

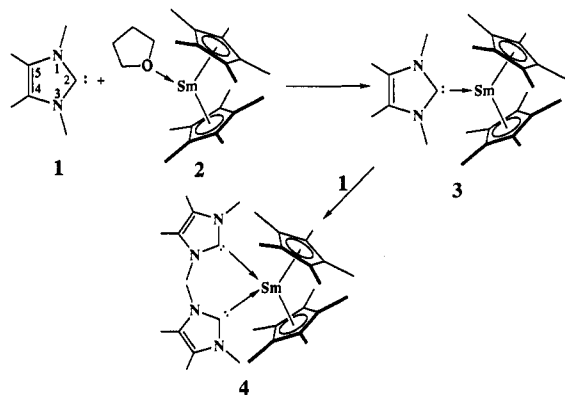
## Carbene-Lanthanide Complexes

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Although carbene-metal complexes are well-known as stable structures and important intermediates, carbene complexes with the lanthanide metals have not been previously characterized.<sup>1</sup> Carbene **1** reacts with bis(pentamethylcyclopentadienyl)-samarium-thf toluene solvate (thf = tetrahydrofuran), **2**, to form the carbene-samarium(II) complex **3**.<sup>3</sup> The carbene-samarium complex **3** is a deep green, high-melting (240–242 °C) solid. Benzene and toluene solutions of **3** retain this dark green color. If the carbene complex **3** is allowed to react with a second equivalent of carbene, the bis(carbene) adduct **4** (mp 184–186 °C) is obtained.<sup>4</sup>



The bis(carbene) adduct **4** is far less soluble in hydrocarbon solvents than **3** and thus tends to crystallize readily. The <sup>1</sup>H NMR spectra of **3** and **4** show rather unusual shifts for the methyl substituents of the carbene as a result of the strong anisotropy

(1) A few isonitrile complexes of lanthanide(III) centers have been reported. See: (a) Fischer, E. O.; Fischer, H. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 246. (b) Fischer, E. O.; Fischer, H. *J. Organomet. Chem.* **1966**, *6*, 141. (c) Burns, J. H.; Baldwin, W. H. *J. Organomet. Chem.* **1976**, *120*, 361. (d) Evans, W. J.; Drummond, D. K. *Organometallics* **1988**, *7*, 797. (e) Evans, W. J.; Drummond, D. K.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *Polyhedron* **1988**, *7*, 1693.

(2) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530.

(3) To a stirred solution of 1.0 g (2 mmol) of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm(thf) (Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941) in 30 mL of toluene was added 252 mg (2 mmol) of 1,3,4,5-tetramethylimidazol-2-ylidene dissolved in 20 mL of toluene. After being stirred for 2 h, the dark green reaction mixture was evaporated, giving the crude compound as a dark green powder. Large dark green crystals of **3** could be obtained from toluene solution at -26 °C: yield, 410 mg (33%); mp 240–242 °C; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 0.38 (s, CCH<sub>3</sub>, 6 H), 6.21 (s, Cp-CH<sub>3</sub>, 30 H), 25.39 (s br, NCH<sub>3</sub>, 6 H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ -92.38 (s, Cp-CCH<sub>3</sub>), 2.38 (s, CCH<sub>3</sub>), 59.85 (s, NCC), 104.07 (Cp-CCH<sub>3</sub>), 104.78 (s, NCH<sub>3</sub>), no NCN resonance found. Anal. Calcd for C<sub>27</sub>H<sub>42</sub>N<sub>2</sub>Sm: C, 59.50; H, 7.77; N, 5.14. Found: C, 59.59; H, 7.76; N, 5.00.

(4) To a stirred solution of 360 mg (0.73 mmol) of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm(thf) in 10 mL of toluene was added 181 mg (1.46 mmol) of 1,3,4,5-tetramethylimidazol-2-ylidene dissolved in 10 mL of toluene. After being stirred for 2 h, the dark green reaction mixture was evaporated, and the residue was carefully treated with 10 mL of benzene. Complex **4** was isolated by filtration as a black-green microcrystalline powder: yield, 210 mg (43%). Black-green crystals suitable for X-ray structure determination could be obtained from toluene solution at -26 °C: mp 184–186 °C; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 2.48 (s, CCH<sub>3</sub>, 12 H), 3.89 (s, Cp-CH<sub>3</sub>, 30 H), 14.81 (s br, NCH<sub>3</sub>, 12 H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>) δ -69.54 (s, Cp-CCH<sub>3</sub>), 7.58 (s, CCH<sub>3</sub>), 85.22 (s, NCH<sub>3</sub>), 91.66 (s, NCC), 101.55 (Cp-CCH<sub>3</sub>), no NCN resonance found. Anal. Calcd for C<sub>34</sub>H<sub>54</sub>N<sub>4</sub>Sm: C, 61.03; H, 8.13; N, 8.37. Found: C, 61.69; H, 7.96; N, 8.30.

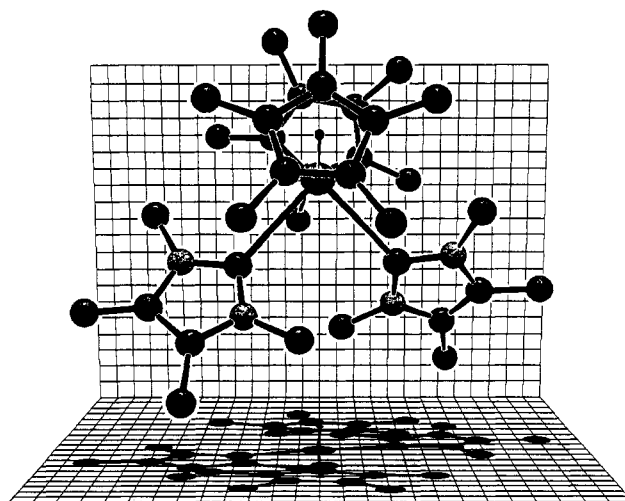


Figure 1. KANVAS<sup>7</sup> drawing of the X-ray structure of bis(carbene)-samarium complex **4**. Hydrogens have been omitted for clarity.

of samarium. In benzene-*d*<sub>6</sub> solution the carbene C-methyls resonate at δ 0.38 in **3** and δ 2.48 in **4** while the *N*-methyls resonate at δ 25.49 and 14.81, respectively. The resonances for the former carbene centers were not observed.

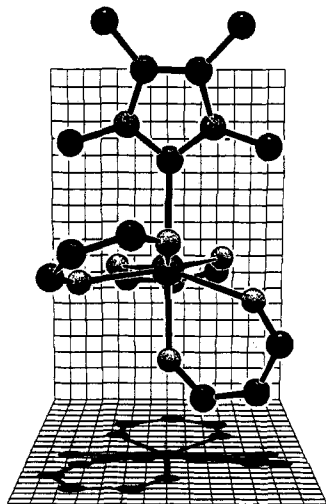
Due to its sparing solubility, crystals of **4** were readily obtained from a toluene solution. The solid state structure of **4** is illustrated in Figure 1.<sup>5</sup> This bis(carbene)-samarium(II) complex shows a pseudotetrahedral geometry with two carbenes and two pentamethylcyclopentadienyl ligands. The angle between the two carbene-samarium bonds is 86.2(5)°, and that between the two pentamethylcyclopentadienyl centroids is 131.2°. There is an approximate molecular 2-fold axis that bisects these angles between like substituents at the samarium. The twist between opposite edges of the tetrahedron is 76.4° along the pseudo 2-fold axis, so that there is a slight distortion toward a square planar structure. The C-Sm distances to the two carbene ligands are 283.7(7) and 284.5(7) pm while the mean C-Sm distance to the pentamethylcyclopentadienyl carbons is 290.3 pm (range 284.2(7)–295.8(7) pm; Sm-Cp\*<sub>cent</sub> = 264.4, 264.7 pm). The ligated carbenes show a geometry that is very similar to that of the uncomplexed carbene<sup>2</sup> with ring internal valence angles at carbon of 101.1(6) and 101.9(6)°. The C-Sm distances to the carbene substituents are longer than any previously reported imidazol-2-ylidene adducts of s-, p-, or d-block elements.<sup>6</sup>

If carbene **1** is allowed to react with tris(2,2,6,6-tetramethylheptane-3,5-dionato)europium(III) (Eu(thd)<sub>3</sub>), a monocarbene adduct of europium(III) (**5**) is obtained.<sup>8</sup> The carbene-europium complex **5** is colorless in solution and in the solid state and melts at 142–145 °C. As in **3** and **4**, the ligated carbene in **5** shows a large lanthanide shift due to the europium center. The carbene C-methyls resonate at δ 11.15 and the *N*-methyls at δ 21.95. In

(5) Crystal data for **4** at -70 °C with Mo Kα radiation: *a* = 1008.0(20) pm, *b* = 1059.4(2) pm, *c* = 1725.2(8) pm, α = 75.95(2)°, β = 74.96(2)°, γ = 65.22(1)°, triclinic, *P*1̄, *Z* = 2, 4480 unique reflections with *I* > 3σ(*I*). The final *R* factors were *R* = 0.056 and *R*<sub>w</sub> = 0.057. See supplementary material.

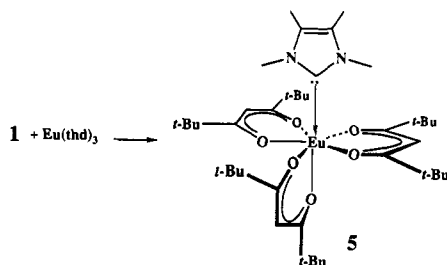
(6) (a) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L. *J. Organomet. Chem.* **1992**, *114*, 9724. (b) Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Inorg. Chem.* **1993**, *32*, 1541. (c) Arduengo, A. J., III; Dias, H. V. R.; Davidson, F.; Harlow, R. L. *J. Organomet. Chem.* **1993**, *462*, 13. (d) Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Organometallics* **1993**, *12*, 3405. (e) Arduengo, A. J., III; Gamper, S. F.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1994**, *116*, 4391. (f) Arduengo, A. J., III; Tamm, M.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 3625.

(7) This drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institut der Universität Freiburg, Germany), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours & Co., Wilmington, DE), to produce the back and shadowed planes. The planes bear a 50-pm grid, and the lighting source is at infinity so that shadow size is meaningful.



**Figure 2.** KANVAS<sup>7</sup> drawing of **5**. Hydrogens and *tert*-butyls have been omitted for clarity.

the <sup>13</sup>C NMR spectrum a resonance for the former carbene center is visible at  $\delta$  46.54 (*cf.*  $\delta$  214 for **1**).



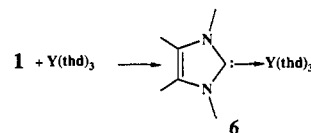
A single crystal of **5** was grown by cooling a pentane solution. The solid state geometry as determined by X-ray crystallography is depicted in Figure 2.<sup>9</sup> The geometry at europium is essentially pentagonal-bipyramidal with the carbene and one of the oxygens from a thd ligand occupying the axial sites. The remaining five oxygens form an approximately planar pentagonal arrangement around the europium. The deviations of the equatorial oxygens

(8)  $\text{Eu}(\text{thd})_3$  (500 mg, 0.7 mmol) was suspended in 30 mL of pentane. To this was added 1,3,4,5-tetramethylimidazol-2-ylidene (89 mg, 0.7 mmol) in solid form. The suspension became gradually clear. After 45 min of stirring, the solvent was removed in vacuo to obtain a white solid: yield, quantitative. Single crystals of **5** could be obtained from pentane solution at  $-26$  °C: mp 142–145 °C; <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ , TMS in  $\text{C}_6\text{D}_6$  as external standard)  $\delta$  5.98 (s, thd  $\text{CH}_3$ , 54 H), 7.01 (s, CH, 3 H), 11.15 (s,  $\text{CCH}_3$ , 6 H), 21.95 (s,  $\text{NCH}_3$ , 6 H),  $\text{C}_6\text{D}_6$  resonance at 13.12 ppm; <sup>13</sup>C NMR ( $\text{C}_6\text{D}_6$ , TMS in  $\text{C}_6\text{D}_6$  as external standard)  $\delta$  4.67 (s, thd  $\text{CCH}_3$ ), 14.04 (s,  $\text{CCH}_3$ ), 34.86 (s, thd  $\text{CH}_3$ ), 46.54 (s br, NCN), 50.01 (s, CH), 59.82 (s,  $\text{NCH}_3$ ), 98.55 (s, NCC), 196.40 (s, CO). Anal. Calcd for  $\text{C}_{40}\text{H}_{69}\text{N}_2\text{O}_6\text{Eu}$ : C, 58.17; H, 8.42; N, 3.39. Found: C, 57.14; H, 8.55; N, 3.10.

(9) Crystal data for **5** at  $-70$  °C with Mo  $\text{K}\alpha$  radiation:  $a = 1070.1(3)$  pm,  $b = 1235.3(1)$  pm,  $c = 1853.5(2)$  pm,  $\alpha = 92.99(1)^\circ$ ,  $\beta = 100.76(1)^\circ$ ,  $\gamma = 110.33(1)^\circ$ , triclinic,  $P\bar{1}$ ,  $Z = 2$ , 7180 unique reflections with  $I > 3\sigma(I)$ . The final  $R$  factors were  $R = 0.033$  and  $R_w = 0.033$ . See supplementary material.

from their best plane are  $-39.2$ ,  $65.5$ ,  $0.2$ ,  $26.1$ , and  $-62.6$  pm. The europium is 2.2 pm above the mean plane of these oxygens. The axial Eu–O bond distance of 230.5(2) pm is slightly shorter than the distances to the equatorial oxygens, which range from 231.0(2) to 235.3(2) pm with an average of 233.2 pm. The Eu–C bond distance to the former carbene center is 266.3(4) pm. This distance is shorter than the Sm–C distances in **4** and is consistent with the higher oxidation state of the europium center. The Eu(III)–C distance in **5** is similar to Pr(III)–C and Sm(III)–C distances reported for some isonitrile complexes.<sup>1e–e</sup> The ring internal angle at the former carbene carbon in **5** is  $103.1(3)^\circ$ , which again is somewhat carbene-like but more relaxed than in **4**.

Finally, we have also prepared the carbene–yttrium complex that is analogous to **5**.<sup>10</sup> In spite of the smaller size of Y(III),  $\text{Y}(\text{thd})_3$  reacts with **1** to form the 7-coordinate monocarbene adduct (**6**). The melting range of this carbene–yttrium complex is 146–148 °C, similar to that of the europium–carbene complex **5**. Unlike the europium and samarium complexes the <sup>1</sup>H NMR resonances for the C–CH<sub>3</sub> and N–CH<sub>3</sub> centers are at more typical positions ( $\delta$  1.33 and 3.53, respectively). The resonance for the former carbene carbon in **6** is at  $\delta$  199.38 (*cf.*  $\delta$  214 for **1**) and shows 33 Hz coupling to the <sup>89</sup>Y nucleus. This indicates that the Y–C bond does not dissociate rapidly on the NMR time scale.



The complexes described above provide interesting structural information on a new class of carbene–lanthanide metal complexes. The carbene–metal bond distances are far longer than in related complexes of s-, p-, and d-block metals. Further work on these unusual complexes is underway.

**Acknowledgment.** The excellent technical assistance of H. A. Craig made this work possible.

**Supplementary Material Available:** A complete description of the X-ray crystallographic determination on **4** and **5**, including tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(10)  $\text{Y}(\text{thd})_3$  (283 mg, 0.44 mmol) was dissolved in 20 mL of pentane. To this was added 1,3,4,5-tetramethylimidazol-2-ylidene (55 mg, 0.44 mmol) in solid form. A clear solution was obtained almost instantly. After 30 min of stirring, the solvent was removed in vacuo to obtain a white solid: yield, quantitative. Crystals could be obtained from pentane solution at  $-26$  °C: mp 146–148 °C; <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.27 (s, thd  $\text{CH}_3$ , 54 H), 1.33 (s,  $\text{CCH}_3$ , 6 H), 3.53 (s,  $\text{NCH}_3$ , 6 H), 5.89 (s, CH, 3 H); <sup>13</sup>C NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  8.56 (s,  $\text{CCH}_3$ ), 29.20 (s, thd  $\text{CH}_3$ ), 34.44 (s,  $\text{NCH}_3$ ), 41.27 (s, thd  $\text{CCH}_3$ ), 90.68 (s, CH), 123.18 (s, NCC), 194.26 (d,  $^1J_{\text{YC}} = 33$  Hz, NCN), 199.38 (s, CO). Anal. Calcd for  $\text{C}_{40}\text{H}_{69}\text{N}_2\text{O}_6\text{Y}$ : C, 62.98; H, 9.12; N, 3.67. Found: C, 61.97; H, 9.31; N, 3.35.