at atmospheric pressure. After 30 min the absorption of gas had ceased, a colourless solid precipitated, and the solution became colourless. The solvent was removed under reduced pressure, and a colourless solid (0.108 g) remained. Its IR spectrum (Nujol) was identical with that of $[Mn_6(O_2CNEt_2)_{12}]$,[1h] but its elemental composition was in agreement with the formulation $[Mn_3(O_2CNEt_2)_6(LiCl)_2]$ (Found: Cl, 7.4; CO_2, 28.0; Mn, 18.0. $C_{30}H_{60}Cl_2Li_2Mn_3N_6O_{12}$ requires Cl, 7.5; CO_2, 27.9; Mn, 17.4%). This product was poorly soluble in ethers or aromatic hydrocarbons, and pure $Mn(O_2CNEt_2)_2$ could not be obtained by recrystallization, chloride always being present. It was unaffected by heating with $NHEt_2$ in a CO_2 atmosphere.

Reaction of $[Mn_2(NPr^i{}_2)_4]$ *with* CO_2.—The orange manganese derivative (0.316 g, 1.24 mmol) was dissolved in thf (15 cm^3), and CO_2 was admitted into the flask. Fast decolouration of the orange solution was observed, and a clear yellowish solution was obtained after a few minutes. Evaporation to dryness left a nearly colourless vitreous solid (0.164 g), whose IR spectrum as a Nujol mull was identical to that of $Mn(O_2CNPr^i{}_2)_2$,[1h] and which had a satisfactory elemental analysis (CO_2, Mn) for this composition.

Reaction of Compounds **1**–**3** *with* CO.—The behaviour of the three compounds was very similar, and only the reaction of **1** is reported as an example; the three cases are compared in the Results and Discussion section.

The pentanuclear complex **1** (0.176 g, 0.16 mmol) was dissolved in thf (10 cm^3), to give a clear orange solution, and exposed to carbon monoxide at atmospheric pressure. Slow absorption of gas was observed, paralleled by a gradual change in colour of the solution from orange to yellow and by the separation of a small amount of a colourless solid (isolated by filtration and identified as LiCl). After 2.5 h the IR spectrum of the solution showed, in the carbonyl stretching region, only the typical absorption of $Et_2NC(O)H$ at 1680m cm^{-1}. After 9 h new bands were present at 2045w, 1965s, 1940ms, 1910m, 1900(sh) and 1860s cm^{-1}, together with a weak absorption around 1610 cm^{-1} suggestive of a Mn–$CONR_2$ moiety. While the aspect of the solution remained unchanged, gas absorption slowed down and the IR spectrum continued to change. After 24 h it displayed bands at 1965m, 1895s + 1860vs {due to $[Mn(CO)_5]^-$}, 1680mw $[Et_2NC(O)H]$, and 1610wm cm^{-1}. After some days only the carbonyl bands of $[Mn(CO)_5]^-$ were observed. No definite product could be isolated from the solution, but the presence of $[Mn(CO)_5]^-$ was confirmed by evaporation of the volatiles [including $Et_2NC(O)H$] and by treatment of the solid orange residue with a few drops of 37% HCl solution, followed by extraction of $[MnH(CO)_5]$ with heptane and air oxidation to $[Mn_2(CO)_{10}]$.

In a separate experiment, gas-volumetric measurements indicated absorption of 2.3 mol of CO per mol of manganese after 24 h, and one of these was found to be fixed in $Et_2NC(O)H$ by spectroscopic determination of the formamide concentration. A similar test for compound **2** indicated absorption of 1.6 mol of CO per mol of manganese after 24 h, 0.5 mol of CO being present as $Pr^i{}_2NC(O)H$.

Reaction between $CoCl_2$ *and* $LiNEt_2$ *under* CO.—The compound $LiNEt_2$ (0.642 g, 8.12 mmol) and $CoCl_2$ (0.513 g, 3.95 mmol) were added to a thf solution (20 cm^3) saturated with CO and cooled to about −80 °C; the cooling bath was then removed. An immediate reaction was observed, with formation of a dark brown solution. Gas absorption began at −80 °C and continued until room temperature was reached. The brown-black solution was stirred under CO for 24 h, after which no gas absorption was evident. The IR spectrum of the final solution had bands in the carbonyl stretching region at 2000w(sh), 1980s, 1930m(sh), 1885vs and 1680w cm^{-1}. The volatiles were removed under reduced pressure and the black gummy residue taken up in water (20 cm^3). The filtered, brown, aqueous solution was treated with an excess of NBu_4Br, and a light brown solid precipitated, was collected and identified as $[NBu_4][Co(CO)_4]$[47] (0.865 g, 55% yield based on $CoCl_2$).

Catalytic Carbonylation of Amines.—All the experiments were conducted under the same conditions, namely thf as solvent at room temperature and at atmospheric pressure of carbon monoxide. The reaction was followed by measuring the gas absorption, and yields were determined spectroscopically from the intensity of the CO stretching absorption of the dialkylformamide (ε = 1000 dm^3 mol^{-1} cm^{-1}). A detailed description of one of the experiments is presented.

A flask (250 cm^3) was charged with thf (25 cm^3) and NEt_2H (3.550 g, 48.54 mmol, 5 cm^3) and the solution was saturated with CO. Then the manganese complex **1** was added (0.398 g, 0.37 mmol). Gas absorption started almost immediately, and continued steadily for several hours. Finally (24 h) a perfectly clear, extremely air-sensitive, orange solution was obtained. Infrared and GC–MS analyses showed $Et_2NC(O)H$ to be the only carbonyl species present. Reaction of this solution with CO_2 afforded an insoluble solid which was collected by filtration. Its IR spectrum as a Nujol mull showed the absorptions observed in the spectrum of $[Mn_3(O_2CNEt_2)_6(LiCl)_2]$.

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