Communications to the Editor

First Isolation of a Tris(ketyl) Metal Complex

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Metal ketyls, as important intermediates in a variety of organic carbonyl-involved reactions, have received continuous attention since their discovery in the previous century.[1−3] Due to their high reactivity and the difficulty in isolation, however, structurally characterized examples of this important class of species remain very rare and are all limited to relatively simple one ketyl per metal ion complexes, which were synthesized recently by reduction of a ketone with one-electron reductants.[4,5] Although reduction of ketones with multielectron reductants was suggested to afford the corresponding multi(ketyl) species,[6] isolation of such species has never been reported. Compared to mono(ketyl) complexes, isolation of a multi(ketyl) metal species is experimentally more difficult and challenging, since intramolecular pinacol coupling of ketyl radicals is also possible besides the common intermolecular reactions. We now found that the use of hexamethylphosphoric triamide (HMPA) as a coordination ligand could sufficiently suppress not only intermolecular but also intramolecular pinacol couplings of ketyl radicals in a multi(ketyl) metal complex. In this communication, we report the successful isolation of a tris(ketyl)samarium(III) complex, which constitutes the first example of structurally characterized multi(ketyl) metal complexes.

Isolation of a tris(ketyl)samarium(III) complex was first attempted by reaction of Sm metal with 3 equiv of fluorenone in THF, but insoluble yellow precipitate was obtained as the only product. When 3 equiv of HMPA was used in this reaction, however, a dark green solution was formed, which upon addition of ether afforded complex **1** as black-green blocks (Scheme 1).[7]

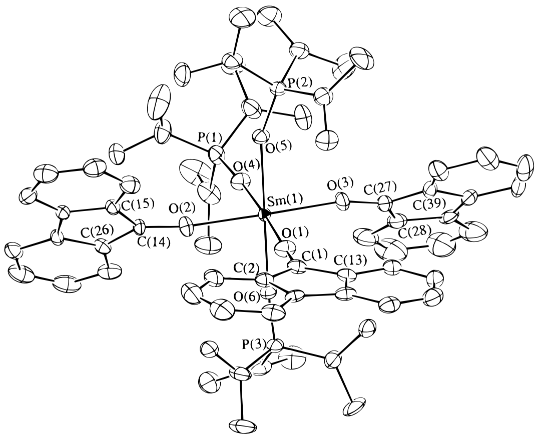
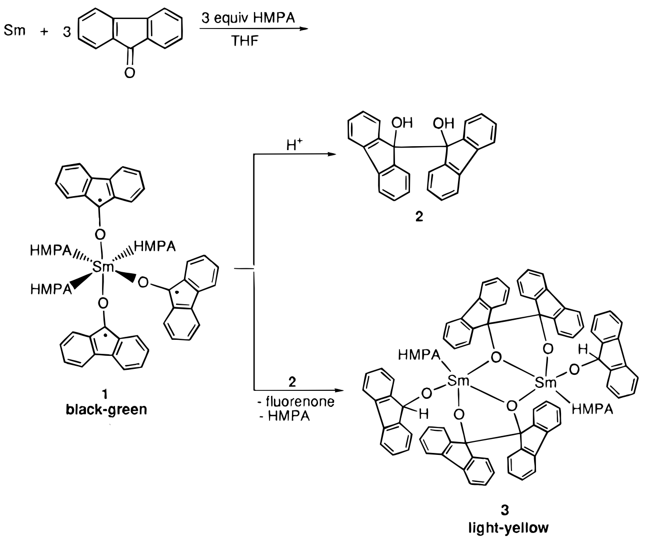


Figure 1. ORTEP drawing of **1** and selected bond lengths (Å) and angles (deg): Sm(1)−O(1), 2.233(9); Sm(1)−O(2), 2.225(10); Sm(1)−O(3), 2.245(9); Sm(1)−O(4), 2.332(9); Sm(1)−O(5), 2.363(8); Sm(1)−O(6), 2.367(7); O(1)−C(1), 1.308(15); O(2)−C(14), 1.297(15); O(3)−C(27), 1.287(15); O(1)−Sm(1)−O(2), 89.9(4); O(1)−Sm(1)−O(3), 93.5(4); O(1)−Sm(1)−O(4), 177.7(3); O(1)−Sm(1)−O(5), 92.1(3); O(1)−Sm(1)−O(6), 89.0(3); O(2)−Sm(1)−O(3), 176.6(4); O(2)−Sm(1)−O(4), 88.4(4); O(3)−Sm(1)−O(4), 88.2(3); O(5)−Sm(1)−O(6), 178.8(3); Sm(1)−O(1)−C(1), 177.2(8); Sm(1)−O(2)−C(14), 170.8(8); Sm(1)−O(3)−C(27), 164.4(8).

Scheme 1



An X-ray analysis reveals that **1** is a monomeric samarium(III) tris(fluorenone ketyl) complex, in which the central Sm atom is coordinated in *mer*-type by three ketyls and three HMPA ligands in an octahedral form (Figure 1).[8] The C−O bond distances in **1** (av 1.297(15) Å) are in the 1.27−1.31 Å range of the C−O(ketyl) bonds found in other fluorenone ketyl complexes such as Sm(ketyl)(OAr)$_2$(THF)$_2$ (Ar = 2,6-^{t}Bu$_2$-4-Me-C$_6$H$_2$),[4] [Na(μ_2-η^1-ketyl)(HMPA)$_2$]$_2$,[5] and [Na(μ_3-η^1-ketyl)(HMPA)]$_4$.[5] The Sm−O(HMPA) bonds (av 2.354(8) Å) are comparable with those reported for Sm(enolate)$_2$(OAr)(HMPA)$_2$ (2.333(10) Å), Sm(OCHPh$_2$)$_2$(OAr)(HMPA)$_2$ (2.363(5) Å), and

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(1) (a) Fittig, R. *Ann.* **1859**, *110*, 23. (b) Bechman, F.; Paul, T. *Ann.* **1891**, *266*, 1. (c) Schlenk, W.; Weichel, T. *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 1182. (d) Schlenk, W.; Thal, A. *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 2480.

(2) Reviews: (a) Fürstner, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 164. (b) Huffman, J. W. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 8, Chapter 1.4. (c) Robertson, G. M. *Ibid.* Vol. 3, Chapter 2.6. (d) McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513. (e) Kahn, B. E.; Riecke, R. T. *Chem. Rev.* **1988**, *88*, 733. (f) Pradhan, S. K. *Tetrahedron* **1986**, *42*, 6351. (g) Huffman, J. W. *Acc. Chem. Res.* **1983**, *16*, 399. (h) McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405. **1974**, *7*, 281. (i) House, H. O. In *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; Chapter 3.

(3) For a recent overview on pinacol coupling, see: Wirth, T. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 61.

(4) Hou, Z.; Miyano, T.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1995**, *117*, 4421.

(5) Hou, Z.; Fujita, A.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1996**, *118*, 2503.

(6) Hirota, N.; Weissman, S. I. *J. Am. Chem. Soc.* **1964**, *86*, 2538.

(7) A typical procedure is as follows. Samarium metal (40 mesh, 0.3 g, 2 mmol) was first activated with 2% of ICH$_2$CH$_2$I) in THF for 1 h. Addition of HMPA (1.06 mL, 6.1 mmol) to this blue suspension gave immediately a purple mixture to which a THF solution of fluorenone (1.08 g, 6 mmol) was syringed. The resulting dark green mixture was stirred at room temperature overnight and was filtered through a frit. Reduction of the solution volume under vacuum and addition of ether precipitated **1** (1.6 g, 65% yield) as black-green blocks. Using less than 3 equiv of HMPA also gave **1** as the only isolable product, but the yield was lower.

(8) **1**: monoclinic, space group $P2_{1/n}$, a = 18.254(3) Å, b = 23.970(5) Å, c = 14.245(3) Å, β = 92.79(2)°, V = 6226(2) Å^3, Z = 4, D_c = 1.31 g cm^{-3}, R = 0.0535 (R_w = 0.0640). **3**: monoclinic, space group $C_{2/c}$, a = 25.605(7) Å, b = 14.037(4) Å, c = 25.884(8) Å, β = 109.37(2)°, V = 8777(4) Å^3, Z = 4, D_c = 1.32 g cm^{-3}, R = 0.0564 (R_w = 0.0785).

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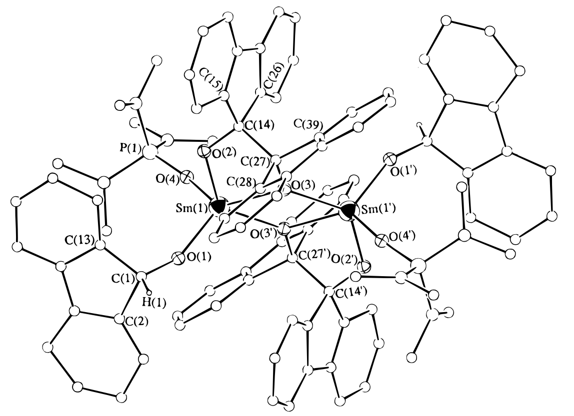

Figure 2. Ball and stick drawing of **3** and selected bond lengths (Å) and angles (deg): Sm(1)−O(1), 2.108(14); Sm(1)−O(2), 2.181(11); Sm(1)−O(3), 2.371(11); Sm(1)−O(3′); 2.293(10); Sm(1)−O(4), 2.293(15); O(1)−C(1), 1.39(3); O(2)−C(14), 1.39(2); O(3)−C(27), 1.44(2); C(14)−C(27), 1.56(3); O(2)−Sm(1)−O(3), 70.1(4); O(3)−Sm(1)−O(3′), 69.2(4); Sm(1)−O(3)−Sm(1′), 110.8(4); Sm(1)−O(1)−C(1), 156.0(15); Sm(1)−O(2)−C(14), 121.1(10); Sm(1)−O(3)−C(27), 114.4(9); Sm(1′)−O(3)−C(27), 133.4(10).

Sm(fluorenoxy)(OAr)$_2$(HMPA)$_2$ (2.391(4) Å).[9] The Sm−O(ketyl) bonds in **1** (av 2.234(9) Å) are longer than that found in Sm(biphenyl-2,2′-diyl ketyl)(OAr)$_2$(THF)$_2$ (2.159(4) Å),[4] probably due to the influence of the HMPA ligands.[10] Similar to other fluorenone ketyl complexes, each ketyl unit in **1** possesses a nearly planar configuration. The two mutually *trans* ketyl planes (O(2)−ketyl and O(3)−ketyl) form a relatively small dihedral angle of 8°, while the dihedral angles formed by the *cis* ketyl planes are almost half of a right angle (O(1)−ketyl/O(2)−ketyl: 49°; O(1)−ketyl/O(3)−ketyl: 43°). In contrast to the previously reported mono(ketyl) Sm(III) complex Sm(biphenyl-2,2′-diyl ketyl)(OAr)$_2$(THF)$_2$, which was ESR silent owing to the antiferromagnetic superexchange interaction between the ketyl radical and the Sm(III) spins,[4] **1** showed a strong ESR signal ($g = 2.0027$) at 22 to −170 °C.[11]

Hydrolysis of **1** gave quantitatively the corresponding pinacol **2**. Interestingly, reaction of **1** with 0.5 equiv of **2** resulted in the formation of light-yellow complex **3** in about 60% yield (Scheme 1). An X-ray analysis shows that **3** is a dimeric Sm(III) fluorenoxide/pinacolate complex, which possesses a crystallographic inversion center at the center of the molecule (Figure 2).[8] The oxygen atom of each fluorenoxy unit in **3** is no longer coplanar with its fluorenyl ring, and the Sm−O(fluorenoxy) bonds (2.108(14) Å) are shorter than the Sm−O(ketyl) bonds in **1** (av 2.234(9) Å). The central C−C bond distances of the pinacolates in **3** (1.56(3) Å) are similar to that of pinacol **2** (1.57(1) Å)[12] but are significantly shorter than that reported for the bulky Sm(III) fluorenone pinacolate [Sm(OAr)$_2$(OEt$_2$)]$_2$[μ-pinacolate] (Ar = 2,6-^{t}Bu$_2$-4-Me-C$_6$H$_2$) (1.613(9) Å).[4] Reflecting this bond length difference between the two pinacolate complexes, cleavage of the pinacolate C−C bonds in **3** to yield a ketyl was not observed in THF,[13] while such bond cleavage occurred very easily in the case of [Sm(OAr)$_2$(OEt$_2$)]$_2$[μ-pinacolate].[4]

Although the formation of **3** from **1** might formally be viewed as hydrogen radical addition to one ketyl and pinacolate substitution of the other two ketyls in **1**, further studies showed that this was not the case. It was found that fluorenone was also formed in this reaction, which probably resulted from dehydrogenation (−H$^\bullet$) and homolytic C−C bond cleavage of **2**. Reaction of **1** with benzopinacol also gave **3** in good yield, and in this reaction formation of benzophenone was confirmed instead of fluorenone. These results clearly demonstrated that the formation of **3** was *via* hydrogen radical abstraction from the pinacol by one ketyl, followed by pinacol coupling of the other two ketyls together with simultaneous release of two HMPA ligands in **1**. It is noteworthy that the steric change, which was caused by the formation of a bulkier fluorenoxy unit from its planar parent fluorenone ketyl, imposed crucial influence on the stability and reactivity of the whole molecule.

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Supporting Information Available: Detailed crystal and elemental analysis data for **1** and **3** and listings of atomic coordinates, thermal parameters, and bond distances and angles for **1** and **3** (22 pages). See any current masthead page for ordering and Internet access instructions.

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[9] Yoshimura, T.; Hou, Z.; Wakatsuki, Y. *Organometallics* **1995**, *14*, 5382.

[10] Hou, Z.; Wakatsuki, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 1205.

[11] Interactions among the three ketyl radicals in **1** were not observed by ESR spectroscopy at 22 to −170 °C in either solid state or in THF.

[12] Hou, Z.; Wakatsuki, Y. Unpublished results.

[13] **3** was ^{1}H NMR detectable in THF-d_8: δ 7.80−6.80 (m, 48 H, fluorenyl), 5.43 (s, 2H, CH), 2.57 (d, $J = 8.0$ Hz, 36 H, NMe).