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The First Structurally Characterized Metal Ketyl Complex: Sm(ketyl)(OAr)$_2$(THF)$_2$ and Its Reversible Coupling to a Disamarium(III) Pinacolate

Zhaomin Hou,*[,†] Takanori Miyano,[‡] Hiroshi Yamazaki,[‡] and Yasuo Wakatsuki*[,†]

The Institute of Physical and Chemical Research (RIKEN)
Hirosawa 2-1, Wako, Saitama 351-01, Japan
Department of Applied Chemistry, Chuo University
Kasuga 1-13-27, Bunkyo, Tokyo 112, Japan

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The formation of ketyls *via* one-electron reduction of ketones by alkali metals was first reported more than 100 years ago.[1] Extensive studies on reactions of ketones and aldehydes with reducing metals have since been carried out,[2] and metal ketyls are now recognized as important intermediates in a variety of organic carbonyl-involved reactions such as reductions,[2a,e,f,h] pinacol couplings,[2b,d] olefin formations (the McMurry reaction),[2b–d,g] and Grignard reactions.[3] Since the metal ketyls are usually very reactive, they have never been isolated and structurally characterized, despite continuous synthetic and mechanistic explorations in this area.[2,4] As a part of our recent project on lanthanide complexes with new ancillary ligands,[5] we have begun to explore the reactivity of divalent lanthanide aryloxide complexes.[6] We report herein the reaction of samarium(II) aryloxide Sm(OAr)$_2$(THF)$_3$ (**1**, Ar = 2,6-^{t}Bu$_2$-4-MeC$_6$H$_2$) with fluorenone, which affords the first structurally characterized metal ketyl complex Sm(biphenyl-2,2′-diyl ketyl)(OAr)$_2$(THF)$_2$ (**2**). More remarkably, the ketyl **2** *reversibly* couples into a structurally characterizable samarium(III) pinacolate (**3**), which thus provides conclusive evidence for the reversibility between a ketyl and a pinacolate.[4,7,8]

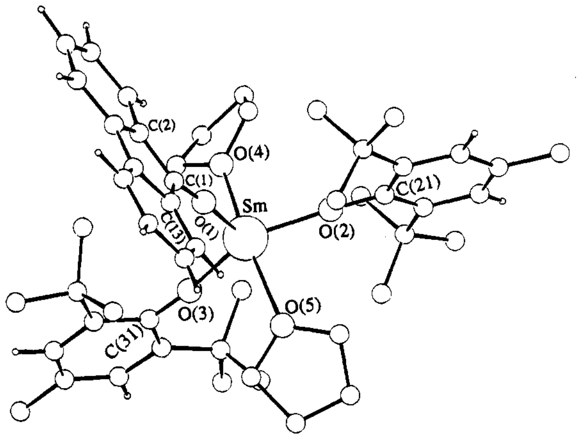
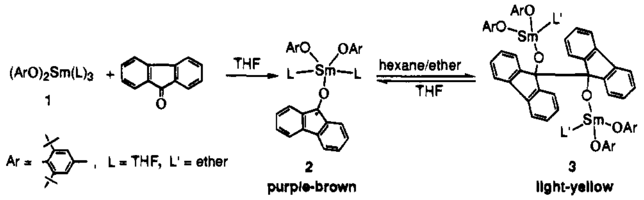


Figure 1. ORTEP drawing of **2** and selected bond lengths (Å) and angles (deg) (the lattice solvent is omitted for clarity): Sm–O(1), 2.159(4); Sm–O(2), 2.165(4); Sm–O(3), 2.161(3); Sm–O(4), 2.438(3); Sm–O(5), 2.475(4); C(1)–O(1), 1.313(7); C(21)–O(2), 1.352(6); C(31)–O(3), 1.352(5); O(1)–C(1)–C(2), 125.9(5); O(1)–C(1)–C(13), 126.1(5); C(2)–C(1)–C(13), 108.1(5).

Scheme 1



Addition of 1 equiv of fluorenone to the samarium(II) aryloxide **1**[9,10] in THF generated immediately a purple-brown solution. Removal of the solvent after stirring at room temperature for 4 h yielded a purple-brown crystalline product, which after recrystallization from THF/benzene gave **2**, as purple-brown blocks in 88% yield (Scheme 1). An X-ray crystallographic study showed that this complex possessed a distorted trigonal bipyramid structure with one fluorenone unit and two ArO ligands at the equatorial and two THF ligands at the apical positions (Figure 1).[10] The average bond distance (2.163(3) Å) of Sm–OAr bonds in **2** is about 0.18 Å shorter than that in **1** but comparable with those (2.14–2.18 Å) reported for the Sm(III)–OR bonds in other five-coordinated Sm(III) alkoxides,[5a] suggesting that the central samarium ion is in a trivalent state.[11] The bond distance between the Sm ion and the oxygen atom of the fluorenone part (Sm–O(1): 2.159(4) Å) is almost the same as those of the Sm–OAr bonds, indicating that the Sm–O(1) bond is an ionic one. Consistent with this bond length, the bond angle (175.2(4)°) of Sm–O(1)–C(1) is also comparable with those of Sm–O–Ar (average 172.8(3)°), which is much larger than those (ca. 130–150°) reported for the η^1-coordinated neutral ketones.[12] The C–O bond distance (C(1)–O(1): 1.313(7) Å) in the fluorenone unit is significantly longer than a C–O double bond[13] but shorter than a C–O single one.[14] The oxygen O(1) and all the carbon atoms in the fluorenone unit are coplanar with $d_{\max} < 0.018$ Å, implying

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[†] The Institute of Physical and Chemical Research (RIKEN).

[‡] Chuo University.

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(9) **1** was obtained in 95% yield as brown-black crystals by reaction of Sm(N(SiMe$_3$)$_2$)$_2$(THF)$_2$ (Evans, W. J.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 575) with 2 equiv of ArOH in THF. During the preparation of this paper, a report on the structure of **1**·THF appeared: Qi, G.-Z.; Shen, Q.; Lin, Y.-H. *Acta Crystallogr., Sect. C* **1994**, *50C*, 1456. In the reaction of **1** with benzophenone, hydrogen abstraction by the ketyl species seemed to occur. Further studies are in progress.

(10) **1**: monoclinic, space group $P2_1$, $a = 9.903(3)$ Å, $b = 16.718(5)$ Å, $c = 13.267(2)$ Å, $\beta = 95.17(2)°$, $V = 2187$ Å^3, $Z = 2$, $D_c = 1.223$ g cm^{-3}, $R = 0.0634$ ($R_w = 0.0738$) for 3111 unique data with $F_o > 5\sigma(F_o)$ and 434 variables. **2**·C$_6$H$_6$: triclinic, space group $P\bar{1}$, $a = 13.326(2)$ Å, $b = 19.651(3)$ Å, $c = 10.705(1)$ Å, $\alpha = 102.22(1)°$, $\beta = 101.87(1)°$, $\gamma = 103.24(1)°$, $V = 2570$ Å^3, $Z = 2$, $D_c = 1.281$ g cm^{-3}, $R = 0.0404$ ($R_w = 0.0510$) for 9935 unique data with $F_o > 5\sigma(F_o)$ and 617 variables. **3**·C$_6$H$_{14}$: triclinic, space group $P\bar{1}$, $a = 13.011(2)$ Å, $b = 17.543(3)$ Å, $c = 12.191(2)$ Å, $\alpha = 97.00(1)°$, $\beta = 111.74(1)°$, $\gamma = 108.06(1)°$, $V = 2367$ Å^3, $Z = 1$, $D_c = 1.244$ g cm^{-3}, $R = 0.0434$ ($R_w = 0.0536$) for 9137 unique data with $F_o > 5\sigma(F_o)$ and 497 variables. Satisfactory micro elemental analyses for **1**–**3** were obtained.

(11) Sm(III) is *ca.* 0.19 Å smaller than Sm(II) in radius when both have the same coordination number. See: Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32A*, 751.

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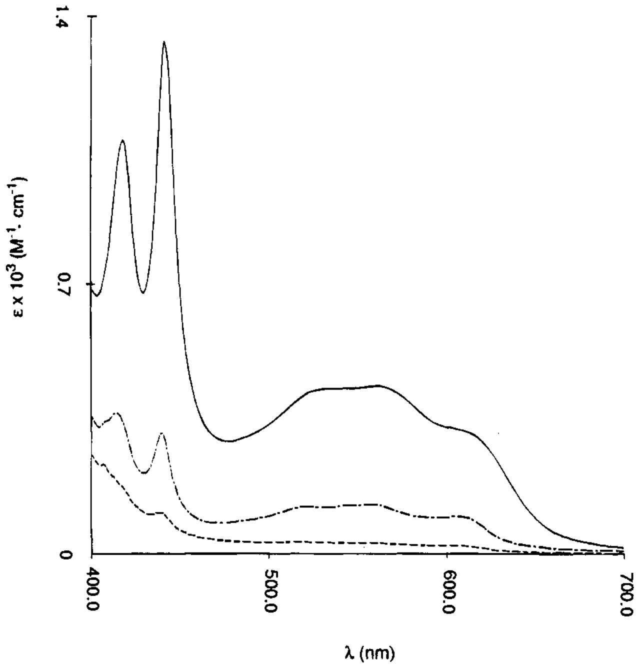

Figure 2. UV−vis spectra. Top: THF solution of **2**. Middle: hexane solution of **2**. Bottom: hexane solution of the powder obtained after evaporation of the hexane solution of **2** (see also the text).

that the carbonyl carbon C(1) is still in an sp^2-hybrid state. These data strongly suggest that **2** is a Sm(III) *ketyl* complex, rather than a Sm(II) species coordinated by a neutral ketone.

Reflecting the influence of the ketyl radical, the ^{1}H NMR spectrum of **2** in THF-d_8 gave unassignable signals which were distributed from δ 0−65. Its UV−vis spectrum in THF was in agreement with those of other metal ketyls which were generated *in situ* (Figure 2, top).[7,15] An X-band ESR spectrum of **2** was not observed at room temperature or −196 °C, apparently owing to the antiferromagnetic superexchange interaction between the ketyl radical and the samarium(III) spins.

The reactivity of **2** demonstrated that the radical was C(1)-centered. Dissolving of **2** into hexane gave a solution whose color was much less intense than that of the THF solution. This color change was also reflected in the UV−vis spectrum (Figure 2, middle). Evaporation of the solvent left a pale powder, which after dissolving into hexane gave an almost colorless solution (Figure 2, bottom).[16] On leaving the hexane solution with a small amount of diethyl ether for a few days, light yellow crystals of **3** precipitated (Scheme 1). An X-ray analysis[10] revealed that **3** was a binuclear samarium(III)−pinacolate complex formed by dimerization of the ketyl **2** at the carbonyl carbon and simultaneous replacement of the two THF ligands with one Et_2O (Figure 3). This molecule possesses a crystallographic inversion center on the C(1)−C(1′) bond. The C(1)−C(1′) bond distance is 1.613(9) Å, which is longer than those (1.56−1.58 Å) found in other pinacolate complexes,[17] and also longer than the central C−C bond (1.59(1) Å) of benzopinacol.[18] This C(1)−C(1′) bond was found to be easily broken to regenerate the ketyl **2** by addition of a strongly coordinative solvent. The light yellow pinacolate **3** turned immediately to purple brown upon addition of THF (Scheme 1). Its UV−vis spectrum in THF was the same as that of **2**, and so was the ^{1}H NMR spectrum in THF-d_8.[19] The ketyl complex **2** could be quantitatively recovered from a THF solution of **3**. This unequivocally demonstrates that the pinacolate formation is reversible, thereby supporting previous investigations in related systems.[4,7,8]

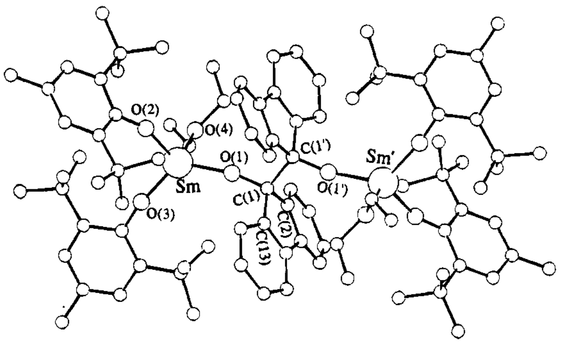

Figure 3. ORTEP drawing of **3** and selected bond lengths (Å) and angles (deg) (the lattice solvent and hydrogen atoms are omitted for clarity): Sm−O(1), 2.099(4); Sm−O(2), 2.115(3); Sm−O(3), 2.141(5); Sm−O(4), 2.435(5); C(1)−O(1), 1.401(7); C(1)−C(1′), 1.613(9); O(1)−C(1)−C(2), 112.5(5); O(1)−C(1)−C(13), 112.5(4); O(1)−C(1)−C(1′), 109.7(4); C(1′)−C(1)−C(2), 111.2(4); C(1′)−C(1)−C(13), 110.3(5); C(2)−C(1)−C(13), 100.5(4).

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Supplementary Material Available: Listings of atomic coordinates, thermal parameters, and bond distances and angles for **1**−**3** (16 pages); listings of observed and calculated structure factors for **1**−**3** (54 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(13) For example, the C−O bond is 1.23(2) Å in free benzophenone (Fleischer, E. B.; Sung, N.; Hawkinson, S. *J. Phys. Chem.* **1968**, *72*, 4311) and 1.248(3) Å in $ZrCl_4(^1\eta\text{-OCMe}^t\text{Bu})$.[11a]

(14) The C−O bond in the fluorenoxy group of $\text{Sm(fluorenoxy)(OAr)}_2\text{(HMPA)}_2$ is 1.404(10) Å (Hou, Z.; Yoshimura, T.; Wakatsuki, Y. Manuscript in preparation).

(15) The influence of the metal ion, the solvent, and the concentration of the ketyls has to be taken into account when comparison of the UV−vis spectra is made. See also ref 7.

(16) The difference in the UV−vis spectra of these two hexane solutions (middle and bottom in Figure 2) arises probably from the influence of traces of THF that is dissociated from **2**.

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(19) Once precipitated, **3** was not soluble in cyclohexane-d_{12} and only slightly soluble in benzene and ether, which precluded its further analysis by ^{1}H NMR spectroscopy.