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William S. Rees, Jr.

Attachment

**INITIAL STRUCTURAL CHARACTERIZATION
OF A LANTHANOID TRIS AGOSTIC INTERACTION**

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Initial Structural Characterization of a
Lanthanoid tris Agostic Interaction**

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As demands for speed and area efficiency in silicon-based electronic circuitry reach near-theoretical limits, attention has been turned increasingly in recent years toward the potential for optical communication, computation and connection. One approach to overcome the intrinsic direct band gap of silicon is to capitalize on the rich electronic manifold inherent in rare earth elements. Such an example was demonstrated by Pomrenke^[1] for ion-implanted samples. In an effort to move this highly promising research out of the laboratory and into the realm of commercial production, techniques which do not demand ultra high vacuum conditions have been sought. The tool of CVD (Chemical Vapor Deposition) is respected widely in the electronic components community as a large volume throughput, economically attractive and rapidly implemented method for fabrication of thin films of exceptional quality materials on non-uniform substrates. The initial work in this area^[2] was followed by a variety of results of CVD grown rare earth doped lattices.^[3] As one component of research in the area of designed dopant sources for CVD use, previous success had been garnered employing metal amide compositions for nitrogen doping of ZnSe.^[4,5] Thus, it was of interest to explore the potential for $\text{RE}(\text{NR}_2)_3$ (RE = rare earth) compounds as dopants in epitaxial semiconducting layers. Following preliminary success in this area,^[6] a demand for higher vapor pressure sources emerged.^[7] During this exploration, a novel interaction of Si-H and

erbium was observed for one of these precursors. The present report contains details related to what is, to the best of our knowledge, the initial finding of what is attributed to be a tris(agostic) interaction for a lanthanoid element.

The initial reports of lanthanide tris(amide) compounds^[8] made reliance upon the well-known bis(trimethylsilyl) moiety popularized by decades of success in Bradley's group.^[9] It was unsurprising that these compounds were observed to be three coordinate, due to the rather large effective cone angle of $\text{N}[\text{Si}(\text{CH}_3)_3]_2^-$ as a ligand, coupled with its electron donating properties to the electropositive Ln^{3+} cation. Subsequent structurally characterized examples include the very recent dysprosium and erbium tris[bis(trimethylsilyl)amide] entries.^[10] As a consequence of this rarity of coordination number three for lanthanides, it was of interest to probe the boundaries of utilizing less spacially demanding, and concomitantly less electron donating, substituents on the nitrogen atom. The first step in such a progression was the preparation of $\text{Er}\{\text{N}[\underline{\text{t}}\text{Bu}][\text{Si}(\text{CH}_3)_3]\}_3$, pseudoisosteric with $\text{Er}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}_3$, yet electronically perturbing to the Er^{3+} ion. Following comparison of the vapor pressure data for these two compounds $\{\text{Er}\{\text{N}[\underline{\text{t}}\text{Bu}][\text{Si}(\text{CH}_3)_3]\}_3$: v.p. = 10^{-3} Torr/ 120°C and $\text{Er}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}_3$: v.p. = 10^{-4} Torr/ 140°C }, attention next was turned toward the selective replacement of substituents at the silyl subunit. During the present investigation,

independent publications of structural characterization of five-coordinate yttrium and neodymium^[10] compounds $[ML_3S_2]$, as well as a four coordinate neodymium^[11] derivative occurred (L = anionic amide ligand; S = neutral coordinated THF). The vapor pressure of $Er\{N[\underline{t}Bu][Si(CH_3)_2(H)]\}_3$ was observed to be surprisingly high, in comparison with other known examples of compounds of this class (Scheme 1). Additionally, the melting point was seen to deviate substantially from the range of derivatives evaluated previously.^[12] Thus, a search for the origin of these properties compelled an appeal to crystallographic characterization of the compound.

Scheme 1.

The molecular configuration^[13] of compound 3 is depicted in Figure 1. Emerging quickly is the noteworthy regiochemistry displayed by the presence of all $\underline{t}Bu$ groups on the same face of the N_3 plane. An additional feature of the structure is the uniform rotation of each $Si[(CH_3)_2(H)]$ subunit to place all six methyl groups toward the periphery of the opposing hemisphere of the molecule. This rotation presumably is dictated by the attraction exhibited between the three silyl hydrides and the erbium center, as no indication of structure-influencing intramolecular forces was found in the unit cell. In 1983 Brookhart and Green^[16] coined

the term agostic to describe interactions of this type. Since then, several examples have been reported^[17] for transition metals and C-H, as well as N-H, units. Very recently, $\eta^2(\text{H}_2)$ interactions^[18] have been extended to $\eta^2(\text{Si-H})$ investigations^[19] for transition elements. A rigorous comparison of agostic and η^2 interactions presently is unwarranted, based on available data. To our knowledge, no earlier publications describe potential interactions between lanthanide elements and Si-H units, either originating from inter- or intramolecular coordination.

Figure 1.

As can be gleaned from an examination of the interatomic distance and angle data (Table 1), the present compound has substantially closer M-N contacts (220 pm vs all other reported data). Furthermore, the N-M-N interatomic angles reside in a tightly clustered group around $116^\circ \pm 2^\circ$. A comparison may be made with the four coordinate entity $\text{Nd}\{\text{N}[\text{C}_6\text{H}_5][\text{Si}(\text{CH}_3)_3]\}_3(\text{THF})$, which exhibits a dispersed average of $111^\circ \pm 3^\circ$. The present case considerably is closer to the predicted value of 120° for a VSEPR-optimized three-coordinate structure. This value is approximated for other sterically demanding homoleptic tris(ligand) lanthanide derivatives.^[20] Additionally, the dihedral angles are grouped closely around

0° [H(n)-Si(n)-N(n)-Er; n = 1: 2.5(13)°; n = 2: -4.6(11)°; n = 3: -0.1(11)°], as the consequence of the above-mentioned rotation of the dimethylsilyl groups. This further reinforces the concept that the structural motif of compound 3 is dominated by the controlling influence of the *tris* agostic Er-H-Si interactions.

Table 1.

In support of the notion of the possible presence of the above-described Er-H-Si interactions, comparative data for $\text{HN}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]$ and $\text{Er}\{\text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]\}_3$ are summarized in Table 2. Most notable is the 253 cm^{-1} shift in the IR vibration attributed to Si-H.^[21] The well documented difficulty in obtaining precise NMR data on lanthanide compounds has hampered an examination of $^2\text{J}(\text{Si},\text{H})$ for the silyl-bound hydrogen atoms present in compound 3. Such a probe of the "unstretched" Si-H character is restricted in the present case.^[22] The Si-H interatomic distances (141 - 148 pm) are, however, within the range of rather rare unstretched complexes, as compared to the typical stretched complexes.^[22a] Presumably such an observation is predominately attributable to the influence of a d^0 metal center. In such instances, the possibility of back donation is eliminated, and all indications favor the highly unusual unstretched case. It is noted, furthermore, that compound 3,

unlike the $\text{CH}(\text{TMS})_2^-$ unit, does not fall under the $\gamma\text{-C-H-Ln}$ vs $\beta\text{-Si-Me-Ln}$ interaction discussion.^[23] Examples of Ln-N-Si-Me also have been reported,^[24] as well as other γ -agostic or β -methyl interactions.^[25] For each of these, the tris agostic M-H-Si described here is unique in its interactions.

Table 2.

In conclusion, a possible source of the origin of the observed high vapor pressure and low melting point for $\text{Er}\{\text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]\}_3$ has been uncovered by an examination of the solid state structure.

Experimental Procedure

An aliquot of ErCl_3 (0.91 g, 3.35 mmole) was suspended in Et_2O (40 mL) and stirred at 0°C for 1 h. Freshly synthesized $\text{LiN}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]$ (1.38 g, 10.07 mmole) in Et_2O (60 mL) was added dropwise with rapid stirring. After attaining ambient temperature, the resultant pink solution was stirred overnight. Subsequently, the clear ether phase was decanted and evaporated. The residue from the ether solution was extracted with hexanes (50 mL). The resultant solution was filtered and its volume reduced in vacuum to 20 mL. Pink crystals of compound 3, obtained from this solution after three days at -80°C , were washed three times with cold (-78°C) hexane and dried at 20°C and 10^{-2} Torr. Ensuing sublimation at 100°C and 10^{-2} Torr yielded an air sensitive, pink powder. M.p. = 48°C . Yield = 0.78 g (42%); ^{13}C NMR (100.569 MHz, C_6D_6 , 22°C , $\text{Si}(\text{CH}_3)_4$ relative to residual $\text{C}_6\text{D}_5\text{H}$): δ = -227.12 (s, $\text{C}(\text{CH}_3)_3$), -127.75 (s, $\text{C}(\text{CH}_3)_3$), -8.99 (s, $\text{Si}(\text{CH}_3)_2$); ^{29}Si NMR (79.4521 MHz, C_6D_6 , 22°C , external standard: $\text{Si}(\text{CH}_3)_4$): δ = 429 (s, $\text{Si}(\text{CH}_3)_2(\text{H})$); MS(EI, 70 eV, 156°C): m/z(%): 559 (6.6) [$\text{M}^+ + 1$], 558 (17.5) [M^+], 543 (20.7) [$\text{M}^+ - \text{Me}$], 528 (1.0) [$\text{M}^+ - 2 \text{ Me}$], 501 (2.0) [$\text{M}^+ - \text{tBu}$], 499 (2.7) [$\text{M}^+ - \text{Si}(\text{CH}_3)_2(\text{H})$], 485 (2.4) [$\text{M}^+ - \text{N}[\text{Si}(\text{CH}_3)_2(\text{H})]$], 428 (3.5) [$\text{M}^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]$], 427 (4.7) [$\text{M}^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})] - (\text{H})$], 412 (21.7) [$\text{M}^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})] - (\text{CH}_3)(\text{H})$], 397 (9.8) [$\text{M}^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})] - (\text{CH}_3)_2(\text{H})$], 369 (12.8) [$\text{M}^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})] - [\text{Si}(\text{CH}_3)_2(\text{H})]$], 355 (8.0) [$\text{M}^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})] - \text{N}[\text{Si}(\text{CH}_3)_2(\text{H})]$], 298 (2.4) [$\text{M}^+ - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})] - \text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]$], 130 (6.5) [$\text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]^+$], 116 (100) [$[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]^+$], 73 (20.3) [$\text{N}[\text{Si}(\text{CH}_3)_2(\text{H})]^+$], 59 (38.1) [$\text{Si}(\text{CH}_3)_2(\text{H})]^+$.

Keywords: homoleptic erbium amide, agostic interactions.

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- [12] A slight increase in vapor pressure for the purified product **3** vs the crude product **2** was noticed. One potential source for the observation of a depression in the vapor pressure in the crude product is the presence of 'ate' complexes. Recently such species have been isolated in this laboratory by reacting ErCl_3 with three equivalents of $\text{LiN}([\text{iBu}][\text{Si}(\text{CH}_3)_3])$ and ensuing crystallization of the reaction product from Et_2O . Details of crystallographic characterization of the obtained $\{[\text{Li}(\text{Et}_2\text{O})_3][\text{Er}\{\text{N}[\text{iBu}][\text{Si}(\text{CH}_3)_3]\}_3\text{Cl}]\}$ will be reported separately. It is noted that the formation of such 'ate' species appears to be irreversible, i.e. once formed, they resist successful removal of

LiCl and subsequent conversion to a neutral, homoleptic lanthanide tris[(silyl)(alkyl)amide] species.

- [13] X-ray crystal structure analysis data: $C_{16}H_{48}N_3Si_3Er$, $M_r = 534.10$ g mol⁻¹, monoclinic, space group $P2_1/n$, $a = 11.128(2)$, $b = 14.430(3)$, $c = 17.943(3)$ Å, $\beta = 90.73(2)^\circ$, $V = 28.810(9)$ Å³, $Z = 4$, $\rho_{calcd} = 1.231$ g cm⁻³, crystal size $0.33 \times 0.53 \times 0.4$ mm³, number of reflections for lattice parameters = 25 ($19.5^\circ \leq 2\theta \leq 26.6^\circ$), $T = 185$ K, $\mu = 3.041$ mm⁻¹, $F(000) = 1100$. Data collection and correction: Enraf-Nonius CAD-4 diffractometer, $MoK\alpha$ radiation ($\lambda = 0.71073$ Å), graphite monochromator, aperture 2.5 mm, scan time variable, max. 45 s, scan angle $(0.93 + 0.35 \tan\theta)^\circ$, scan technique $\omega-2\theta$, range $2^\circ < 2\theta < 48^\circ$, hkl boundaries: $-12 \leq h \leq 12$, $0 \leq k \leq 16$, $0 \leq l \leq 20$, total number of measured reflections: 4971, unique reflections: 4346 ($R = 0.0227$), observed reflections with $[|F_o| \geq 4\sigma|F_o|]$: 4340, corrections: Lorentz, polarization, absorption (DIFABS: correction factors: min.: 0.917, max.: 1.164). Solution and refinement: structure solution by Patterson method, full-matrix least-squares refinement, 236 parameters refined. The methyl groups in the t Bu moiety attached to nitrogen N1 were found to be disordered over two sites (C14-C16/C141-C161), each occupying a population parameter of 0.5. The disordered carbon atoms and the agostic hydrogen atoms H1, H2, H3 each were refined with isotropic, whereas all other non-hydrogen atoms were refined with anisotropic, thermal parameters. All hydrogen atoms were calculated in idealized positions (C-H 96 pm, $U_{iso} = 0.08$ Å², final residue value $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o| = 0.0190$, $R_2 = [\Sigma_w(|F_o| -$

$|F_c|)^2 / \sum_w (|F_o|^2)^{1/2} = 0.0417$ ($w = 1/\sigma^2(F_o)$), $\text{Goof} = [\sum_w (|F_o| - |F_c|)^2 / (n-p)]^{1/2} = 1.051$, $\Delta\rho(\text{max./min.}) = \text{max. } 0.404 \text{ e\AA}^{-3}$ and $\text{min. } -0.300 \text{ e\AA}^{-3}$. All refinements were performed using the SHELXL-93 program system.^[14] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Loepoldshafen (Germany) on quoting the dispository number CSD-XXXXX.

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Scheme 1: Synthetic route to $\text{Er}\{\text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]\}_3$.

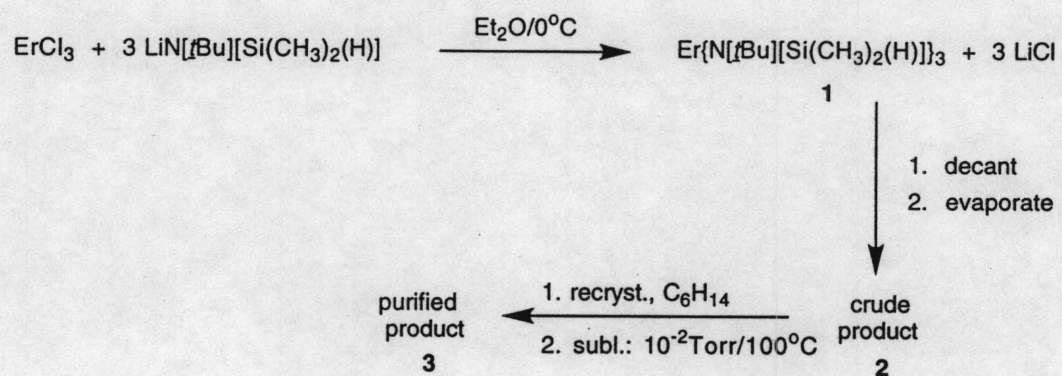


Fig. 1: ZORTEP plot^[15] of $\text{Er}\{\text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]\}_3$ (thermal ellipsoids are scaled to the 30% probability level). Selected interatomic angles [°] and distances [pm] (standard deviations are given in parentheses):

Er-N1 220.6(2), Er-N2 220.6(2), Er-N3 220.6(2), Er-H1 232(3), Er-H2 241(3), Er-H3 237(3), N1-Si1 168.9(3), N1-C13 147.6(4), N2-Si2 169.1(3), N2-C23 146.3(4), N3-Si3 168.6(3), N3-C33 147.5(4); Si1-H1 141.1(3), Si2-H2 146.1(3), Si3-H3 148.1(3), N1-Er-N2 118.97(9), N1-Er-N3 114.60(9), N2-Er-N3 116.85(9), Er-N1-Si1 99.34(11), Si1-N1-C13 126.2(2), Er-N1-C13 133.6(2), Er-N2-Si2 99.85(11), Si2-N2-C23 126.9(2), Er-N2-C23 133.1(2), Er-N3-Si3 99.73(11), Si3-N3-C33 127.1(2), Er-N3-C33 133.1(2).

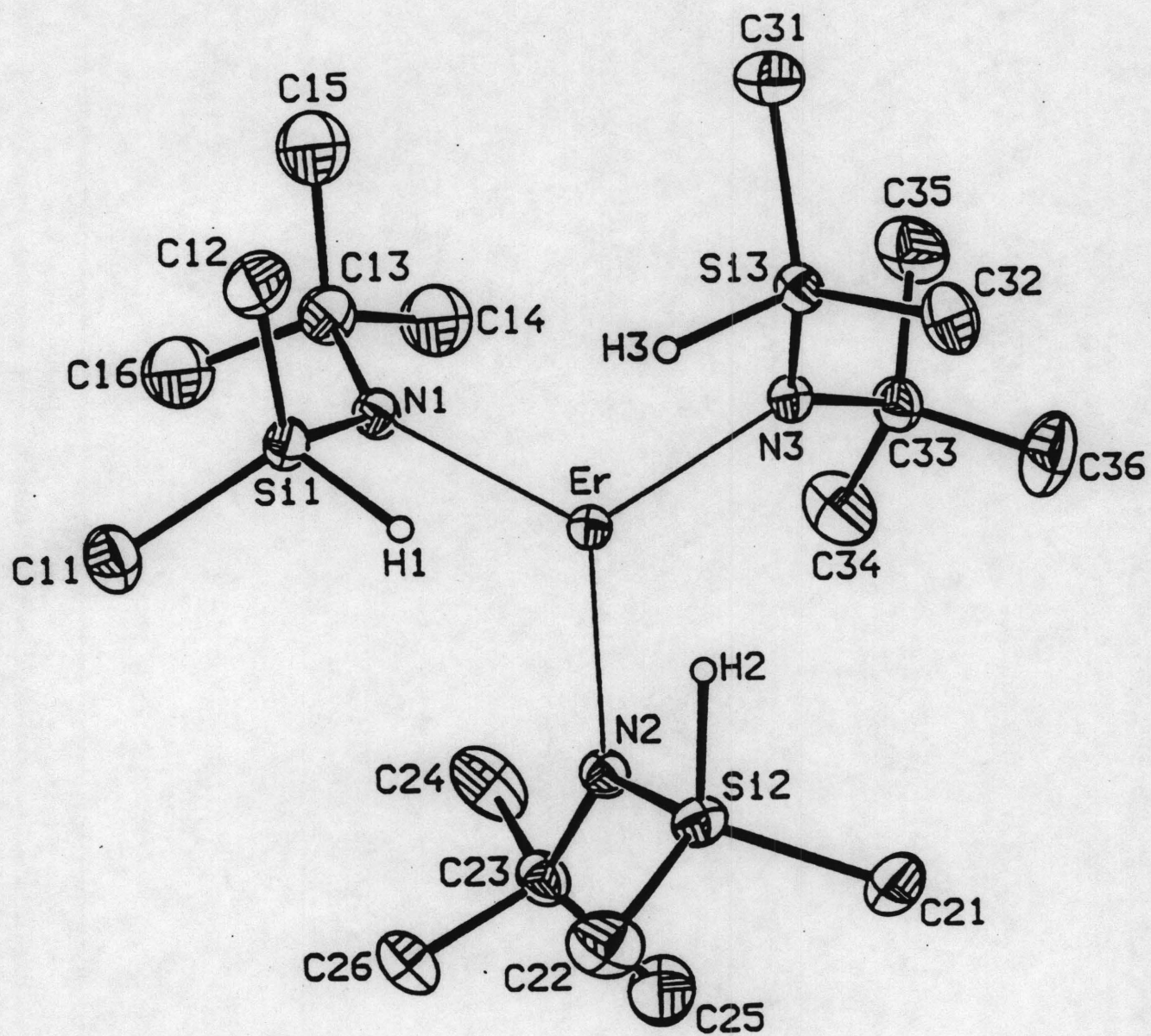


Table 1: Interatomic angles [°] and distances [pm] involving M-N interactions for homoleptic lanthanide *tris*(amide) compounds.

	M-N distances	MN ₂ angles
Er{N[<i>i</i> Bu][Si(CH ₃) ₂ (H)]} ₃ } ^[a]	Er-N1 220.6(2)	N1-Er-N2 118.97(9)
	Er-N2 220.6(2)	N1-Er-N3 114.60(9)
	Er-N3 220.6(2)	N2-Er-N3 116.85(9)
Nd{N[C ₆ H ₅][Si(CH ₃) ₃]} ₃ (THF) ^[11]	Nd-N1 230.8(3)	N1-Nd-N2 107.8(1)
	Nd-N2 229.8(2)	N1-Nd-N3 109.4(1)
	Nd-N3 232.0(3)	N2-Nd-N3 114.0(1)
Nd{N[Si(CH ₃) ₂ (H)] ₂ } ₃ (THF) ₂ ^[10]	Nd-N1 235.3(4)	N1-Nd-N2 113.7(2)
	Nd-N2 232.6(5)	N1-Nd-N3 129.9(2)
	Nd-N3 235.1(5)	N2-Nd-N3 129.2(2)
Y{N[Si(CH ₃) ₂ (H)] ₂ } ₃ (THF) ₂ ^[10]	Y-N1 227.5(4)	N1-Y-N2 111.1(1)
	Y-N2 222.9(4)	N1-Y-N3 134.8(1)
	Y-N3 227.6(4)	N2-Y-N3 116.9(2)

[a] This work.

Table 2: Infrared spectroscopic data for compounds possessing metal-(Si-H) interactions and representative values for non-interacting systems.

Compound	Si-H (cm ⁻¹)	Reference
HN[<i>i</i> Bu][Si(CH ₃) ₂ (H)]	2111	This work ^[a]
Er{N[<i>i</i> Bu][Si(CH ₃) ₂ (H)]} ₃	1858	This work ^[a]
unperturbed Si-H	2081-1972	[26]
Mo η ² (Si-H)	1750-1730	[26]

[a] In C₆D₆ solution

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Structural characterization of $\text{Er}\{\text{N}[\text{tBu}][\text{Si}(\text{CH}_3)_2(\text{H})]\}_3$ has revealed that all the tBu groups reside on the same face of the N_3 plane, whereas all Si-CH₃ groups are rotated toward the periphery of the molecule. This results in erbium-hydrogen interatomic distances of 231.7-236.7 pm for the silyl hydride moieties folding into the metal center.