Title

DIVALENT LANTHANIDE CHEMISTRY. REACTION OF BASE-FREE BIS |BIS(TRIMETHYLSILYL)AMIDE] YTTERBIUM (II) WITH SUBSITUTED CYCLOPENTADIENES; PREPARATIONS OF BASE-FREE BIS(PENTAMETHYLCYCLOPENTADIENYL) YTTERBIUM (II)

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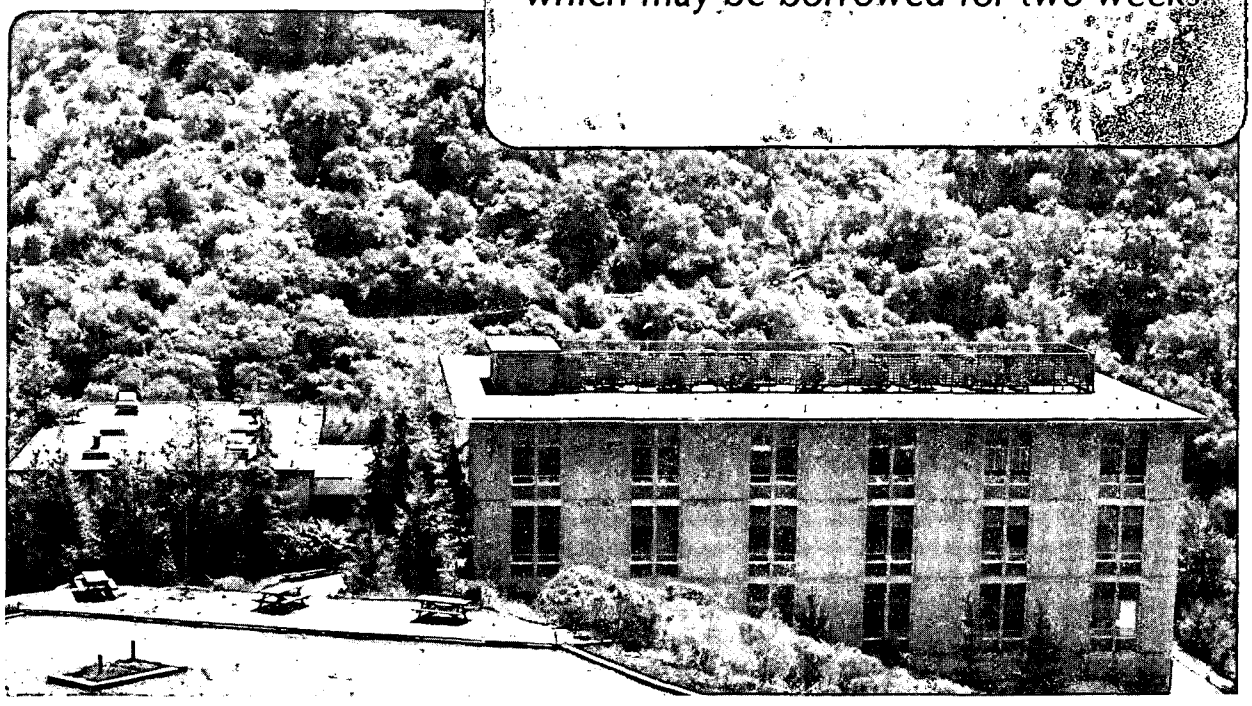

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Divalent Lanthanide Chemistry. Reaction of Base-Free Bis[bis(trimethylsilyl)amide] Ytterbium(II) with Substituted Cyclopentadienes; Preparations of Base-Free Bis(Pentamethylcyclopentadienyl) Ytterbium(II)

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Abstract

One molar equivalent of Me_5C_5H, per Yb(II), reacts with $Yb_2[\mu\text{-}N(SiMe_3)_2]_2[N(SiMe_3)_2]_2$ to give $(Me_5C_5)_2Yb_2[\mu\text{-}N(SiMe_3)_2]_2$ as shown by X-ray crystallography. The space group is Pbca with a = 17.031(1), b = 16.002(2), c = 14.099(2) Å, V = 3843 Å, and z =4. The centrosymmetric dimer is composed of two terminal Me_5C_5 groups bonded to each ytterbium atom, Yb-C (ave.) = 2.72 ± 0.02 Å, and the ytterbium atoms are bridged by $N(SiMe_3)_2$ groups, Yb-N (ave.) = 2.54 ± 0.10 Å. The diene, Me_4EtC_5H, behaves similarly, giving $(Me_4EtC_5)_2Yb_2[\mu\text{-}N(SiMe_3)_2]_2$. Two molar equivalents of Me_5C_5H, per Yb(II), react with $Yb_2[\mu\text{-}N(SiMe_3)_2]_2[N(SiMe_3)_2]_2$ to give $(Me_5C_5)_2Yb_2[N(H)(SiMe_3)_2]$ which gives base-free $(Me_5C_5)_2Yb$ on dissolution in toluene or vacuum sublimation (90°C/10^{-3}mm). The diene, Me_4EtC_5H, behaves similarly giving base-free $(Me_4EtC_5)_2Yb$.

In the previous paper in this journal, we described the synthesis of the base-free complex, $Yb_2[\mu\text{-}N(SiMe_3)_2]_2[N(SiMe_3)_2]_2$.[1] Reactions of the amide with protic acids allowed us to estimate the pK_a of $(Me_3Si)_2NH$ to be between 30 and 35. This suggested to us that we could use Me_5C_5H (pK_a, dmso = 26.1)[2] to make the base-free complex $(Me_5C_5)_2Yb$, a complex that we have wanted to prepare for several years,[3] since the deprotonation could be done in hydrocarbon solvents and $(Me_3Si)_2(H)N$ is a poor Lewis base.[4] The ability to work in non-basic or very weakly basic solvents is the crucial ingredient in the synthetic scheme since even the relatively weak base, diethyl ether, cannot be removed from $(Me_5C_5)_2Yb(OEt_2)$ by sublimation. This result is to be contrasted with the ready removal of tetrahydrofuran from $(Me_5C_5)_2Sm(thf)_2$ by sublimation.[5] In this paper we describe the reaction of Me_5C_5H and Me_4EtC_5H with $Yb_2[\mu\text{-}N(SiMe_3)_2]_2[N(SiMe_3)_2]_2$.

Addition of one molar equivalent of Me_5C_5H to the ytterbium silylamide (reckoned as monomer) in toluene gives a red solution from which red prisms may be isolated. The complex is insoluble in pentane and only sparingly soluble in hot toluene, and it is non-volatile. The ^1H NMR spectrum shows that the Me_5C_5 and the $N(SiMe_3)_2$ groups at δ2.10 and 0.090, respectively, are present in a 1:1 ratio, and that the compound is diamagnetic. The complex reacts with $Me_2PCH_2CH_2PMe_2$ to give the monomeric complex $(Me_5C_5)YbN(SiMe_3)_2(dmpe)$. The unsymmetrically substituted diene, Me_4EtC_5H, behaves similarly with $Yb_2[\mu\text{-}N(SiMe_3)_2]_2[N(SiMe_3)_2]_2$ giving red, pentane soluble $(Me_4EtC_5)_2Yb_2[\mu\text{-}N(SiMe_3)_2]_2$, which is probably dimeric in the gas phase as the $[M\text{-}N(SiMe_3)_2]^+$ ion is observed in the mass spectrum. The dimeric nature of $(Me_5C_5)_2Yb_2[\mu\text{-}N(SiMe_3)_2]_2$ in the condensed phase is proved by X-ray crystal structure analysis.

The $(Me_5C_5)_2Yb_2[\mu\text{-}N(SiMe_3)_2]_2$ crystallizes in the orthorhombic space group Pbca with four molecules in the unit cell. The molecule has a crystallographically imposed inversion center and the molecule has C_{2h} symmetry as shown in the ORTEP diagram in the Figure. The positional and thermal parameters for the low temperature data set (-95°C) are in Table I, some bond lengths and angles are in Table II, and crystal data are in Table III.

The bridging ytterbium to nitrogen distances are very unsymmetrical. The Yb(1)-N(1) distance is 2.630(3) Å and the Yb(1)-N(1') distance is 2.445(3) Å with an averaged distance of 2.538 ± 0.096 Å which is 0.036 Å longer than that found in $Yb_2[\mu\text{-}N(SiMe_3)_2]_2[N(SiMe_3)_2]_2$.[1] The Yb...Yb distance of 3.793(1) Å is also longer by 0.318 Å relative to that in the binary silylamide. The N(1)-Yb(1)-N(1') angle is 83.3(1)°, ca. 10° smaller than the equivalent angle in $Yb_2[\mu\text{-}N(SiMe_3)_2]_2[N(SiMe_3)_2]_2$. The Yb(1)-N(1)-Yb(1) angle is 96.7(1)°, ca. 10° larger than the equivalent angle in $Yb_2[\mu\text{-}N(SiMe_3)_2]_2[N(SiMe_3)_2]_2$. The averaged ytterbium to ring carbon distance is 2.72 ± 0.02 Å, and the values range from 2.719(4) to 2.767(4) Å. The ytterbium to ring centroid distance is 2.465 Å and the center of the Me_5C_5-centroid is only 0.001 Å out of the plane defined by Yb(1)N(1)N(1')Yb(1') and the dihedral angle between the latter plane and the plane defined by Si(1)N(1)Si(2) is 91.5°.

The ytterbium to ring carbon distances in $(Me_5C_5)_2Yb_2[\mu\text{-}N(SiMe_3)_2]_2$ are long and the spread among the distances is large. The averaged Yb-C distance in $(Me_5C_5)_2Yb(py)_2$,[6a] a molecule whose coordination number is 8 if the pentamethylcyclopentadienyl ligand occupies three coordination sites, is 2.74(4) Å and the averaged Yb-C distance in $(Me_5C_5)_2Yb(thf)$[6b] and in $(Me_5C_5)_2Yb(OEt_2)$[6c] is 2.66 ± 0.01 Å and 2.70 ± 0.02 Å, respectively. Hence, a Yb-C distance of ca. 2.55 Å might have been expected for the five coordinate ytterbium atom in $(Me_5C_5)_2Yb_2[\mu\text{-}N(SiMe_3)_2]_2$ rather than 2.72 ± 0.023 Å. The elongation can be

explained by examining the intramolecular contacts. There are three rather short carbon-carbon contacts; C(11)...C(35) is 3.41 Å, C(22')...C(36) is 3.55 Å, and C(12')...C(37) is 3.56 Å. These contact distances are less than the sum of the van der Waals radius of two methyl groups of 4.0 Å.[7] The methyl carbon atoms C(35,36,37,38,39) are out of the mean plane of the C_5-ring by 0.23, 0.26, 0.19, 0.16, and 0.19Å, respectively. The close contacts cause the planar (to within 0.004 Å) C_5-ring to tilt away from the ytterbium atom with the result that the Yb-C distances fall into two groups. The averaged Yb-C (30, 31, 32) distance is 2.757 ± 0.009 Å and the averaged Yb-C (33, 34) distance is 2.724 ± 0.004 Å. Hence the ring carbon atoms that are bonded to the methyl groups that are in close contact with the silylamide methyl groups are pushed away from the ytterbium atom by ca. 0.03 Å. The result of all of the intra-ligand repulsions is that the averaged Yb-C distance is longer than expected on the basis of simple coordination number considerations and the molecule might be referred to as being sterically overcrowded.[8]

In addition, the Me_5C_5 ring shows substantial deviations from cylindrical C_5-symmetry. The carbon-carbon distances associated with the longer Yb-C (30, 31, 32) distances are shorter, C(30)-C(34) = 1.403(6) Å, C(30)-C(31) = 1.391(6) Å, and C(31)-C(32) = 1.409(6) Å, than those that are associated with the shorter Yb-C (33, 34) distances, C(33)-C(34) = 1.437(6) Å and C(33)-C(32) = 1.425(5) Å.

Reaction of two molar equivalents of Me_5C_5H with $Yb_2[\mu\text{-}N(SiMe_3)_2]_2[N(SiMe_3)_2]_2$ per monomeric unit in pentane over 24 h gives a dark brown-orange solution from which green crystals of the coordination complex, $(Me_5C_5)_2Yb_2[N(H)(SiMe_3)_2]$, can be crystallized. The ^1H NMR spectrum shows two resonances at δ1.93 and 0.087 due to the Me_5C_5 and $N(SiMe_3)_2$ protons, respectively. The NH proton was not observed. The $^{13}C\{^1H\}$ NMR spectrum shows the

resonances due to the Me_5C_5 carbons at δ113.8 and 10.7 and $(Me_3Si)_2N$ carbons at δ2.62. The chemical shifts and line widths of the resonances clearly show that the complex is diamagnetic and therefore the ytterbium atom is divalent. The infrared spectrum shows a νNH stretching frequency at 3205 cm^{-1}, 170 cm^{-1} lower in energy than that of the free silylamine.[9]

The $(Me_5C_5)_2Yb_2[N(H)(SiMe_3)_2]$ is one of the few complexes known in which the $(Me_3Si)_2$ NH is acting as a Lewis base. In the other complexes the ν NH of the coordinated $N(H)(SiMe_3)_2$ is reduced by ca. 240 cm^{-1} relative to free silylamine.[4] In this context, it is generally observed that νNH decreases upon coordination of ammonia to transition metals.[10] The usual reason given for this energy lowering is that the s-character of the N-H bond decreases on coordination. This contention seems to be reasonable in the present case since $N(H)(SiMe_3)_2$ is planar at nitrogen[4d] and coordination of the lone pair on the nitrogen to the ytterbium atom results in a hybridization change from sp^2 to sp^3.

Reaction of two molar equivalents of Me_5C_5H (per Yb) with $Yb_2[\mu\text{-}N(SiMe_3)_2]_2[N(SiMe_3)_2]_2$ in toluene takes a different course. Stirring the amide and the diene in toluene for 24 h yields a brown-orange solution. Evaporation of the toluene at room temperature yields a green solid which gives green needles from pentane. The crystals crumble to a brown-green powder when exposed to vacuum. The powder is base-free $(Me_5C_5)_2Yb$. When heated in a sealed tube the green metallocene turns brown-orange at ca. 130°C and melts to a red liquid at 190°C. These changes are reversible. The metallocene sublimes at 90°C at 10^{-3}mm without decomposition and it gives a monomeric molecular ion in the mass spectrum (see Experimental section for details). The ^1H NMR spectrum in benzene is a single resonance at δ1.92 and the $^{13}C\{^1H\}$ NMR spectrum consists of two resonances at δ113.4 and δ10.6 due to

the ring and methyl carbons respectively. If a toluene solution of $(Me_5C_5)_2Yb$ is concentrated and cooled, dark green crystals of $(Me_5C_5)_2Yb(PhMe)$ may be isolated. Base-free $(Me_5C_5)_2Yb$ can be isolated on exposure of the toluene solvate to vacuum or recrystallization from pentane. Thus the reaction or/and crystallization solvent plays a crucial role in the synthesis of $(Me_5C_5)_2Yb$, as it does in the synthesis of $Yb_2[N(SiMe_3)_2]_2$.[1]

In order to explore the solvent effects in a qualitative way, $(Me_5C_5)_2Yb[N(H)(SiMe_3)_2]$ was dissolved in pentane. Removal of the pentane gives $(Me_5C_5)_2Yb$-$[N(H)(SiMe_3)_2]$. Addition of toluene to the amine complex followed by evaporation to dryness then crystallization from toluene gives $(Me_5C_5)_2Yb(PhMe)$ and the toluene is displaced by addition of a large amount of pentane or on exposure to vacuum. Addition of diethyl ether to the amine complex gives $(Me_5C_5)_2Yb(OEt_2)$ which then gives the base-free compound when a hot toluene solution is slowly evaporated to dryness under reduced pressure. The coordination chemistry of these very weak Lewis bases with $(Me_5C_5)_2Yb$ is being studied by solid state NMR techniques.

The diene, $EtMe_4C_5H$, behaves similarly giving $[EtMe_5C]_2Yb[N(H)(SiMe_3)_2]$ as a brown-orange semi-solid, which gives brown-orange $(EtMe_5C_5)_2Yb$ on sublimation at 90°C at 10^{-3}mm. The metallocene melts at 158-165°C and gives a monomeric molecular ion in the mass spectrum (see Experimental Section for details).

The obvious thermal stability suggests that the gas phase physical chemistry of these relatively simple metallocenes will be extensive and rewarding. Gas electron diffraction studies show that $Yb(C_5Me_5)_2$[11a] and the alkaline earth analogues $M(C_5Me_5)_2$ where M = Ca,[11a] Sr, [11b] or Ba[11b] are bent metallocenes as are $M(C_5Me_5)_2$ where M is Sm or Eu in the solid state.[5] The gas phase photoelectron spectroscopic studies of $M(C_5Me_5)_2$ where M is Sm, Eu, or Yb[11c] and Ca, Sr, or Ba[11d] are consistent with a bent sandwich structure.

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 the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a JEOL-FX90Q instrument operating at 90 MHz (^{1}H) and 22.5 MHz (^{13}C). Chemical shifts are expressed in δ-values, positive values are to high frequency of Me_4Si at δ = 0.

$(Me_5C_5)_2Yb_2[\mu\text{-}N(SiMe_3)_2]_2$. Pentamethylcyclopentadiene (0.20 mL, 0.0013 mol) in toluene (20 mL) was added to $\{Yb[N(SiMe_3)_2]_2\}_2$ (0.63g, 0.0013 mol.) in toluene (40 mL). The mixture turned dark red during the course of 1 h. The red solution was stirred for 12 h then filtered. The filtrate was concentrated to ca. 40 mL and then cooled to -10°C. The large red octahedra were isolated and dried under reduced pressure to give 0.28 g (46% yield) of product, mp 315-320°C (dec). **Anal.** Calcd for $C_{16}H_{33}NSi_2Yb$: C, 41.0; H, 7.10; N, 2.99. Found: C, 36.7; H, 6.81; N, 2.30. As we have observed previously,[1] ytterbium amides give terrible combustion analyses. The solution spectroscopic studies and in this case the X-ray structure analysis leave no doubt as to the correct composition of the compound. When a sample of the compound was hydrolyzed with D_2O, a C_6D_6 extract of the hydrolysate showed the presence of $(Me_3Si)_2ND$, δ0.081 and Me_5C_5D, δ0.97 (t, J_{H-D} = 1.1 Hz, 3 H), 1.73 (s, 6 H), and 1.78 (s,6H) in a 1:1 area ratio. IR (Nujol): 2725w, 1250s, 1050w, 1003vs, 854s, 826vs, 809s, 759m, 732s, 690w, 663m, 614w, 585w, 567m, 394s, 360m, 260s, 240s, 218m, cm^{-1}.

$(Me_5C_5)Yb[N(SiMe_3)_2](Me_2PCH_2CH_2PMe_2)$. The phosphine, $Me_2PCH_2CH_2PMe_2$ (0.10 mL, 0.090 g, 0.00060 mol) was added to $(Me_5C_5)_2Yb_2N(SiMe_3)_2]_2$ (0.28 g, 0.0060 mol) in toluene (30 mL). The purple solution was stirred for 1 h, then

filtered. The filtrate was concentrated to ca. 5 mL and cooled to -10°C for 2 d. The large purple prisms were isolated and dried under reduced pressure. The mother liquor produced a second crop of crystals. The combined yield was 0.35 g (95% yield), mp 226-229°C. Anal. Calcd for $C_{22}H_{49}NPSi_2Yb$: C, 42.7; H, 7.98; N, 2.26. Found: C, 41.5; H, 8.00; N, 2.08. IR (Nujol): 2720w, 1417m, 1298w, 1283w, 1243s, 1230s, 1051s, 936m, 922m, 870s, 825sh, 812s, 758m, 742m, 719m, 690w, 657m, 600w, 585w, cm^{-1}. ^1H NMR(C_6D_6, 31°C): δ2.26 (s, Me_5C_5, 15 H), δ0.97 (an apparent triplet with separation between the outermost lines of 6.3 Hz, CH_2P, 4H), 0.73 (an apparent singlet, Me_2P, 12 H), 0.30 (s, Me_3Si, 18 H). $^{31}P\{^1H\}$ NMR (C_6D_6, 31°C): δ-36.0s.

$(EtMe_4C_5H)_2Yb_2[)-N(SiMe_3)_2]_2$. Tetramethylethylcyclopentadiene (0.22 g, 0.0015 mol) in pentane (10 mL) was added to $Yb_2[N(SiMe_3)_2]_4$ (0.72g, 0.0015 mol) in pentane (30 mL). The mixture slowly turned dark red over 15 h. The solution was filtered and the filtrate was concentrated to ca. 10 mL. Cooling (-20°C) yielded large red prisms which were collected and dried under reduced pressure. A second crop of crystals was obtained from the mother liquor giving a combined yield of 0.50 g (69% yield), mp 252-255°C. Anal. Calcd for $C_{17}H_{35}NSi_2Yb$: C, 42.3; H, 7.31; N, 2.90. Found: C, 34.3; H, 7.50; N, 1.89. The combustion analysis is awful, but the spectroscopy leaves no doubt about the composition, along with a $[M-N(SiMe_3)_2]^+$ ion at 816 amu in the mass spectrum. ^1H NMR (PhMe-d_8, 30°C, 200 MHz): δ2.55 (q, J_{HH} = 7.3 Hz, 2H $\underline{CCH_2}Me$), 2.12 (s, 6H, $C\underline{Me_2}$), 0.23 (s, 18H, $N(Si\underline{Me_3})_2$). IR (Nujol): 2730m, 1375m, 1314w, 1260sh, 1243vs, 1125brw, 1062w, 1048w, 1013m, 948sbt, 855vs, 825sbr, 760s, 745s, 664s, 613m, 584s, 402s, 353m, 305s, 268m, 240w cm^{-1}.

$(Me_5C_5)_2Yb[N(H)(SiMe_3)_2]$. Pentamethylcyclopentadiene (0.59 mL, 0.0038 mol) in pentane (10 mL) was added to $Yb_2[N(SiMe_3)_2]_4$ (0.93 g, 0.0019 mol) in pentane

(30 mL). The reaction mixture slowly darkened and an orange-red precipitate formed within 15 minutes which dissolved over 15 h with stirring. The brown-orange solution was filtered and the filtrate was concentrated to ca. 7 mL then cooled to -20°C. Green feathers were isolated and dried under reduced pressure. The mother liquor afforded a second crop of crystals in a combined yield of 0.56g, 49%. Anal. Calcd for $C_{26}H_{49}NSi_2Yb$: C, 51.6; H, 8.16; N, 2.31. Found: C, 50.6; H, 7.84; N, 2.16. ^1H NMR (C_6D_6, 31°C): δ1.93 (s, 30H), 0.087 (s, 18H). $^{13}C\{^1H\}$ NMR: δ113.8 ($Me_5\underline{C}_5$), 10.7 ($\underline{Me}_5C_5$), 2.62 (Me_3Si). IR (Nujol): 3205s, 2725m, 1305w, 1265s, 1260s, 1250s, 1163s, 1056s, 1015m, 977m, 930m, 850sbr, 797msh, 790wsh, 763s, 719w, 698s, 679wsh, 653s, 620m, 586m, 551s, 365sbr, 260s cm^{-1}.

$(Me_5C_5)_2Yb$. Pentamethylcyclopentadiene (0.42 mL, 0.0026 mol) in toluene (20 mL) was added to $Yb_2[N(SiMe_3)_2]_4$ (0.66g, 0.0013 mL) in toluene (20 mL). The mixture was stirred for 24h and the toluene was removed under reduced pressure from the brown-orange solution giving a green residue. The residue was dissolved in pentane (30 mL), filtered, and the filtrate was concentrated to ca. 10 mL and cooling (-25°C) afforded large green needles that crumbled and turned brown-tan upon isolation and exposure to vacuum. A second crop of crystals was isolated and the combined yield was 0.45g (78%). When heated in a sealed capillary the compound gradually turned orange as the temperature was raised above 130°C until it melted from 189-191°C to a red liquid that turned green as it cooled to 20°C. This behavior is reversible. The compound sublimed at 90°C/10^{-3}mm or at 200°C at 1 atm without much decomposition. Anal. Calcd for $C_{20}H_{20}Yb$: C, 54.2; H, 6.82. Found: C, 53.8; H, 6.96. MS; nominal mass, observed intensity (calculated intensity): 440, 6.21 (8.65); 441, 47.6 (41.8); 442, 71.0 (70.2); 443, 59.1 (59.8); 444, 100 (100); 445, 15.2 (20.9); 446, 36.2 (37.6). ^1H NMR (C_6D_6, 30°C): δ1.92s. $^{13}C\{^1H\}$ NMR:

δ113.4 ($\underline{C}_5Me_5$), 10.6 ($C_5\underline{Me}_5$). IR (Nujol): 2725w, 1155w, 1015m, 792m, 718m, 665w, 584w, 352m, 274s cm^{-1}.

The residue from reaction of the silylamide and the diene was dissolved in toluene and it was concentrated to ca. 3 mL and cooled (-20°C). The large green crystals formed were collected and dried in a stream of nitrogen. Examination of the hydrolysis product from D_2O in C_6D_6 showed the presence of Me_5C_5D and toluene in a 1:1 ratio. Mulling the green prisms in Nujol gives an infrared spectrum identical to that of the base-free complex.

The green solution from $(Me_5C_5)_2Yb(OEt_2)$[6b] (3 g) in toluene (200 mL) was heated to 100°C and the toluene was removed slowly under reduced pressure (4-5h). The residue was dissolved in toluene (200 mL) and the reflux procedure was repeated. The residue was crystallized from pentane (150 mL, -25°C) as fine green needles that collapsed to brown-tan powder under reduced pressure. The yield of the base-free compound was 87%.

$(EtMe_4C_5)_2Yb$. Tetramethylethylcyclopentadiene (1.6 mL, 0.0087 mol) in pentane (20 mL) was added to $Yb_2[N(SiMe_3)_2]_4$ (2.2 g, 0.0043 mol) in pentane (30 mL). The mixture was stirred for 20h, the brown-orange solution was filtered, and the filtrate was concentrated to ca. 15 mL and cooled to -70°C. The deep green crystals were isolated at low temperature though they melted to a sticky brown-orange material at 20°C. The infrared spectrum showed νNH for free and coordinated $HN(SiMe_3)_2$ at 3379 and 3205 cm^{-1}. The brown-orange material was sublimed at ca. 170°C at 1 atm or at ca. 90°/10^{-3}mm without significant decomposition as a brown-orange material which is base-free $(Me_4EtC_5)_2Yb$, mp 158-165°C. Anal. Calcd for $C_{22}H_{34}Yb$: C, 56.0; H, 7.28. Found: C, 56.2; H, 7.34. MS, nominal mass, observed intensity (calculated intensity): 467, 0.18 (0.07); 468, 10.1 (8.53); 469, 44.1 (41.5); 470, 73.2 (70.2); 471, 62.0 (60.5); 472, 100 (100); 473, 22.5 (22.8); 474, 36.5

(37.6); 475, 7.54 (8.76); 476, 0.40 (1.01). ^{1}H NMR (C_6D_6, 30°C): δ2.40 (q, J = 7.2 Hz, 4H, $CC\underline{H}_2Me$); 1.98 (s, 12H, C_2Me_2); 1.90 (s, 12H, C_2Me_2); 0.97 (t, J = 7.2 Hz, 6H, CCH_2 $\underline{Me}$). IR (Nujol): 2722m, 1605w, 1308w, 1158w, 1146wsh, 1037w, 1017w, 866w, 747w, 716w, 549w, 438w, 360w, 301s, 277m cm^{-1}.

X-ray Crystallography on $(Me_5C_5)_2Yb_2[)\text{-}N(SiMe_3)_2]_2$.[12] A dark red octahedron of approximate dimension 0.22x0.22x0.32mm was lodged into a thin walled quartz capillary in an argon filled dry box. The capillary was subsequently flame sealed. Preliminary precession photographs indicated orthorhombic (mmm) Laue symmetry, and yielded preliminary cell dimensions.

The crystal was transferred to an Enraf-Nonius CAD4 automated diffractometer, cooled to -95° and centered in the beam. Automatic peak search and indexing yielded the same unit cell as the precession photographs and confirmed the Laue symmetry. Examination of the h01, 0k1, and kk0 zones showed the following systematic absences: 0k1; k ≠ 2n+1, h01; l ≠ 2n+1, hk0; h ≠ 2n+1 consistent only with the space group Pbca. Accurate cell parameters and the orientation matrix were determined by a least-squares fit to the setting angles of the unresolved MoKα components of 24 symmetry related reflections with 2θ between 25 and 28°. The results as well as data collection parameters are found in Table (III).

2849 data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz-polarization effects. Examination of the azimuthal scan data showed a significant variation I_{min}/I_{max} = 0.812 for the average relative intensity curve. An analytical absorption correction using the measured size and indexed faces of the crystal and a 8x10x8 gaussian grid of internal points was performed. The maximum and minimum transmission factors were .482 and .374, respectively.

Rejection of systematically absent data gave a set of 2506 unique data which were used to solve and refine the structure. The positions of the Yb and Si atoms were found using a three-dimensional Patterson map. The remaining atom positions were found using standard Fourier and difference Fourier techniques. The heavy atoms were refined anisotorpically using full matrix least-squares techniques. The hydrogen atoms were located, and placed in idealized positions with fixed thermal parameters, and were included in structure factor calculations, but not refined.

The final residuals for 182 variables refined against the 1878 data for which $F^2 > 3\sigma(F^2)$ were R = 2.76%, wR = 3.60% and GOF = 1.925. The R value for all 2506 data was 4.61%.

The quantity minimized by the least-squares program was $\Sigma w(|F_o|-|F_c|)^2$, where w is the weight of a given observation. The p-factor, used to reduce the weight of intense reflections, was set to .025 in the final stages of the refinement. 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 a secondary extinction and a correction was applied.

The largest peak in the final difference Fourier map had an electron density of 1.05 $e^-/Å^3$ associated with the Yb atom.

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Supplementary Material. Table of General Temperature factors, root mean square amplitudes of thermal vibration and structure factor tables (12 pages).

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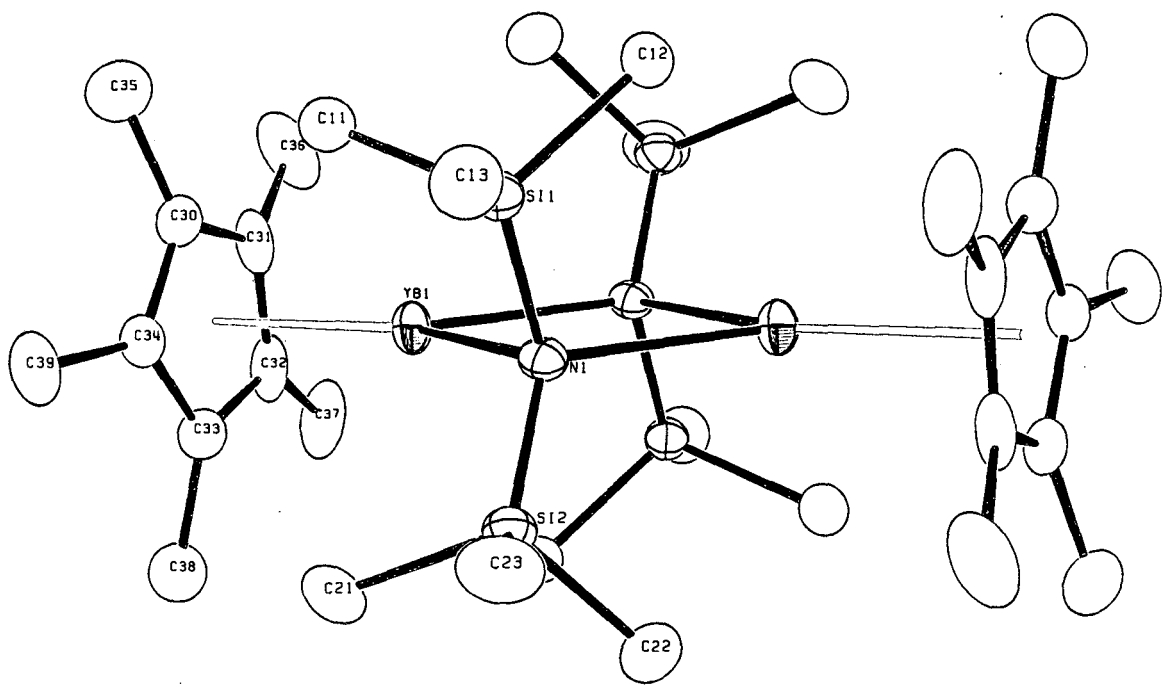
Figure Caption

ORTEP diagram of $(Me_5C_5)_2Yb_2[\mu\text{-}N(SiMe_3)_2]_2$. The atoms that are related by the inversion center are labeled with a prime.



XBL 847-3161

Table I. Positional and Thermal Parameters.

Atom	x	y	z	$B(Å^2)$
YB1	Ø.ØØ342(1)	Ø.Ø7913(1)	Ø.1ØØ13(2)	1.664(6)
SI1	-Ø.11472(9)	-Ø.Ø891(1)	Ø.Ø953(1)	1.74(3)
SI2	-Ø.16492(9)	Ø.Ø476(1)	-Ø.Ø446(1)	1.8Ø(3)
N1	-Ø.Ø977(3)	-Ø.Ø157(2)	Ø.ØØ91(3)	1.5(1)
C11	-Ø.Ø914(4)	-Ø.Ø467(4)	Ø.2161(4)	2.8(1)
C12	-Ø.Ø451(4)	-Ø.18Ø2(4)	Ø.Ø773(4)	2.4(1)
C13	-Ø.2155(4)	-Ø.1333(4)	Ø.1Ø63(5)	2.9(1)
C21	-Ø.1728(4)	Ø.15ØØ(4)	Ø.Ø183(5)	2.8(1)
C22	-Ø.1334(4)	Ø.Ø722(4)	-Ø.1677(4)	3.Ø(1)
C23	-Ø.2675(3)	Ø.ØØ64(4)	-Ø.Ø542(5)	3.2(2)
C3Ø	Ø.Ø2Ø2(3)	Ø.1314(4)	Ø.2847(4)	2.2(1)
C31	Ø.Ø919(3)	Ø.1511(4)	Ø.243Ø(4)	2.3(1)
C32	Ø.Ø8Ø6(3)	Ø.215Ø(4)	Ø.1756(4)	2.3(1)
C33	-Ø.ØØØ8(3)	Ø.2354(4)	Ø.1757(4)	2.Ø(1)
C34	-Ø.Ø379(4)	Ø.1828(3)	Ø.245Ø(4)	1.9(1)
C35	Ø.ØØ9Ø(4)	Ø.Ø767(4)	Ø.3717(6)	3.4(2)
C36	Ø.1716(4)	Ø.1235(4)	Ø.2773(5)	4.3(2)
C37	Ø.1443(4)	Ø.2611(4)	Ø.1254(5)	3.7(2)
C38	-Ø.Ø385(4)	Ø.3Ø63(4)	Ø.1243(5)	3.1(1)
C39	-Ø.1215(3)	Ø.19Ø8(4)	Ø.2787(5)	2.8(1)
C1ØØ	Ø.Ø3Ø8	Ø.1831	Ø.2248	4.Ø**
H111	-Ø.Ø997	-Ø.Ø872	Ø.265Ø	4.Ø**
H112	-Ø.Ø358	-Ø.Ø3Ø6	Ø.22Ø2	4.Ø**
H113	-Ø.121Ø	Ø.ØØ21	Ø.23Ø8	4.Ø**
H121	-Ø.Ø886	-Ø.1982	Ø.Ø382	3.3**
H122	-Ø.Ø652	-Ø.1646	Ø.1375	3.3**
H123	-Ø.Ø1Ø8	-Ø.2272	Ø.Ø852	3.3**
H131	-Ø.2157	-Ø.1739	Ø.1576	4.Ø**
H132	-Ø.2517	-Ø.Ø912	Ø.12ØØ	4.Ø**
H133	-Ø.2291	-Ø.1617	Ø.Ø496	4.Ø**
H211	-Ø.21Ø8	Ø.1856	-Ø.Ø112	4.Ø**
H212	-Ø.1891	Ø.1419	Ø.Ø834	4.Ø**
H213	-Ø.1236	Ø.1786	Ø.Ø193	4.Ø**
H221	-Ø.1714	Ø.1Ø91	-Ø.1974	4.Ø**
H222	-Ø.Ø841	Ø.1Ø2Ø	-Ø.1668	4.Ø**
H223	-Ø.1282	Ø.Ø24Ø	-Ø.2Ø46	4.Ø**
H231	-Ø.3Ø16	Ø.Ø452	-Ø.Ø851	4.Ø**
H232	-Ø.2688	-Ø.Ø451	-Ø.Ø899	4.Ø**
H233	-Ø.2891	-Ø.ØØ55	Ø.ØØ75	4.Ø**
H351	Ø.Ø193	Ø.1Ø93	Ø.427Ø	4.6**
H352	-Ø.Ø417	Ø.Ø557	Ø.3726	4.6**
H353	Ø.Ø466	Ø.Ø322	Ø.3691	4.6**
H361	Ø.1912	Ø.1565	Ø.3266	5.2**
H362	Ø.1723	Ø.Ø655	Ø.2964	5.2**
H363	Ø.2Ø96	Ø.127Ø	Ø.2242	5.2**
H371	Ø.1643	Ø.3Ø62	Ø.1617	4.6**
H372	Ø.188Ø	Ø.2237	Ø.1116	4.6**
H373	Ø.1268	Ø.2826	Ø.Ø65Ø	4.6**
H381	-Ø.Ø362	Ø.3571	Ø.1618	4.Ø**
H382	-Ø.Ø159	Ø.3162	Ø.Ø651	4.Ø**
H383	-Ø.Ø945	Ø.2948	Ø.1153	4.Ø**
H391	-Ø.1238	Ø.23Ø3	Ø.3311	3.6**
H392	-Ø.1547	Ø.21ØØ	Ø.23Ø3	3.6**
H393	-Ø.14Ø2	Ø.1384	Ø.3Ø23	3.6**

** -- Atoms included but not refined.

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

$$(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos\ \text{gamma})*B(1,2) + ac(\cos\ \text{beta})*B(1,3) + bc(\cos\ \text{alpha})*B(2,3)]$$

Table II. Some Selected Bond Lengths and Angles.

ATOM 1	ATOM 2	DISTANCE
YB1	N1	2.63Ø(3)
YB1	N1	2.445(3)
YB1	C3Ø	2.749(4)
YB1	C31	2.767(4)
YB1	C32	2.754(4)
YB1	C33	2.719(4)
YB1	C34	2.724(4)
YB1	C1ØØ	2.465(1)
SI1	N1	1.715(3)
SI1	C11	1.876(5)
SI1	C12	1.895(5)
SI1	C13	1.862(5)
SI2	N1	1.7Ø6(3)
SI2	C21	1.868(5)
SI2	C22	1.86Ø(5)
SI2	C23	1.872(4)
C3Ø	C31	1.391(6)
C31	C32	1.4Ø9(6)
C32	C33	1.425(5)
C33	C34	1.437(6)
C34	C3Ø	1.4Ø3(6)
C3Ø	C35	1.52Ø(7)
C31	C36	1.5Ø8(6)
C32	C37	1.49Ø(6)
C33	C38	1.492(7)
C34	C39	1.5Ø6(6)

Intramolecular Angles

ATOM 1	ATOM 2	ATOM 3	ANGLE
YB1	N1	YB1	96.72(11)
YB1	N1	SI1	99.21(14)
YB1	N1	SI2	1Ø8.25(14)
YB1	N1	SI1	1Ø5.87(14)
YB1	N1	SI2	114.ØØ8(16)
SI1	N1	SI2	127.39(2Ø)
N1	YB1	N1	83.28(11)
N1	YB1	C1ØØ	149.51(7)
N1	YB1	C1ØØ	127.22(7)
N1	SI1	C11	111.1Ø(18)
N1	SI1	C12	1Ø8.99(18)
N1	SI1	C13	118.34(2Ø)
C11	SI1	C12	1Ø5.53(2Ø)
C11	SI1	C13	1Ø4.88(21)
C12	SI1	C13	1Ø7.18(22)
N1	SI2	C21	111.Ø4(18)
N1	SI2	C22	11Ø.25(2Ø)
N1	SI2	C23	116.74(19)
C21	SI2	C22	1Ø6.12(21)
C21	SI2	C23	1Ø5.99(22)
C22	SI2	C23	1Ø6.Ø5(23)

Table III. Crystal Data (-95°C) for $(Me_5C_5)_2Yb_2[\mu\text{-}N(SiMe_3)_2]_2$.

Space Group	Pbca
a, Å	17.031(1)
b, Å	16.002(2)
c, Å	14.099(2)
V, $Å^3$	3843
z	4
fw	937.35
d(calcd), g cm^{-3}	1.62
μ(calcd), cm^{-1}	46.69
size, mm	0.23x0.22x0.32
reflcns, collected	2849
reflcns, unique	2506
reflcns, $F_o^2 > 3\sigma(F_o^2)$	1878
R, %	2.76
R_w, %	3.60
GOF	1.925
monochromater	highly oriented graphite
radiation	MoKα (λ = 0.71073Å)
scan range, type	$3° \leq 2\theta \leq 45°$, $\theta - 2\theta$
scan speed, deg min^{-1}	0.69 - 6.7
scan width, deg	$\delta\theta = 0.50 + 0.347 \tan\theta$
decay	less than 0.5%

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