

Reaction of AlMe_3 with $[\text{Mn}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{thf})]$ to form the unique methyl-bridged compound $[\{\text{Mn}(\mu\text{-Me})[\text{N}(\text{SiMe}_3)_2\text{AlMe}_3]\}_2]$

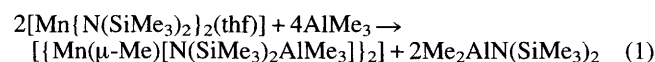
Mark Niemeyer and Philip P. Power*

Department of Chemistry, University of California, Davis, California 95616, USA

The synthesis and structural characterization of the novel transition-metal amido/alkyl compound $[\{\text{Mn}(\mu\text{-Me})[\text{N}(\text{SiMe}_3)_2\text{AlMe}_3]\}_2]$ **1** via the reaction of AlMe_3 with $[\text{Mn}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{thf})]$ are reported; **1** features a unique $\text{Mn}(\mu\text{-Me})_2\text{Mn}$ type of bridged structure stabilized by Mn–Me interactions involving a methyl group from AlMe_3 .

Manganese(II) alkyl derivatives have played an important role in the development of transition organo-metal chemistry.¹ Neutral manganese(II) alkyls have been known for almost 60 years² but the first well characterized manganese(II) alkyls were not reported until 1976³ with the disclosure of the structures and spectroscopies of $[\{\text{Mn}(\text{CH}_2\text{SiMe}_3)_2\}_\infty]$, $[\{\text{Mn}(\text{CH}_2\text{Bu}^t)_4\}]$ and $[\{\text{Mn}(\text{CH}_2\text{CMe}_2\text{Ph})_2\}_2]$. Interestingly, these compounds were also the first alkyl-bridged transition-metal species to be well characterized. Increasing the size of the alkyl group has resulted in monomeric or dissociated species as in the crystal structure of $[\text{Mn}\{\text{C}(\text{SiMe}_3)_3\}_2]$ ⁴ and the vapour-phase structures of $[\{\text{Mn}(\text{CH}_2\text{Bu}^t)_2\}_2]$ ⁵ or $[\{\text{Mn}[\text{CH}(\text{SiMe}_3)_2]\}_2]$.⁶ The research on manganese(II) alkyls has often been paralleled by work on amides, owing to the close electronic and steric relationship of alkyl and amide groups.⁷ Thus, derivatives of the $-\text{CH}(\text{SiMe}_3)_2$ and $-\text{N}(\text{SiMe}_3)_2$ groups are isoelectronic and frequently isostructural. By the same token the $-\text{C}(\text{SiMe}_3)_3$ and $-\text{N}(\text{SiMe}_3)_2\text{AlMe}_3$ groups have been recognized⁸ as isoelectronic and the structures of their derivatives can be compared. Indeed, work has shown that the compounds $[\text{Yb}\{\text{C}(\text{SiMe}_3)_3\}_2]$ ⁹ and $[\text{Yb}\{\text{N}(\text{SiMe}_3)_2\text{AlMe}_3\}_2]$ ¹⁰ have very similar structures. In contrast, the lithium derivatives $[\{\text{LiC}(\text{SiMe}_3)_3\}_2]$ ¹¹ and $[\{\text{LiN}(\text{SiMe}_3)_2\text{AlMe}_3\}_\infty]$ ⁸ differ structurally, a circumstance that can be traced to the greater polarity of the aluminium nitrogen or carbon bonds. In this paper a new application of the $-\text{N}(\text{SiMe}_3)_2\text{AlMe}_3$ ligand in the stabilization of a bridged methyl manganese complex, as well as a novel type of transition-metal amido/alkyl, are reported.

The title compound $[\{\text{Mn}(\mu\text{-Me})[\text{N}(\text{SiMe}_3)_2\text{AlMe}_3]\}_2]$ **1** was synthesized as described† in eqn. (1) and proceeds with



the elimination of $\text{Me}_2\text{AlN}(\text{SiMe}_3)_2$. **1** is a pale yellow, extremely air-sensitive, crystalline material. Although it decomposes rapidly at 115–118 °C, it becomes a black oil at room temperature over a period of two days and, even in a –20 °C freezer, slow decomposition is apparent over a period of several weeks.

The structure§ of **1** was determined at 130 K. A centre of symmetry is crystallographically required in the methyl-bridged dimer as shown in Fig. 1. In addition to two bridging methyls, the manganese atoms are coordinated by a nitrogen and a $\text{CH}_3[\text{C}(10)]$ group from the $-\text{N}(\text{SiMe}_3)_2\text{AlMe}_3$ ligand. The two bridging methyls have slightly different bond lengths to the manganese atoms, $[\text{Mn}–\text{C}(1)/\text{C}(1a)]$ 2.201(11)/2.285(11) Å. These distances are also close to the $\text{Mn}–\text{C}(10)$ interaction of 2.323(11) Å, involving the methyl group bridging to aluminium. The $\text{Al}(1)–\text{C}(10)$ bond distance, 2.105(12) Å, is 0.12 Å

longer than the other two $\text{Al}–\text{C}$ interactions. The $\text{Mn}–\text{N}$ and $\text{Al}–\text{N}$ distances are 2.177(8) and 1.966(8) Å, and the $\text{Mn}\cdots\text{Mn}$ separation is 2.712(3) Å. Further important structural parameters are given in the figure legend.

The bridged methyl structure observed in **1** is quite rare in transition-metal alkyl chemistry where most examples involve β -stabilized alkyl groups.³ For first-row transition metals only a handful of methyl-bridged species have been structurally characterized,¹² all of which involve stabilizing phosphine, cyclopentadiene or π -allyl¹³ co-ligands. The observation of unequal bridging metal–methyl distances has been explained^{12a} on the basis of an agostic¹⁴ $\text{M}–\text{H}–\text{CH}_2–\text{M}$ interactions. The difference between the two $\text{Mn}–\text{C}$ distances in **1** is 0.084 Å, which is somewhat smaller than the differences (0.16–0.2 Å) seen in the adducts¹⁵ $[\text{Mn}_2(\text{CH}_2\text{Bu}^t)_4(\text{PMe}_3)_2]$, $[\text{Mn}_2(\text{CH}_2\text{SiMe}_3)_4(\text{PMe}_3)_2]$, $[\text{Mn}_2(\text{CH}_2\text{SiMe}_3)_4(\text{PMePh}_2)_2]$ or $[\text{Mn}_2(\text{CH}_2\text{Ph})_4(\text{PMe}_3)_2]$, suggests that possible agostic interactions are weak. Furthermore, the locations of the hydrogens on the bridging methyl groups C(1) and C(1a) do not support the existence of a strong agostic effect in **1** since none of the hydrogens appear to be in the Mn_2C_2 plane where the $\text{C}–\text{H}–\text{M}$ interaction can be maximized. It appears that the bridging methyls are primarily bound to the manganese atoms through a simpler interaction involving an sp^3 orbital on each of the carbons. It is also notable that the bridging $\text{Mn}–\text{C}$ bond lengths are on average somewhat shorter than those in the phosphine adducts excepting the benzyl derivative. These parameters suggest that the Mn centres in **1** are slightly less crowded than those in the phosphine adducts. The $\text{Mn}\cdots\text{Mn}$ distance in **1** also supports this argument¹⁵ where only the benzyl compound has a slightly shorter $\text{Mn}\cdots\text{Mn}$ separation.

The $\text{Mn}–\text{N}$ bond length, 2.177(8) Å, is almost identical to the bridging $\text{Mn}–\text{N}$ distance, 2.174(3) Å, observed in $[\{\text{Mn}[\text{N}(\text{SiMe}_3)_2]\}_2]$.¹⁶ This observation is consistent with the four-coordination, and the bridging character, of the amide nitrogen. The $\text{N}–\text{Si}$ distances can be similarly rationalized

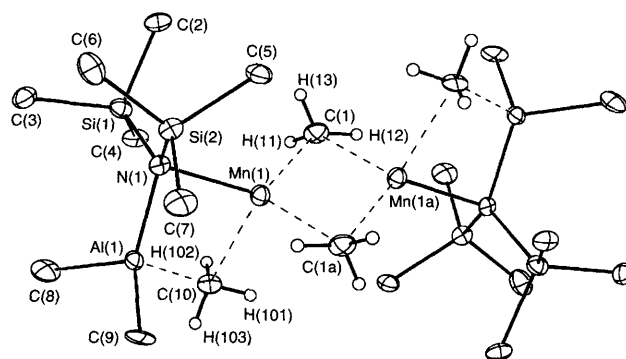


Fig. 1 Thermal ellipsoidal plot of **1** including bridging methyl hydrogens. Important bond distances (Å) and angles (°) not given in text are as follows: $\text{Al}(1)–\text{C}(8)$ 1.976(11), $\text{Al}(1)–\text{C}(9)$ 1.985(10), $\text{N}(1)–\text{Si}(1)$ 1.807(8), $\text{N}(1)–\text{Si}(2)$ 1.769(8); $\text{C}(1)–\text{Mn}–\text{C}(1a)$ 105.6(3), $\text{Mn}–\text{C}(1)–\text{Mn}(1a)$ 74.4(3), $\text{N}(1)–\text{Mn}(1)–\text{C}(1)$ 123.7(4), $\text{N}(1)–\text{Mn}(1)–\text{C}(1a)$ 116.9(3), $\text{C}(1)–\text{Mn}(1)–\text{C}(10)$ 115.2(4), $\text{C}(1a)–\text{Mn}(1)–\text{C}(10)$ 103.4(4), $\text{Al}(1)–\text{C}(10)–\text{Mn}(1)$ 77.7(4), $\text{N}(1)–\text{Al}(1)–\text{C}(10)$ 102.6(4).

although these distances are on average slightly (*ca.* 0.03 Å) longer than those observed in $[\{\text{LiN}(\text{SiMe}_3)_2\text{AlMe}_3\}_\infty]$.⁸ The Al–N bond length is similar to those observed for amine–organoaluminium adducts.¹⁷

The most striking feature of the coordination at aluminium concerns the Al(1)–C(10) bond which is at least 0.12 Å longer than either of the other two non-manganese interactive Al–C bonds. This elongation is consistent with the close [2.323(11) Å] Mn–C(10) interaction which is only 0.05 Å longer than the Mn–C(1a) bond distance. In effect, the manganese binds almost equally strongly with three bridging methyl groups. Further evidence for the strong Mn–C(10) interaction comes from the relatively acute Mn(1)–N(1)–Al(1) angle of 84.2(3)°. The magnetic susceptibility of **1** at 298 K is 2.9(1) μ_{B} and is consistent with strong antiferromagnetic coupling. ¹H NMR (*ca.* 1 mol dm^{−3}, 298 K) spectroscopy of **1** in [²H₈]toluene did not show a ‘clean’ pattern. Instead, a multiplicity of peaks was observed that was indicative of dissociative behaviour.

In summary, a new aspect of the chemistry of the –N(SiMe₃)₂AlMe₃ ligand has been shown in the cleavage of Mn–N and Al–C bonds to form **1**. In addition, the efficacy of the –N(SiMe₃)₂AlMe₃ group in the stabilization of hitherto unknown transition metal-bridging methyl moieties, as well as a novel class of transition-metal amido/alkyls has been demonstrated.

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Footnotes

† A 2 mol dm^{−3} solution of AlMe₃ (2.46 ml, 4.92 mmol) in toluene was added, with cooling in a dry ice–acetone bath, to $[\text{Mn}\{\text{N}(\text{SiMe}_3)_2(\text{thf})\}]^{18}$ (1.10 g, 2.46 mmol) in toluene (10 ml). The solution was stirred for 1 h whereupon the cooling bath was removed. The resulting pale amber solution was then stirred for a further hour at room temperature. Removal of the volatile materials under reduced pressure afforded an amber oil which was redissolved in *ca.* 3 ml of *n*-hexane. Cooling in a −20 °C freezer for 6 days afforded the product as pale yellow, extremely air-sensitive crystals. The crystals decompose in 2 days to a black oil. In a −20 °C freezer some decomposition is observed within one week. Yield 0.48 g, 65%, mp 115–118 °C (decomp.) $\mu_{\text{eff}} = 2.9 \mu_{\text{B}}$ (298 K). IR (Nujol, cm^{−1}) 1922vs, 1399w, 1297w, 1255vs, 1222s, 1187s, 1018w, 968s, 865vs, br, 779vs, 765(sh), 703vs, 669(sh), 628s, 618s, 583s, 513s, 481s, 415(sh), 380(sh), 295m 215w.

‡ This compound has not been characterized. It appears to disproportionate into Al₂Me₃N(SiMe₃)₂ and MeAl[N(SiMe₃)₂]₂ as described in: N. Wiberg, W. Baumeister and P. Zahn, *J. Organomet. Chem.*, 1972, **36**, 267; M. Trapp, H.-D. Hausen, G. Weckler and J. Weidlein, *J. Organomet. Chem.*, 1993, **450**, 53.

§ Crystal data for **1**: at 130 K with Cu–K α ($\lambda = 1.54178$ Å) radiation; monoclinic, space group $P2_1/n$, $a = 14.206(7)$, $b = 8.865(3)$, $c = 15.137(6)$ Å, $\beta = 117.13(3)^\circ$, $Z = 4$, $R = 0.087$ for 1528 [$I > 2\sigma(I)$] data. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/111.

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