positional parameters, anisotropic thermal parameters, bond angles, bond distances, and observed and calculated structures for III and IV (63 pages). Ordering information is given on any current masthead page.

Preparation of Yb[N(SiMe₃)₂]₂[AlMe₃]₂. A Complex with Four Yb–Me–Al Interactions[†]

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Summary: Trimethylaluminum reacts with base-free ytterbium bis[bis(trimethylsilyl)amide] to give Yb[N-(SiMe₃)₂]₂[AlMe₃]₂. The X-ray crystal structure provides evidence for four Yb–Me–Al and two Yb–Me–Si bridging interactions.

Bridging alkyl compounds formed by interaction of aluminum alkyls with early d- and f-element organometallic compounds are of interest relative to structure and bonding[1] as well as to the mechanism of Ziegler–Natta polymerization processes.[2] Several compounds have been isolated in which two methyl groups of an aluminum alkyl forms bridges between the main-group and f-block metal,[3] as in $Me_4Al_2(\mu\text{-}Me)_2$;[4] viz., the methyl group contributes one σ-type molecular orbital and a single electron to the bridge bonding.

Base-free $Yb_2[N(SiMe_3)_2]_4$[5] is a dimer with two terminal and two bridging silylamide groups and both ytterbium atoms are three-coordinate. The overall geometry is similar to that found for $Mn_2[N(SiMe_3)_2]_4$[6a,b] and $Co_2[N(SiMe_3)_2]_4$.[6b] The Yb–N–Yb bridge in $Yb_2[N(SiMe_3)_2]_4$ can be cleaved by Lewis bases, such as phosphines, to give $Yb[N(SiMe_3)_2]_2(Me_2PCH_2CH_2PMe_2)$,[7a] and by molecules that have Lewis acidic and basic sites present in the same
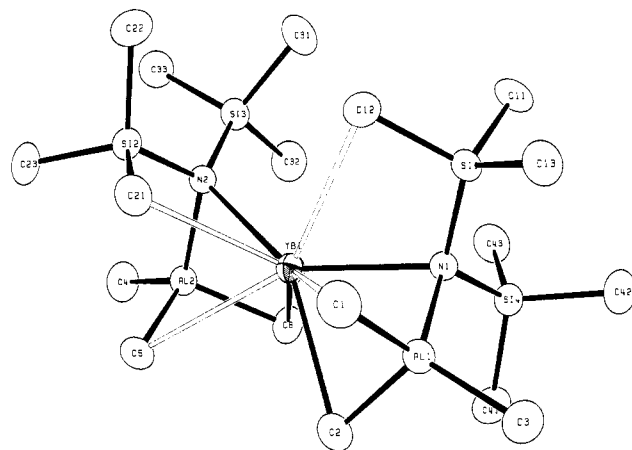
Figure 1. An ORTEP drawing of I, Yb[N(SiMe₃)₂]₂(AlMe₃)₂, showing the divalent ytterbium atom in eight-coordination.

molecule, such as $NaN(SiMe_3)_2$ to give $NaYb[N(SiMe_3)_2]_3$.[7b] The latter complex contains two silylamide groups that bridge the metal atoms with the lone pair of electrons on the nitrogen atoms acting as donors toward the alkali and lanthanide metal atoms. In this communication we describe a complex formed between $Yb_2[N(SiMe_3)_2]_4$ and the Lewis acid Me_6Al_2 that contains two bridging and two semibridging Yb–Me–Al interactions.

Two molar equivalents of Me_6Al_2 react with $Yb_2[N(SiMe_3)_2]_4$ in pentane to give a bright yellow solution from which yellow plates of diamagnetic $Yb[N(SiMe_3)_2]_2$-$(Me_3Al)_2$ (I) were obtained by crystallization from pentane at -20 °C in essentially quantitative yield.[8] Triethylaluminum behaves similarly giving the yellow, low melting $Yb[N(SiMe_3)_2]_2(Et_3Al)_2$.[9] Figure 1 shows an ORTEP of I. The complex can be thought of as being derived from a monomeric $Yb[N(SiMe_3)_2]_2$ fragment in which each lone pair of electrons on the nitrogen atoms is coordinated to aluminum atoms so that the coordination number of the nitrogen and aluminum atoms is four. The averaged Al–N distance of 1.963 (5) Å and the averaged Yb–N–Al angle of 80.5 (7)° are similar to those found in $Me_4Al_2(\mu\text{-}NPh_2)(\mu\text{-}Me)$[10a] of 2.003 (3) Å and 85.6 (1)° and Me_4Al_2-$(\mu\text{-}NMe_2)_2$[10c] of 1.96 (1) Å and 91.6 (2)°, respectively. The Yb–N(1) and Yb–N(2) bond lengths of 2.510 (2) and 2.573

[†] This paper is dedicated to the memory of the late Professor E.L. Muetterties with thanks for his wisdom and guidance.

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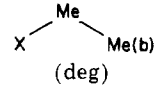
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(8) (a) NMR: ¹H, δ 0.28 (s, 36 H), –0.25 (s, 18 H), temperature independent to –85 °C; ¹³C{¹H}, δ 5.36 and 0.85 due to Me₃Si and Me₃Al, respectively; IR (Nujol) 1260 (m), 1250 (s), 1212 (w), 1185 (w), 880 (s), 832 (s), 775 (m), 755 (m), 725 (m), 715 (w), 625 (s), 615 (w), 532 (w), 505 (w), 442 (m), 360 (w) cm⁻¹; MS (CI CH₅⁺): 637 (M – 1)⁺, the experimental (M – 1)⁺ ion matched the simulated spectrum beautifully. Crystal data (–95 °C): triclinic, $P\bar{1}$, a = 9.8707 (17) Å, b = 12.9348 (17) Å, c = 13.1081 (20) Å, α = 68.12 (11)°, β = 83.19 (15)°, γ = 84.39 (14)°, V = 1539.5 Å³, Z = 2, d(calcd) = 1.39 g cm⁻³, μ = 32.456 cm⁻¹, crystal size, 0.33 × 0.36 × 0.22 mm, Mo Kα (λ = 0.710 73 Å). The 4012 raw intensity data were reduced to structure factor amplitudes and their esd's by correction for background, scan speed, and Lorentz and Polarization effects.[8d] A 2.75% linear decay in three standard reflections was observed, and the data were corrected. A three-dimensional Patterson synthesis revealed the position of the Yb, Al, and Si atoms and the remaining atoms were located by Fourier techniques. An empirical absorption correction using azimuthal scan data was applied.[8d] The final residuals for 245 variables refined against 3814 data for which $F^2 > 3\sigma(F^2)$ were R = 0.0169, R_w = 0.0258, and GOF = 1.857. The R for all 4012 data was 0.019. (c) The hydrogen atoms on C(2) and C(6) were located in the Fourier difference maps, but they were not refined since we did not collect high angle data ($2\theta > 45°$). (d) Boncella, J. M.; Andersen, R. A. *Inorg. Chem.* **1984** *23*, 432.

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Table I

compound	Al-C_b,[a] Å	Al-C_t,[b] Å	Δ,[c] Å	Me M⟋ ⟍Al (deg)	Me X⟋ ⟍Me(b) (deg)	ref
$Me_4Al_2(\mu\text{-}Me)_2$	2.125 (2)	1.953 (2)	0.17	75.7 (1)	104.3 (1)	4
$Me_4Al_2(\mu\text{-}Me)(\mu\text{-}NPh_2)$	2.142 (2)	1.948 (5)	0.19	78.9 (2)	94.7 (2)	10a
$Me_4Al_2(\mu\text{-}Me)_4Mg$	2.13 (2)	1.96 (1)	0.17	77.7 (3)	105.7 (1)	10b
$Me_2Al(\mu\text{-}Me)_2YCp_2$	2.10 (1)	1.94 (1)	0.16	80.8 (4)	112 (1)	3b
$Me_2Al(\mu\text{-}Me)_2YbCp_2$	2.13 (2)	2.00 (1)	0.13	78.9 (6)	113.3 (8)	3a
I	2.009 (2)	1.959 (2)	0.05	65.9 (7)	107.7 (4)	this work
	2.029 (1)		0.07	73.8 (1)	104.5 (6)	

[a] b = bridging carbon atom.   [b] t = terminal carbon atom.   [c] Δ is [Al-C_b]-[Al-C_t].

(2) Å are longer than the equivalent bond length of 2.46 (2) Å in $NaYb[N(SiMe_3)_2]_3$.[7b] The N(1)–Yb–N(2) angle of 131.56 (5)° is similar to that found in $Yb[N(SiMe_3)_2]_2(Me_2PCH_2CH_2PMe_2)$[7a] of 123.6 (6)°.

The methyl groups C(1,2) and C(5,6) bridge the aluminum and ytterbium atoms with Al(1)–C(1,2) and Al(2)–C(5,6) distances of 2.005 (2), 2.030 (2), 2.012 (2), and 2.027 (2) Å, respectively, with an average of 2.019 (11) Å. The averaged bridge distance is significantly shorter than that found for the Al–C bridging distance in $Me_4Al_2(\mu\text{-}Me)_2$ and $Me_4Al_2(\mu\text{-}Me)(\mu\text{-}NPh_2)$ of 2.125 (2)[4] and 2.142 (2) Å,[10a] respectively. The averaged Al–C(2,6)–Yb and Al–C-(1,5)–Yb angles of 73.8 (1) and 65.9 (7)°, respectively, are similar to the equivalent angles in $Cp_2Yb(\mu\text{-}Me)_2AlMe_2$ and $Cp_2Y(\mu\text{-}Me)_2AlMe_2$ of 78.9 (6)[3a] and 80.8 (4)°,[3b] respectively. The averaged N(1)–Al(1)–C(1,2) and N(2)–Al-(2)–C(5,6) angle is 106.1 (1.6)° and the averaged N(1)–Al(1)–C(3) and N(2)–Al(2)–C(4) angle is 116.6 (4)°, similar to the equivalent angles in $Me_4Al_2(\mu\text{-}Me)(\mu\text{-}NPh_2)$ of 108.9 (1.0) and 113.1 (1.1)°,[10a] respectively. The averaged terminal Al–C distance in I of 1.959 (2) Å is identical with that found for the equivalent distance in $Me_4Al_2(\mu\text{-}Me)_2$[4] of 1.953 (2) Å and in other related compounds as shown in Table I. Inspection of Table I shows that the bridging Al–C distances in I are ca. 0.1 Å shorter than this distance in related compounds. This concept may be expressed quantitatively by defining Δ, the averaged terminal Al–C distance minus the averaged bridging Al–C distance, for the series of related complexes in Table I. The Δ values show that the bridge bonds in I are approximately midway between bridging and terminal Al–C bonds in length and presumably in strength. As a consequence of the shorter bridging Al–C lengths in I, the bridging Yb–C bonds might be proportionately longer and therefore weaker.

The Yb–μ-C bond lengths fall into three ranges: two short distances, Yb–C(2,6) of 2.788 (2) and 2.756 (2) Å, respectively [average 2.767 (6) Å] with Yb–C–Al angles of 74.03 (7) and 73.65 (7)°, respectively, one intermediate distance, Yb–C(5) of 3.042 (2) Å and the Yb–C(5)–Al angle of 67.21 (7)°, and one long distance, Yb–C(1) of 3.202 (3)Å [average 2.95 (17) Å]. Further, the shortest Al–C distances are pairwise related to the longest Yb–C distances. The two short Yb–C distances are close to those found in $Cp_2Yb(\mu\text{-}Me)_2AlMe_2$ and $Cp_4Y_2(\mu\text{-}Me)_2$ of 2.59 (2) and 2.54 (1) Å, respectively,[3a] since the radius of Yb(II) is ca. 0.1 Å larger than that of Yb(III) or Y(III).[11] The two longer Yb–C distances are still shorter than the sum (3.3 Å) of the van der Waals radius of a carbon atom[12a] and the metallic radius of divalent ytterbium (1.7 Å).[12b] The relative weakness of the Yb–Me–Al interaction in I in the solid state is apparently true in solution since the line

shape in the ^1H NMR resonance experiment does not change to –80 °C. With the assumption of a chemical shift difference for the bridging and terminal methyl groups of 1 Hz at –80 °C, the upper limit for $\Delta G^\ddagger(T_c)$ is ca. 10 kcal mol^{-1}. This may be compared with $\Delta G^\ddagger(T_c)$ for bridge-terminal exchange in $Me_4Al_2(\mu\text{-}Me)_2$[13] and in $Cp_2Y(\mu\text{-}Me)_2AlMe_2$[3a] of ca. 11 and 16 kcal mol^{-1}, respectively. As a consequence of the Yb–C(2,6)–Al bridge bond, two hydrogen atoms on each carbon atom, H(2,3) on C(2) and H(4,6) on C(6), approach the ytterbium atom. The Yb–H(2,3,4,6) distances are 2.63, 2.72, 3.13, and 2.53 Å, respectively,[8c] suggesting that the Yb–Me–Al interaction is not just be way of the carbon atom, but the hydrogen atoms on the bridging methyl groups also are involved.

In addition to the short Yb–C–Al distances, two of the methyl groups on the silicon atoms have short Yb–C contacts. The Yb–C (12,21) distances are 3.067 (2) and 3.039 (2) Å, respectively, and all other intramolecular contacts are >3.5 Å. A similar phenomenon was noted in $Yb[N(SiMe_3)_2]_2(Me_2PCH_2CH_2PMe_2)$,[7a] in which the ytterbium to carbon contact distance is 3.04 Å and discussed in some detail in ref 7b.

In summary, the coordination at ytterbium in I may be described as either four- or eight-coordinate. However, the geometry is so irregular that it is impossible to describe the stereochemistry in a precise fashion using the dihedral angle formalism advocated by Muetterties.[14] Even though the bridging interaction in I is weak, the chemistry of I is substantially different than trimethylaluminum or its coordination complexes. In particular, I polymerizes ethylene at 20 °C and 12 atm whereas trimethylaluminum does not polymerize ethylene under such mild conditions.[15] These and other reactions will be described later.

Supplementary Material Available: Tables of bond lengths and angles and positional and thermal parameters and structure factors (25 pages). Ordering information is given in any current masthead page.

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