

Manganese(II) Amides: The Synthesis and X-Ray Crystal Structures of $\text{Mn}[\text{N}(\text{SiMe}_3)(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)]_2[\text{THF}]$ and $\text{Mn}_3[\text{N}(\text{H})2,6\text{-Pr}^i_2\text{C}_6\text{H}_3]_4[\text{N}(\text{SiMe}_3)_2]_2$

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Manganese Complexes, X-Ray

A series of manganese(II) amides (**1–4**), derived from 2,6-diisopropylaniline (H_2NAr ; where $\text{Ar} = 2,6\text{-Pr}^i_2\text{C}_6\text{H}_3$) and its N-silylated derivative $\text{H}(\text{SiMe}_3)\text{NAr}$, has been prepared and characterized. The crystal structure of $\text{Mn}[\text{N}(\text{SiMe}_3)\text{Ar}]_2[\text{THF}]$ (**2**) reveals a monomeric species with a planar three-coordinate Mn(II) center. Crystal data for **2**: trigonal (hexagonal axes), $a = 30.119(2) \text{ \AA}$, $c = 10.589(1) \text{ \AA}$, $V = 8319(1) \text{ \AA}^3$, $T = 153 \text{ K}$, space group $P3_1$ (No. 144), $Z = 9$ ($R/R_w = 0.053/0.050$). In contrast, $\text{Mn}_3[\text{N}(\text{H})\text{Ar}]_4[\text{N}(\text{SiMe}_3)_2]_2 \cdot \text{C}_7\text{H}_8$ (**4**) is shown to be a novel trinuclear compound held together by nitrogen-bridges. The two terminal Mn(II) atoms have a distorted trigonal planar arrangement of nitrogen donors whereas the central Mn(II) is surrounded by a distorted tetrahedral array of nitrogen donors. Crystal data for **4**: orthorhombic, $a = 21.301(5) \text{ \AA}$, $b = 17.021(6) \text{ \AA}$, $c = 20.519(7) \text{ \AA}$, $V = 7439(4) \text{ \AA}^3$, $T = 153 \text{ K}$, space group $Pbcn$ (No. 60), $Z = 4$ ($R/R_w = 0.050/0.070$).

Introduction

Despite growing interest in exploring the chemistry of various transition metal amide systems, the number of manganese amide complexes reported is quite meagre [1–3]. This may be due in part to the practical difficulties arising from working with compounds containing extremely reactive Mn–N bonds. Nevertheless, a limited number of amido-manganese compounds are known, including $\text{Me}_2\text{NMn}(\text{CO})_5$ [4], $\text{Mn}[\text{N}(\text{CN})_2]_2$ [5], $\text{Mn}[\text{N}(\text{SiMe}_3)_2]_2[\text{THF}]$ [6], $\text{Mn}[\text{phthalimide}]_2 \cdot 4\text{NH}_3$ [7], and more recently $\text{Mn}[\text{N}(\text{SiMe}_3)_2]_3$ [2] and $\text{Mn}_3[\text{NET}_2]_6\text{Cl}_2[\text{Li}(\text{THF})_2]_2$ [3]. X-ray structural analyses have been rare, with the exception of the amido species containing $\text{N}(\text{SiMe}_3)_2$ which have been studied in more depth. The structures of the monomers $\text{Mn}[\text{N}(\text{SiMe}_3)_2]_3$ [2] and $\text{Mn}[\text{N}(\text{SiMe}_3)_2]_2[\text{THF}]$ [8], and the dimer $[\text{Mn}(\text{N}(\text{SiMe}_3)_2)_2]_2$ [9] are known. In each case the manganese atoms are three-coordinated. A series of yellow tetrahedral compounds $\text{Mn}[\text{N}(\text{SiMe}_3)_2]_2(\text{L})_2$ (where $\text{L} = \text{THF}$, py or Bu^nCN) has also been prepared [10], and the structure of $\text{Mn}[\text{N}(\text{SiMe}_3)_2]_2[\text{THF}]_2$ was recently reported [11]. An example of a four-coordinate purely amidomanganese(II) center is found in the unusual molecular structure of

$\text{Mn}_3[\text{NET}_2]_6\text{Cl}_2[\text{Li}(\text{THF})_2]_2$ which contains three tetrahedrally coordinated manganese atoms [3].

Herein we report the preparation and characterization of a series of manganese(II) amides (**1–4**), including the low temperature X-ray structure determinations of the mononuclear manganese compound $\text{Mn}[\text{N}(\text{SiMe}_3)\text{Ar}]_2[\text{THF}]$ (**2**), where $\text{Ar} = 2,6\text{-Pr}^i_2\text{C}_6\text{H}_3$, and the trinuclear manganese compound $\text{Mn}_3[\text{N}(\text{H})\text{Ar}]_4[\text{N}(\text{SiMe}_3)_2]_2 \cdot \text{C}_7\text{H}_8$ (**4**). To our knowledge, the almost linear arrangement of three manganese(II) atoms bound exclusively by nitrogen donors makes **4** unique.

Experimental

General procedures

The reactants $\text{Mn}[\text{N}(\text{SiMe}_3)_2]_2$ [8] and $\text{HN}(\text{SiMe}_3)\text{Ar}$ [12] were prepared according to published methods. H_2NAr was obtained from Janssen and purified by initial drying over KOH and subsequent distillation from CaH_2 . Anhydrous MnCl_2 was obtained from Fluka, and Bu^nLi (1.6 M in hexane) from Janssen. Both were used without further purification. All solvents were dried and distilled before use. Infrared spectra were recorded with a BIORAD FTS 7 spectrometer using halo oil or nujol mulls and KBr plates. All manipulations were carried out either on a vacuum line or in a dry box under dry oxygen-free nitrogen. Owing to the extreme oxygen sensitivity of these manganese amides, all reactions were carried out in H-vessels, which consist of two compartments separated by a glass frit. Melting points

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were determined on samples sealed in melting point capillaries and are uncorrected.

Preparation of Mn[N(H)Ar]₂[THF] (1) and Mn[N(SiMe₃)Ar]₂[THF] (2)

A sample of (a) H₂NAr (1.64 g, 9.27 mmol) or (b) HN(SiMe₃)Ar (1.43 g, 5.74 mmol) was dissolved in THF and cooled to 0 °C in one compartment of an H-vessel. To this stirred solution an equivalent amount of BuⁿLi was added by syringe. The solution was allowed to warm to room temperature and was stirred for a further hour. The H-vessel was tilted to allow the LiN(R)Ar (R = H, SiMe₃) solution to pass through the glass frit into the second compartment containing one half equivalent of MnCl₂ (a) 0.57 g, 4.5 mmol or (b) 0.35 g, 2.8 mmol. This mixture was stirred at room temperature for 3 h. The solvent was removed under vacuum to leave a solid, which was extracted using hexane. The H-vessel was again tilted to allow the hexane solution to pass through the glass frit to the first compartment filtering out any solid (LiCl). Solvent was again removed in vacuum leaving a white solid yield: (a) 1.76 g, 81% of Mn[N(H)Ar]₂[THF] (1), m. p. 178–181 °C.

$C_{28}H_{44}MnON_2$				
Calcd	C 70.12	H 9.25	N 5.84,	
Found	C 67.6	H 9.0	N 5.6.	

(b) Yield 2.6 g, 72% of Mn[N(SiMe₃)Ar]₂[THF] (2), m. p. 131–134 °C.

$C_{34}H_{60}MnON_2Si_2$				
Calcd	C 65.45	H 9.69	N 4.49,	
Found	C 64.7	H 9.5	N 4.4.	

Preparation of Mn[N(H)Ar]₂ (3) and Mn₃[N(H)Ar]₄[N(SiMe₃)₂]₂ (4)

A sample of Mn[N(SiMe₃)₂]₂ ((a) 1.89 g, 5.04 mmol or (b) 1.61 g, 4.29 mmol) was weighed out into an H-vessel. The appropriate amount of H₂NAr ((a) 1.80 g, 10.2 mmol or (b) 0.76 g, 4.3 mmol) was added by syringe. The mixture was stirred and warmed to 90 °C for 10 min. After cooling to room temperature the volatile product, HN(SiMe₃)₂, was removed under vacuum. The remaining solid was recrystallized from toluene to afford: (a) colorless crystals (yield 1.4 g, 68%, m. p. 130–132 °C) of 3.

$C_{24}H_{36}MnN_2$				
Calcd	C 70.74	H 8.90	N 6.87,	
Found	C 69.2	H 9.0	N 6.7.	

(b) large ruby-red crystals (yield 1.3 g, 76%, m. p. 169–172 °C) of 4.

$C_{67}H_{116}Mn_3N_6Si_4$				
Calcd	C 62.73	H 9.11	N 6.55,	
Found	C 62.4	H 9.1	N 6.6	

X-ray crystallography

Using an inert mounting oil we were able to rapidly isolate and mount suitable single crystals [13]. These were transferred immediately to the low temperature gas stream of the diffractometer in which the crystals were stable. Data for both crystals were collected at –120 °C on a Siemens-Stoë AED four circle diffractometer using graphite monochromated Mo-K_α radiation. 2θ–ω scans, with online profile fitting [14] and variable scan speeds, were employed. Empirical absorption corrections based on ψ-scan data were applied in each case. Both structures were solved by Direct Methods (SHELXS-86) [15] and refined by full-matrix least squares techniques (SHELX-76, modified by the author).

Crystal data for

Mn[N(SiMe₃)(2,6-Prⁱ₂C₆H₃)]₂[THF] (2)

C₃₄H₆₀N₂OSi₂Mn, Mr = 624.0, colorless, crystal dimensions 0.3×0.4×0.6 mm, trigonal (hexagonal axes) *a* = *b* = 30.119(2) Å, *c* = 10.589(1) Å, *V* = 8319(1) Å³, space group P3₁, *Z* = 9, *F*(000) = 3051, 7812 reflections collected (8 < 2θ < 45°), 7806 unique and 6578 observed reflections with *F* > 3.0σ(*F*). The manganese, silicon, oxygen, nitrogen, and THF and methyl carbon atoms (with the exception of C328, C329 and C330) were refined anisotropically. Hydrogen atoms were inserted at calculated positions. The space group was confirmed to be P3₁ by an eta refinement [16], η = +0.95(7). The full-matrix refinement of 825 parameters converged with *R* = 0.053, *R*_w = 0.050, w^{–1} = σ²(*F*) + 0.0005 *F*² and maximum/minimum rest electron density +0.6/–0.4 eÅ^{–3}.

Crystal data for

Mn₃[NH(2,6-Prⁱ₂C₆H₃)]₄[N(SiMe₃)₂]₂·C₇H₈ (4)

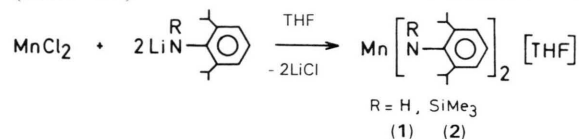
C₆₀H₁₀₈Mn₃N₆Si₄·C₇H₈, Mr = 1282.8, red, crystal dimensions 0.6×0.6×0.7 mm, orthorhombic, *a* = 21.301(5) Å, *b* = 17.021(6) Å, *c* = 20.519(7) Å, *V* = 7439(4) Å³, space group Pbcn, *Z* = 4, *F*(000) = 2764, 6436 reflections collected (8 < 2θ < 45°), 4832 unique and 3964 observed reflections with *F* > 4.0σ(*F*). All non-hydrogen atoms were refined anisotropically and hydrogen atoms were inserted at calculated positions. (The hydrogen atoms

on N30 and N50 had been previously detected in difference Fourier maps, close to their calculated positions). The half occupancy toluene solvent molecule was refined as a rigid group with common anisotropic temperature factors for the carbon atoms, since poor convergence was obtained with more general models. The full-matrix refinement of 342 parameters converged with $R = 0.050$, $R_w = 0.070$, $w^{-1} = \sigma^2(F) + 0.0006F^2$ and maximum/minimum rest electron density $+0.7/-0.6 \text{ e}\text{\AA}^{-3}$.

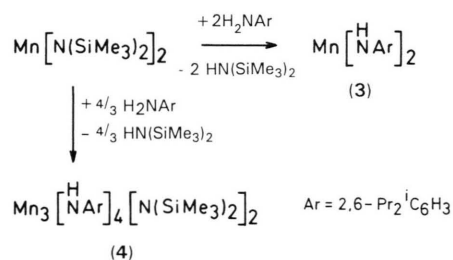
Results and Discussion

These Mn–N compounds (**1–4**) are thermally stable solids which are not only sensitive to moisture but also to oxygen. An almost instantaneous color change to black is observed in the presence of O_2 .

Compounds **1** and **2** are prepared by transmetalation reactions; combining anhydrous MnCl_2 with two equivalents of the corresponding lithiated aniline derivative affords the colorless solids (Scheme I).



The remarkable and novel trinuclear manganese(II) compound (**4**) was prepared by a different synthetic route. The reaction of $\text{Mn}[\text{N}(\text{SiMe}_3)_2]_2$ with H_2NAr affords an entirely nitrogen-bridged linear trinuclear manganese complex in 76% yield (Scheme II). Unlike the other Mn–N compounds (**1–3**) this compound is ruby-red in color. **3** can also be prepared from these reagents by simply altering the reaction stoichiometry (Scheme II).



Crystals of $\text{Mn}[\text{N}(\text{SiMe}_3)\text{Ar}]_2[\text{THF}]$ (**2**) and $\text{Mn}_3[\text{N}(\text{H})\text{Ar}]_4[\text{N}(\text{SiMe}_3)_2]_2 \cdot \text{C}_7\text{H}_8$ (**4**) were obtained from hexane and toluene solutions, respectively, and their X-ray crystal structures were de-

termined. Atomic coordinates are listed in Tables I and II and selected interatomic distances and angles are given in Tables III and IV.

Table I. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for $\text{Mn}[\text{N}(\text{SiMe}_3)(\text{Ar})]_2[\text{THF}]$ (**2**).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
Mn(1)	2069(1)	4368(1)	9791	24(1)
N(1)	2634(2)	4708(2)	11053(6)	23(3)
C(1)	2951(3)	5242(3)	10885(7)	25(2)
C(2)	2918(3)	5600(3)	11715(7)	24(2)
C(3)	3219(3)	6127(3)	11463(7)	25(2)
C(4)	3538(3)	6314(3)	10442(7)	29(2)
C(5)	3564(3)	5968(3)	9631(7)	27(2)
C(6)	3287(3)	5442(3)	9823(7)	22(2)
C(7)	2555(3)	5419(3)	12862(7)	31(2)
C(8)	2091(3)	5479(3)	12604(8)	46(5)
C(9)	2843(3)	5714(3)	14050(8)	47(5)
C(10)	3349(3)	5095(3)	8881(7)	30(2)
C(11)	3909(3)	5249(3)	8658(9)	49(5)
C(12)	3092(3)	5074(3)	7629(8)	50(5)
Si(1)	2831(1)	4380(1)	12038(2)	30(1)
C(13)	3455(3)	4434(3)	11528(9)	47(4)
C(14)	2942(4)	4595(3)	13744(8)	54(5)
C(15)	2311(3)	3695(3)	12057(8)	39(4)
N(2)	1692(2)	3752(2)	8708(5)	23(3)
C(16)	1180(3)	3621(3)	8364(7)	21(2)
C(17)	1082(3)	3749(3)	7139(7)	26(2)
C(18)	584(3)	3628(3)	6848(8)	34(2)
C(19)	183(3)	3399(3)	7707(8)	42(2)
C(20)	285(3)	3275(3)	8894(8)	36(2)
C(21)	775(3)	3377(3)	9230(7)	26(2)
C(22)	1503(3)	4025(3)	6182(7)	33(2)
C(23)	1682(3)	4602(3)	6164(8)	46(5)
C(24)	1345(4)	3800(4)	4836(8)	57(5)
C(25)	863(3)	3246(3)	10547(7)	34(2)
C(26)	454(4)	2711(4)	10984(10)	69(6)
C(27)	911(4)	3648(4)	11495(8)	67(6)
Si(2)	1874(1)	3308(1)	8333(3)	32(1)
C(28)	2577(3)	3618(3)	8486(9)	45(4)
C(29)	1577(3)	2721(3)	9369(9)	51(5)
C(30)	1679(3)	3040(3)	6704(8)	48(5)
O(1)	1771(2)	4889(2)	9443(5)	32(2)
C(31)	2079(3)	5429(3)	9119(8)	33(4)
C(32)	1714(3)	5645(3)	9164(8)	32(4)
C(33)	1212(3)	5178(3)	8756(8)	41(4)
C(34)	1224(3)	4737(3)	9387(9)	39(4)
Mn(2)	2248(1)	1411(1)	12759(1)	26(1)
N(3)	2815(2)	1802(2)	13975(5)	24(3)
C(201)	2883(3)	2297(3)	14259(7)	24(2)
C(202)	3124(3)	2700(3)	13377(7)	29(2)
C(203)	3149(3)	3175(3)	13654(8)	40(2)
C(204)	2948(3)	3240(3)	14727(8)	42(2)
C(205)	2729(3)	2858(3)	15604(8)	38(2)
C(206)	2688(3)	2380(3)	15390(7)	25(2)
C(207)	3331(3)	2650(3)	12146(8)	44(2)
C(208)	3889(4)	3085(4)	11891(10)	71(5)
C(209)	2986(4)	2608(4)	11044(8)	69(6)
C(210)	2411(3)	1958(3)	16386(8)	40(2)
C(211)	2593(4)	2152(4)	17756(8)	62(6)
C(212)	1843(3)	1739(3)	16280(9)	51(5)

Table I (continued).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
Si(3)	3278(1)	1670(1)	14511(3)	35(1)
C(213)	3926(3)	2099(4)	13820(9)	68(6)
C(214)	3083(4)	1005(4)	14166(12)	85(7)
C(215)	3398(4)	1755(4)	16254(9)	64(6)
N(4)	1980(2)	857(2)	11447(6)	28(3)
C(216)	1446(3)	494(3)	11625(7)	23(2)
C(217)	1285(3)	174(3)	12702(7)	31(2)
C(218)	761(3)	– 158(3)	12907(8)	34(2)
C(219)	399(3)	– 187(3)	12075(8)	36(2)
C(220)	550(3)	114(3)	10999(8)	35(2)
C(221)	1071(3)	457(3)	10760(7)	24(2)
C(222)	1660(3)	179(3)	13672(8)	34(2)
C(223)	1602(4)	– 345(3)	13899(10)	61(5)
C(224)	1612(4)	415(3)	14945(8)	59(5)
C(225)	1205(3)	785(3)	9575(7)	35(2)
C(226)	954(3)	468(3)	8398(7)	48(4)
C(227)	1064(3)	1204(3)	9731(8)	48(5)
Si(4)	2375(1)	746(1)	10507(3)	36(1)
C(228)	3027(3)	1338(4)	10553(10)	67(5)
C(229)	2407(4)	166(4)	10990(9)	60(6)
C(230)	2202(4)	633(4)	8783(8)	57(6)
O(2)	1676(2)	1661(2)	12928(5)	32(3)
C(231)	1788(3)	2190(3)	12852(9)	41(4)
C(232)	1316(4)	2177(4)	13369(11)	65(6)
C(233)	898(3)	1660(3)	13090(12)	66(5)
C(234)	1133(3)	1327(3)	13204(8)	37(4)
Mn(3)	5742(1)	4674(1)	6047(1)	27(1)
N(5)	6299(2)	4853(2)	4791(6)	27(3)
C(301)	6551(3)	4560(3)	4932(7)	25(2)
C(302)	6457(3)	4162(3)	4035(7)	28(2)
C(303)	6669(3)	3853(3)	4242(8)	36(2)
C(304)	6970(3)	3913(3)	5301(8)	38(2)
C(305)	7066(3)	4292(3)	6127(8)	39(2)
C(306)	6865(3)	4619(3)	5974(7)	27(2)
C(307)	6126(3)	4067(3)	2853(8)	38(2)
C(308)	6401(4)	4039(4)	1665(8)	58(5)
C(309)	5608(3)	3577(3)	3012(9)	59(5)
C(310)	6996(3)	5038(3)	6940(8)	47(2)
C(311)	7572(3)	5389(4)	7071(11)	70(5)
C(312)	6745(4)	4800(4)	8240(9)	80(7)
Si(5)	6539(1)	5403(1)	3902(3)	35(1)
C(313)	7065(4)	5984(4)	4708(10)	76(6)
C(314)	6827(4)	5371(3)	2371(9)	72(6)
C(315)	5998(3)	5524(4)	3584(10)	63(5)
N(6)	5438(2)	4972(2)	7205(6)	29(3)
C(316)	4899(3)	4611(3)	7477(7)	25(2)
C(317)	4761(3)	4329(3)	8612(8)	37(2)
C(318)	4257(3)	3954(3)	8803(9)	46(2)
C(319)	3889(3)	3862(3)	7915(8)	46(2)
C(320)	4016(3)	4139(3)	6840(8)	42(2)
C(321)	4523(3)	4524(3)	6586(7)	31(2)
C(322)	5156(4)	4403(4)	9621(9)	57(3)
C(323)	5262(4)	3977(4)	9582(9)	77(7)
C(324)	4993(4)	4468(4)	10969(9)	79(6)
C(325)	4647(3)	4823(3)	5362(9)	50(2)
C(326)	4316(5)	5065(6)	5148(12)	130(12)
C(327)	4597(4)	4479(4)	4235(9)	78(7)
Si(6)	5698(1)	5587(1)	7749(3)	50(1)
C(328)	6374(5)	5842(6)	8157(15)	129(5)
C(329)	5716(8)	6040(7)	6617(18)	197(9)
C(330)	5368(4)	5650(4)	9158(9)	71(3)
O(3)	5332(2)	3849(2)	6197(5)	35(3)

Table I (continued).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
C(331)	5562(3)	3530(3)	6504(9)	38(4)
C(332)	5119(3)	2978(3)	6446(10)	56(5)
C(333)	4662(3)	3025(3)	6753(12)	70(5)
C(334)	4775(3)	3519(3)	6098(10)	50(4)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table II. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for $\text{Mn}_3[\text{N}(\text{H})\text{Ar}]_4[\text{N}(\text{SiMe}_3)_2]_2 \cdot \text{C}_7\text{H}_8$ (**4**).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
Mn(1)	5935(1)	3019(1)	1398(1)	38(1)
Mn(2)	5000	2869(1)	2500	28(1)
Si(1)	6745(1)	2425(1)	192(1)	80(1)
C(1)	6339(3)	1506(4)	447(3)	117(3)
C(2)	7604(2)	2185(4)	189(3)	93(2)
C(3)	6504(3)	2600(6)	– 672(3)	156(4)
N(1)	6568(2)	3189(2)	706(2)	55(1)
Si(2)	6941(1)	4082(1)	687(1)	68(1)
C(10)	7612(3)	4117(4)	1265(3)	99(3)
C(11)	7249(3)	4360(4)	– 136(3)	104(3)
C(12)	6385(3)	4871(3)	912(3)	83(2)
N(30)	5196(1)	2225(2)	1618(1)	34(1)
C(30)	4811(2)	1945(2)	1090(2)	37(1)
C(31)	4671(2)	1141(3)	1035(2)	49(1)
C(32)	4347(2)	876(3)	493(3)	66(2)
C(33)	4139(2)	1388(3)	23(3)	72(2)
C(34)	4252(2)	2172(3)	92(2)	56(2)
C(35)	4580(2)	2474(2)	617(2)	40(1)
C(36)	4860(3)	542(3)	1545(3)	67(2)
C(37)	5430(4)	111(5)	1398(4)	182(5)
C(38)	4357(4)	– 14(5)	1740(4)	153(4)
C(39)	4656(2)	3359(3)	649(2)	45(1)
C(40)	5053(2)	3688(3)	76(3)	66(2)
C(41)	4030(2)	3785(3)	645(2)	59(2)
N(50)	5781(1)	3618(2)	2302(1)	30(1)
C(50)	6343(2)	3817(2)	2659(2)	35(1)
C(51)	6464(2)	4612(2)	2824(2)	45(1)
C(52)	7014(2)	4790(3)	3153(2)	63(2)
C(53)	7438(2)	4218(4)	3307(3)	74(2)
C(54)	7317(2)	3451(3)	3151(2)	61(2)
C(55)	6771(2)	3228(3)	2830(2)	43(1)
C(56)	5997(2)	5272(2)	2677(2)	51(1)
C(57)	5549(2)	5397(3)	3244(2)	63(2)
C(58)	6331(3)	6046(3)	2511(3)	87(2)
C(59)	6674(2)	2366(3)	2688(2)	52(2)
C(60)	6773(2)	1843(3)	3286(3)	75(2)
C(61)	7102(3)	2081(3)	2141(3)	81(2)
C(80)	– 330(5)	2785(4)	2909(5)	144(4)
C(81)	114	2861	3381	144(4)
C(82)	719	3020	3214	144(4)
C(83)	881	3102	2575	144(4)
C(84)	437	3025	2103	144(4)
C(85)	– 169	2867	2270	144(4)
C(86)	– 659	2782	1750	144(4)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Mn(1)–N(1)	1.998(6)	Mn(1)–N(2)	1.985(5)
Mn(1)–O(1)	2.194(7)	N(1)–C(1)	1.414(8)
N(1)–Si(1)	1.732(7)	N(2)–C(16)	1.435(10)
N(2)–Si(2)	1.727(8)	Mn(2)–N(3)	1.986(5)
Mn(2)–N(4)	2.004(6)	Mn(2)–O(2)	2.203(7)
N(3)–C(201)	1.430(11)	N(3)–Si(3)	1.729(8)
N(4)–C(216)	1.434(8)	N(4)–Si(4)	1.709(8)
Mn(3)–N(5)	1.994(6)	Mn(3)–N(6)	1.991(8)
Mn(3)–O(3)	2.158(5)	N(5)–C(301)	1.430(13)
N(5)–Si(5)	1.719(6)	N(6)–C(316)	1.463(8)
N(6)–Si(6)	1.711(7)		
N(1)–Mn(1)–N(2)	143.8(3)	N(1)–Mn(1)–O(1)	107.2(2)
N(2)–Mn(1)–O(1)	109.0(2)	Mn(1)–N(1)–C(1)	114.6(5)
Mn(1)–N(1)–Si(1)	123.9(3)	C(1)–N(1)–Si(1)	119.8(5)
Mn(1)–N(2)–C(16)	115.9(5)	Mn(1)–N(2)–Si(2)	127.1(4)
C(16)–N(2)–Si(2)	116.2(5)	N(3)–Mn(2)–N(4)	144.3(3)
N(3)–Mn(2)–O(2)	109.4(3)	N(4)–Mn(2)–O(2)	106.3(3)
Mn(2)–N(3)–C(201)	112.8(5)	Mn(2)–N(3)–Si(3)	129.1(4)
C(201)–N(3)–Si(3)	117.3(4)	Mn(2)–N(4)–C(216)	112.1(5)
Mn(2)–N(4)–Si(4)	122.4(3)	C(216)–N(4)–Si(4)	123.5(5)
N(5)–Mn(3)–N(6)	143.4(2)	N(5)–Mn(3)–O(3)	106.3(3)
N(6)–Mn(3)–O(3)	110.3(2)	Mn(3)–N(5)–C(301)	113.5(4)
Mn(3)–N(5)–Si(5)	121.1(4)	C(301)–N(5)–Si(5)	123.7(5)
Mn(3)–N(6)–C(316)	112.0(5)	Mn(3)–N(6)–Si(6)	129.1(3)
C(316)–N(6)–Si(6)	118.4(6)		

Table III. Selected bond lengths (Å) and angles (°) for Mn[N(SiMe₃)Ar]₂[THF] (**2**).

Mn(1)–Mn(2)	3.023(1)	Mn(1)–N(1)	1.980(3)
Mn(1)–N(30)	2.123(3)	Mn(1)–N(50)	2.141(3)
Mn(2)–N(30)	2.157(3)	Mn(2)–N(50)	2.135(3)
Mn(2)–N(30a)	2.157(3)	Mn(2)–N(50a)	2.135(3)
Si(1)–N(1)	1.717(4)	N(1)–Si(2)	1.716(4)
N(30)–C(30)	1.439(5)	N(50)–C(50)	1.444(4)
N(1)–Mn(1)–N(30)	138.6(1)	N(1)–Mn(1)–N(50)	131.0(1)
N(30)–Mn(1)–N(50)	90.4(1)	N(30)–Mn(2)–N(50)	89.6(1)
N(30)–Mn(2)–N(30a)	118.9(2)	N(50)–Mn(2)–N(30a)	127.9(1)
N(30)–Mn(2)–N(50a)	127.9(1)	N(50)–Mn(2)–N(50a)	106.6(2)
N(30a)–Mn(2)–N(50a)	89.6(1)	Mn(1)–N(1)–Si(1)	118.7(2)
Mn(1)–N(1)–Si(2)	117.5(2)	Si(1)–N(1)–Si(2)	123.7(2)
Mn(1)–N(30)–Mn(2)	89.9(1)	Mn(1)–N(30)–C(30)	118.2(2)
Mn(2)–N(30)–C(30)	133.6(2)	Mn(1)–N(50)–Mn(2)	90.0(1)
Mn(1)–N(50)–C(50)	115.1(2)	Mn(2)–N(50)–C(50)	133.6(2)

Table IV. Selected interatomic distances (Å) and angles (°) for Mn₃[N(H)Ar]₄[N(SiMe₃)₂]₂·C₇H₈ (**4**).

In **2** there are three similar, but independent Mn[N(SiMe₃)Ar]₂[THF] monomers in the asymmetric unit. One of these is shown in Fig. 1. Each manganese(II) atom binds two amide ligands and one THF molecule, resulting in a distorted trigonal planar geometry. The maximum displacement of a manganese atom from its N₂O plane is 0.021 Å, for Mn(1). The average N–Mn–N angle is 143.8 ± 0.5°, whereas the N–Mn–O angles range from 106.3 to 110.3(3)°. This simply reflects the greater steric requirements of the N(SiMe₃)(Ar) groups. Similar compression of the

N–Mn–O angle relative to the N–Mn–N angle is also observed in related THF adducts (Table V). Both the average Mn–N (terminal) and the Mn–O distances of 1.993 ± 0.011 Å and 2.185 ± 0.018 Å in **2** are similar to those found in related structures (Table V). The geometry about the nitrogen atoms is also approximately planar (N is at most 0.113 Å above its MnCSi plane) suggesting that π -delocalization with Si and the metal center is possible. The MnCSi planes are twisted by 52 ± 3° relative to each other allowing the bulky aromatic groups to be well separated in space.

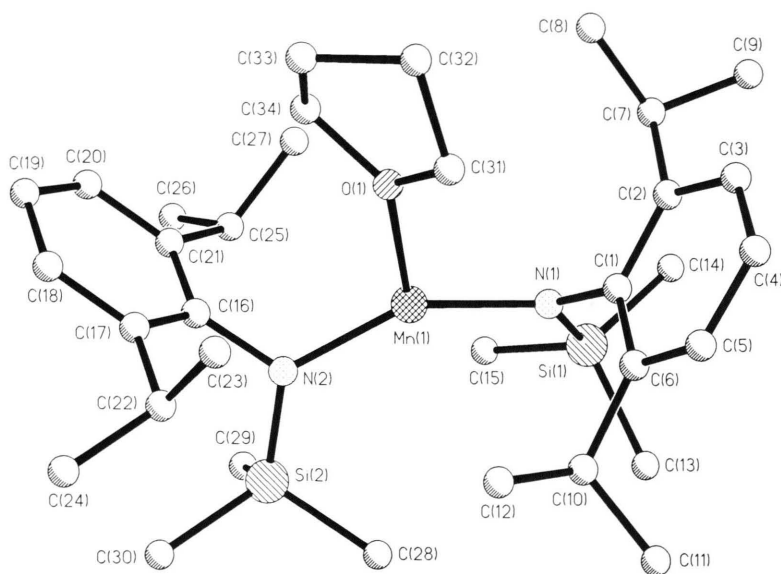


Fig. 1. Perspective view of one of the three similar but independent $\text{Mn}[\text{N}(\text{SiMe}_3)\text{Ar}]_2[\text{THF}]$ molecules in the asymmetric unit of **2**. The hydrogen atoms have been omitted for clarity.

The structure of $\text{Mn}[\text{N}(\text{H})\text{Ar}]_2[\text{THF}]$ (**1**) is expected to be very similar to that of **2** and $\text{Mn}[\text{N}(\text{SiMe}_3)_2]_2[\text{THF}]$ [8]. In addition, with the absence of THF as a coordinating solvent, $\text{Mn}[\text{N}(\text{H})\text{Ar}]_2$ (**3**) is expected to be a polynuclear manganese species which may possess a geometry similar to **4** or to $[\text{Mn}[\text{N}(\text{SiMe}_3)_2]_2]$ [6].

The X-ray structural analysis of $\text{Mn}_3[\text{N}(\text{H})\text{Ar}]_4[\text{N}(\text{SiMe}_3)_2] \cdot \text{C}_7\text{H}_8$ (**4**) (Fig. 2) reveals an almost linear ($170.3(1)^\circ$) array of three manganese(II) atoms bridged by four nitrogen (NHAr) atoms and capped at both ends by a terminal nitrogen ($\text{N}(\text{SiMe}_3)_2$). The four-membered Mn–N rings have internal angles of $90.4(1)^\circ$ at

Mn(1) and $89.6(1)^\circ$ at Mn(2). The planes (maximum displacement from least squares plane is $0.031 \text{ \AA}$) formed by these rings are twisted by 75.7° to each other resulting in a distorted tetrahedral arrangement of nitrogen atoms around Mn(2) and a distorted trigonal planar (maximum displacement of Mn(1) from the N_3 plane is $0.028 \text{ \AA}$) arrangement of nitrogen atoms around Mn(1) and Mn(1a). As in **2** the geometry about the terminal nitrogens is planar (N is at most $0.033 \text{ \AA}$ above its MnSi_2 plane), however the bridging nitrogens (N30, N50) do not have a planar environment which suggests that H atoms are attached to them. The hydrogen atoms on the bridging nitrogens

Table V. Bond lengths ($\text{\AA}$) and angles ($^\circ$) for related manganese(II) compounds (at room temperature except where noted)

Compound	Mn–N _t ^d	Mn–N _b ^e	Mn–O _{THF}	N _t –Mn–N _t ^d	N–Mn–O	Ref.
$\text{Mn}[\text{N}(\text{SiMe}_3)(2,6\text{-Pr}_2\text{C}_6\text{H}_3)]_2[\text{THF}]^a$ (2)	1.985–2.004(6)	–	2.158–2.203(7)	143.4–144.3(3)	106.3–110.3(3)	this work
$\text{Mn}[\text{N}(\text{SiMe}_3)_2]_2[\text{THF}]$	1.99(2)	–	2.16(2)	145–150	101–113	[8]
$\text{Mn}[\text{N}(\text{SiMe}_3)_2]_2[\text{THF}]_2$	2.033–2.048(5)	–	2.226–2.249(5)	131.7(2)	98.4–117.3(2)	[11]
$\text{Mn}[\text{C}(\text{H})(\text{SiMe}_3)_2]_2[\text{THF}]$	–	–	2.19(2)	160.1(9) ^f	100.0(6) ^g	[24]
$\text{Mn}[\text{N}(\text{SiMe}_3)_2]_2\text{Li}(\text{THF})$	2.023(3)	–	–	–	–	[9b]
$\text{Mn}[\text{N}(\text{SiMe}_3)_2]_2^b$	1.994	2.184	–	98.9 ^h	–	[9a]
$\text{Mn}[\text{N}(\text{SiMe}_3)_2]_2^c$	1.997–1.999(3)	2.170–2.174(3)	–	99.2(1) ^h	–	[9b]
$\text{Mn}_3[\text{N}(\text{H})2,6\text{-iPr}_2\text{C}_6\text{H}_3]_4[\text{N}(\text{SiMe}_3)_2]_2^a$ (4)	1.980(3)	2.123–2.157(3)	–	89.6–90.4(1) ^h	–	this work
$\text{Mn}_3(\text{NEt}_2)_6(\text{Cl})_2[\text{Li}(\text{THF})_2]_2$	–	2.089–2.203(5)	–	91.5–94.7(2) ^h	–	[3]
$\text{Mn}_3(\text{mesityl})_6$	–	–	–	98.0–98.6(4) ⁱ	–	[20]

^a This work, 153 K; ^b high thermal motion, treat numbers with caution; ^c 140 K; ^d N_t is a terminal nitrogen; ^e N_b is a bridging nitrogen; ^f C–Mn–C angle; ^g C–Mn–O angle; ^h internal N_b–Mn–N_b angle within the Mn_2N_2 ring; ⁱ internal C_b–Mn–C_b angle within the Mn_2C_2 ring.

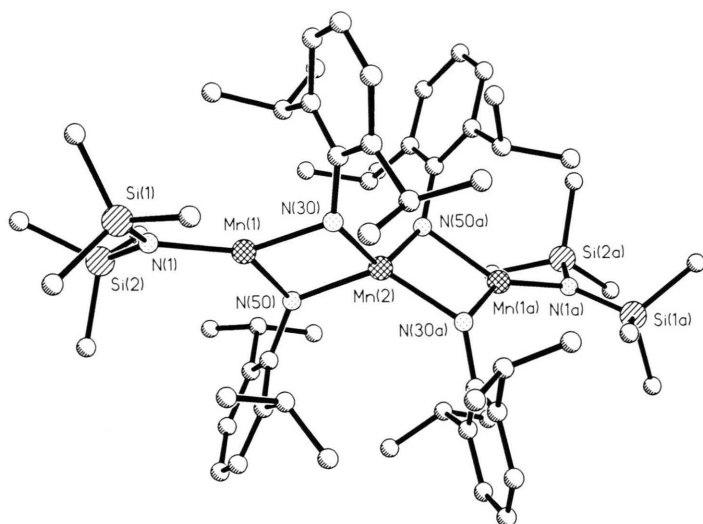


Fig. 2. Perspective view of $\text{Mn}_3[\text{N}(\text{H})\text{Ar}]_4[\text{N}(\text{SiMe}_3)_2]_2$ (**4**). The hydrogen atoms and the toluene solvent molecule have been omitted for clarity.

were detected in difference Fourier maps and their presence is further supported by the observation of an N–H absorbance (3290 cm^{-1}) in the IR spectrum.

The Mn(1)–N(1) distance of $1.980(3)\text{ \AA}$ is comparable to the terminal Mn–N distances found in $\text{Mn}[\text{N}(\text{SiMe}_3)_2][\text{THF}]$ [8] and $[\text{Mn}[\text{N}(\text{SiMe}_3)_2]_2]$ [9] (Table V). As expected, the bridging Mn–N distances in **4** ($2.123\text{--}2.157(3)\text{ \AA}$) are significantly longer than the terminal Mn–N distances in **4** and **2** ($1.980(3), 1.993(8)\text{ \AA}$ respectively). However, this bridging Mn–N bond length is slightly shorter than, although comparable to, the other bridging Mn–N distances found in $\text{Mn}_3[\text{NEt}_2]_6\text{Cl}_2[\text{Li}(\text{THF})_2]_2$ ($2.150\text{ \AA}$) [3] and $[\text{Mn}[\text{N}(\text{SiMe}_3)_2]_2]$ ($2.184\text{ \AA}$) [9].

Several non-linear trinuclear complexes of manganese(II) are known [17] and there are also two examples of linear mixed-valence (Mn(II)/Mn(III))

complexes, $\text{Mn}_3(\text{O}_2\text{CMe})_4(\text{saladhp})_2(\text{MeOH})$ [18] and $[\text{PPh}_4]_2[\text{Mn}_3(\text{pdt})_5]$ [19]. However, examples containing a linear arrangement of three manganese(II) centers are rare. Discrete linear trinuclear compounds of manganese(II) have only been encountered in a handful of derivatives, $\text{Mn}_3^{\text{II}}(\text{mesityl})_6$ [20], $\text{Mn}_3^{\text{II}}[\text{NEt}_2]_6\text{Cl}_2[\text{Li}(\text{THF})_2]_2$ [3], $\text{Mn}_3^{\text{II}}(\text{O}_2\text{CCMe}_3)_6(\text{biphme})_2$ [21], $\text{Mn}_3^{\text{II}}(\text{OC}(\text{H})\text{Bu}^t)_6$ [22], and recently $\text{Mn}_3^{\text{II}}(\text{O}_2\text{CCF}_3)_6$ [23], which was also prepared in our research group. To our knowledge, **4** is the first such compound with exclusively nitrogen donors [25].

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