

# Thermally Stable Half-Sandwich Benzhydryl Ln(II) (Ln = Sm, Yb) Complexes Supported by Sterically Demanding Carbazolyl and Fluorenyl Ligands

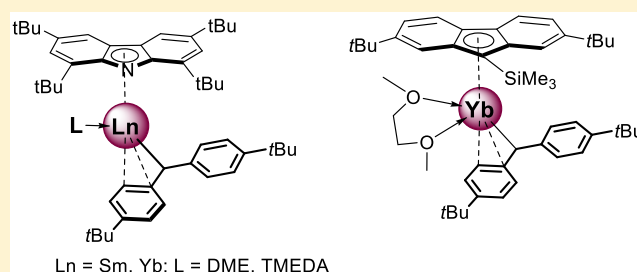
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## Supporting Information

**ABSTRACT:** A series of new isolable and thermally stable half-sandwich Ln(II) benzhydryl complexes coordinated by the sterically demanding ligands *tert*-butylcarbazol-9-yl [*t*Bu<sub>4</sub>Carb]Ln[(*p*-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH](L) (Ln = Sm, L = DME (4); Ln = Yb, L = DME (5); Ln = Yb, L = TMEDA (6)) and 2,7-di-*tert*-butyl-fluorenyl-9-trimethylsilylyl [2,7-*t*Bu<sub>2</sub>-9-Me<sub>3</sub>Si-C<sub>13</sub>H<sub>6</sub>]<sub>2</sub>Yb[(*p*-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH](DME) (7) were synthesized by the alkane elimination reaction of [(*p*-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH]<sub>2</sub>Ln(L<sub>n</sub>) (Ln = Sm, Yb) with *t*Bu<sub>4</sub>CarbH and 2,7-*t*Bu<sub>2</sub>-9-Me<sub>3</sub>Si-C<sub>13</sub>H<sub>7</sub>. X-ray analysis revealed that in 4, 5, and 7 the benzhydryl ligand is coordinated to the metal ion in an η<sup>3</sup> coordination mode, while in 6 it is η<sup>1</sup>-bound. The type of coordination of the benzhydryl ligands in diamagnetic 5–7 is retained in their C<sub>6</sub>D<sub>6</sub> solutions. Complexes 4–7 demonstrated unprecedented thermal stability and do not undergo decomposition after heating their solutions in C<sub>6</sub>D<sub>6</sub> or toluene at 100 °C for 72 h. The reactions of [*t*Bu<sub>4</sub>Carb]Ln[(*p*-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH](DME) (Ln = Sm (4), Ln = Yb (5)) with an excess of DME led to the formation of the symmetrical bis(carbazolyl) complex products [*t*Bu<sub>4</sub>Carb]<sub>2</sub>Ln(DME)<sub>4</sub> (Ln = Sm (8), Yb (9)) isolated in the form of separated ion pairs.



## INTRODUCTION

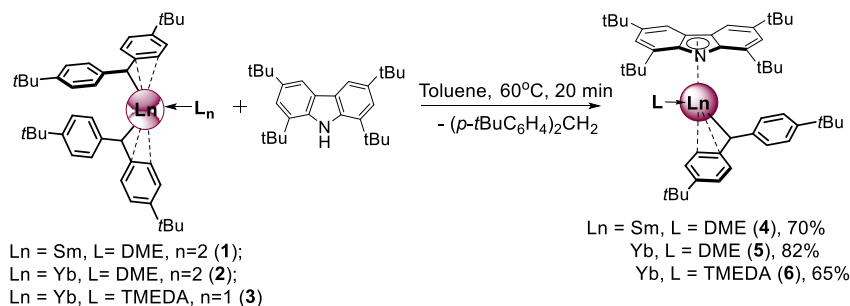
The impressive progress achieved in the design, synthesis, characterization, and reactivity studies of  $\sigma$ -bonded alkyl complexes of trivalent lanthanides<sup>1</sup> was inspired by their unique reactivity and great promise in catalysis of a wide range of transformations.<sup>2</sup> At the same time the hydrocarbyl derivatives of divalent lanthanides still remain poorly explored.<sup>3</sup> This chemistry started recently in the early 1990s with the discovery of Yb(II) complexes with bulky silyl-substituted ligands.<sup>3a–h</sup> The presence of two highly reactive centers ( $\sigma$ -Ln–C bonds and a metal ion in a low oxidation state) provides two different patterns of rich and diverse reactivity of these alkyl species. Due to the Ln–C bonds they can undergo insertions of multiple C=C and C=E bonds<sup>4</sup> and  $\sigma$ -bond metathesis<sup>1b,4</sup> and mediate activation of normally inert C–H bonds,<sup>5</sup> while the Ln(II) ion is responsible for a reductive chemistry. The development of the field was hampered by the extremely high air sensitivity of these complexes as well as by the synthetic problems associated with difficulties in stabilization of the coordination sphere of large electropositive Ln(II) ions<sup>6</sup> prone to ligand exchange reactions and  $\beta$ -hydrogen elimination or  $\beta$ -hydrogen abstraction of hydrocarbyl ligands.<sup>7</sup> The kinetic stabilization of Ln(II) alkyl species can be

achieved by coordination and steric saturation of the coordination spheres of the metal ions as well as the rational selection of alkyl ligands. As a general rule bulky hydrocarbyl ligands which lack  $\beta$ -hydrogen atoms ([C(SiMe<sub>3</sub>)<sub>3</sub>],<sup>3a,c–e</sup> [C(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub>CH=CH<sub>2</sub>)],<sup>3d</sup> benzyl<sup>3i,j,m</sup>) or contain Lewis base groups able to coordinate to the metal center ([C(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub>OMe)],<sup>3d,h</sup> [Me<sub>3</sub>SiCH(C<sub>6</sub>H<sub>4</sub>)NMe<sub>2</sub>],<sup>3i</sup> bis(phosphinimino)methanide<sup>3k</sup>) have been successfully used for this purpose. Sadow and co-workers proposed an original way of stabilization of Ln(II) bis(alkyl) species via  $\beta$ -SiH agostic interactions between Ln(II) and [C(SiHMe<sub>2</sub>)<sub>3</sub>] ligands.<sup>8</sup> It should be noted that mixed-ligand Ln(II) alkyl species coordinated by a supporting ligand are even more rare because of the pronounced tendency for Schlenk-type equilibrium and symmetrization reactions.<sup>9</sup>

Recently we successfully introduced into Ln(II) chemistry the new bulky benzhydryl ligand [(*p*-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH]<sup>–</sup>, which proved to be suitable for the synthesis of isolable thermally stable Yb(II), Sm(II), and Ca(II) bis(hydrocarbyl) complexes.<sup>10</sup> In this work we report on the synthesis of a series of

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## Scheme 1. Synthesis of Complexes 4–6



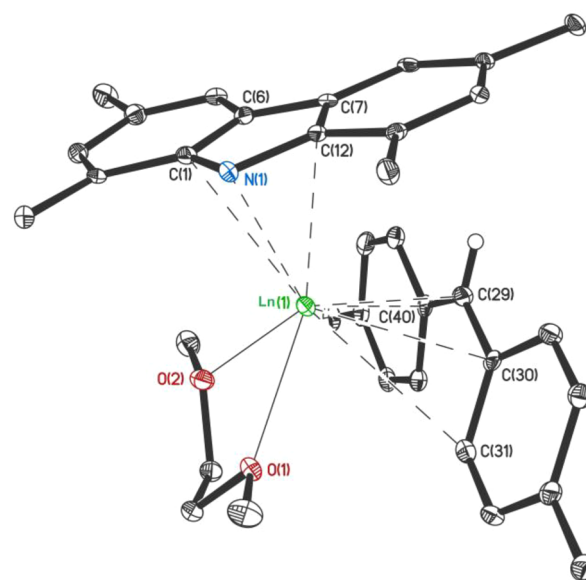
Ln(II) half-sandwich benzhydryl complexes coordinated by the 1,3,6,8-tetra-*tert*-butylcarbazol-9-yl and 2,7-di-*tert*-butylfluoren-9-trimethylsilylyl ligands. The application of these supporting ligands allowed us to synthesize new half-sandwich Yb(II) and Sm(II) alkyl complexes.

## RESULTS AND DISCUSSION

The reactions of equimolar amounts of  $[(p\text{-}t\text{Bu-C}_6\text{H}_4)_2\text{CH}]_2\text{Ln}(\text{L}_n)$  (Ln = Sm, L = DME,  $n = 2$  (1); Ln = Yb, L = DME,  $n = 2$  (2); Ln = Yb, L = TMEDA,  $n = 1$  (3)) and 1,3,6,8-tetra-*tert*-butylcarbazole in toluene at 60 °C (20 min) (Scheme 1) afford the half-sandwich alkyl complexes  $[t\text{Bu}_4\text{Carb}]\text{Ln}[(p\text{-}t\text{Bu-C}_6\text{H}_4)_2\text{CH}](\text{L})$  (Ln = Sm, L = DME (4); Ln = Yb, L = DME (5); Ln = Yb, L = TMEDA (6)). Recrystallization of the reaction products from toluene resulted in the isolation of the complexes as black (4) and orange (5 and 6) air- and moisture-sensitive crystals in 70, 82, and 65% yields, respectively.

Complexes 4–6 are highly soluble in THF and aromatic hydrocarbons but poorly soluble in hexane. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the diamagnetic complexes 5 and 6 in  $\text{C}_6\text{D}_6$  present a single set of signals characteristic for 1,3,6,8-tetra-*tert*-butylcarbazolyl ( $(p\text{-}t\text{Bu-C}_6\text{H}_4)_2\text{CH}$ ) fragments and coordinated base (DME or TMEDA). No changes were detected in the spectra over 1 month, thus giving evidence that these compounds are not prone to a Schlenk-type equilibrium and no symmetrization reaction occurs in aromatic solvents.

The crystal structures of half-sandwich alkyl complexes 4–6 were established by X-ray analysis. The X-ray diffraction studies revealed that complexes 4–6 crystallize in the monoclinic space group  $P2_1/n$ . The molecular structures of 4 and 5 are depicted in Figure 1, and the crystal and structural refinement data are summarized in Table S1 in the Supporting Information. The Ln(II) cations in complexes 4 and 5 are coordinated by carbazoyl and benzhydryl ligands and one DME molecule. The lanthanide ions are located above the plane of the benzhydryl ligands. The Yb–C<sub>benzhydryl</sub> bond length in 5 (2.540(4) Å) is consistent with those in the related benzyl ytterbium complexes  $[\text{C}_6\text{H}_5\text{CH}_2]_2\text{Yb}(\text{DME})_2$  (2.572(2) and 2.585(2) Å)<sup>3j</sup> and in the mixed-ligand Yb(II) alkyl derivative coordinated by a tris(pyrazolyl)borate ligand  $\text{Tp}^{t\text{Bu},\text{Me}}\text{YbCH}_2\text{SiMe}_3(\text{THF})$  (2.526(4) Å).<sup>9k</sup> However, this distance is noticeably shorter in comparison to the six-coordinate benzyl complexes containing more sterically demanding ligands  $[\text{C}_6\text{H}_5\text{CH}_2]_2\text{Yb}(\text{thp})_4$  (2.617(3) Å, thp = tetrahydropyran)<sup>3j</sup> and  $[\text{Yb}\{\text{CH}(\text{SiMe}_3)\text{C}_6\text{H}_4\text{NMe}_2\}_2(\text{thf})_2]$  (2.640(3) and 2.661(3) Å).<sup>3i</sup> The bond length between the Sm cation and the methine carbon in 4 (2.670(4) Å) is comparable with the bond length in the six-coordinate mixed-ligand complex  $\text{Tp}^{t\text{Bu},\text{Me}}\text{SmCH}(\text{SiMe}_3)_2(\text{THF})$



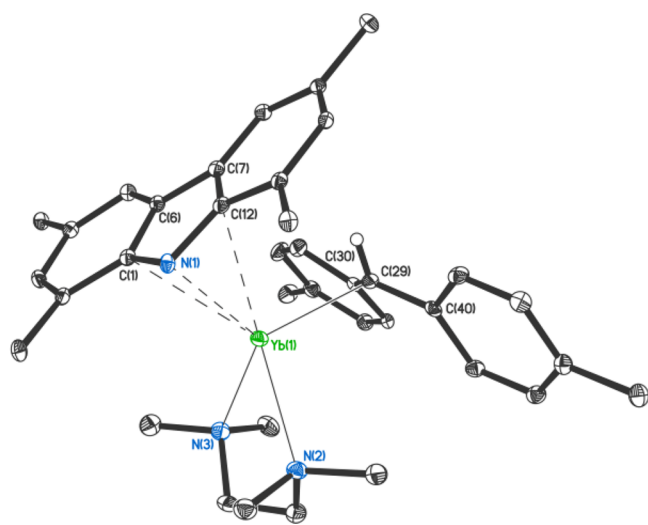
**Figure 1.** Molecular structure of complexes 4 (Sm) and 5 (Yb). Ellipsoids are given at 30% the probability level. Methyl fragments of *t*Bu groups and all hydrogen atoms except the methine hydrogen are omitted for clarity. Selected bonds distance (Å) and angles (deg): 4, Sm(1)–N(1) 2.596(3), Sm(1)–C(1) 2.858(3), Sm(1)–C(6) 3.164(3), Sm(1)–C(7) 3.095(3), Sm(1)–C(12) 2.756(3), Sm(1)–C(29) 2.670(4), Sm(1)–H(29A) 2.94(4), Sm(1)–C(30) 2.904(3), Sm(1)–C(31) 3.220(4), Sm(1)–C(40) 3.125(4), Sm(1)–O(1) 2.605(2), Sm(1)–O(2) 2.529(3), Sm(1)–C(29)–C(30) 84.1(2), Sm(1)–C(29)–C(40) 94.0(2); 5, Yb(1)–N(1) 2.491(3), Yb(1)–C(1) 2.668(4), Yb(1)–C(6) 2.928(4), Yb(1)–C(7) 2.926(4), Yb(1)–C(12) 2.678(4), Yb(1)–C(29) 2.540(4), Yb(1)–H(29A) 2.76(4), Yb(1)–C(30) 2.806(4), Yb(1)–C(31) 3.084(4), Yb(1)–C(40) 3.350(4), Yb(1)–O(1) 2.433(3), Yb(1)–O(2) 2.373(3), Yb(1)–C(29)–C(30) 84.9(2), Yb(1)–C(29)–C(40) 111.3(3).

(2.697(4) Å)<sup>9k</sup> but much shorter than in the Sm(II) complex with bulkier aminobenzyl ligands  $[\text{Sm}\{\text{CH}(\text{SiMe}_3)\text{C}_6\text{H}_4\text{NMe}_2\}_2(\text{thf})_2]$  (2.768(3) and 2.789(3) Å)<sup>3i</sup> and in the parent bis(alkyl) complex  $[(p\text{-}t\text{Bu-C}_6\text{H}_4)_2\text{CH}]_2\text{Sm}(\text{DME})_2$  (2.760(3) Å).<sup>10</sup> It is noteworthy that despite the higher coordination numbers of the lanthanide ions in 4 and 5 in comparison to those in the parent bis(alkyl) complexes the short contacts between the Ln(II) and *ipso*-C<sub>Ph</sub> atoms of the phenyl rings (4, 2.904(3), 3.125(4) Å; 5, 2.806(4) Å) persist. The benzhydryl ligand is coordinated unsymmetrically: the dihedral angles between the planes of six-membered carbon cycles are 154.6(4)° (4) and 159.7(2)° (5). Also, one of the Ln–*o*-C<sub>Ph</sub> distances (4, 3.220(4) Å; 5, 3.084(4) Å) is significantly shorter than the others (4, 3.690(4)–3.901(4) Å; 5, 3.701(4)–4.182(4) Å). Thus, short contacts between the

lanthanide ion and one of the  $o$ -C<sub>ph</sub> atoms were detected in these complexes.

The bulky 1,3,6,8-tetra-*tert*-butylcarbazoyl ligands in **4** and **5** are  $\pi$ -coordinated to the Ln(II) ions.<sup>11</sup> Their coordination mode is similar to those in the previously described sandwich and half-sandwich complexes (*t*Bu<sub>4</sub>Carb)<sub>2</sub>Ln,<sup>11c</sup> (*t*Bu<sub>4</sub>Carb)-LnR(THF)<sub>*n*</sub> (Ln = Yb, Sm, Eu; R = I, N(SiMe<sub>3</sub>)<sub>2</sub>, CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>*o*-NMe<sub>2</sub>; *n* = 1, 2)<sup>9c,11a</sup> and can be considered as  $\eta^5$  coordinated noticeably tilted toward the  $\eta^3$  mode. The Ln-*t*Bu<sub>4</sub>Carb<sub>center</sub> (**4**, 2.637(2) Å; **5**, 2.466(2) Å) distances are comparable to the values measured in sandwich complexes [*t*Bu<sub>4</sub>Carb]<sub>2</sub>Ln (Ln = Yb (2.506(2) Å), Sm (2.614(2) Å)). The bond distances from the metal ions to the carbons neighboring the nitrogen (**4**, 2.756(3), 2.858(3) Å; **5**, 2.668(4), 2.678(4) Å) are much shorter in comparison to the distances to two other carbon atoms (**4**, 3.164(3), 3.095(3) Å; **5**, 2.926(4), 2.928(4) Å) indicating significant contribution of  $\eta^3$ -bonding mode.

As in **4** and **5**, complex **6** crystallizes as a solvate with one molecule of hexane in the monoclinic space group *P*2<sub>1</sub>/*n* (Figure 2). The nature of the bonding of the benzhydryl ligand



**Figure 2.** Molecular structure of complex **6**. Thermal ellipsoids are given at the 30% probability level. Methyl fragments of *t*Bu groups and all hydrogen atoms except the methine hydrogen are omitted for clarity. Selected bond distances (Å) and angles (deg): Yb(1)–N(1) 2.509(2), Yb(1)–C(1) 2.807(2), Yb(1)–C(6) 3.187(3), Yb(1)–C(7) 3.182(3), Yb(1)–C(12) 2.772(3), Yb(1)–C(29) 2.597(3), Yb(1)–H(29A) 2.69(3), Yb(1)–C(30) 3.316(3), Yb(1)–C(40) 3.277(3), Yb(1)–N(2) 2.617(3), Yb(1)–N(3) 2.561(2), Yb(1)–C(29)–C(30) 106.4(2), Yb(1)–C(29)–C(40) 104.7(2).

with Yb(II) ion in **6** proved to be different from that in **4** and **5**. The benzhydryl ligand is bonded to the Yb(II) ion exclusively through the central CH fragment, and no short contacts with *ipso* or *ortho* phenyl carbon atoms were detected. The Yb–CH<sub>benzhydryl</sub> bond (2.597(3) Å) in **6** is somewhat longer than in **5** (2.540(4) Å). The distances between the metal ion and *ipso*-C<sub>benzhydryl</sub> atoms are very similar (3.316(3), 3.277(3) Å) and reflect a symmetrical arrangement of the benzhydryl coordination. Thus, the coordination type of the benzhydryl ligand in **6** is definitely  $\eta^1$ .<sup>12</sup> However, similarly to **4** and **5** the metal ion in **6** is located above the plane of the ligand. Also, the Yb-*t*Bu<sub>4</sub>Carb<sub>center</sub> (2.643(2) Å) and Yb–C<sub>carb</sub> (2.772(3)–3.187(3) Å) distances are slightly longer than those in **5**. Most likely such a difference in bonding in **6** and **5** is due

to steric repulsion caused by the larger size of TMEDA in comparison to that of DME.

The differences in the structures of **5** and **6** were also detected in solution by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} spectroscopy as well as a 2D <sup>171</sup>Yb–<sup>1</sup>H NMR long-range correlation. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of diamagnetic complexes **5** and **6** were recorded in benzene-*d*<sub>6</sub> at ambient temperature. In the <sup>1</sup>H NMR spectra of **5** and **6** the CH aryl and *t*Bu protons of the *t*Bu<sub>4</sub>Carb ligands give nearly identical sets of signals: four singlets at 8.37, 7.65, 1.84, and 1.54 ppm for **5** and 8.19, 7.65, 1.92, and 1.49 ppm for **6**. In contrast, the signals corresponding to the methanide CH protons of benzhydryl ligands in **5** and **6** differ noticeably (3.28 (**5**) and 3.00 (**6**) ppm). It is noteworthy that these signals are significantly shifted toward the strong-field region in comparison to the related signal of the parent bis(alkyl) ytterbium complex **3** (4.10 ppm), whereas one could expect a weak-field shift of the signals as a result of a decrease in electron density on the methanide CH fragment caused by the electron-withdrawing nature of the carbazoyl ligand. A similar situation took place when one benzyl group in the bis(aminobenzyl) complex [Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH(SiMe<sub>3</sub>)<sub>2</sub>Yb(THF)<sub>2</sub> was replaced by a fluorenyl ligand: the signal assigned to the methine CH proton also shifted to the strong-field region (from 1.15 to 0.74 ppm).<sup>31</sup> It is important to note that in complex **5** the signal corresponding to the *o*-CH aryl protons (6.57 ppm) is strong-field-shifted by 0.41 ppm in comparison to the appropriate signal in the spectrum of complex **6** (6.98 ppm) (see Table 1), giving evidence of the

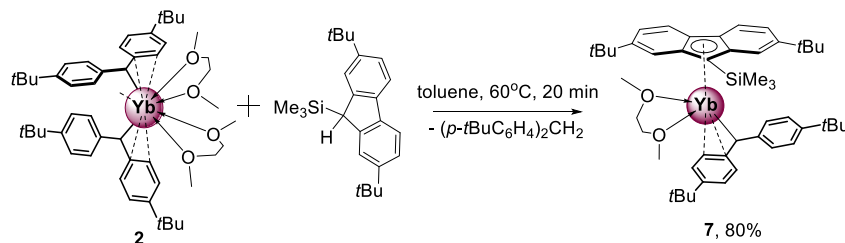
**Table 1.** Selected Distances (Å) and Chemical Shifts in NMR Spectra (ppm) for Yb(II) Alkyl Complexes **3** and **5**–**7**

	<b>3</b>	<b>5</b>	<b>6</b>	<b>7</b>
Yb–CH <sub>benzhydryl</sub> <sup>a</sup>	2.555(2)	2.540(4)	2.597(3)	2.589(2)
$\delta$ ( <sup>1</sup> H) CH	4.10	3.28	3.00	3.13
$\delta$ ( <sup>13</sup> C) CH	71.2	69.59	67.89	67.73
Yb... <i>o</i> -CH(C <sub>6</sub> H <sub>4</sub> )	2.889(2)	3.084(4)	3.616(4)	2.737(2)
$\delta$ ( <sup>1</sup> H) <i>o</i> -CH(C <sub>6</sub> H <sub>4</sub> )	7.01	6.57	6.98	6.79
$\delta$ ( <sup>13</sup> C) <i>o</i> -CH(C <sub>6</sub> H <sub>4</sub> )	117.80	117.55	118.84	117.60
Yb... <i>ipso</i> -CH(C <sub>6</sub> H <sub>4</sub> ) <sup>a</sup>	2.617(2)	2.806(4)	3.316(3)	2.721(2)
$\delta$ ( <sup>13</sup> C) <i>ipso</i> -CH(C <sub>6</sub> H <sub>4</sub> )	143.10	143.66	146.48	144.48
$\delta$ ( <sup>171</sup> Yb)	507	259	178	280

<sup>a</sup>The shortest distances are given.

retention of Yb–*o*-CH interaction in C<sub>6</sub>D<sub>6</sub> solution. In order to get a deeper insight into the structures of complexes **5** and **6** in solution, 2D <sup>171</sup>Yb–<sup>1</sup>H NMR long-range correlations were obtained. The 2D <sup>1</sup>H–X correlation via heteronuclear zero- and double-quantum coherence with gradient pulse correlation selection without decoupling was used. The experiment was optimized to *J* ≈ 15 Hz. The 2D <sup>171</sup>Yb–<sup>1</sup>H *ge*-HMBC NMR experiments for **5** and **6** reveal significant differences between these complexes. The chemical shift of <sup>171</sup>Yb in **5** is 259 ppm, while for **6** it is noticeably shifted to high field (178 ppm). Moreover, the <sup>171</sup>Yb–<sup>1</sup>H NMR spectrum of **6** has no cross-peaks reflecting the interaction of <sup>171</sup>Yb with *o*-phenyl CH, whereas this signal is clearly visible in the spectrum of **5**. The aforementioned facts are in good agreement with the X-ray data and give evidence for the difference in the structures of complexes **5** and **6** in solution. The chemical shifts corresponding to C<sub>*ipso*</sub> carbons in the <sup>13</sup>C{<sup>1</sup>H} spectra of **5** and **6** are in line with the tendency described above: for **6**

## Scheme 2. Synthesis of Complex 7



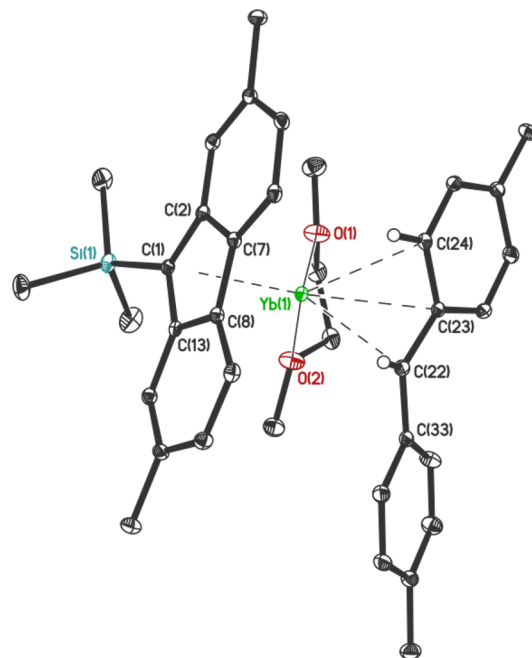
(146.48 ppm) it is shifted to low field in comparison to that of **5** (143.66 ppm) (Table 1).

The paramagnetism of **4**<sup>13</sup> and its low solubility in C<sub>6</sub>D<sub>6</sub> do not allow for the registration of tractable <sup>1</sup>H NMR spectra of this compound. The low solubility of **5**–**7** in C<sub>6</sub>H<sub>7</sub> also hampered variable-temperature NMR investigation of these complexes.

The successful application of a sterically demanding 9-trimethylsilyl-substituted fluorenyl ligand in the chemistry of oxophilic metals and catalytic performance of these derivatives in a variety of catalytic transformations<sup>14</sup> (particularly in stereospecific styrene polymerization<sup>3i,14a</sup>) prompted us to evaluate its applicability to the synthesis of a half-sandwich benzhydryl Yb(II) complex. To provide higher solubility of the Yb(II) species, a 9-trimethylsilylfluorenyl ligand bearing two *t*Bu substituents in 2- and 7-positions was applied. Complex **2** readily reacts with 2,7-di-*tert*-butyl-9-trimethylsilylfluorene in toluene at 60 °C (Scheme 2). The slow concentration of the reaction mixture affords large blood red crystals of **7** in 80% yield.

Complex **7** is soluble in THF and toluene and sparingly soluble in hexane. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra recorded in a C<sub>6</sub>D<sub>6</sub>/THF-*d*<sub>8</sub> mixture (90/10) within 1 month do not give any evidence for ligand redistribution reactions. The methine proton of the benzhydryl ligand appears as a singlet with a chemical shift at 3.13 ppm partially overlapping with the DME signals (–CH<sub>2</sub>CH<sub>2</sub>–). The *o,m*-CH benzhydryl protons give rise to two doublets at 6.79 (<sup>3</sup>J<sub>HH</sub> = 7.7 Hz) and 7.01 (<sup>3</sup>J<sub>HH</sub> = 8.4 Hz) ppm. The signals corresponding to the aromatic protons of the fluorenyl ligands were assigned by <sup>1</sup>H–<sup>13</sup>C HSQC and <sup>1</sup>H–<sup>1</sup>H COSY NMR experiments. A singlet at 8.07 ppm corresponds to the fluorenyl protons at positions 1, 8, and two doublets at 7.98 (<sup>3</sup>J<sub>HH</sub> = 8.2 Hz) and 7.20 (<sup>3</sup>J<sub>HH</sub> = 9.8 Hz) ppm correspond to the protons at positions 3,6 and 4,5, respectively. The protons of the *t*Bu substituents in the benzhydryl and fluorenyl groups appear as singlets at 1.24 and 1.44 ppm, respectively. The SiMe<sub>3</sub> protons give rise to a singlet with chemical shift of 0.64 ppm similarly to the related complexes of Ca<sup>14a,c</sup> and Sc.<sup>14d</sup> A cross-peak of the Yb(II) ion with the *o*-CH<sub>benzhydryl</sub> proton is observed in the <sup>171</sup>Yb–<sup>1</sup>H NMR long-range correlation for **7**; the chemical shift of <sup>171</sup>Yb extracted from the 2D spectrum is 280 ppm and is in good agreement with the value measured for **5** (259 ppm).

According to X-ray analysis complex **7** crystallizes in the monoclinic space group P2<sub>1</sub>/c (Figure 3). The arrangement of the Yb(II) ion relative to the benzhydryl fragment in **7** is even less symmetrical than in **5** as a result of a more pronounced shift toward one of the Ph rings (the dihedral angle between six-membered carbon rings is 163.53(6)° vs 159.7(2)° in **5**). In complex **7** the distances Yb–*ipso*-C<sub>Ph</sub> (2.721(2) Å) and Yb–*o*-C<sub>Ph</sub> (2.737(2) Å) have close values and are noticeably longer

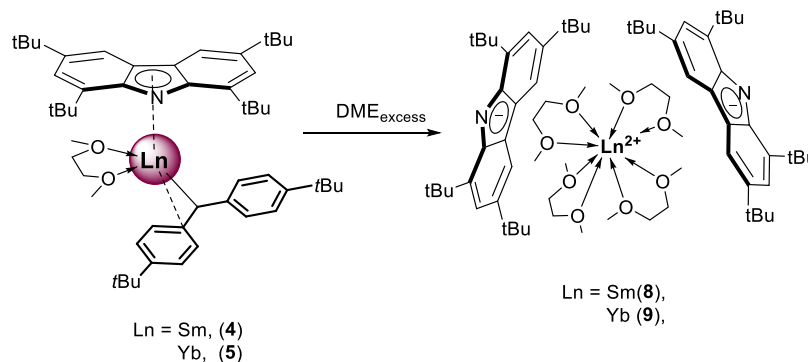


**Figure 3.** Molecular structure of complex **7**. Ellipsoids are given at the 30% probability level. All hydrogen atoms are omitted for clarity. Selected bonds distances (Å) and angles (deg): Yb(1)–C(1) 2.692(2), Yb(1)–C(2) 2.663(2), Yb(1)–C(7) 2.711(2), Yb(1)–C(8) 2.764(2), Yb(1)–C(13) 2.750(2), Yb(1)–C(22) 2.589(2), Yb(1)–H(22A) 2.69(2), Yb(1)–C(23) 2.721(2), Yb(1)–C(24) 2.737(2), Yb(1)–O(1) 2.417(2), Yb(1)–O(2) 2.340(2), Yb(1)–C(22)–C(23) 79.5(2).

in comparison to the Yb–C<sub>bzh</sub> bond (2.589(2) Å). The coordination mode of the benzhydryl ligand formally can be classified as η<sup>3</sup>. The fluorenyl ligand is coordinated to the Yb(II) ion in an η<sup>5</sup> fashion. The average Yb–C<sub>CP</sub> distance (2.716(2) Å) and the Yb–C<sub>center</sub> distance (2.425(2) Å) are somewhat longer in comparison to those in the bis(fluorenyl) Yb(II) complex (C<sub>13</sub>H<sub>9</sub>)<sub>2</sub>Yb(THF)<sub>2</sub> (2.503(3) and 2.513(3) Å).<sup>15</sup>

The half-sandwich complexes **5**–**7** demonstrated high (on the scale appropriate for organolanthanide complexes) thermal stability. Studies of the thermal stability of diamagnetic complexes **5**–**7** were carried out under the control of <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} spectroscopy as well as 2D <sup>171</sup>Yb–<sup>1</sup>H NMR long-range correlation, and no evidence of decomposition was observed after heating the solutions of complexes in C<sub>6</sub>D<sub>6</sub> at 100 °C over 72 h. Complex **4** was also recovered in quantitative yield after heating in benzene for 72 h. It is worth noting that in contrast to the parent bis(benzhydryl) species [(*p*-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH]<sub>2</sub>Ln(DME)<sub>2</sub> (Ln = Sm, Yb), which completely decomposes at 40 °C in 8 h, the half-sandwich complexes **4**, **5**, and **7** proved to be much more stable vs

Scheme 3. Reactions of 4 and 5 with DME



temperature. Most likely this is the result of a decrease in the negative charge at the benzhydryl carbanion caused by the electron-withdrawing nature of carbazoyl and fluorenyl ligands. However, an increase in temperature to 120 °C or increase in the reaction time leads to a gradual destruction of the complexes. Approximately 70% decomposition was achieved for 5 and 6 in 48 h, while 7 turned out to be somewhat more resistant; the same value of decomposition was reached in 54 h. The volatile reaction products were identified by both GC/MS chromatography and NMR spectroscopy (see the Supporting Information). In all cases (*p*-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH<sub>2</sub> together with the sandwich Ln(II) complexes [tBu<sub>4</sub>Carb]<sub>2</sub>Ln (Ln = Yb, Sm) and [2,7-*t*Bu<sub>2</sub>-9-SiMe<sub>3</sub>C<sub>13</sub>H<sub>6</sub>]<sub>2</sub>Yb(DME) were isolated as the major thermal decomposition products. Surprisingly, unlike the decomposition of the parent [(*p*-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH]<sub>2</sub>Ln(DME)<sub>2</sub> (Ln = Sm, Yb) complexes, no formation of the methylated diphenylmethane (*p*-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CHMe<sup>10</sup> was detected. On the other hand, the reaction affords methyl vinyl ether, MeOCH=CH<sub>2</sub>, which is one of the expected decomposition products of organolanthanide adducts with DME.<sup>16</sup> In the case of complex 6, other than (*p*-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH<sub>2</sub> no volatile decomposition products were found. Obviously, the cleavage of the DME molecule is facilitated by the thermodynamically favorable formation of strong Ln–O bonds. However, all our attempts to isolate and identify the other metal-containing byproducts failed.

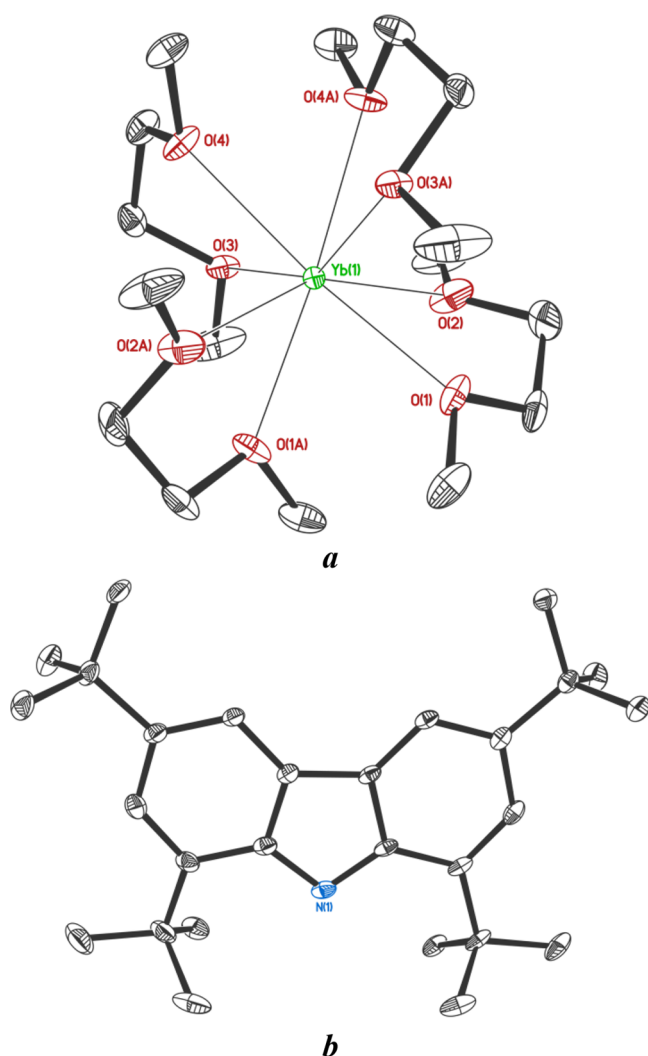
Unlike cationic alkyl Ln(III) complexes,<sup>17</sup> structurally characterized cationic alkyl Ln(II) species still remain scarce.<sup>8</sup> Recently we demonstrated that Sm(II) complexes coordinated by 1,3,6,8-tetra-*tert*-butylcarbazol-9-yl ligands ([tBu<sub>4</sub>Carb]<sub>2</sub>Sm, [tBu<sub>4</sub>CarbSm(μ-I)(THF)<sub>2</sub>]<sub>2</sub>) on treatment with DME or crown ether easily undergo heteroleptic dissociation of tBu<sub>4</sub>Carb–Ln bonds, affording a solvent-separated ionic pair.<sup>9c,11c</sup> We intended to apply this approach to the synthesis of cationic alkyl Ln(II) complexes, and the reactions of complexes 4 and 5 with an excess of DME were carried out. Indeed, both complexes react instantly with DME on dissolution in a DME/THF (3/2) mixture. Unfortunately, the reaction does not allow for the synthesis of the desired cationic alkyl species but rather leads to the formation of the symmetric products—the ionic bis(carbazoyl) complexes [tBu<sub>4</sub>Carb]<sub>2</sub>Ln(DME)<sub>4</sub> (Ln = Sm (8), Yb (9)). (Scheme 3). The complexes were isolated as deep blue (8) and straw yellow (9) crystals in 88% and 86% yields, respectively. After separation of the crystals the GC/MS analysis detected in the mother liquor the presence of (*p*-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH<sub>2</sub> (55%) and (*p*-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CHMe (45%). The formation of the same

products was observed in the decomposition reactions of the parent bis(benzhydryl) complexes 1 and 2.<sup>10</sup> Unfortunately the attempts at isolation of lanthanide-containing products other than 8 and 9 were unsuccessful. The mechanism of the dissociation of the Yb(II)–carbazoyl bond in sandwich complexes has been explored and supported by DFT calculations.<sup>11c</sup>

The monocrystalline samples of complexes 8 and 9 were obtained by slow concentration of their THF solutions. X-ray studies revealed that 8 and 9 are isomorphous and crystallize as solvates with three THF molecules, [tBu<sub>4</sub>Carb<sup>−</sup>]<sub>2</sub>[Ln<sup>2+</sup>(DME)<sub>4</sub>]·3THF (Ln = Sm(8), Yb (9)), in the trigonal space group P3<sub>2</sub>2<sub>1</sub>. The molecular structure of complex 8 has been previously determined and reported in 2015.<sup>11c</sup> The single-crystal structure determination of 9 confirmed that, similarly to the Sm(II) congener, [tBu<sub>4</sub>Carb<sup>−</sup>]<sub>2</sub>[Yb<sup>2+</sup>(DME)<sub>4</sub>] exists as a separated ion pair (Figure 4). The Yb(II) cation coordinated by four chelating DME molecules is surrounded by two carbazoyl anions (tBu<sub>4</sub>Carb<sup>−</sup>); however, the distance between the metal and the ligand excludes the existence of any bonding between them except an ionic bond. The shortest distance between the cation of Yb<sup>2+</sup> and the centroid of a five-membered heterocycle in crystal is 6.319(2) Å. The planes of the carbazoyl ligands form a dihedral angle of 62.0(2)°. The Yb–O distances fall into the range of 2.481(3)–2.570(2) Å. The structures of complexes 8 and 9 present a rather rare example of organometallic Ln(II) compounds belonging to the type “metal in box”,<sup>18</sup> where the coordinatively saturated cation [Yb<sup>2+</sup>(DME)<sub>4</sub>] is located in a box built of planar carbazoyl ligands.<sup>18b,c</sup>

## CONCLUSION

The application of sterically demanding carbazoyl (tBu<sub>4</sub>Carb) and fluorenyl (2,7-*t*Bu<sub>2</sub>-9-SiMe<sub>3</sub>-C<sub>13</sub>H<sub>6</sub>) ligands allows for the synthesis of isolable half-sandwich Ln(II) benzhydryl complexes. X-ray analysis revealed a variety of coordination modes of [(*p*-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH] ligands to the Ln(II) centers, depending on the type of the ancillary ligand and the coordinated Lewis base. In DME-containing complexes 4, 5, and 7, in addition to a covalent bond between the metal ion and the methanide carbon, short contacts with *ipso* and *ortho* phenyl carbon atoms were detected, resulting in an η<sup>3</sup> coordination mode of the benzhydryl ligands. In contrast, in TMEDA complex 6 no short contacts between the Ln(II) centers and phenyl carbons were measured giving evidence for η<sup>1</sup> coordination of the [(*p*-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH] ligand to the Yb(II) ion. Multinuclear NMR spectroscopic studies of diamagnetic Yb(II) complexes 5–7 indicate retention of the coordination



**Figure 4.** Molecular structure of the dicationic (a) and anionic (b) parts of complex **9**. Ellipsoids are set at 30% probability. All hydrogen atoms are omitted for clarity. Selected bond distances (Å): Yb(1)–O(1) 2.481(3), Yb(1)–O(2) 2.494(3), Yb(1)–O(3) 2.570(2), Yb(1)–O(4) 2.500(2).

fashion of benzhydryl fragments in  $C_6D_6$  solutions. All complexes demonstrate enhanced thermal stability in comparison to the parent bis(benzhydryl) complexes. Interestingly, thermal decomposition of  $[(p\text{-}t\text{Bu-C}_6\text{H}_4)_2\text{CH}]_2\text{Ln}(\text{DME})_2$  (Ln = Sm, Yb) and half-sandwich complexes **4**, **5**, and **7** is accompanied by different transformations of benzhydryl and DME ligands. Thermolysis of **1** and **2** affords  $(p\text{-}t\text{Bu-C}_6\text{H}_4)_2\text{CHMe}$  and  $(p\text{-}t\text{Bu-C}_6\text{H}_4)_2\text{CH}_2$  mixtures, while that of **4**, **5**, and **7** leads to the formation of  $(p\text{-}t\text{Bu-C}_6\text{H}_4)_2\text{CH}_2$  and  $\text{MeOCH}=\text{CH}_2$  along with sandwich complexes.

## EXPERIMENTAL SECTION

**General Consideration.** All experiments were performed in evacuated tubes using standard Schlenk-flask or nitrogen-filled MBraun glovebox techniques with rigorous exclusion of traces of moisture and air. After being dried over KOH, THF and DME were purified by distillation from sodium/benzophenone ketyl; hexane and toluene were purified by distillation from sodium/potassium alloy prior to use.  $C_6D_6$  and THF- $d_8$  were dried with sodium/benzophenone ketyl and condensed under vacuum prior to use. Bis-alkyl complexes  $[p\text{-}t\text{BuC}_6\text{H}_4\text{CH}]_2\text{Ln}(\text{L})_n$  (Ln = Yb, L = TMEDA,  $n = 1$ ; Ln = Yb, Sm, L = DME,  $n = 2$ ),<sup>10</sup> 2,7- $t\text{Bu}_2$ -9-SiMe $_3$ C $_3$ H $_6$ <sup>14d</sup> and

$t\text{Bu}_4\text{CarbH}^{19}$  were prepared according to literature procedures. All other reagents and solvents were used as purchased from commercial suppliers.

**Instruments and Measurements.** NMR spectra were recorded on a Bruker DPX 200 or Bruker Avance DRX-400 spectrometer. Chemical shifts for  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  spectra were referenced internally using the residual solvent resonances and are reported relative to TMS; coupling constants are given in Hz. The assignment of  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  resonances was assisted with gHSQC and gHMBC spectra. The hmbcgp1pndqf (2D H/X correlation via heteronuclear zero and double quantum coherence optimized on long-range couplings with low-pass  $J$  filter to suppress one-bond correlations without decoupling during acquisition, using gradient pulses for selection) pulse program was used for Yb–H long-range correlation. The delay between pulses (d1) was set to 1.5 s. The gpz1, gpz2, and gpz3 parameters were set to 70%, 30%, and 57.5%, respectively. The cnst2 parameter was set to 250 and that of cnst13 to 15. IR spectra were recorded as Nujol mulls or KBr plates on FSM 1201 and Bruker Vertex 70 instruments. The N, C, H elemental analyses were carried out in the microanalytical laboratory of the IOMC by means of a Carlo Erba Model 1106 elemental analyzer with an accepted tolerance of 0.4 unit on carbon (C), hydrogen (H), and nitrogen (N). Lanthanide metal analysis was carried out by complexometric titration.<sup>20</sup>

**X-ray Crystallography.** The X-ray data for **4**–**7** and **9** were collected on Agilent Xcalibur (4) and Bruker D8 Quest (5–7, 9) diffractometers (Mo  $K\alpha$  radiation,  $\omega$ -scan technique,  $\lambda = 0.71073$  Å) using APEX3<sup>21</sup> and CrysAlis Pro<sup>22</sup> software packages. The structures were solved by direct methods and were refined by full-matrix least squares on  $F^2$  for all data using SHELX.<sup>23</sup> SADABS<sup>24</sup> and CrysAlis Pro were used to perform absorption corrections. All non-hydrogen atoms in **4**–**7** and **9** were found from Fourier syntheses of electron density and were refined anisotropically. Methine hydrogen atoms of benzhydryl ligands in **4**–**7** also were found from Fourier syntheses of electron density. Other hydrogen atoms in **4**–**7** and **9** were placed in calculated positions and were refined in the “riding” model with  $U(\text{H})_{\text{iso}} = 1.2U_{\text{eq}}$  of their parent atoms ( $U(\text{H})_{\text{iso}} = 1.5U_{\text{eq}}$  for methyl groups).

The crystallographic data and structure refinement details for **4**–**7** and **9** are given in Table S1. CCDC 1950152 (4), 1950153 (5), 1950154 (6), 1950155 (7), and 1950156 (9) contain supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre: [ccdc.cam.ac.uk/structures](http://ccdc.cam.ac.uk/structures).

**Synthesis of  $[\text{tBu}_4\text{Carb}]\text{Sm}[\text{CH}(\text{C}_6\text{H}_4\text{-}p\text{-}t\text{Bu})_2](\text{DME})$  (4).** Complex **1** (0.614 g, 0.69 mmol) was suspended in cold toluene (20 mL) with rigorous stirring, and 1,3,6,8-tetra-*tert*-butylcarbazole (0.270 g, 0.69 mmol) was added slowly. The temperature of the reaction mixture was increased rapidly to 60 °C and kept there for 20 min until complete dissolution of **1**. The resulting deep brown solution was brought to ambient temperature. Slow concentration of the reaction mixture at room temperature afforded complex **4** as black crystals in 70% yield (0.564 g). IR (KBr, Nujol):  $\nu$  1594 (s), 1490 (s), 1390 (m), 1365 (s), 1311 (s), 1270 (w), 1220 (w), 1188 (s), 1040 (s), 1015 (w), 932 (w), 906 (w), 860 (s), 835 (m), 821 (s), 805 (s), 777 (m), 672 (s), 653 (m), 633 (w), 556 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{53}\text{H}_{77}\text{NO}_2\text{Sm}$  (910.50  $\text{g mol}^{-1}$ ): C, 69.91; H, 8.52; N, 1.54; Sm, 16.51. Found: C, 69.59; H, 8.25; N, 1.23; Sm, 16.59.

**Synthesis of  $[\text{tBu}_4\text{Carb}]\text{Yb}[\text{CH}(\text{C}_6\text{H}_4\text{-}p\text{-}t\text{Bu})_2](\text{DME})$  (5).** **3** (0.579 g, 0.69 mmol) was dissolved in toluene (10 mL), and excess DME (1 mL) was added. A bright yellow powder of **2** formed instantly. The suspension was stirred at room temperature for 20 min, and the volatiles were removed under vacuum. The solid residue was resuspended in toluene (15 mL), and 1,3,6,8-tetra-*tert*-butylcarbazole (0.273 g, 0.70 mmol) was added slowly. The temperature of the reaction mixture was increased rapidly to 60 °C and kept there for 20 min until complete dissolution of **2**. The resulting bright orange solution was brought to ambient temperature. Slow concentration of the reaction mixture at room temperature afforded **5** as red-orange crystals in 82% yield (0.557 g).  $^1\text{H}$  NMR (400 MHz,  $C_6D_6$ , 298 K):  $\delta$  8.37 (s, 2H, CH-carbazoly), 7.65 (s, 2H, CH-carbazoly), 7.04 (d,

4H, *m*-CH, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz), 6.57 (d, 4H, *o*-CH, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz), 3.28 (s, 1H, CH-benzhydryl), 2.34 (br s, 4H, -CH<sub>2</sub>CH<sub>2</sub>-, DME), 2.03 (br s, 6H, OMe-DME), 1.84 (s, 18H, *t*Bu-carbazoyl), 1.54 (s, 18H, *t*Bu-carbazoyl), 1.29 (s, 18H, *t*Bu-benzhydryl). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 293 K): δ 145.64 (s, C-carbazoyl), 143.66 (s, *ipso*-C, benzhydryl), 140.31 (s, C-carbazoyl), 139.05 (s, C-carbazoyl), 135.19 (s, *ipso*-C, benzhydryl), 126.50 (s, *m*-CH, C<sub>6</sub>H<sub>4</sub>), 124.51 (s, C-carbazoyl), 119.84 (s, CH-carbazoyl), 117.55 (s, *o*-CH, C<sub>6</sub>H<sub>4</sub>), 115.22 (s, CH-carbazoyl), 70.11 (br s, -CH<sub>2</sub>CH<sub>2</sub>-, DME), 69.59 (s, CH-benzhydryl), 59.70 (s, OMe-DME), 35.93 (s, C(CH<sub>3</sub>)<sub>3</sub>, carbazoyl), 34.80 (s, C(CH<sub>3</sub>)<sub>3</sub>, carbazoyl), 33.38 (s, C(CH<sub>3</sub>)<sub>3</sub>, benzhydryl), 31.88 (s, C(CH<sub>3</sub>)<sub>3</sub>, carbazoyl), 31.44 (s, C(CH<sub>3</sub>)<sub>3</sub>, benzhydryl), 29.80 (s, C(CH<sub>3</sub>)<sub>3</sub>, carbazoyl). IR (KBr, Nujol): ν 1592 (s), 1499 (s), 1399 (m), 1365 (s), 1311 (s), 1284 (w), 1269 (w), 1245 (w), 1219 (w), 1188 (s), 1049 (s), 1018 (w), 934 (w), 907 (w), 861 (s), 841 (m), 822 (s), 803 (s), 776 (m), 672 (s), 650 (m), 634 (w), 553 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>53</sub>H<sub>77</sub>NO<sub>2</sub>Yb (933.19 g mol<sup>-1</sup>): C, 68.21; H, 8.32; N, 1.50; Yb, 18.54. Found: C, 67.83; H, 8.04; N, 1.28; Yb, 18.39.

**Synthesis of [tBu<sub>4</sub>Carb]Yb[CH(C<sub>6</sub>H<sub>4</sub>-*p*-tBu)<sub>2</sub>](TMEDA) (6). 3** (0.776 g, 0.92 mmol) was dissolved in toluene (15 mL), and 1,3,6,8-tetra-*tert*-butylcarbazole (0.360 g, 0.92 mmol) was added. The solution was heated for 20 min at 80 °C, the volatiles were removed under vacuum, and freshly distilled hexane (10 mL) was added to the residue. Orange crystals of complex **6** were obtained by slow concentration of a hexane solution in 65% yield (0.570 g). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 8.19 (br s, 2H, CH-carbazoyl), 7.65 (s, 2H, CH-carbazoyl), 7.17–7.07 (m, 4H, *m*-CH, C<sub>6</sub>H<sub>4</sub>), 6.98 (d, 4H, *o*-CH, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz), 3.00 (s, 1H, CH-benzhydryl), 1.92 (s, 18H, *t*Bu-carbazoyl), 1.49 (s, 18H, *t*Bu-carbazoyl), 1.31 (s, 18H, *t*Bu-benzhydryl), 1.21 (s, 12H, NMe<sub>2</sub>-TMEDA), 1.11 (br s, 4H, -CH<sub>2</sub>CH<sub>2</sub>- TMEDA). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 293 K): δ 147.13 (br s, C-carbazoyl), 146.48 (br s, *ipso*-C, benzhydryl), 140.07 (s, C-carbazoyl), 139.61 (s, C-carbazoyl), 136.52 (s, *ipso*-C, benzhydryl), 126.22 (s, *m*-CH, C<sub>6</sub>H<sub>4</sub>), 125.24 (s, C-carbazoyl), 120.27 (s, CH-carbazoyl), 118.84 (s, *o*-CH, C<sub>6</sub>H<sub>4</sub>), 115.30 (s, CH-carbazoyl), 67.89 (s, CH-benzhydryl), 55.97 (s, -CH<sub>2</sub>CH<sub>2</sub>- TMEDA), 45.13 (br s, NMe<sub>2</sub>-TMEDA), 36.26 (s, C(CH<sub>3</sub>)<sub>3</sub>, carbazoyl), 34.78 (s, C(CH<sub>3</sub>)<sub>3</sub>, carbazoyl), 33.47 (s, C(CH<sub>3</sub>)<sub>3</sub>, carbazoyl), 31.95 (s, C(CH<sub>3</sub>)<sub>3</sub>, carbazoyl), 31.52 (s, C(CH<sub>3</sub>)<sub>3</sub>, benzhydryl), 30.57 (s, C(CH<sub>3</sub>)<sub>3</sub>, carbazoyl). IR (KBr, Nujol): ν 1302 (m), 1280 (m), 1244 (s), 1216 (m), 1188 (w), 1120 (w), 1084 (m), 1020 (w), 970 (w), 900 (m), 865 (s), 841 (s), 777 (m), 757 (w), 670 (w), 651 (s), 580 (m), 541 (w), 510 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>61</sub>H<sub>97</sub>N<sub>3</sub>Yb (1043.51 g mol<sup>-1</sup>): C, 70.21; H, 9.18; N, 4.03; Yb, 16.58. Found: C, 69.86; H, 8.84; N, 3.71; Yb, 16.45.

**Synthesis of [2,7-*t*Bu<sub>2</sub>-9-SiMe<sub>3</sub>C<sub>13</sub>H<sub>7</sub>]Yb[CH(C<sub>6</sub>H<sub>4</sub>-*p*-tBu)<sub>2</sub>](DME) (7).** A synthetic protocol analogous to that for **5** was applied. **3** (0.579 g, 0.69 mmol) in toluene (10 mL) and 2,7-*t*Bu<sub>2</sub>-9-SiMe<sub>3</sub>C<sub>13</sub>H<sub>8</sub> (0.241 g, 0.69 mmol) were used in the synthesis. The reaction was carried out in toluene at 60 °C, and the reaction time was 20 min. Deep red crystals of complex **7** were obtained by slow concentration of the reaction mixture in 80% yield. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>/THF-*d*<sub>8</sub> 90/10, 298 K): δ 8.07 (s, 2H, 1,8-CH-fluorenyl), 7.98 (d, 2H, 3,6-CH-fluorenyl, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz), 7.20 (d, 2H, 4,5-CH-fluorenyl, <sup>3</sup>J<sub>HH</sub> = 9.8 Hz), 7.01 (d, 4H, *m*-CH-benzhydryl, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz), 6.79 (d, 4H, *o*-CH-benzhydryl, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz), 3.32–3.07 (compl. m, 5H, -CH<sub>2</sub>CH<sub>2</sub>- DME and CH-benzhydryl), 3.01 (br s, 6H, OMe-DME), 1.44 (s, 18H, *t*Bu-fluorenyl), 1.24 (s, 18H, *t*Bu-benzhydryl), 0.64 (s, 9H, SiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>/THF-*d*<sub>8</sub> 90/10, 293 K): δ 145.51 (s, *ipso*-C-fluorenyl), 144.48 (br s, *ipso*-C, benzhydryl), 141.09 (s, *ipso*-C-fluorenyl), 135.51 (s, *ipso*-C, benzhydryl), 126.34 (s, *m*-CH, benzhydryl), 121.04 (s, *ipso*-C-fluorenyl), 120.77 (s, CH-fluorenyl), 117.60 (s, *o*-CH-benzhydryl), 116.20 (s, 1,8-CH-fluorenyl), 115.13 (s, CH, fluorenyl), 85.81 (s, 9-C, fluorenyl), 71.61 (br s, -CH<sub>2</sub>CH<sub>2</sub>- DME), 67.73 (br s, CH-benzhydryl), 58.43 (br s, OMe-DME), 34.82 (s, C(CH<sub>3</sub>)<sub>3</sub>-fluorenyl), 33.38 (s, C(CH<sub>3</sub>)<sub>3</sub>-benzhydryl), 31.60 (s, C(CH<sub>3</sub>)<sub>3</sub>-fluorenyl), 31.41 (s, C(CH<sub>3</sub>)<sub>3</sub>-benzhydryl), 2.12 (s, SiMe<sub>3</sub>). IR (KBr, Nujol): ν 1592 (s), 1326 (w), 1303 (w), 1265 (m), 1245 (w), 1199 (m), 1180 (s),

1095 (s), 1053 (m), 1015 (w), 976 (s), 942 (w), 861 (s), 822 (s), 807 (s), 661 (s), 630 (s), 553 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>49</sub>H<sub>70</sub>O<sub>2</sub>SiYb (892.24 g mol<sup>-1</sup>): C, 65.96; H, 7.91; Yb, 19.40. Found: C, 65.64; H, 7.65; Yb, 19.33.

**Thermolysis of Complex 5.** Complex **5** (0.100 g, 0.11 mmol) was dissolved in C<sub>6</sub>D<sub>6</sub> (0.7 mL) and placed into an NMR tube. The tube was heated at 120 °C for 48 h to achieve a 70% conversion of the complex. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of the reaction mixture indicated the formation of (*p*-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH<sub>2</sub> (lit.<sup>10</sup>), methyl vinyl ether MeOCH=CH<sub>2</sub> (lit.<sup>16c-e</sup>), and [tBu<sub>4</sub>Carb]<sub>2</sub>Yb (lit.<sup>11c</sup>) (Figures S2 and S5 in the Supporting Information).

**Thermolysis of Complex 7.** Complex **7** (0.100 g, 0.11 mmol) was dissolved in C<sub>6</sub>D<sub>6</sub> (0.7 mL) and placed into an NMR tube. The tube was heated at 120 °C for 54 h to achieve a 70% conversion of the complex. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of the reaction mixture indicated the formation of (*p*-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH<sub>2</sub> (lit.<sup>10</sup>), methyl vinyl ether MeOCH=CH<sub>2</sub> (lit.<sup>16c-e</sup>), and [2,7-*t*Bu<sub>2</sub>-9-SiMe<sub>3</sub>C<sub>13</sub>H<sub>7</sub>]<sub>2</sub>Yb(DME) (Figures S12–S14 in the Supporting Information). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) for [2,7-*t*Bu<sub>2</sub>-9-SiMe<sub>3</sub>C<sub>13</sub>H<sub>7</sub>]<sub>2</sub>Yb(DME): δ 7.80 (s, 4H, 1,8-CH-fluorenyl), 7.78 (d, 4H, 4,5-CH-fluorenyl, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz), 7.03 (d, 4H, 3,6-CH-fluorenyl, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz), 2.33 (s, 6H, OMe-DME), 2.12 (s, 4H, -CH<sub>2</sub>CH<sub>2</sub>-DME), 1.46 (s, 36H, *t*Bu), 0.47 (s, 18H, SiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) for [2,7-*t*Bu<sub>2</sub>-9-SiMe<sub>3</sub>C<sub>13</sub>H<sub>7</sub>]<sub>2</sub>Yb(DME): δ 148.42 (s, *ipso*-C), 144.54 (s, *ipso*-C), 142.22 (s, *ipso*-C), 120.45 (s, 4,5-CH-fluorenyl), 115.72 (s, 1,8-CH-fluorenyl), 113.69 (s, 3,6-CH-fluorenyl), 87.57 (s, C9), 69.80 (s, -CH<sub>2</sub>CH<sub>2</sub>- DME), 60.28 (s, OMe-DME), 34.80 (s, C(CH<sub>3</sub>)<sub>3</sub>), 31.80 (s, C(CH<sub>3</sub>)<sub>3</sub>), 2.32 (s, SiMe<sub>3</sub>).

**Reaction of Complex 5 with an Excess of DME.** Orange crystals of complex **5** (0.300 g, 0.32 mmol) were dissolved in a minimal amount of THF (3 mL) to form a brownish yellow solution. DME (2 mL, 19.3 mmol) was added to the solution, and a voluminous straw yellow precipitate formed instantly. When the mixture was heated to 60 °C, the precipitate dissolved completely, and subsequent slow cooling to room temperature afforded light yellow crystals of complex **9** (0.18 g, 86%). <sup>1</sup>H NMR (400 MHz, pyridine-*d*<sub>5</sub>, 293 K): δ 8.52 (br s, 4 H, CH-carbazoyl), 7.68 (br s, 4 H, CH-carbazoyl), 3.61 (br s, 8 H, THF), 3.42 (s, 16 H, -CH<sub>2</sub>CH<sub>2</sub>-DME), 3.10 (s, 24 H, OMe-DME), 2.32 (br s, 36 H, *t*Bu), 1.66 (br s, 36 H, *t*Bu), 1.58 (br s, 12 H, THF). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, pyridine-*d*<sub>5</sub>, 298 K): δ 143.74 (s, C-carbazoyl), 138.03 (br s, C-Carbazoyl), 134.18 (br s, C-carbazoyl), 133.50 (s, C-carbazoyl), 116.81 (br s, CH-carbazoyl), 114.87 (br s, CH-carbazoyl), 73.24 (s, -CH<sub>2</sub>CH<sub>2</sub>- DME), 69.06 (s, α-CH<sub>2</sub>, THF), 59.85 (s, OMe, DME), 38.08 (s, C(CH<sub>3</sub>)<sub>3</sub>), 36.36 (s, C(CH<sub>3</sub>)<sub>3</sub>), 34.47 (s, CH<sub>3</sub>), 32.62 (s, CH<sub>3</sub>), 27.02 (s, β-CH<sub>2</sub>, THF). IR (KBr, Nujol): ν 1292 (m), 1245 (w), 1220 (w), 1186 (w), 1114 (w), 1060 (s), 851 (s), 776 (w), 650 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>84</sub>H<sub>144</sub>N<sub>2</sub>O<sub>11</sub>Yb (1529.12 g mol<sup>-1</sup>): C, 65.98; H, 9.36; N, 1.83; Yb, 11.32. Found: C, 65.67; H, 9.08; N, 1.45; Yb, 11.23. The mother liquor was separated from the crystals and analyzed. GC/MS analysis of the products detected the presence of (*p*-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH<sub>2</sub> and (*p*-*t*Bu-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CHMe in the ratio 55:45 (Figure S22 in the Supporting Information).

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.9b00624>.

Crystal data for **4–7** and **9** and characterization data for all complexes (PDF)

### Accession Codes

CCDC 1950152–1950156 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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## Notes

The authors declare no competing financial interest.

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