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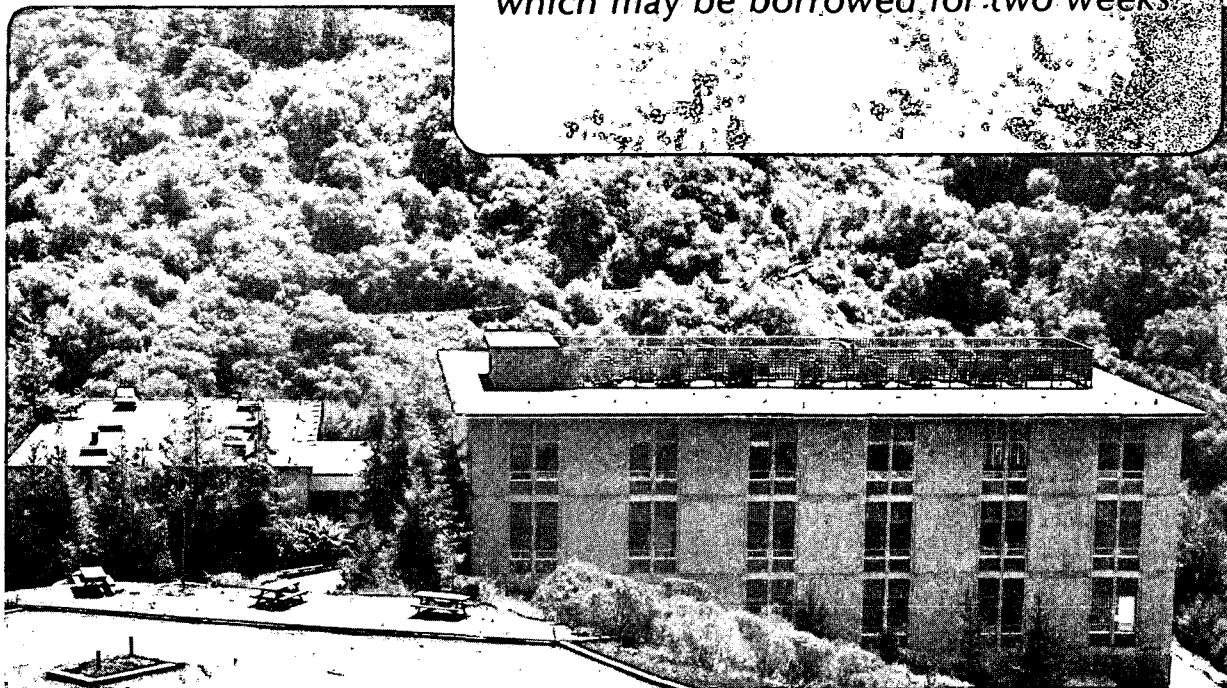
DIVALENT LANTHANIDE CHEMISTRY. PREPARATION
OF BASE-FREE DIMERIC BIS[BIS(TRIMETHYLSILYL)
AMIDO]-YTTERBIUM(II) AND SOME OF
ITS REACTIONS WITH PROTIC ACIDS

J.M. Boncella, T.D. Tilley, and R.A. Andersen

December 1986

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**Divalent Lanthanide Chemistry. Preparation of Base-Free
Dimeric Bis[bis(trimethylsilyl)amido]-Ytterbium(II)
and Some of its Reactions with Protic Acids**

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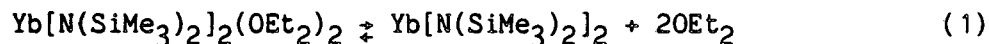
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Abstract

Base-free $\text{Yb}_2[\text{N}(\text{SiMe}_3)_2]_4$ can be prepared by gently heating a solution of $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2[\text{OEt}]_2$ in toluene while removing the volatile material under reduced pressure. The amide is dimeric in gas phase, by mass spectroscopy, in toluene solution, and in the solid phase by X-ray crystallography at -95°C . The space group is $P\bar{1}$, $a=8.868(1)\text{\AA}$, $b=12.561(2)\text{\AA}$, $c=21.560(3)\text{\AA}$, $\alpha=73.81(1)^\circ$, $\beta=86.70(1)^\circ$, $\gamma=71.26(1)^\circ$, and $V=2225(\text{\AA})^3$. The averaged Yb-N (terminal) distance is $2.305 \pm 0.003 \text{\AA}$ and the averaged Yb-N (bridge) distance is $2.502 \pm 0.035 \text{\AA}$. There are two short Yb...C contact distances per dimeric unit. In solution, the $\Delta G^\ddagger(\text{tc})$ for bridge-terminal exchange is $11.3 \text{ kcal mol}^{-1}$. On the basis of some acid-base reactions the pK_a of $\text{HN}(\text{SiMe}_3)_2$ is estimated to be between 30 and 35.

In an earlier paper,¹ we outlined our interests in and strategies for synthesis of divalent silylamides of the lanthanide elements of the type $M[N(\text{SiMe}_3)_2]_2$. We expected that these complexes with low coordination numbers enforced by sterically bulky ligands to undergo intra- and perhaps intermolecular reactions to remove the coordinative unsaturation at the large, electropositive metal centers. In this paper we describe the preparation of the base-free ytterbium complex, $\text{Yb}_2[\mu\text{-N}(\text{SiMe}_3)_2]_2[\text{N}(\text{SiMe}_3)_2]_2$, its crystal structure that shows four intra-molecular $\text{Yb}\dots\text{CH}_3\text{Si}$ bridge interactions, and some of its reactions with protic acids.

The orange diethylether complex, $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{OEt}_2)_2$,^{1a} turns red on dissolution in toluene. This suggested to us that the equilibrium shown in equation 1 exists



in toluene solution, assuming that the base-free complex is red in color. If this suggestion is correct, then removing the toluene-diethylether solvent mixture at elevated temperature and reduced pressure should drive the equilibrium to the right as diethyl ether is the most volatile component. Exposing a warm (60-70°C) solution of $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{OEt}_2)_2$ in toluene to a dynamic vacuum yields a red solution that gives red needles of $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2$ from pentane. The complex is dimeric in gas phase since it gives a molecular ion in the mass spectrum at 986 amu.

The ¹H NMR spectrum shows a single resonance at $\delta 0.32$ at room temperature and two equal area resonances at $\delta 0.48$ and 0.36 at -92°C. The low temperature spectrum suggests that the stereochemically rigid structure consists of a dimer with two terminal and two bridging $\text{N}(\text{SiMe}_3)_2$ groups so that each

ytterbium is three coordinate. This structure is similar to that found in the solid state for the divalent transition metal complexes $M_2[\mu-N(SiMe_3)_2]_2$, where M is $Mn^{2a,b}$ or Co^{2b} . At $-56^\circ C$ the two singlets in $Yb_2[\mu-N(SiMe_3)_2][N(SiMe_3)_2]_2$ coalesce. Using the simple two site exchange approximation with $T_c=217K$ and $\Delta\nu = 8$ Hz at coalescence gives $\Delta G^\ddagger(T_c) = 11.3$ kcal mol $^{-1}$ for bridge-terminal exchange. The $^{13}C\{^1H\}$ NMR spectrum at $25^\circ C$ consists of a singlet at $\delta 6.47$ and a pair of single resonances at $\delta 6.05$ and 5.88 at $-92^\circ C$.

The crystal structure at $-95^\circ C$ confirms the spectroscopic deductions. An ORTEP diagram is shown in Figure I, positional and thermal parameters are shown in Table I, bond lengths and bond angles are shown in Tables II and III, respectively, and crystal data are shown in Table V. The complex crystallizes in the triclinic space groups $P\bar{1}$ with one dimer in the asymmetric unit. The molecule has no crystallographically imposed symmetry and the molecule has no apparent symmetry. The ytterbium-ytterbium separation is $3.475(1)\text{\AA}$.

The Yb(1)-N(4) and Yb(2)-N(1) terminal distances are $2.300(3)\text{\AA}$ and $2.310(3)\text{\AA}$, respectively, with an averaged value of $2.305 \pm 0.003\text{\AA}$. The Yb(1)-N(2,3) and Yb(2)-N(2,3) bridging distances are $2.492(3)\text{\AA}$, $2.445(3)\text{\AA}$, $2.573(2)\text{\AA}$, and $2.497(3)\text{\AA}$, respectively, with an averaged value of $2.502 \pm 0.035\text{\AA}$. The ytterbium atoms appear to be three coordinate; however, close examination of the structure reveals that there are four rather short Yb...C contacts, two for each ytterbium atom. Hence, the coordination number of each ytterbium atom is greater than three and the Yb...C contacts are responsible for the rather large differences in the Yb-N (bridging) distances and the lack of symmetry in the molecule. The Yb(1)...C(11,19) and Yb(2)...C(5,8) distances are $2.823(4)\text{\AA}$, $2.888(4)\text{\AA}$, $2.785(4)\text{\AA}$, and $2.820(4)\text{\AA}$, respectively, with an averaged value of $2.829 \pm 0.030\text{\AA}$.

Table IV lists some ytterbium and lutetium compounds that contain either short intra-molecular M...C contacts or with two center-three electron bridge bonds. The first two compounds have Yb...C distances and Yb-C-Si angles that are similar to the corresponding values in $\text{Yb}_2[\mu\text{-N}(\text{SiMe}_3)_2]_2[\text{N}(\text{SiMe}_3)_2]_2$. These features are reminiscent of the geometries found in compounds containing electron-deficient alkyl bridges. The Yb...C contact distance in $\text{Yb}_2[\mu\text{-N}(\text{SiMe}_3)_2]_2[\text{N}(\text{SiMe}_3)_2]_2$ is ca. 0.3Å longer and the Yb...C-Si angle is closed by ca. 6° relative to these parameters in $\text{Yb}_2\text{Cp}_4(\mu\text{-Me})_2$, a compound in which the methyl group symmetrically bridges the two ytterbium centers in a three center-two electron bond. The last compound in Table IV contains a nearly linear Lu...C-Lu bridge, with a secondary Lu...C contact distance of 2.76(1)Å, which is only ca. 0.1Å shorter than the the Yb...C contacts of $\text{Yb}_2[\mu\text{-N}(\text{SiMe}_3)_2]_2[\text{N}(\text{SiMe}_3)_2]_2$. It is clear that the Yb...C contacts in the title compound fall well within the region expected for Yb-C bonding interactions.¹ Based upon the comparisons in Table IV it may be useful to regard the methyl group of Yb...C(Me)-Si linkages as semibridging, using the language that has been developed in metal carbonyl chemistry to describe carbonyl groups that asymmetrically bridge two metals.⁵ However, the term secondary bonding interaction may be more appropriate in cases where one M...C distance is much longer than the Si-C distance, but still shorter than the van der Waals contact distance.⁶

We¹ and others⁷ have suggested that these secondary interactions are by way of a Yb...C interaction, rather than due to donation of C-H bond electron density in the C-H bond to the metal (i.e., Yb...H-C.) In order to obtain more data pertinent to this question, the X-ray diffraction data were collected at -95°C. All hydrogen atoms were located but not refined, and placed in calculated positions. Difference Fourier maps in the region of C(8)

with H(81,82,83) missing indicated that the calculated hydrogen positions were accurate. The shortest Yb...H distance (2.23Å) is between Yb(2) and H(82) of C(8). Other short Yb...H distances ranged from 2.52 to 2.96Å. The Yb(2)...H(82) distance is well within the sum of the van der Waals radius of hydrogen and the metallic radius of ytterbium(II) in eight coordination which is (1.2 + 1.8) = 3.0Å. However, since only one Yb...H separation in the dimer is very short, and since the geometry about the methyl groups appear unperturbed, the Yb...C(Me) interactions appear to be primarily due to an attraction between the electropositive metal and the electronegative carbon atoms of the Me₃Si groups though a neutron diffraction structure would be helpful. The room-temperature X-ray diffraction data for Y₂Cp₄(μ-Me)₂ was accurate enough to allow location of the hydrogen atoms.^{4a} Based on consideration of the hydrogen positions (Y...H distances ranged from 2.54 to 3.45Å), the authors described the methyl groups as bridging the two ytterbium centers by way of their carbon atoms, in a classical three center-two electron bond as found in Me₄Al₂(μ-Me)₂.⁹

The Yb...C or Yb...HC contacts appear to be responsible for the distortions of the bond angles about the planar Yb(1,2)N(2,3) ring. Bonding between Yb(2) and carbon atoms C(5) and C(8) is responsible for displacement of N(1) from the Yb(1,2)N(2,3) least squares plane by 0.25Å. Similarly, N(4) is displaced by 1.07Å above this plane to allow interaction of Yb(1) with C(11) and C(19). The dihedral angle defined by Yb(1,2)N(2,3) and N(2)Si(3,4) is 118°, and that between Yb(1,2)N(2,3) and N(3)Si(5,6) is 79°. The twisting of the bridging (Me₃Si)₂N(2) group towards Yb (1) and Yb(2) is undoubtedly largely due to secondary Yb...C interactions. The Yb...C contacts also cause distortions in the terminal silylamide ligands. The dihedral angle defined by Yb(1,2)N(2,3) and Yb(2)Si(1,2) planes is 115° and that defined by

Yb(1,2)N(2,3) and Yb(1)Si(7,8) planes is 57° . The Yb...C interactions are strong enough to distort the geometry of the terminal nitrogen atoms from planarity, a feature that has not been observed previously.^{2,10} The Si-C(5,8,11,19) distances, which average to $1.888 \pm 0.007\text{\AA}$, are not significantly different from all of the other Si-C distances within the molecule which average to $1.864 \pm 0.012\text{\AA}$.

The degree to which a ytterbium atom will engage in secondary Yb...C bonding to increase its coordination number appears to be determined largely by steric factors. These interactions are probably quite weak since the low-temperature solution NMR spectra (^1H and ^{13}C) show no evidence for them. Also, no unusual features were observed in the C-H stretching region of the infrared spectrum of a solid sample. Our view is that the Yb...C interactions are worth less than 5 kcal mol^{-1} , which is on the order of crystal packing forces and solvation energies. Studies designed to obtain more quantitative information from solid state NMR spectroscopy are planned for the future.

The base-free ytterbium silylamide should undergo a wide variety of reactions with protic acids.^{11a} We could predict the thermodynamic feasibility of these reactions if we knew the pK_a of $(\text{Me}_3\text{Si})_2\text{NH}$. Unfortunately, this value was not known when we began these studies, but it must be less than NH_3 ($\text{pK}_a = 35$) since sodium amide deprotonates the silylamine,¹² and greater than phenylacetylene (pK_a in dmsO = 28.7)¹³ since the acetylene reacts with the silylamide to give the known complex $\text{Yb}(\text{C}\equiv\text{CPh})_2$.¹⁴ The pK_a of $(\text{Me}_3\text{Si})_2\text{NH}$ has recently been estimated to be 26 in tetrahydrofuran.¹⁵

As expected, $\text{Yb}_2[\mu\text{-N}(\text{SiMe}_3)_2]_2[\text{N}(\text{SiMe}_3)_2]_2$ reacts with $\text{CpW}(\text{CO})_3\text{H}$ (pK_a in MeCN is 16.1)¹⁶ to give $\text{Yb}[\text{CpW}(\text{CO})_3]_2[\text{thf}]_3$ after crystallization from thf. The infrared spectrum in the CO-stretching frequency region, 1895s, 1755vs, and 1675vs cm^{-1} (Nujol) is identical to that found for $\text{Mg}[\text{CpMo}(\text{CO})_3]_2[\text{thf}]_4$ in

which the magnesium atom is coordinated to four tetrahydrofuran groups and two trans disposed carbonyl oxygen atoms of $\text{CpMo}(\text{CO})_3$.¹⁷ The low energy CO stretching frequency at 1675 cm^{-1} is consistent with Yb-OC-W interactions,¹⁸ though the precise structure is unknown. A related lanthanum complex, $\text{La}[\text{CpMo}(\text{CO})_3]_3[\text{thf}]_5$, has one carbonyl ligand on each $\text{CpMo}(\text{CO})_3$ unit is acting as an isocarbonyl link towards the lanthanum atom.¹⁹

Experimental Section. All operations were carried out under nitrogen. Microanalyses were performed by the Microanalytical Laboratory of this department. Infrared spectra were recorded on a Perkin-Elmer 597 instrument and ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR were recorded on a JEOL-FX90Q instrument operating at 90 MHz (^1H) and 22.5 MHz (^{13}C). The chemical shifts are expressed in δ -values, positive values are to high frequency of Me_4Si at $\delta = 0$.

$\text{Yb}_2[\mu\text{-N}(\text{SiMe}_3)_2]_2[\text{N}(\text{SiMe}_3)_2]_2$. The diethyl ether complex, $\text{Yb}[\text{N}(\text{SiMe}_3)_2][\text{OEt}_2]_2$ ^{1a} (1.0 g, 0.0016 mol) was dissolved in toluene (20 mL) and the red solution was heated to 80° for 2 hours then the toluene was slowly removed under reduced pressure while keeping the solution at ca. 80°C . The orange-red residue was dissolved in pentane (40 mL), filtered, and the filtrate was concentrated to ca. 10 mL. Cooling to -20°C gave orange-red needles which were collected and dried under reduced pressure. Concentration of the mother liquor to ca. 1 mL and cooling to -20°C gave a second crop of product in a combined yield of 0.60 g (76%), mp $150 - 153^\circ\text{C}$. IR: 1250s, 1175w, 1020s, 930s, 875s, 820s, 755s, 660s, 605msh, 595s, 410s, 390msh, 375s, 362ssh, 285w, 245w, cm^{-1} . Anal. Calcd for $\text{C}_{12}\text{H}_{36}\text{N}_2\text{Si}_4\text{Yb}$: C, 29.2; H, 7.35; N, 5.67. Found: C, 27.4; H, 7.19; N, 4.85. As explained earlier^{1a} the combustion analysis results on lanthanide silylamides are frequently poor, presumably due to formation of lanthanide carbides, silicides and nitrides. The

spectroscopy and crystallography of this compound leaves no doubt as to the identity and purity of the product, however.

Yb(thf)₃[CpW(CO)₃]₂. The diethyl ether complex, Yb[N(SiMe₃)₂]₂[OEt₂]₂ (0.34 g, 0.00053 mol) in toluene (10 mL) was added to CpW(CO)₃H (0.35 g, 0.0010 mol) in toluene (30 mL). The yellow precipitate was stirred for 1 hour then the toluene was removed under reduced pressure. The yellow residue was dissolved in tetrahydrofuran (20 mL) and the solution was concentrated to ca. 2 mL. Cooling afforded yellow prisms in 73% (0.41 g) yield. Anal. Calcd for C₂₈H₃₄O₉W₂Yb: C, 31.9; H, 3.25. Found: C, 31.6; H, 3.25.

Yb(C≡CPh)₂. Phenylacetylene (0.16 mL, 1.5 mmol) in toluene (10 mL) was added to Yb[N(SiMe₃)₂]₂[OEt₂]₂ (0.48 g, 0.00075 mol) in toluene (20 mL) at 0°C. After stirring for 1 hour, a dark purple solid was deposited from solution. The solid was isolated by filtration and then crystallized from tetrahydrofuran (8 mL, -70°C). The acetylide was identified by its infrared spectrum, $\nu_{CC} = 2040, 2010 \text{ cm}^{-1}$ and analysis.¹⁴ Anal. Calcd for C₁₆H₁₀Yb: C, 51.2; H, 2.69. Found: C, 51.6; H, 2.83.

X-ray Crystallography. Red-orange platelets of Yb₂[N(SiMe₃)₂]₄ were grown by slowly cooling a saturated pentane solution to -25°C. A plate of approximate dimensions 0.4 mm x 0.32 mm x 0.10 mm was lodged into a thin walled quartz capillary in an argon filled dry box. The capillary was then flame sealed. Examination of the crystals with preliminary precession photography indicated triclinic Laue symmetry. The crystal was then mounted on an Enraf-Nonius CAD4 automated diffractometer,²⁰ cooled to -95°C and centered in the beam. Automatic peak search and indexing confirmed the Laue symmetry and yielded cell parameters. The space group PI was confirmed by successful solution and refinement of the structure.

Accurate cell parameters were determined by a least-squares fit to the setting angles of the unresolved MoK α components of 24 symmetry related reflections having 2θ between 25 and 30°. The cell parameters are given in Table V along with the data collection parameters.

The 6005 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz-polarization effects. Analysis of the azimuthal scan data showed a significant variation, $I_{\min}/I_{\max} = 0.478$ for the average relative intensity curve. An analytical absorption correction using the measured size of the crystal, its indexed faces, and a $6 \times 10 \times 14$ gaussian grid of internal points was performed. The maximum and minimum transmission factors were 0.492 and 0.232, respectively.

Rejection of redundant data gave a unique set of 5821 data which were used to solve and refine the structure. The Yb atom positions were determined by analysis of a three-dimensional Patterson map. The remaining atoms were found by conventional Fourier and difference Fourier techniques. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were placed in calculated positions with fixed thermal parameters, and were included in structure factor calculation, but were not refined. The large thermal motion on C(16,17,18) is due to a rotational disorder which could not be resolved.

The final residuals for 344 variables refined against the 4844 data for which $F^2 > 3\sigma(F^2)$ were $R = 2.19\%$, $wR = 2.72\%$, and $GOF = 1.669$. The R value for all 5821 data was 3.44%.

The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The p -factor,²⁰ used to reduce the weight of intense reflections, was set to 0.02 throughout the refine-

ment. The analytical forms for the scattering factor tables for the neutral atoms were used and all non-hydrogen scattering factors were corrected for both the real and imaginary components of anomalous dispersion.

Inspection of the residuals ordered in ranges of $\sin\theta/\lambda$, $|F_o|$, and parity and value of the individual indexes showed no unusual features or trends. There was evidence of secondary extinction in the low-angle, high-intensity data, and a secondary extinction correction was applied.

The largest peak in the final difference Fourier map had an electron density of $0.97 \text{ e}^{-1}/\text{\AA}^3$ and was associated with Yb(1).

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Supplementary Material. General Temperature Factors, Amplitudes of thermal vibration, and Structure factor tables (29 pages).

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20. For a description of the CHEXRAY facility and the computer programs used, see ref. 18.

Figure Captions

Figure I. ORTEP Diagram of $\text{Yb}_2[\mu\text{-N}(\text{SiMe}_3)_2]_2[\text{N}(\text{SiMe}_3)_2]_2$

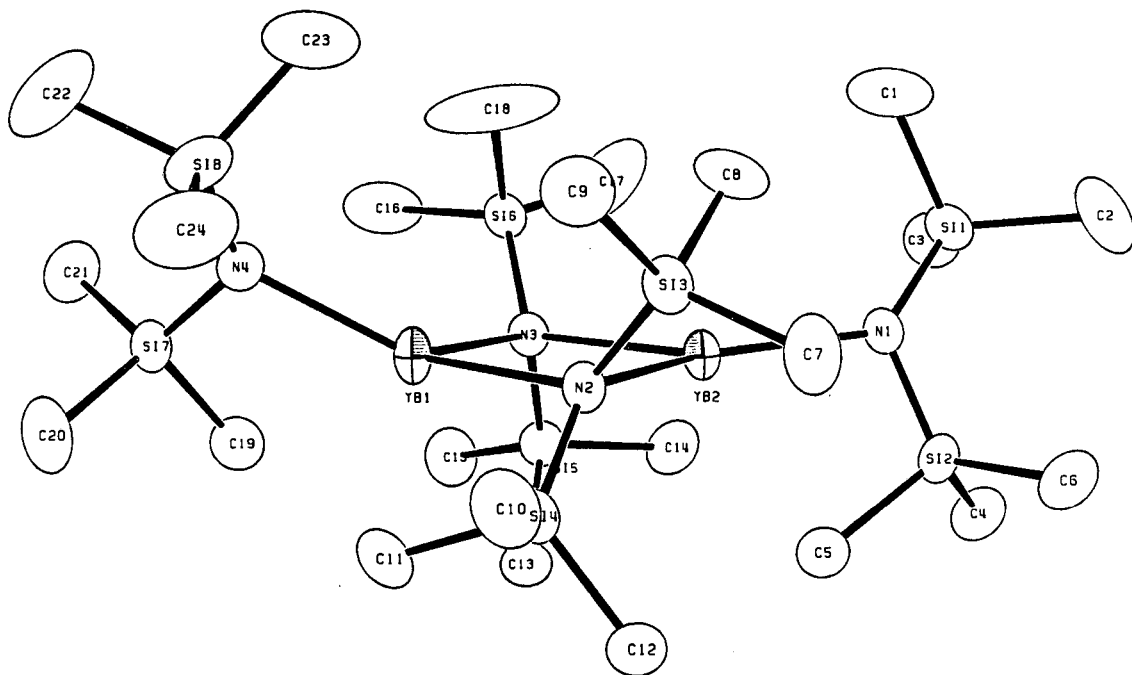


Table I.

Positional and Thermal Parameters

Atom	x	y	z	.2 B(A ²)
----	-	-	-	-----
YB1	0.14117(2)	0.45535(2)	0.29097(1)	2.433(5)
YB2	0.30502(2)	0.24259(2)	0.21182(1)	2.160(4)
SI1	0.5813(1)	0.1180(1)	0.09814(6)	2.73(3)
SI2	0.3242(1)	0.0262(1)	0.16153(6)	2.58(3)
SI3	0.4738(1)	0.1628(1)	0.34924(6)	2.71(3)
SI4	0.1400(1)	0.2062(1)	0.38473(6)	2.50(3)
SI5	-0.0081(1)	0.4548(1)	0.14431(6)	2.41(3)
SI6	0.2631(1)	0.5491(1)	0.13953(6)	2.59(3)
SI7	-0.0357(2)	0.6961(1)	0.32175(6)	2.76(3)
SI8	0.2925(2)	0.5973(1)	0.38376(7)	3.73(3)
N1	0.4333(4)	0.1178(3)	0.1516(2)	2.37(8)
N2	0.2754(4)	0.2402(3)	0.3293(2)	2.13(8)
N3	0.1597(4)	0.4571(3)	0.1793(2)	2.00(8)
N4	0.1518(4)	0.6011(3)	0.3332(2)	2.62(9)
C1	0.7156(6)	0.1947(6)	0.1158(3)	6.1(2)
C2	0.7141(7)	-0.0309(5)	0.0971(3)	5.1(2)
C3	0.5007(6)	0.1961(5)	0.0152(2)	3.9(1)
C4	0.2263(6)	0.0262(4)	0.0888(2)	3.9(1)
C5	0.1568(5)	0.0763(4)	0.2153(2)	3.4(1)
C6	0.4300(6)	-0.1304(4)	0.2040(3)	4.4(1)
C7	0.5160(6)	0.0006(5)	0.3713(3)	4.5(1)
C8	0.5952(5)	0.1920(5)	0.2771(3)	4.4(1)
C9	0.5633(6)	0.1998(5)	0.4125(3)	4.6(1)
C10	0.2159(6)	0.1496(5)	0.4692(2)	4.3(1)
C11	-0.0321(6)	0.3426(4)	0.3840(2)	3.6(1)
C12	0.0493(6)	0.0983(4)	0.3725(2)	3.6(1)
C13	-0.1183(5)	0.3809(4)	0.2085(2)	3.2(1)
C14	0.0470(6)	0.3677(4)	0.0849(2)	3.5(1)
C15	-0.1537(6)	0.5973(4)	0.1021(2)	3.8(1)
C16	0.1541(7)	0.7053(5)	0.1234(5)	8.7(3)
C17	0.3390(9)	0.5214(6)	0.0639(3)	11.9(2)
C18	0.4318(7)	0.5308(6)	0.1901(4)	10.9(2)
C19	-0.1488(6)	0.6519(4)	0.2685(3)	3.7(1)
C20	-0.1516(7)	0.6955(5)	0.3943(3)	5.3(2)
C21	-0.0548(6)	0.8523(4)	0.2801(3)	4.4(1)
C22	0.2746(8)	0.7427(5)	0.3959(3)	7.5(2)
C23	0.4985(6)	0.5436(6)	0.3532(3)	6.0(2)
C24	0.2852(7)	0.4965(6)	0.4637(3)	6.4(2)
H11	0.7970	0.1923	0.0859	7.2**
H12	0.6563	0.2720	0.1144	7.2**
H13	0.7634	0.1541	0.1574	7.2**
H21	0.7929	-0.0245	0.0666	6.0**
H22	0.7640	-0.0717	0.1379	6.0**
H23	0.6522	-0.0735	0.0866	6.0**
H31	0.5861	0.1940	-0.0125	5.0**
H32	0.4334	0.1584	0.0041	5.0**
H33	0.4408	0.2747	0.0133	5.0**
H41	0.1691	-0.0279	0.0997	5.0**
H42	0.1561	0.1023	0.0701	5.0**
H43	0.3060	0.0043	0.0596	5.0**
H51	0.0915	0.0276	0.2222	5.0**
H52	0.2004	0.0725	0.2545	5.0**
H53	0.0942	0.1550	0.1955	5.0**
H61	0.3607	-0.1747	0.2070	5.5**
H62	0.5205	-0.1595	0.1802	5.5**
H63	0.4651	-0.1351	0.2447	5.5**
H71	0.6269	-0.0370	0.3816	5.4**
H72	0.4563	-0.0218	0.4067	5.4**
H73	0.4882	-0.0206	0.3364	5.4**
H81	0.7045	0.1496	0.2879	5.3**
H82	0.5608	0.1675	0.2448	5.3**
H83	0.5815	0.2731	0.2628	5.3**
H91	0.6719	0.1523	0.4201	5.5**
H92	0.5559	0.2794	0.3996	5.5**
H93	0.5071	0.1841	0.4506	5.5**

Table I - continued

Atom	x	y	z	.2 B(A)
H101	0.1344	0.1328	0.4961	5.3**
H102	0.3043	0.0792	0.4739	5.3**
H103	0.2504	0.2058	0.4803	5.3**
H111	-0.1060	0.3237	0.4144	5.0**
H112	0.0071	0.3983	0.3938	5.0**
H113	-0.0826	0.3747	0.3429	5.0**
H121	-0.0228	0.0850	0.4052	5.0**
H122	-0.0053	0.1277	0.3326	5.0**
H123	0.1314	0.0265	0.3740	5.0**
H131	-0.2122	0.3786	0.1907	5.0**
H132	-0.0527	0.3039	0.2280	5.0**
H133	-0.1476	0.4239	0.2392	5.0**
H141	-0.0466	0.3675	0.0663	5.0**
H142	0.1079	0.4016	0.0528	5.0**
H143	0.1091	0.2895	0.1055	5.0**
H151	-0.2400	0.5835	0.0854	5.0**
H152	-0.1928	0.6426	0.1313	5.0**
H153	-0.1031	0.6376	0.0689	5.0**
H161	0.2172	0.7512	0.1014	9.5**
H162	0.0588	0.7253	0.0981	9.5**
H163	0.1221	0.7258	0.1623	9.5**
H171	0.3956	0.5736	0.0432	12.1**
H172	0.4099	0.4427	0.0709	12.1**
H173	0.2530	0.5311	0.0362	12.1**
H181	0.4925	0.5807	0.1703	10.9**
H182	0.3953	0.5493	0.2297	10.9**
H183	0.5022	0.4515	0.2013	10.9**
H191	-0.2549	0.7043	0.2616	5.0**
H192	-0.0981	0.6538	0.2294	5.0**
H193	-0.1513	0.5747	0.2884	5.0**
H201	-0.2555	0.7511	0.3834	6.2**
H202	-0.1614	0.6199	0.4119	6.2**
H203	-0.1000	0.7154	0.4236	6.2**
H211	-0.1656	0.8982	0.2763	5.3**
H212	-0.0001	0.8810	0.3043	5.3**
H213	-0.0130	0.8576	0.2394	5.3**
H221	0.3569	0.7332	0.4248	8.4**
H222	0.2836	0.7952	0.3567	8.4**
H223	0.1738	0.7727	0.4131	8.4**
H231	0.5761	0.5422	0.3820	7.1**
H232	0.5186	0.4669	0.3492	7.1**
H233	0.5070	0.5945	0.3129	7.1**
H241	0.3652	0.4960	0.4913	7.4**
H242	0.1838	0.5225	0.4809	7.4**
H243	0.3049	0.4197	0.4602	7.4**

** -- Atoms included but not refined.

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:

$$\begin{aligned}
 & \frac{4}{3} * [a^2 * B(1,1) + b^2 * B(2,2) + c^2 * B(3,3) + ab(\cos \gamma) * B(1,2) \\
 & + ac(\cos \beta) * B(1,3) + bc(\cos \alpha) * B(2,3)]
 \end{aligned}$$

Table II.

Bond Lengths

Intramolecular Distances

ATOM 1	ATOM 2	DISTANCE
YB1	N2	2.492(3)
YB1	N3	2.445(3)
YB1	N4	2.300(3)
YB2	N1	2.310(3)
YB2	N2	2.573(3)
YB2	N3	2.497(3)
SI1	N1	1.710(3)
SI1	C1	1.870(5)
SI1	C2	1.868(5)
SI1	C3	1.870(4)
SI2	N1	1.691(3)
SI2	C4	1.862(4)
SI2	C5	1.898(4)
SI2	C6	1.875(4)
SI3	N2	1.728(3)
SI3	C7	1.873(5)
SI3	C8	1.881(4)
SI3	C9	1.872(4)
SI4	N2	1.726(3)
SI4	C10	1.872(4)
SI4	C11	1.891(4)
SI4	C12	1.866(4)
SI5	N3	1.726(3)
SI5	C13	1.871(4)
SI5	C14	1.876(4)
SI5	C15	1.860(4)
SI6	N3	1.721(3)
SI6	C16	1.829(6)
SI6	C17	1.837(5)
SI6	C18	1.831(5)
SI7	N4	1.691(3)
SI7	C19	1.881(4)
SI7	C20	1.845(4)
SI7	C21	1.876(4)
SI8	N4	1.699(3)
SI8	C22	1.873(5)
SI8	C23	1.887(5)
SI8	C24	1.869(5)
YB1	C11	2.823(4)
YB1	C18	3.492(7)
YB1	C19	2.888(4)
YB2	C5	2.785(4)
YB2	C8	2.820(4)
YB2	C14	3.387(4)

Table III.

Bond Angles

Intramolecular Angles

ATOM 1	ATOM 2	ATOM 3	ANGLE
YB1	N2	SI3	129.69(14)
YB1	N2	SI4	98.57(12)
YB2	N2	SI3	94.06(12)
YB2	N2	SI4	132.60(14)
SI3	N2	SI4	116.24(16)
N2	SI3	C7	112.95(17)
N2	SI3	C8	108.94(16)
N2	SI3	C9	115.82(18)
C7	SI3	C8	103.61(22)
C7	SI3	C9	108.55(21)
C8	SI3	C9	106.05(20)
N2	SI4	C10	115.56(17)
N2	SI4	C11	109.80(16)
N2	SI4	C12	115.47(16)
C10	SI4	C11	103.55(19)
C10	SI4	C12	105.49(20)
C11	SI4	C12	105.91(19)
YB1	N3	SI5	115.96(13)
YB1	N3	SI6	110.24(13)
YB2	N3	SI5	98.81(12)
YB2	N3	SI6	117.93(13)
SI5	N3	SI6	120.16(16)
N3	SI5	C13	107.30(15)
N3	SI5	C14	111.03(16)
N3	SI5	C15	117.88(17)
C13	SI5	C14	108.01(18)
C13	SI5	C15	106.59(19)
C14	SI5	C15	105.62(18)
N3	SI6	C16	115.35(19)
N3	SI6	C17	113.13(20)
N3	SI6	C18	108.88(22)
C16	SI6	C17	107.4(4)
C16	SI6	C18	102.7(3)
C17	SI6	C18	108.7(4)
N2	YB1	C11	67.36(10)
N2	YB1	C18	99.09(14)
N2	YB1	C19	149.17(10)
N3	YB1	C11	127.20(11)
N3	YB1	C18	54.91(13)
N3	YB1	C19	93.04(11)
N4	YB1	C11	100.48(11)
N4	YB1	C18	84.95(15)
N4	YB1	C19	66.70(11)
C11	YB1	C18	165.88(14)
C11	YB1	C19	84.82(12)
C18	YB1	C19	109.28(14)

Intramolecular Angles

ATOM 1	ATOM 2	ATOM 3	ANGLE
N2	YB1	N3	93.54(9)
N2	YB1	N4	129.37(10)
N3	YB1	N4	126.87(10)
N1	YB2	N2	138.81(10)
N1	YB2	N3	130.40(10)
N2	YB2	N3	90.37(9)
YB1	N2	YB2	86.64(9)
YB1	N3	YB2	89.38(9)
YB2	N1	SI1	133.45(16)
YB2	N1	SI2	103.27(13)
SI1	N1	SI2	122.59(17)
N1	SI2	C4	116.44(18)
N1	SI2	C5	106.26(16)
N1	SI2	C6	115.51(17)
C4	SI2	C5	106.04(19)
C4	SI2	C6	106.89(20)
C5	SI2	C6	104.66(20)
N1	SI1	C1	111.08(18)
N1	SI1	C2	114.19(19)
N1	SI1	C3	112.17(17)
C1	SI1	C2	105.66(25)
C1	SI1	C3	106.34(23)
C2	SI1	C3	106.87(20)
YB1	N4	SI7	104.02(14)
YB1	N4	SI8	128.31(16)
SI7	N4	SI8	125.28(19)
N4	SI7	C19	108.13(17)
N4	SI7	C20	114.66(20)
N4	SI7	C21	115.94(18)
C19	SI7	C20	105.21(22)
C19	SI7	C21	104.51(20)
C20	SI7	C21	107.40(21)
N4	SI8	C22	114.44(22)
N4	SI8	C23	110.74(20)
N4	SI8	C24	110.87(19)
C22	SI8	C23	105.6(3)
C22	SI8	C24	107.0(3)
C23	SI8	C24	107.8(3)

N1	YB2	C5	67.92(11)
N1	YB2	C8	89.98(12)
N1	YB2	C14	82.80(10)
N2	YB2	C5	97.27(11)
N2	YB2	C8	65.84(11)
N2	YB2	C14	132.65(9)
N3	YB2	C5	122.54(10)
N3	YB2	C8	111.43(12)
N3	YB2	C14	58.31(9)
C5	YB2	C8	123.63(13)
C5	YB2	C14	76.25(11)
C8	YB2	C14	154.28(12)

Table IV.

<u>Compound</u>	<u>X</u>	<u>Me</u> <u>X Yb(Lu)</u> <u>in deg.</u>	<u>Me-Yb(Lu)</u> <u>in Å</u>	<u>Ref.</u>
$\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2\text{dmpe}$	Si	80	3.04	1b
$\text{NaYb}[\text{N}(\text{SiMe}_3)_2]_3$	Si	78.6(3)	2.88(3)	1a
$\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\mu\text{-Me})_4\text{Al}_2\text{Me}_2$	Al	73.8(1)	2.767(6)	3
	Al	65.9(7)	3.12(8)	
	Si	83.5(3)	3.05(2)	
$\text{Yb}_2[\mu\text{-N}(\text{SiMe}_3)_2]_2[\text{N}(\text{SiMe}_3)_2]$	Si	82(1)	2.83(4)	this work
$\text{Yb}_2\text{Cp}_4(\mu\text{-Me})_2$	Yb	87.7(3)	2.55(1)	4a
$\text{YbCp}_2(\mu\text{-Me})_2\text{AlMe}_2$	Al	98.9(6)	2.59(3)	4b
$\text{Lu}_2(\text{Me}_5\text{C}_5)_4(\mu\text{-Me})(\text{Me})$	Lu	170(4)	2.76(1)	4c

Table V.

Crystal Data (-95°C) for $\text{Yb}_2[\text{N}(\text{SiMe}_3)_2]_4$

<u>Space Group</u>	<u>P1</u>
a, Å	8.868(1)
b, Å	12.561(2)
c, Å	21.560(3)
α , deg	73.84(1)
β , deg	86.70(1)
γ , deg	71.26(1)
V, Å ³	2225
z	2
fw	987.64
d(calcd), g cm ⁻³	1.474
μ (calcd), cm ⁻¹	43.97
size, mm	0.45 x 0.32 x 0.10
reflens, collected	6005
reflens, unique	5821
reflens, $F_o^2 > 3\sigma(F_o^2)$	4844
R, %	2.19
R_w , %	2.72
GOF	1.669
monochromator	highly oriented graphite
radiation	MoK α ($\lambda = 7.1073\text{\AA}$)
scan range, type	$3^\circ \leq 2\theta \leq 45^\circ$
scan speed, deg min ⁻¹	0.69 - 6.7
scan width, deg	$\Delta\theta = 0.55 + 0.347 \tan \theta$
decay	4.7%, corrected

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