

## Sounding out the Reactivity of Trimethylttrium

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The fundamental reactivity of amorphous  $[\text{YMe}_3]_n$  was representatively examined: toward  $\text{GaMe}_3$  as a Lewis acid, 9-fluorenone as a carbonyl substrate, and tetramethyldisilazane ( $\text{HN}(\text{SiHMe}_2)_2$ ) as a Brønsted acid. The products obtained from the 3-equiv reactions were spectroscopically and X-ray crystallographically identified.  $\text{Y}(\text{GaMe}_4)_3$  shows Y–Ga distances of 3.0393(4) and 3.0502(3) Å, which are significantly shorter than the Y–Al distances in  $\text{Y}[\text{AlMe}_4]_3[\text{Al}_2\text{Me}_6]_{0.5}$  (av 3.068 Å). The homoleptic alkoxide  $[\text{Y}(\text{OC}_{14}\text{H}_{11})_3]_x$  bearing sterically demanding 9-Me-fluorenoxy ligands documents high methyl group transfer economy via the 1,2-addition reaction of  $[\text{YMe}_3]_n$  to 9-fluorenone; it was obtained in single-crystalline form in a minor byproduct, the asymmetric dimer  $[\text{Y}(\text{OC}_{14}\text{H}_{11})_2(\mu\text{-OC}_{14}\text{H}_{11})_2(9\text{-fluorenone})]$ . The previously elusive unsolvated complex  $\{\text{Y}[\text{N}(\text{SiHMe}_2)_2]_3\}$  also shows a dimeric molecular composition,  $\{\text{Y}[\text{N}(\text{SiHMe}_2)_2]_2[\mu\text{-N}(\text{SiHMe}_2)_2]\}_2$ , featuring asymmetrically bridging silylamide ligands and Y–SiH multi- $\beta$ -agostic interactions in the solid state  $[(\text{Y}-\text{Si})_{\text{min}} 3.0521(7)$  Å,  $(\text{Y}-\text{H})_{\text{min}} 2.41(3)$  Å,  $\nu(\text{Si}-\text{H})_{\text{agostic}} 1931$   $\text{cm}^{-1}$ ].

### Introduction

The reactivity and structural chemistry of organolanthanide complexes are intrinsically controlled by the steric features of spectator and actor ligands as well as by the presence of any coordinating donor molecules.<sup>1</sup> Unsolvated methyl complexes are classified as the most reactive organolanthanide complexes due to the enhanced basicity and concomitant small size of the methyl actor ligand.<sup>2</sup> Methane activation<sup>3</sup> and multiple hydrogen abstraction<sup>4</sup> promoted by  $\text{Cp}^*\text{Lu}(\text{CH}_3)$  and  $[\text{Cp}^*\text{Y}(\mu\text{-CH}_3)_2]_3$ , respectively, provide examples of this extraordinary reactivity. The synthetic accessibility of unsolvated discrete methyl complexes depends crucially on the availability of suitable precursors and/or efficient multistep reaction sequences.<sup>5</sup> The formation of highly reactive and sterically unsaturated rare-earth metal centers is often indicated by solvent degradation,<sup>6</sup> self-degradation,<sup>7</sup> and/or occurrence of secondary agostic interactions.<sup>8</sup> Structurally characterized non-ate higher alkyl and aryl compounds include  $\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ ,<sup>9,10</sup>  $\text{Ln}[\text{CH}(\text{SiMe}_3)_2]_3$ ,<sup>11</sup>

$\text{Yb}(\text{CH}_2\text{tBu})_3(\text{THF})_2$ ,<sup>12</sup>  $\text{Ln}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$ ,<sup>13</sup>  $\text{Ln}(\text{C}_6\text{H}_5)_3(\text{THF})_3$ , and  $\text{Ln}(o\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_3$ .<sup>14</sup> However, until now only the silylalkyl derivatives have found widespread use in alkane elimination reactions.<sup>15</sup> Moreover, methyl derivatives are available in the form of ate complexes  $[\text{Li}_3(\text{donor})_3][\text{Ln}(\text{CH}_3)_6]$  (donor = TMEDA (*N,N,N',N'*-tetramethylethylenediamine), DME (1,2-dimethoxyethane))<sup>16</sup> and adduct complexes  $\text{Ln}(\text{MMe}_4)_3 = \text{LnMe}_3(\text{MMe}_3)_3$  (M = Al, Ga)<sup>17</sup> as well as their solvated cationic variants  $[\text{YMe}_2(\text{THF})_5]^+[\text{BPh}_4]^-$  and  $[\text{YMe}(\text{THF})_6]^{2+}[\text{BPh}_4]^{2-}$ .<sup>18</sup> Recently, we described the synthesis of the elusive trimethylttrium,  $[\text{YMe}_3]_n$  (**1**), from the homoleptic tetramethylaluminate  $\text{Y}(\text{AlMe}_4)_3$ <sup>19</sup> utilizing Lapperts donor(ether)-induced aluminate cleavage reaction.<sup>20</sup> Herein, we report the results of a preliminary reactivity study on  $[\text{YMe}_3]_n$ , which suggests a multifaceted applicability in organometallic synthesis.

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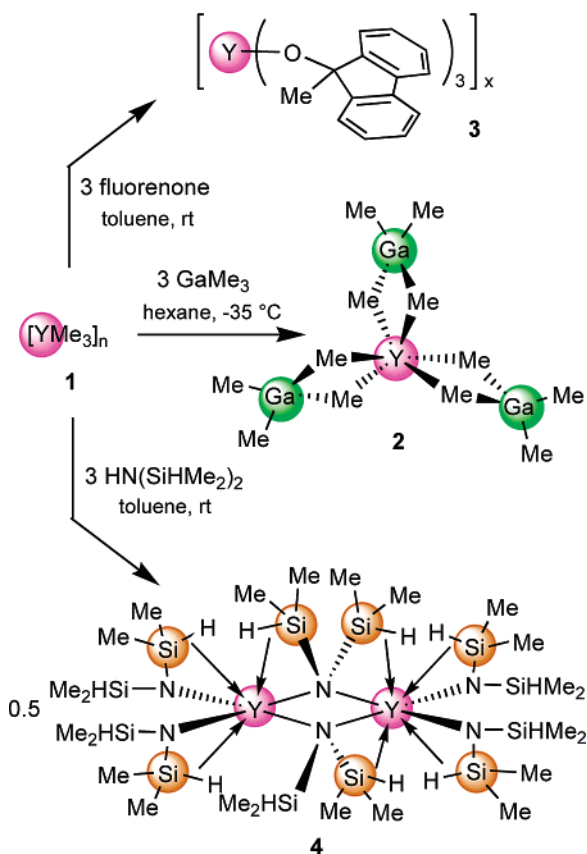
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Scheme 1. Three Different Reaction Pathways of  $[YMe_3]_n$ 

## Results and Discussion

**Lewis Acid–Base Addition Reactions.** The feasibility of the addition of Lewis acid main group metal alkyls to  $[YMe_3]_n$  was communicated previously.<sup>19</sup> Accordingly, mixed alkylalumininate  $YAl_3Me_3Et_9$  and homoleptic gallate  $Y(GaMe_4)_3$  (2) were obtained from the reaction of 1 with  $AlEt_3$  and  $GaMe_3$ , respectively, in almost quantitative yield (Scheme 1).

Thus far, only two investigations of molecular rare-earth metal gallate complexes have been carried out.<sup>17a,21</sup> Our synthesis route using the detour via aluminate formation  $\rightarrow$  donor-induced cleavage  $\rightarrow$   $GaMe_3$  addition avoids excessive use of expensive  $GaMe_3$  and undesired gallium-containing byproducts inherent to the originally applied amide elimination reaction.<sup>17a</sup>

Unlike the neodymium congener (tetragonal space group  $I4_1/a$ ),  $Y(GaMe_4)_3$  (2) crystallized in the monoclinic space group  $C2/c$  with two crystallographically equivalent tetramethylgallate ligands (Figure 1; Tables 1 and 4). The Y–C distances of 2.505(2)–2.521(2) Å lie in the same range as those in  $Y[AlMe_4]_3[Al_2Me_6]_{0.5}$  (2.505(6)–2.514(8) Å).<sup>17b</sup> Surprisingly, the Y–Ga distances ranging from 3.0393(4) to 3.0502(3) Å are significantly shorter than the Y–Al distances in  $Y[AlMe_4]_3[Al_2Me_6]_{0.5}$  (av 3.068 Å), which is also reflected in less acute C–Y–C angles (86.40(7)° and 87.16(10)° versus 84.33–84.81°). As unambiguously evidenced by the neutron diffraction study of  $Nd[AlMe_4]_3[Al_2Me_6]_{0.5}$ ,<sup>17c</sup> complex 2 also shows five-coordinate bridging carbon atoms with two of the hydrogen atoms in each tilted toward the larger Lewis-acidic metal center.

**1,2-Addition to Ketones.** Nucleophilicity-driven addition of M–CH<sub>3</sub> moieties to carbonyl functionalities are routine reactions in organic synthesis, utilizing organometallics such as MeLi,

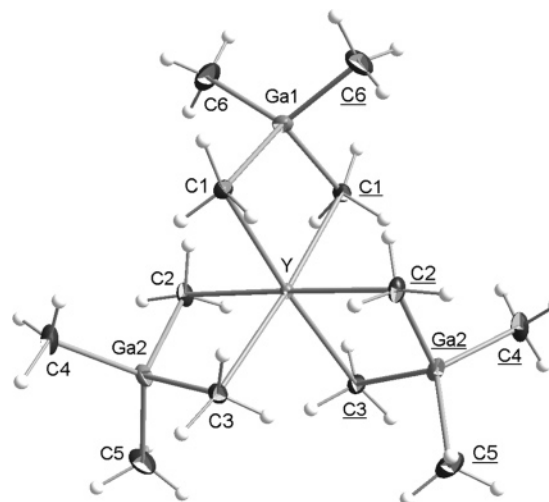


Figure 1. Molecular structure of  $Y(GaMe_4)_3$  (2) shown with atomic displacement parameters at the 30% level. Underlined atomic labels indicate symmetry-related atoms  $[-x, y, 0.5-z]$ .

Table 1. Selected Interatomic Distances and Angles for  $Y(GaMe_4)_3$  (2)

Bond Lengths (Å)			
Y–Ga1	3.0393(4)	Y–Ga2	3.0502(3)
Y–C1	2.505(2)	Y–C2	2.516(2)
Y–C3	2.521(2)	Y–H1B	2.48(2)
Y–H1C	2.48(2)	Y–H2A	2.50(2)
Y–H2C	2.43(2)	Y–H3A	2.50(2)
Y–H3B	2.49(2)	Ga1–C1	2.117(2)
Ga1–C6	1.971(3)	Ga2–C2	2.110(2)
Ga2–C3	2.108(2)	Ga2–C4	1.974(2)
Ga2–C5	1.976(2)		
Bond Angles (deg)			
Y–C1–Ga1	81.76(7)	Y–C2–Ga2	82.00(7)
Y–C3–Ga2	81.93(7)	C1–Y–C1	87.16(10)
C1–Y1–C3	86.40(7)	C1–Ga1–C6	105.07(11)
C1–Ga1–C1	109.32(11)	C2–Ga2–C3	86.40(7)

Table 2. Selected Interatomic Distances and Angles for  $[Y(OC_{14}H_{11})_2(\mu-OC_{14}H_{11})_2(9\text{-fluorenone})]_2$  (3a)

Bond Lengths (Å)			
Y1–O1	2.028(4)	Y1–O2	2.049(4)
Y1–O3	2.227(4)	Y1–O4	2.252(4)
Y2–O3	2.251(4)	Y2–O4	2.301(4)
Y2–O5	2.028(4)	Y2–O6	2.092(4)
Y2–O7	2.319(4)		
Bond Angles (deg)			
Y1–O3–Y2	107.72(15)	Y1–O4–Y2	105.18(15)
O1–Y1–O2	116.26(17)	O2–Y1–O3	121.75(15)
O1–Y1–O4	116.41(15)	O1–Y1–O3	115.53(15)
O2–Y1–O4	104.77(15)	O3–Y2–O4	72.73(14)
O3–Y2–O5	101.43(15)	O3–Y2–O6	100.18(14)
O3–Y2–O7	158.06(14)	O4–Y2–O5	114.77(15)
O4–Y2–O6	137.04(15)	O4–Y2–O7	87.87(14)
O5–Y2–O6	108.18(16)	O5–Y2–O7	93.52(16)
O6–Y2–O7	90.13(15)	Y1–O1–C1	168.8(4)
Y1–O2–C15	156.1(4)	Y1–O3–C29	115.0(3)
Y1–O4–C43	120.1(3)	Y2–O3–C29	136.9(3)
Y2–O4–C43	133.7(3)	Y2–O5–C57	175.6(4)
Y2–O6–C71	145.4(4)	Y2–O7–C85	152.7(4)

MeMgX, and  $Al_2Me_6$ .<sup>22</sup> An important limitation of the synthetic value of aluminum alkyls is that often only the addition of one Al–C bond of the reagent to C=O functionalities occurs.<sup>23</sup> Importantly, poorly defined organocerium reagents of the type  $CeX_3/RLi$  (X = Cl, I; R = alkyl, alkenyl, alkynyl, phenyl) and

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**Table 3. Selected Interatomic Distances and Angles for {Y[N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>(μ-N(SiHMe<sub>2</sub>)<sub>2</sub>)<sub>2</sub>}<sub>2</sub> (4)**

Bond Lengths (Å)			
Y1–N1	2.2535(18)	Y1–N2	2.2612(19)
Y1–N3	2.4985(18)	Y1–N4	2.5036(18)
Y2–N3	2.4581(18)	Y2–N4	2.4556(18)
Y2–N5	2.237(2)	Y2–N6	2.2436(19)
Y1–Si2	3.0569(7)	Y1–Si3	3.0521(7)
Y1–Si8	3.1375(7)	Y2–Si6	3.1620(7)
Y2–Si7	3.1012(7)	Y2–Si9	3.1990(7)
Y2–Si11	3.0929(7)	Y1–H2	2.47(3)
Y1–H3	2.44(3)	Y1–H8	2.41(3)
Y2–H6	2.57(3)	Y2–H7	2.43(3)
Y2–H11	2.49(3)		
Bond Angles (deg)			
Y1–O3–Y2	107.72(15)	Y1–O4–Y2	105.18(15)
O1–Y1–O2	116.26(17)	O2–Y1–O3	121.75(15)
O1–Y1–O4	116.41(15)	O1–Y1–O3	115.53(15)
O2–Y1–O4	104.77(15)	O3–Y2–O4	72.73(14)
Y1–N1–Si1	100.19(9)	Y1–N1–Si2	136.71(11)
Y1–N2–Si3	99.98(9)	Y1–N2–Si4	135.65(11)
Y1–N3–Si5	108.40(9)	Y1–N3–Si6	118.45(9)
Y1–N4–Si7	129.73(9)	Y1–N4–Si8	93.79(8)
Y2–N3–Si5	118.73(9)	Y2–N3–Si6	96.33(8)
Y2–N4–Si7	93.96(8)	Y2–N4–Si8	126.18(9)
Y2–N5–Si9	108.05(10)	Y2–N5–Si10	127.27(11)
Y2–N6–Si11	102.50(9)	Y2–N6–Si12	133.64(11)
Y2–N6–Si11	102.50(9)	Y2–N6–Si12	133.64(11)

CeCl<sub>3</sub>/RMgX (R = alkyl, phenyl; X = Cl, Br), being less basic than organolithium or Grignard reagents, belong to the most prominent organolanthanide reagents in organic synthesis.<sup>23,24</sup> Organocerium additions to hydrazones revealed the beneficial effect of a 1:1 CeCl<sub>3</sub>/LiCH<sub>3</sub> reagent stoichiometry on efficiency and selectivity,<sup>25</sup> while soluble cerium salts [CeCl<sub>3</sub>·LiCl] were employed for the improved addition to carbonyl compounds.<sup>26</sup> There is a dearth of data on Ln-promoted alkylation reactions of C=O moieties utilizing *well-defined* rare-earth metal alkyl complexes.<sup>27,28</sup> Ate complexes [Li<sub>3</sub>(TMEDA)<sub>3</sub>][Ln(CH<sub>3</sub>)<sub>6</sub>] (Ln = Pr, Sm) were reacted with α,β-unsaturated aldehydes and ketones and found to favor 1,2-methylation (80–95%) over 1,4-methylation.<sup>27</sup> Metalated products, i.e., alkoxide derivatives, were isolated from the reaction of YbPh<sub>2</sub> with 9-fluorenone, yielding YbPh(9-Ph-fluorenoxy).<sup>28</sup> Noteworthy, by targeting selective ketone functionalization, rare-earth metal alkoxide derivatives [Ln(OCR'<sub>2</sub>Me)<sub>3</sub>] of tertiary alcohols would be accessible via the addition of all three Ln–C bonds of [YMe<sub>3</sub>]<sub>n</sub> (1) to substrates O=CR'<sub>2</sub>.<sup>29</sup> The resulting soluble/volatile alkoxide complexes would complement the library of important precursor compounds for advanced ceramics via MOCVD and sol gel processes.<sup>30</sup>

To test the methylating capability of 1, we examined its reaction with 3 equiv of 9-fluorenone in toluene (Scheme 1).<sup>31</sup>

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This transformation afforded the envisaged methylation product containing three sterically demanding 9-Me-fluorenoxy ligands.<sup>32</sup> The new homoleptic alkoxide [Y(OC<sub>14</sub>H<sub>11</sub>)<sub>3</sub>]<sub>x</sub> (3) is soluble in toluene and was identified by NMR (CH<sub>3</sub>, s, 1.53 ppm) and IR spectroscopy as well as elemental analysis. As indicated by <sup>1</sup>H NMR spectroscopy, pure complex 3 is preferentially obtained if the reaction is performed with substoichiometric amounts of 9-fluorenone (e.g., 2.5 equiv). A slight excess of 9-fluorenone produced adduct complex {[Y(OC<sub>14</sub>H<sub>11</sub>)<sub>3</sub>]<sub>3</sub>(9-fluorenone)<sub>0.5</sub>} (3a) as a byproduct, whereas >3.5-equiv reactions form adduct complex {[Y(OC<sub>14</sub>H<sub>11</sub>)<sub>3</sub>]<sub>3</sub>(9-fluorenone)} (3b). In the <sup>1</sup>H NMR spectrum, the coordinated 9-fluorenone showed signals that are considerably shifted to higher field compared to noncoordinated 9-fluorenone. Byproduct 3a could be separated by fractional crystallization and was X-ray crystallographically characterized as [Y(OC<sub>14</sub>H<sub>11</sub>)<sub>2</sub>(μ-OC<sub>14</sub>H<sub>11</sub>)<sub>2</sub>](9-fluorenone) (Figure 2, Tables 2 and 4). The preferred crystallization of dinuclear rare-earth metal alkoxide complexes in the presence of an additional donor molecule has been reported previously.<sup>33</sup>

The asymmetric coordination environment of the dimeric complex 3a is to some extent reflected in the Y–O bond lengths. The four-coordinate yttrium centers show average terminal and bridging Y–O bond distances of 2.039 and 2.240 Å, respectively, while those of the five-coordinate yttrium center average 2.060 and 2.276 Å.<sup>33</sup> The overall steric bulk of the 9-Me-fluorenoxy ligand can be compared with that of OCH<sub>2</sub>Bu<sub>2</sub>, OCPH<sub>3</sub>, and OSiMe<sub>2</sub>tBu, giving likewise dimeric complexes of the smaller-sized rare-earth metal cations.<sup>30</sup> For comparison, the smaller OrBu ligand results in the formation of trinuclear complexes.<sup>30</sup> The Y–O–C bond angles indicate enhanced conformational flexibility ranging from 145.40(4)° to 175.6(4)° for the terminal and from 115.0(3)° to 136.9(3)° for the bridging alkoxide ligands. The Y–O(flourenone) donor bond of 2.319(4) Å is considerably elongated compared to the Y–O(phosphine oxide) distance of 2.263(3) Å in Y(OSiPh<sub>3</sub>)<sub>3</sub>-(OP<sub>n</sub>Bu<sub>3</sub>)<sub>2</sub>.<sup>33a</sup>

**Alkane Elimination Reactions.** Methane elimination reactions of 1 proceed readily as initially found for the formation of Ln[N(SiMe<sub>2</sub>)<sub>2</sub>]<sub>3</sub> and [Y(OCH<sub>2</sub>Bu<sub>2</sub>)<sub>3</sub>] via the 3-equiv reactions of silylamine and alcohol, respectively.<sup>19,34</sup> Rare-earth metal bis-(trimethylsilyl)amide complexes are known as routine synthesis precursors in organolanthanide chemistry.<sup>32</sup> Since our group introduced the extended silylamide route based on the sterically more flexible Ln[N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>x</sub> (x = 1, 2), we have been intrigued by its solvent-free variant.<sup>34b,35</sup> In our hands, various attempts to isolate Ln[N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>3</sub> failed, including (a) a silylamine elimination with Ln[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>, (b) an alkane elimination with Ln[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>, and (c) complete THF donor displacement either by the toluene reflux method or by AlMe<sub>3</sub>-mediated Lewis-acid competition.<sup>36</sup> For heteroleptic complexes, the [N(SiHMe<sub>2</sub>)<sub>2</sub>] ligand was found to be prone to extensive

(31) A 9-fluorenone/fluorenyl radical/9-H-fluorenoxy-based coordination chemistry has been comprehensively studied for Ln<sup>II</sup>/Ln<sup>III</sup> redox systems. For example, see: Hou, Z.; Fujita, A.; Zhang, Y.; Miyano, T.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 754.

(32) Obrey, S. J.; Bott, S. G.; Barron, A. R. *Organometallics* **2001**, *20*, 5162.

(33) For examples, see: (a) McGeary, M. J.; Coan, P. S.; Foltling, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 1723: Y<sub>2</sub>-(OSiMe<sub>2</sub>tBu)<sub>6</sub>(HOSiMe<sub>2</sub>tBu) [Y–O(terminal) 2.05(2)–2.10(2) Å, Y–O(bridging) 2.24(2)–2.28(2) Å]. (b) Herrmann, W. A.; Anwender, R.; Scherer, W. *Chem. Ber.* **1993**, *126*, 1533: Nd<sub>2</sub>(OCH<sub>2</sub>Bu<sub>2</sub>)<sub>6</sub>(NCCH<sub>3</sub>).

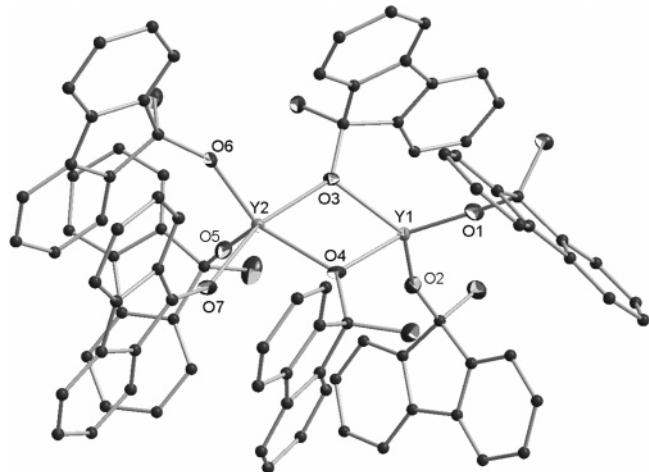
(34) (a) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1021. (b) Anwender, R. *Top. Curr. Chem.* **1996**, *179*, 33.

(35) Herrmann, W. A.; Anwender, R.; Munck, F. C.; Scherer, W.; Dufaud, V.; Huber, N. W.; Artus, G. R. *J. Z. Naturforsch.* **1994**, *49B*, 1789.

Table 4. Crystal Data and Data Collection Parameters of Complexes 2, 3a and 4

	2	3a	4
chem formula	C <sub>12</sub> H <sub>36</sub> Ga <sub>3</sub> Y	C <sub>104</sub> H <sub>82</sub> O <sub>7</sub> Y <sub>2</sub>	C <sub>24</sub> H <sub>84</sub> N <sub>6</sub> Si <sub>2</sub> Y <sub>2</sub>
fw	478.48	1621.52	971.87
color/shape	colorless/flat prism	yellow/plate	colorless/plate
cryst size (mm)	0.40 × 0.13 × 0.03	0.15 × 0.13 × 0.03	0.38 × 0.09 × 0.07
cryst syst	monoclinic	monoclinic	triclinic
space group	C2/c (no. 15)	P2 <sub>1</sub> /c (no. 14)	P1̄ (no. 2)
a (Å)	10.8817(6)	26.548(1)	11.0213(4)
b (Å)	15.7284(8)	13.4330(5)	11.1534(4)
c (Å)	12.5031(7)	25.284(1)	25.1661(9)
α (deg)			79.470(1)
β (deg)	101.850(1)	116.120(1)	80.359(1)
γ (deg)			60.812(1)
V (Å <sup>3</sup> )	2094.3(2)	8095.7(6)	2644.2(2)
Z	4	4	2
T (K)	123(2)	123(2)	123(2)
ρ <sub>calcd</sub> (g cm <sup>-3</sup> )	1.517	1.330	1.221
μ (mm <sup>-1</sup> )	6.543	1.486	2.478
F <sub>000</sub>	960	3360	1032
θ range (deg)	2.31–30.06	1.61–25.25	2.11–26.42
data collected (h,k,l)	15, 22, 17	31, 16, 30	13, 13, 31
no. of reflns collected	17 532	93 890	34 529
no. of indep reflns (all)/R <sub>int</sub>	3080/0.027	14 653/0.203	10 831/0.039
no. of obsd reflns (I > 2σ(I))	2854	9220	8892
no. of params refined	107	1024	457
R1 (obsd/all) <sup>a</sup>	0.0227/0.0257	0.0773/0.1384	0.0286/0.0427
wR2 (obsd/all) <sup>a</sup>	0.0661/0.0677	0.1506/0.1710	0.0647/0.0703
GOF (obsd/all) <sup>a</sup>	1.112/1.108	1.119/1.119	1.017/1.017
largest diff peak and hole (e Å <sup>-3</sup> )	+1.007/−0.968	+0.597/−1.115	+0.512/−0.431

<sup>a</sup> R1 =  $\sum(|F_o| - |F_c|)/\sum|F_o|$ ; wR2 =  $\{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$ ; GOF =  $\{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ .

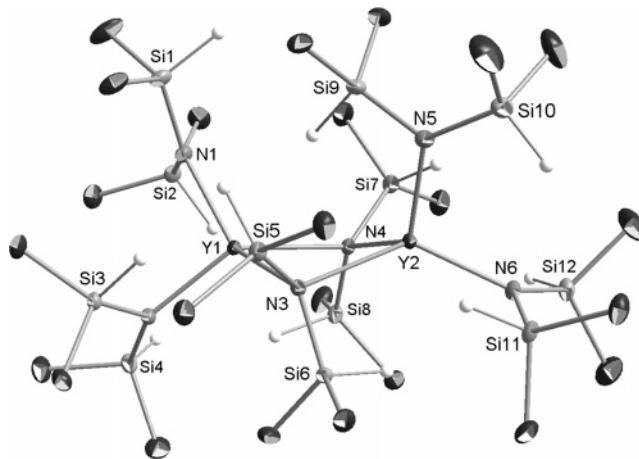


**Figure 2.** Molecular structure of [Y(OC<sub>14</sub>H<sub>11</sub>)<sub>2</sub>(μ-OC<sub>14</sub>H<sub>11</sub>)]<sub>2</sub>(9-fluorenone) (**3a**) with atomic displacement parameters at the 30% level. For clarity the C atoms in the ring systems are given with an arbitrary radius and H atoms omitted.

β-SiH...Ln agostic interactions.<sup>37</sup> Surprisingly, treatment of [YMe<sub>3</sub>]<sub>n</sub> (**1**) with HN(SiHMe<sub>2</sub>)<sub>2</sub> even at ambient temperature led to the isolation of Y[N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>3</sub> (**4**) (Scheme 1). The reaction mixture in toluene cleared up after 2 h, accompanied by slow gas evolution. Although the <sup>1</sup>H NMR spectrum of the oily product indicated different silylamide ligand environments, the homoleptic bis(dimethylsilyl)amide complex **4** could be crystallized as the main product from hexane (41% yield). An X-ray structure analysis revealed a dimeric molecular composition, {Y[N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>[μ-N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>}<sub>2</sub> (Figure 3, Tables 3 and 4).<sup>38</sup>

(36) (a) Anwander, R.; Runte, O.; Eppinger, J.; Gerstberger, G.; Herdtweck, E.; Spiegler, M. *J. Chem. Soc., Dalton Trans.* **1998**, 5, 847. (b) Eppinger, J. Ph.D. Thesis, Technische Universität München, 1999.

(37) For an example, see: Eppinger, J.; Spiegler, M.; Hieringer, W.; Herrmann, W. A.; Anwander, R. *J. Am. Chem. Soc.* **2000**, 122, 3080.



**Figure 3.** Molecular structure of {Y[N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>[μ-N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>}<sub>2</sub> (**4**) shown with atomic displacement parameters at the 30% level. Methyl H atoms are omitted for clarity.

The asymmetrically bridged molecule exhibits Y–N bond distances of average 2.249 (terminal) and 2.479 Å (bridging), which lie in the expected range. For comparison, the Y–N bond lengths in Y[N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>3</sub>(THF)<sub>2</sub> range from 2.229(4) to 2.276(4) Å.<sup>35</sup> The most striking structural feature is the appearance of Y...SiH multi-β-agostic interactions (cf., Scheme 1: interacting Si atoms are highlighted in orange). Each of the terminal silylamide ligands shows one close Y...SiH contact with minimum Y...Si and Y...H distances of 3.0521(7) and 2.41(3) Å, respectively. One of the bridging ligands features a β-diagostic interaction with both metal centers (Y1...Si8,

(38) For related donor-functionalized complexes see: (a) Müller-Buschbaum, K. *Z. Anorg. Allg. Chem.* **2003**, 629, 2127: [Ln(N(C<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>)<sub>2</sub>]<sub>2</sub> (Ln = La, Gd, Yb). (b) Deacon, G. B.; Forsyth, C. M.; Gitlits, A.; Harika, R.; Junk, P. C.; Skelton, B. W.; White, A. H. *Angew. Chem.* **2002**, 114, 3383; *Angew. Chem., Int. Ed.* **2002**, 41, 3249: [Sc<sub>2</sub>(Ph<sub>2</sub>p<sub>z</sub>)<sub>6</sub>]. (c) Deacon, G. B.; Gitlits, A.; Roesky, P. W.; Bürgstein, M. R.; Lim, K. C.; Skelton, B. W.; White, A. H. *Chem. Eur. J.* **2001**, 7, 127: [Ln<sub>2</sub>(Bu<sub>2</sub>p<sub>z</sub>)<sub>6</sub>] (Ln = La, Nd, Yb, Lu).

3.1375(7) Å, Y2- -Si7 3.1012(7) Å), while the other bridging ligand shows only one close contact of 3.1620(7) Å (Y- -Si6). The noninteracting Y- -Si distances range from 3.4720(7) to 3.6942(7) Å and Si-N-Si angles from 117.34(10)° to 124.02-(11)°. As a result, the plane with Y centers Y1, Y2 and bridging N atoms N3, N4 is nonplanar, with Y1 and Y2 lying -0.2203-(7) and -0.2278(7) Å below and N3 and N4 0.2242(7) and 0.2249(7) Å above the plane. Similar bonding phenomena were previously reported for the trinuclear partially solvated Sm(II) derivative  $\text{Sm}\{[\mu\text{-N}(\text{SiHMe}_2)_2]\text{Sm}[\text{N}(\text{SiHMe}_2)_2](\text{THF})\}_2$ .<sup>39</sup>

The IR spectrum of complex **4** (Nujol mull) clearly supports the occurrence of agostic interactions in the solid state, as indicated by two separate SiH stretching frequencies at 2095 (nonagostic) and 1931  $\text{cm}^{-1}$  (agostic), respectively (see Supporting Information). In contrast, the ambient-temperature solution <sup>1</sup>H NMR spectrum displays only one signal set for the silylamide ligands ( $\delta_{\text{SiH}}$  4.89 ppm), which is in accordance with their high mobility and weak agostic interactions.

### Conclusion

This preliminary reactivity study on  $[\text{YMe}_3]_n$  revealed straightforward access to peralkylated heterobimetallic complexes such as  $\text{YGa}_3\text{Me}_{12}$ , which are of relevance for materials science. A highly efficient methylation of carbonylic functionalities (high yield, high group transfer economy) was evidenced for the synthesis of a new sterically crowded rare-earth metal alkoxide complex. For comparison, the organocerium reagent  $\text{CeCl}_3/\text{LiR}$  (1:1 molar ratio), which is broadly used in organic synthesis for nucleophilic addition reactions to carbonylic groups, usually transfers one alkyl group per rare-earth metal center. Moreover, optimal reproducibility and specificity in reactivity of the exceptional organocerium reagent seems to be hampered by precise control of the  $\text{CeCl}_3/\text{LiR}$  molar ratio.<sup>24,25</sup> Finally, the easy formation of unsolvated homoleptic complexes  $\text{YL}_3$  via alkane elimination reactions, as shown for  $\{\text{Y}[\text{N}(\text{SiHMe}_2)_2][\mu\text{-N}(\text{SiHMe}_2)_2]\}_2$ , suggests the feasibility of unsolvated heteroleptic organolanthanide compounds of type  $\text{YL}_2\text{Me}$  and  $\text{YLMe}_2$ . The latter are prioritized target molecules in organolanthanide catalysis and might give access to unprecedented strong secondary metal- -ligand interactions.

### Experimental Details

**General Procedures.** All operations were performed with rigorous exclusion of air and water, using standard Schlenk, high-vacuum, and glovebox techniques (MBraun MB150B-G-II; <1 ppm  $\text{O}_2$ , <1 ppm  $\text{H}_2\text{O}$ ). Hexane and toluene were purified using Grubbs columns (MBraun SPS, solvent purification system).  $\text{C}_6\text{D}_6$  was obtained from Aldrich, degassed, dried over Na for 24 h, filtered, and stored in a glovebox. Tetramethyldisilazane,  $\text{HN}(\text{SiHMe}_2)_2$ , was purchased from Aldrich and degassed (freeze-pump-thaw) before use. Fluorenone was received from Aldrich and degassed under high vacuum overnight before use. Complexes  $[\text{YMe}_3]_n$  (**1**) and  $\text{Y}(\text{GaMe}_4)_3$  (**2**) were synthesized according to the literature (ref 19). NMR spectra were recorded at 25 °C on a Bruker-AVANCE-DMX400 (<sup>1</sup>H: 400.13 MHz; <sup>13</sup>C: 100.62 MHz), a Bruker-BIOSPIN-AV500 (5 mm BBO, <sup>1</sup>H: 500.13 MHz; <sup>13</sup>C: 125.77 MHz), and a Bruker-BIOSPIN-AV600 (5 mm cryo probe, <sup>1</sup>H: 600.13 MHz; <sup>13</sup>C: 150.91 MHz). <sup>1</sup>H and <sup>13</sup>C shifts are referenced to internal solvent resonances and reported in parts per million relative to TMS. IR spectra were recorded on a Nicolet-Impact 410

FTIR spectrometer as Nujol mulls sandwiched between CsI plates. Elemental analyses were performed on an Elementar Vario EL III.

**$\text{Y}(\text{OC}_{14}\text{H}_{11})_3$  (**3**).** Freshly prepared  $[\text{YMe}_3]_n$  (**1**, 30 mg, 0.22 mmol) was suspended in 5 mL of hexane. 9-Fluorenone (121 mg, 0.67 mmol) in 5 mL of hexane was added with vigorous stirring at ambient temperature. After this mixture had been stirred for 12 h, the solvent was removed in a vacuum to yield 149 mg of a yellowish powder, **3**. Product **3** is almost insoluble in hexane and dissolves in toluene and benzene to give an orange solution. Crystallization of **3** from a toluene/hexane (5:1) mixture gave a small amount of byproduct,  $[\text{Y}(\text{OC}_{14}\text{H}_{11})_3]_2(9\text{-fluorenone})$  (**3a**), in the form of yellow plates. Characterization of the crude product **3**: IR (Nujol):  $\nu = 1675$  w, 1585 w, 1295 m, 1238 s, 1211 s, 1124 m, 1093 vs, 974 m, 936 m, 763 vs, 733 vs, 630 w, 590  $\text{m cm}^{-1}$ . <sup>1</sup>H NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  7.41 (d, 6H, ar), 7.33 (d, 6H, ar), 7.08 (m, 12H, ar), 1.53 (s, 9H,  $\text{CH}_3$ ) ppm. <sup>13</sup>C NMR (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  152.9, 138.3, 128.7, 127.9, 125.1, 122.3, 119.7, 82.7 ppm. Anal. Calcd for  $\text{C}_{42}\text{H}_{33}\text{O}_3\text{Y}$  (674.627  $\text{g mol}^{-1}$ ): C 74.78, H 4.93. Found: C 75.03, H 5.25. Homoleptic 9-fluorenone-free **3** was obtained when substoichiometric amounts of 9-fluorenone were employed: <sup>1</sup>H NMR (600 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  7.38 (d, 6H, ar), 7.32 (d, 6H, ar), 7.09 (m, 12H, ar), 1.40 (s, 8H,  $\text{CH}_3$ ) ppm. <sup>13</sup>C (151 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  138.9, 129.7, 128.7, 128.5, 128.3, 122.6, 120.5, 83.1 ppm. Byproduct **3a** was also obtained in the presence of a slight excess of 9-fluorenone: <sup>1</sup>H NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  7.50 (d, 12H, ar), 7.25 (d, 12H, ar), 7.04 (m, 24H, ar), 6.81 (t, 2H, 9-fluorenone), 6.62 (d, 2H, 9-fluorenone), 6.46 (t, br, 2H, 9-fluorenone), 6.28 (d, br, 2H, 9-fluorenone), 1.65 (s, 18H, Me) ppm. <sup>13</sup>C NMR (126 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  153.8, 144.5, 138.8, 128.6, 128.3, 128.2, 123.3, 120.1, 83.4 ppm. Anal. Calcd for  $\text{C}_{97}\text{H}_{74}\text{O}_7\text{Y}_2$  (1529.43  $\text{g mol}^{-1}$ ): C 76.17, H 4.88; no satisfactory analysis was obtained. The equimolar reaction of **3** (81 mg, 0.05 mmol) and 9-fluorenone (9 mg, 0.05 mmol) in hexane gave  $\{[\text{Y}(\text{OC}_{14}\text{H}_{11})_3]_3(9\text{-fluorenone})\}$  (**3b**) (85 mg) in almost quantitative yield. IR (Nujol):  $\nu = 1722$  s, 1689 s, 1613 m, 1293 m, 1244 m, 1213 m, 1152 w, 1095 m, 976 w, 939 w, 912 w, 763 s, 738 vs, 677 w, 631 w, 589  $\text{m cm}^{-1}$ . <sup>1</sup>H NMR (600 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  7.53 (s, br, 6H, ar), 7.28 (s, br, 6H, ar), 7.07 (m, 12H, ar), 7.00 (d, br, 2H, 9-fluorenone), 6.88 (t, br, 2H, 9-fluorenone), 6.80 (s, br, 2H, 9-fluorenone), 6.63 (s, br, 2H, 9-fluorenone), 1.70 (s, 9H,  $\text{CH}_3$ ) ppm. <sup>13</sup>C (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C): 144.6, 128.9, 138.7, 129.7, 128.9, 128.3, 128.2, 124.7, 124.6, 123.5, 120.3, 120.0, 119.9, 81.9 ppm. Anal. Calcd for  $\text{C}_{55}\text{H}_{41}\text{O}_4\text{Y}$  (854.82  $\text{g mol}^{-1}$ ): C 77.28, H 4.83. Found: C 75.03, H 5.16.

**$[\text{Y}(\text{SiHMe}_2)_3]_2$  (**4**).** Freshly prepared  $[\text{YMe}_3]_n$  (**1**, 40 mg, 0.23 mmol) was suspended in 3 mL of toluene. Disilazane  $\text{HN}(\text{SiHMe}_2)_2$  (119 mg, 0.90 mmol) in 3 mL of toluene was added with vigorous stirring at ambient temperature. Instant gas evolution was observed. After 20 min the reaction mixture cleared up, indicating the consumption of **1**. The solution was filtered and the solvent removed under vacuum to give 143 mg of a colorless oil. Complex **4** could be crystallized from hexane as large colorless plates (46 mg, 41%) at -35 °C. IR (Nujol):  $\nu = 2095$  br s, 1931 br s, 1250 vs, 1028 vs, 943 vs, 896 vs, 840 vs, 791 s, 775 s, 765 s, 419 m, 409  $\text{m cm}^{-1}$ . <sup>1</sup>H NMR (400 MHz, toluene-*d*<sub>8</sub>, 25 °C):  $\delta$  4.89 (m, 1H), 0.41 (d, 6H) ppm. <sup>13</sup>C NMR (100 MHz, toluene-*d*<sub>8</sub>, 25 °C):  $\delta$  2.9 ppm. Anal. Calcd for  $\text{C}_{12}\text{H}_{12}\text{N}_3\text{Si}_6\text{Y}$  (485.904  $\text{g mol}^{-1}$ ): C 29.66, H 8.71, N 8.65. Found: C 30.13, H 8.61, N 8.24.

**X-ray Crystallography and Crystal Structure Determination of **2**, **3a**, and **4**.** Crystals suitable for diffraction experiments were selected in a glovebox and mounted in Paratone-N inside a nylon loop (Hampton Research). Data collection was done on a Bruker AXS SMART 2K CCD diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$ ) performing  $\omega$ -scans in four  $\varphi$  positions, employing the SMART software package.<sup>40</sup> A total

(39) Nagl, I.; Scherer, W.; Tafipolsky, M.; Anwender, R. *Eur. J. Inorg. Chem.* **1999**, 9, 1405.

(40) SMART, v. 5.054, Data Collection Software for Bruker AXS CCD; Bruker AXS Inc.: Madison, WI, 1999.

of 1880 collected images were processed using SAINT.<sup>41</sup> Numerical absorption correction was done using SHELXTL.<sup>42</sup> The structures were solved by direct methods and refined with standard difference Fourier techniques.<sup>42</sup> Compound **2**: All H atoms of the methyl groups bonded to Al were found in the difference Fourier maps. H atoms of coordinating methyl groups were refined as manually constructed rigid groups with C–H 0.98 Å, H–H distances of 1.600 Å, and  $U_{\text{iso}}(\text{H})$  of 1.5 that of the parent C atom. All other H atoms were placed in calculated positions (riding model). Compound **3a**: All H atoms were placed in calculated positions (riding

(41) SAINT, v. 6.45a, Data Integration Software for Bruker AXS CCD; Bruker AXS Inc.: Madison, WI, 2002.

(42) SHELXTL, v. 6.14, Structure Determination Software Suite; Bruker AXS Inc.: Madison, WI, 2000.

model). Compound **4**: The H atoms on Si were refined with an  $U_{\text{iso}}$  1.5 times that of the parent Si atom. All other H atoms were geometrically constrained.

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**Supporting Information Available:** IR spectrum of **4**. CIF files and text giving tables of atomic coordinates, atomic displacement parameters, and bond distances and angles for complexes **2**, **3a**, and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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