DALTON

Nucleophilic substitution *vs*. acid–base reactions of $[Mn\{N(SiMe_3)_2\}_2]\cdot 2thf$; syntheses and structures of $2[Li(thf)_4]^+[Mn(C_{12}H_8N)_4]^{2-}\cdot C_6H_5Me$ and $[Mn(C_{12}H_8N)_2]\cdot 3thf$ (thf = tetrahydrofuran, $C_{12}H_8N$ = carbazol-9-yl)

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The ion-separated complex $2[Li(thf)_4]^+[Mn(C_{12}H_8N)_4]^{2-}$ **1** has been obtained from the nucleophilic substitution reaction of $[Mn\{N(SiMe_3)_2\}_2]\cdot 2thf$ with $Li[C_{12}H_8N]$ (1 : 4 equivalents) (thf = tetrahydrofuran, $C_{12}H_8N$ = carbazol-9-yl), and the molecular species $[Mn(C_{12}H_8N)_2]\cdot 3thf$ **2** from the acid–base reaction of $[Mn\{N(SiMe_3)_2\}_2]\cdot 2thf$ and $C_{12}H_8NH$ (1 : 2 equivalents). They are among the few amidomanganese(II) complexes containing simple (sterically undemanding) dialkyl- or diaryl-amido groups to be characterised. The crystal structures of both were determined: **1** contains the first tetraamidomanganese(II) dianion and **2** possesses the highest co-ordination number for Mn^{II} in such a compound.

Previous work has shown that the reactions of transition- and main-group metal bis(trimethylsilyl)amido complexes, $[M_x\{N(SiMe_3)_2\}_y]$, with weaker organic acids can be used in the preparation of a wide range of metalloorganic complexes.[1] However, we recently extended the utility of these reagents by illustrating that nucleophilic substitution of the $(Me_3Si)_2N$ groups in Group 12 and 13 silylamide complexes with various organic anions is an effective route to a broad range of Group 12 and 13 metal complexes.[2] It should be noted that Lappert and co-workers[3] had employed a similar approach to $E[CH(SiMe_3)_2]_2$ using substitution of $E[N(SiMe_3)_2]_2$ (E = Si or Ge). This approach allows the incorporation of organic groups for which the conjugate acids are not acidic enough to react directly with the metal silylamides, so that organometallic complexes as well as metalloorganic compounds can be accessed. The ease of substitution of the $(Me_3Si)_2N$ groups in these species has allowed, for example, the preparation of the homoleptic cadmium phosphide $2[Li(thf)_4]^+[Cd_4(PPh_2)_{10}]^{2-}$ (thf = tetrahydrofuran),[2d] a complex which appears to be impossible to prepare by existing means in the presence of halide ions.[4] In general, the outcome of the nucleophilic substitution reactions of metal silylamides is controlled by the strength of the organic nucleophiles employed, the presence of Lewis-base solvation and the potential nature of the Group 12 or 13 metals.

We report here the extension of our previous work on main-group metal silylamides to transition metals, and make the comparison of the reactivity of $[Mn\{N(SiMe_3)_2\}_2]\cdot 2thf$ towards nucleophilic substitution (with R^-) [equation (1)]

$$[Mn\{N(SiMe_3)_2\}_2] + 2LiR \longrightarrow MnR_2 + 2\,Li[N(SiMe_3)_2] \quad (1)$$

and the reaction with the corresponding organic acid (RH) [equation (2)].

$$[Mn\{N(SiMe_3)_2\}_2] + 2RH \longrightarrow MnR_2 + 2NH(SiMe_3)_2 \quad (2)$$

Results and Discussion

The ion-separated complex $2[Li(thf)_4]^+[Mn(C_{12}H_8N)_4]^{2-}\cdot C_6H_5Me$ **1** was obtained from the nucleophilic substitution reaction of $[Mn\{N(SiMe_3)_2\}_2]\cdot 2thf$ with $Li[C_{12}H_8N]$ (1 : 1–4 equivalents) ($C_{12}H_8N$ = carbazol-9-yl) and the molecular species $[Mn(C_{12}H_8N)_2]\cdot 3thf$ **2** was the product of the acid–base reaction of $[Mn\{N(SiMe_3)_2\}_2]\cdot 2thf$ with $[C_{12}H_8NH]$ (1 : 2 equivalents), both in thf–toluene solvent. Complex **1** can also be obtained by the reaction of **2** with $Li[C_{12}H_8N]$ (1 : 2 equivalents) (see Experimental section). Although the reactions of $[Mn\{N(SiMe_3)_2\}_2]$ with various organic acids have been employed previously in the preparation of manganese(II) alkoxides, amides, selenides, phosphides and arsenides,[1] to our knowledge this current work is the first study involving a nucleophilic substitution reaction of this precursor. The formation of **1** and **2** illustrates, with the same organic functionality being incorporated, that the nature of the products can be kinetically controlled by the mode of reaction of the metal silylamide precursor.

The basic characterisation of complex **2** was by elemental analysis. The ^1H NMR spectrum was paramagnetically broadened, however, it was sufficiently clear to discern the aromatic and thf ligand environments. This preliminary characterisation gave an initial indication of the differing outcomes of the nucleophilic substitution and acid–base reactions producing both complexes. The stability of these complexes (**1** decomposing at > 300 °C and **2** at *ca.* 120 °C), which are among the few simple amidomanganese(II) compounds to be prepared in which there is no stabilisation imparted by sterically bulky substituents, is worthy of note.[5]

Low-temperature (153 K) X-ray crystallographic studies were undertaken on both complexes. Selected bond lengths and angles for **1** and **2** are listed in Tables 1 and 2, respectively. Details of the structural refinements are given in Table 3. The structure of **1** is that of the ion-separated complex $2[Li(thf)_4]^+[Mn(C_{12}H_8N)_4]^{2-}\cdot C_6H_5Me$ (Fig. 1) arising from nucleophilic substitution of the $N(SiMe_3)_2$ groups followed by addition of another two anions. In addition, there is one toluene molecule per formula unit of **1** in the lattice. The outcome of the nucleophilic substitution reaction of $[Mn\{N(SiMe_3)_2\}_2]\cdot 2thf$ with $[C_{12}H_8N]^-$ is identical to the substitution reaction of $[Cd\{N(SiMe_3)_2\}_2]$ with the same anion under similar conditions,[2a] even though there is a considerable difference in the ionic radii of Mn^{2+} and Cd^{2+} (0.80 and 0.97 Å, respectively). Although there is some distortion in the pseudo-tetrahedral $[Mn(C_{12}H_8N)_4]^{2-}$ dianion arising from the accommodation of four $C_{12}H_8N$

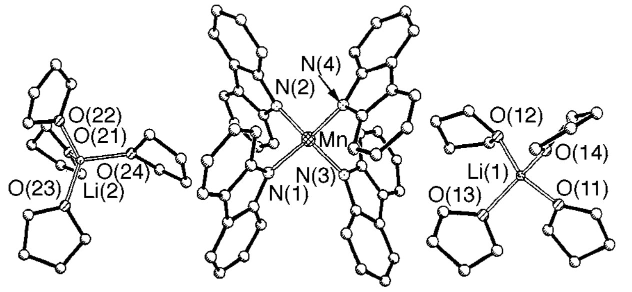

Fig. 1 Molecular structure of complex **1**. Hydrogen atoms have been omitted for clarity

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Mn–N(1)	2.121(5)	Mn–N(2)	2.122(5)
Mn–N(3)	2.107(5)	Mn–N(4)	2.121(5)
Li(1,2)–O	1.92 (average)		
N(3)–Mn–N(1)	110.6(2)	N(3)–Mn–N(4)	104.4(2)
N(1)–Mn–N(4)	114.3(2)	N(3)–Mn–N(2)	113.4(2)
N(1)–Mn–N(2)	103.4(2)	N(4)–Mn–N(2)	111.1(2)

groups around the smaller Mn^{2+} cation [range N–Mn–N 103.4(2)–114.3(2)°], the Mn–N bonds are all of similar lengths (average 2.12 Å), *cf.* Mn–N 2.04 Å in $[Mn\{N(SiMe_3)_2\}_2]\cdot 2thf$[5f] where the manganese(II) centre is also pseudo-tetrahedral.

The structure of complex **2** is that of a monomeric complex $[Mn(C_{12}H_8N)_2]\cdot 3thf$ in the solid state, in which the manganese centre has a distorted trigonal-bipyramidal geometry (Fig. 2). The greatest distortion occurs within the trigonal plane of the molecule, with the Mn^{2+} ion being co-ordinated within this plane by two $C_{12}H_8N$ ligands [average Mn–N 2.08 Å and N–Mn–N 146.25(6)°] and by one thf ligand [Mn–O(2) 2.157(1) Å and average O–Mn–N 106.9°]. The Mn–O bonds made with the axial thf ligands (average 2.32 Å) are considerably longer than that occurring in the axial plane and are similar to those found in the structure of $[Mn\{N(SiMe_3)_2\}_2]\cdot 2thf$ (average 2.24 Å).[5f]

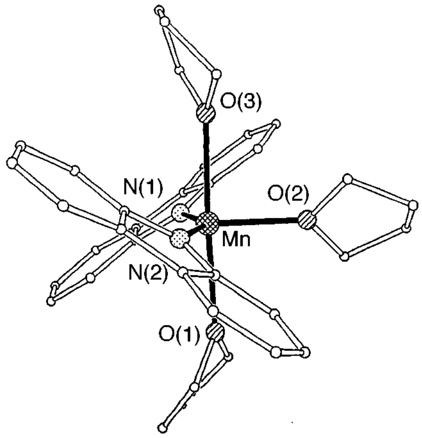

Fig. 2 Molecular structure of complex **2**. Hydrogen atoms have been omitted for clarity

Table 2 Selected bond lengths (Å) and angles (°) for complex **2**

Mn–N(1)	2.080 (2)	Mn–N(2)	2.082(2)
Mn–O(1)	2.319(1)	Mn–O(3)	2.311(1)
Mn–O(2)	2.157(1)		
N(1)–Mn–N(2)	146.25(6)	N(1)–Mn–O(2)	107.79(5)
N(2)–Mn–O(2)	105.96(5)	N(1)–Mn–O(3)	99.99(5)
N(2)–Mn–O(3)	90.25(5)	O(2)–Mn–O(3)	88.66(5)
N(1)–Mn–O(1)	87.77(5)	N(2)–Mn–O(1)	92.81(5)
O(2)–Mn–O(1)	88.24(5)	O(3)–Mn–O(1)	176.15(5)

Comparatively few examples of homoleptic manganese(II) amido complexes have been structurally characterised.[5] The majority of the structurally elucidated complexes contain sterically bulky substituents (particularly trimethylsilylamido and its variants) which not only stabilise them but also encourage generally low co-ordination numbers at the metal centres, *e.g.* $[\{Mn[\mu\text{-}N(SiMe_3)_2][N(SiMe_3)_2]\}_2]$,[5b,c] $[Mn\{N(SiMe_3)_2\}_2]\cdot 2thf$[5f] and $[\{(Me_3Si)_2N\}Mn\{\mu\text{-}N(SiMe_3)_2\}_2Li]\cdot thf$[5c] (all of which contain four-co-ordinated Mn) and $[Mn\{N(SiMe_3)_2\}_2]\cdot thf$ (three-co-ordinate),[5a] $[Mn\{N(SiMePh_2)_2\}_2]$[5e] and $[Mn\{N(mes)[B(mes)_2]\}_2]$[5d] (mes = mesityl) (both containing two-co-ordinate Mn). The co-complex $[Mn_3(\mu\text{-}NEt_2)_6(\mu\text{-}Cl)_2\{Li(thf)\}_2]\cdot C_6H_5Me$ (containing four-co-ordinate Mn) and the dimer $[\{Mn_2(\mu\text{-}NPr^i_2)(NPr^i_2)\}]_2$ (three-co-ordinate Mn) are the only well characterised compounds containing simple diaryl- or dialkylamido groups.[5g] The most closely related amido complex to **1** is $[\{Me_3Si)_2N\}Mn\{\mu\text{-}N(SiMe_3)_2\}_2Li]\cdot thf$,[5c] in which a tris(amido)manganese(II) anion is linked through two bridging trimethylsilyl groups to a thf-solvated Li^+ cation. However, complex **1** is the first example containing a tetraamidomanganese(II) dianion. Although trigonal-bipyramidal geometries are not unknown for complexes of Mn^{2+} in general,[6] **2** is the first example of an amidomanganese(II) complex with this co-ordination geometry (previously only two- to four-co-ordinate geometries had been found). Evidently the occurrence of the tetraamidomanganese(II) anion of **1** and the relatively high co-ordination number of the Mn of **2** result from the very low steric requirements of the planar $C_{12}H_8N$ groups present compared to those previously employed. This is stressed particularly in a comparison of **2** with the solvated complexes $[Mn\{N(SiMe_3)_2\}_2]\cdot n\,thf$ ($n = 1$ or 2),[5a,f] in which the presence of the more sterically demanding bis(trimethylsilyl)amido substituents precludes further solvation by more than two thf molecules. The low steric demands of $C_{12}H_8N$ groups are also seen in their equatorial arrangement in **2**, which can be compared to the axial arrangements found in the similar complexes $MnL_2\cdot 3Y$ in which sterically demanding metalloorganic ligands are present [$L = \{2,4,6\text{-}(F_3C)_3C_6H_2O\}$, Y = thf;[6e] $L = OSi(OBu^t)_3$, Y = pyridine[1e]].

One important conclusion of this study is that, as with the Group 12 and 13 derivatives, nucleophilic substitution of the silylamido groups is demonstrated in the formation of complex **2**. The preparation of $2[Li(thf)_4]^+[Cd_4(PPh_2)_{10}]^{2-}$[2d] by nucleophilic substitution of $[Cd\{N(SiMe_3)_2\}_2]$ with $Li[PPh_2]$ has illustrated that by using silylamido precursors the inclusion of halide ions in the frameworks of cage complexes can be avoided. Several studies have shown that the nature of the products formed by the transmetallation reactions of MnX_2 (X = halide) with metalloorganic alkali- or alkaline-earth-metal complexes can be complicated by the intimate inclusion of the halide ions and/or alkali- or alkaline-earth metal halides into their structures, *e.g.* as occurs in the formation of $[Mn_3(\mu\text{-}NEt_2)_6(\mu\text{-}Cl)_2\{Li(thf)\}_2]\cdot C_6H_5Me$[5g] from MCl_2 and $Li[NEt_2]$ or in the preparation of the imido cage complex $[\{Mn_6(\mu_3\text{-}NPh)_4Br_3(thf)_4\}\{Mg_2(\mu\text{-}NHPh)(\mu\text{-}Br)_2Br_2(thf)_4\}]$.[7] We are currently pursuing the preparation of homoleptic imido (RN^{2-}) and phosphinidene (RP^{2-}) cage complexes of Mn^{II} and other transition metals utilising nucleophilic substitution reactions of the metal silylamides, as a means of avoiding the incorporation of these species.

Experimental

General

The products **1**, **2** and the starting material $[Mn\{N(SiMe_3)_2\}_2]\cdot 2thf$ are all air-sensitive. They were handled on a vacuum line using standard inert-atmosphere techniques and under dry O_2-free Ar.[8] The complex $[Mn\{N(SiMe_3)_2\}_2]\cdot 2thf$ was prepared in the manner described in the literature and purified by distillation.[9] The toluene and thf solvents were dried using sodium–benzophenone and degassed prior to the reactions. All compounds were isolated and characterised with the aid of an argon-filled glove-box (Miller-Howe) fitted with an oxygen- and water-recirculation system (Belle). Melting points were determined by using a conventional apparatus and sealing samples in capillaries under Ar. Infrared spectra were recorded as Nujol mulls (NaCl windows) on a Perkin-Elmer Paragon 1000 spectrometer and ^1H NMR spectra using a Bruker WH 250 MHz spectrometer using the dimethylformamide (dmf) solvent resonances as the internal reference.

Syntheses

Complex 1. To a suspension of $Li[C_{12}H_8N]$ (4.98 mmol) in toluene–hexanes [prepared by the reaction of $LiBu^n$ (3.15 cm^3, 4.98 mmol, 1.5 mol dm^{-3} in hexanes) with carbazole (1.62 g, 4.98 mmol) in toluene (15 cm^3)] was added $[Mn\{N(SiMe_3)_2\}_2]\cdot 2thf$ (0.67 g, 1.25 mmol) in toluene (10 cm^3) and thf (10 cm^3). The resulting dark orange solution was filtered while hot (porosity 3, Celite) and the filtrate reduced in volume to *ca.* 20 cm^3 under vacuum. The yellow powder produced was heated gently back into solution. Crystals of complex **1** were grown by storage at room temperature (12 h). The same product was formed regardless of the stoichiometry of the reaction. For the 1:4 reaction described above, yield 1.01 g (62%). Complex **1** can also be obtained in similar yield by the reaction of **2** with $Li[C_{12}H_8N]$. The reaction of **1** with $Li[C_{12}H_8N]$ (1:2 equivalents) in an identical solvent mixture to the above gives **2** in similar yield to that of the 1:4 reaction. Isolation of **1** under vacuum produces a dry powder from which lattice-bound toluene, present in the crystal structure, has been removed. The following data refer to the unsolvated material. M.p. decomp. >300 °C. IR (Nujol): $\tilde{\nu}_{max}/cm^{-1} = 1232w, 1147w, 1116w, 1039m, 886m, 800m, 757s$ and 724s. ^1H NMR (25 °C, 250 MHz, dmf): δ 7.0–8.5 (br, m, $C_{12}H_8N$), 3.60 (m) and 1.75 (m) (Found: C, 73.2; H, 7.2; N, 4.4. Calc.: C, 73.3; H, 7.3; N, 4.3%).

Complex 2. To a suspension of carbazole (0.97 g, 5.8 mmol) in toluene was added $[Mn\{N(SiMe_3)_2\}_2]\cdot 2thf$ (1.50 g, 2.8 mmol). A dark grey suspension formed, which lightened to beige on heating and stirring. This solubilises on addition of a few drops of thf and gentle heating, forming a dark orange solution. Storage at room temperature (24 h) gave yellow cubic crystals of complex **2**; yield 1.07 g (61%), m.p. *ca.* 120 °C (decomp.). IR (Nujol): $\tilde{\nu}_{max}/cm^{-1} = 1261m, 1140m, 1075m, 748s$ and 726s. ^1H NMR (25 °C, 250 MHz, dmf): broad and uninformative (Found: C, 71.7; H, 6.6; N, 4.6. Calc.: C, 72.5; H, 6.4; N, 4.4%).

X-Ray crystallography

Crystals of complexes **1** and **2** were mounted directly from solution at room temperature under Ar using a perfluorocarbon oil which protects them from atmosphere moisture and oxygen (Reidel-de Haën). The oil 'freezes' at reduced temperatures and holds the crystal static in the X-ray beam.[10] Data were collected on a Stoe AED diffractometer, and a semiempirical absorption correction based on ψ scans was employed. The structures were solved by the direct method (SHELXTL PLUS)[11] and refined by full-matrix least squares on F^2 (SHELXL 93).[12] All non-hydrogen atoms of **1** and the non-hydrogen atoms of the dianion of **2** only were refined anisotropically. The $[Li(thf)_4]^+$ cations of **1** were refined isotropically. Seven of the eight thf ligands were disordered; they were modelled using distance restraints. The H atoms were fixed geometrically in both structures. Details of the structure solutions and refinements for **1** and **2** are listed in Table 3.

Table 3 Crystal data and structure solutions of complexes **1** and **2**

	1	**2**
Empirical Formula[a]	$C_{87}H_{104}Li_2MnN_2O_8$	$C_{36}H_{40}MnN_2O_3$
M	1402.56	603.64
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Crystal size/mm	0.4 × 0.4 × 0.3	0.3 × 0.2 × 0.2
a/Å	12.972(3)	12.429(2)
b/Å	13.937(4)	18.037(5)
c/Å	22.342(6)	14.730(3)
α/°	78.03(2)	—
β/°	78.00(2)	113.61(2)
γ/°	82.45(2)	—
$U/Å^3$	3849(2)	3026(1)
$\mu(Mo\text{-}K\alpha)/mm^{-1}$	0.230	0.475
Z	2	4
$D_c/Mg\ m^{-3}$	1.210	1.325
θ range/°	3.00–22.48	4.08–22.50
Reflections collected	11 918	6444
Independent reflections (R_{int})	9992 (0.023)	3926 (0.055)
$R1\ [F > 4\sigma(F)]$[b]	0.083 (7515 reflections)	0.028 (3501 reflections)
$wR2$ (all data)[c]	0.236	0.075
Peak, hole/e $Å^{-3}$	0.920, −0.581	0.280, −0.235

[a] Data in common: $T = 153(2)$ K, $\lambda = 0.710\ 73$ Å. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{\frac{1}{2}}, w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$; for complex **1**, $x = 0.1007$, $y = 14.407$, for **2**, $x = 0.0294$, $y = 1.748$.

Atomic co-ordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/502.

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