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First Isolation of a Metal Ketyl in Aggregated Forms. X-ray Structures of Dimeric and Tetrameric Sodium Fluorenone Ketyl Complexes: $[\mathrm{Na}(\mu_2\text{-}\eta^1\text{-ketyl})(\mathrm{HMPA})_2]_2$ and $[\mathrm{Na}(\mu_3\text{-}\eta^1\text{-ketyl})(\mathrm{HMPA})]_4$

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Alkali metal ketyls, formed *via* one-electron reduction of ketones or aldehydes, have been known since the last century.[1−3] It was suggested on the basis of UV−vis and ESR spectra that these ketyls may exist in solution in an equilibrium between monomeric and dimeric forms.[4] However, the isolation and structural characterization of these ketyls have never been achieved due to their high reactivity. Although several metal pinacolates have been isolated,[5−9] only one ketyl has been described.[9] Studies on this ketyl complex $[(\mathrm{ArO})_2\mathrm{Sm}(\text{fluorenone ketyl})(\mathrm{THF})_2$ ($\mathrm{Ar} = 2,6\text{-}{}^t\mathrm{Bu}_2\text{-}4\text{-Me-}\mathrm{C_6H_2}$)] showed that a decrease in the steric hindrance around the central metal by substitution of the THF ligands with $\mathrm{Et_2O}$ resulted in the immediate coupling of the ketyl to yield a pinacolate, rather than the formation of a dimeric ketyl.[9]

By the use of hexamethylphosphoric triamide (HMPA) as a ligand, we have now isolated the dimeric and tetrameric sodium fluorenone ketyl complexes, $[\mathrm{Na}(\mu_2\text{-}\eta^1\text{-biphenyl-2,2}'\text{-diyl ketyl})(\mathrm{HMPA})_2]_2$ (**1**) and $[\mathrm{Na}(\mu_3\text{-}\eta^1\text{-biphenyl-2,2}'\text{-diyl ketyl})(\mathrm{HMPA})]_4$ (**2**), from the reaction of fluorenone with sodium metal in THF. These complexes are the first examples of structurally characterized alkali metal ketyls, as well as the first examples of metal ketyl aggregates. In this communication, we report the X-ray analysis of these complexes. Formation of these ketyl complexes *via* C−C bond cleavage of a pinacol is also demonstrated.

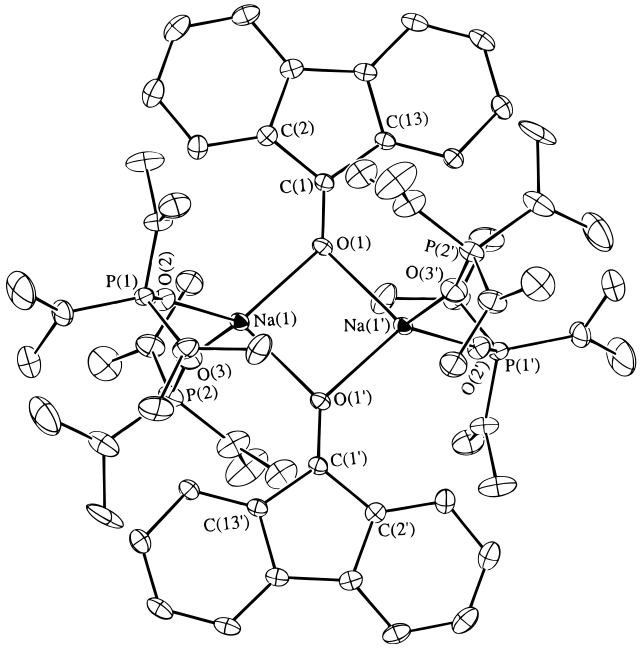

Figure 1. ORTEP drawing of **1**. Selected bond lengths (Å) and angles (deg): Na(1)−O(1), 2.292(5); Na(1)−O(1′), 2.316(5); Na(1)−O(2), 2.236(4); Na(1)−O(3), 2.199(5); O(1)−C(1), 1.275(7); O(1)−Na(1)-O(1′), 91.9(2); O(1)−Na(1)−O(2), 123.3(2); O(1)−Na(1)−O(3), 106.9(2); O(1′)−Na(1)−O(2), 112.6(2); O(1′)−Na(1)−O(3), 108.9(2); O(2)−Na(1)−O(3), 111.2(2); Na(1)−O(1)−Na(1′), 88.1(2); Na(1)−O(1)−C(1), 134.7(4); Na(1′)−O(1)−C(1), 133.4(4); O(1)−C(1)−C(2), 127.1(5); O(1)−C(1)−C(13), 127.0(5); C(2)−C(1)−C(13), 105.9(5).

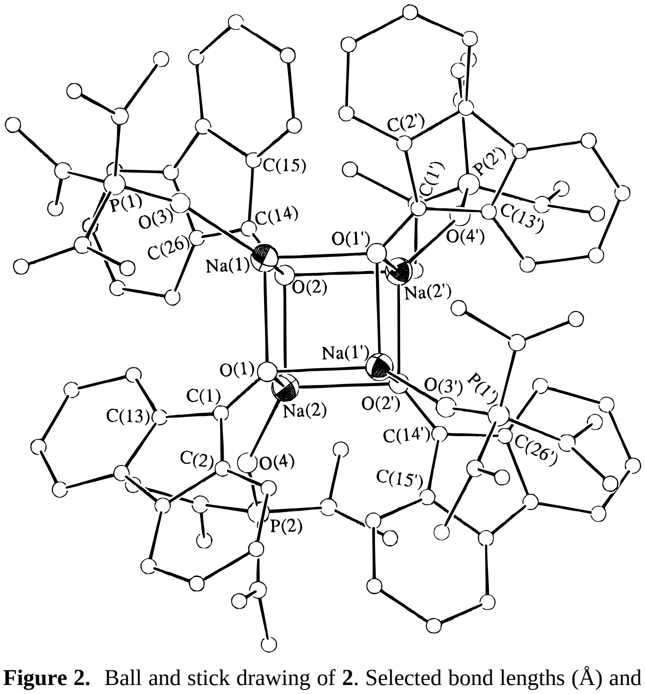

Figure 2. Ball and stick drawing of **2**. Selected bond lengths (Å) and angles (deg): Na(1)−O(1), 2.290(14); Na(1)−O(1′), 2.315(15); Na(1)−O(2), 2.418(17); Na(2)−O(1), 2.453(18); Na(2)−O(2), 2.328(15); Na(2)−O(2′), 2.290(16); Na(1)−O(3), 2.129(19); Na(2)−O(4), 2.171(19); O(1)−C(1), 1.27(3); O(2)−C(14), 1.30(3); O(1)−C(1)−C(2), 126.6(17); O(1)−C(1)−C(13), 125.0(18); C(2)−C(1)−C(13), 108.2(16); O(2)−C(14)−C(15), 126.0(18), O(2)−C(14)−C(26), 126.2(17); C(15)−C(14)−C(26), 107.8(17).

Addition of 1 equiv of fluorenone to fresh sodium chips in THF gave a brown mixture, which was stirred at room temperature for about 3 h. During this time, the sodium chips gradually disappeared, and a green solution was obtained. Addition of 2 equiv of HMPA gave a red-brown solution which, after concentration and addition of hexane, precipitated **1** as brown blocks in 81% isolated yield (Scheme 1).[10] The UV−vis and ESR spectra[11] of **1** in THF were almost the same as

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

(3) Sodium benzophenone ketyl is used in almost every chemistry laboratory for dehydration of etheral solvents.

(4) For examples, see: (a) Hirota, N.; Weissman, S. I. *J. Am. Chem. Soc.* **1964**, *86*, 2538. (b) Hirota, N. *J. Am. Chem. Soc.* **1967**, *89*, 32.

(5) Coutts, R. S. P.; Wailes, P. C.; Martin, R. L. *J. Organomet. Chem.* **1973**, *50*, 145.

(6) (a) Hillgärtner, H; Newmann, W. P.; Schröder, B. *Liebigs Ann. Chem.* **1975**, 586. (b) Ziebarth, M; Newmann, W. P. *Liebigs Ann. Chem.* **1978**, 1765.

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

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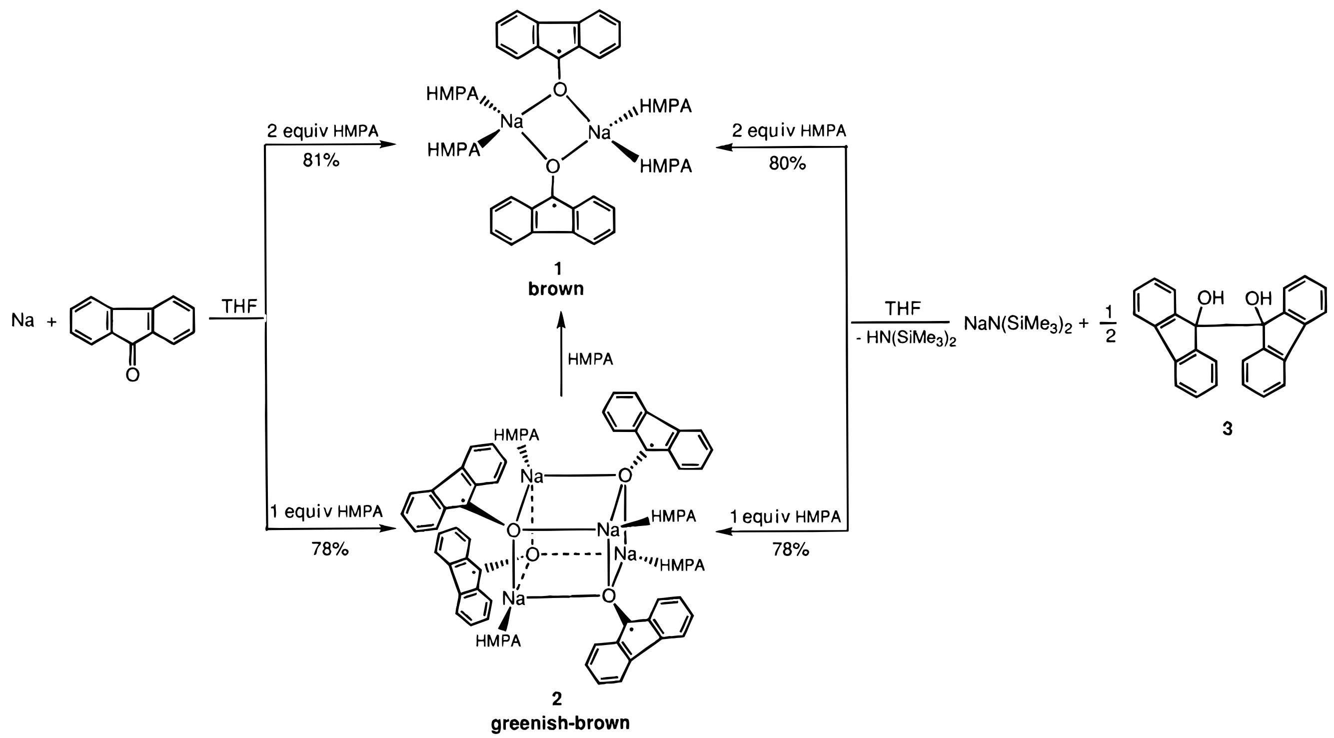
Scheme 1



those reported for the *in-situ*-generated sodium fluorenone ketyl.[4a] An X-ray analysis reveals that **1** is a ketyl-bridged dimeric sodium complex in which each sodium atom is also bonded to two terminal HMPA ligands (Figure 1).[12] The ketyl unit in **1** possesses a nearly planar configuration, which is similar to that of the Sm ketyl, $(ArO)_2Sm(ketyl)(THF)_2$.[9] This molecule has a crystallographic inversion center at the center of the Na(1)O(1)Na(1′)O(1′) plane. The two ketyl moieties are therefore identical and coplanar, forming a dihedral angle of 17° with the Na(1)O(1)Na(1′)O(1′) plane. The C−O bond (1.275(7) Å) in **1** is shorter than that (1.313(7) Å) in the Sm ketyl,[9] probably reflecting the difference between terminal and bridged ketyls. The bond lengths of the Na−O(ketyl) bonds (2.292(5) and 2.316(5) Å) are comparable with those of the Na−OAr bonds (2.231(6) and 2.296(7) Å) found in the dimeric sodium aryl oxide complex $[Na(\mu\text{-OAr})(THF)_2]_2$ (Ar = 2,6-$(CF_3)_2$-4-(CF_3)-C_6H_2).[13] The similarity in bond lengths between Sm−O(ketyl) and Sm−O(aryl oxide) bonds was previously observed.[9,14,15] The lengths of the Na−O(HMPA) bonds (2.199(5) and 2.236(4) Å) in **1** are comparable with those (2.239(4) Å) found for the terminal HMPA ligands in $[Na(\mu\text{-HMPA})(NCS)(HMPA)]_2$.[16]

If only 1 equiv of HMPA was used in the reaction of fluorenone with Na, greenish-brown crystals of **2** were obtained in 78% isolated yield (Scheme 1). Although the UV−vis and ESR spectra in THF are very similar to those of **1**,[11] an X-ray analysis shows that **2** is a μ_3-ketyl-bridged tetrameric complex which possesses an Na_4O_4 cubane core (Figure 2).[12] A crystallographic C_2 axis exists at the center of and perpendicular to the Na(1)O(1)Na(1′)O(1′) plane. Each Na atom in **2** is coordinated to one terminal HMPA. The C−O bonds (1.27(3) and 1.30(3) Å) of the ketyls in **2** are similar to those in **1**. The Na−O(ketyl) bonds in **2** range from 2.290(14) to 2.453(18) Å, due to the unsymmetrical ketyl bridges. In a cubane sodium pinacolone enolate complex, the Na−O(enolate) bonds were found to vary from 2.241(2) to 2.332 (3) Å.[17]

The formation of **2** can formally be regarded as the dimerization of two molecules of **1** by removal of one of the two HMPA ligands attached to each Na atom. It is surprising that this dimerization is not pinacol-coupling of the ketyls, but aggregation of the ketyls *via* Na−O(ketyl) interactions. The behavior of this sodium ketyl is in contrast to what was observed in the case of lanthanide ketyls, where pinacol-coupling occurred when the steric hindrance around the central metal was decreased.[9,15,18] Reaction of tetramer **2** with 4 or more equiv of HMPA yielded only dimer **1** (Scheme 1); a monomeric ketyl was not isolated.

Ketyl complexes **1** and **2** could also be obtained by reaction of a pinacol, 1,2-(biphenyl-2,2′-diyl)ethane-1,2-diol (**3**), with $NaN(SiMe_3)_2$ *via* C−C bond cleavage of the pinacolate (Scheme 1). This demonstrates that deprotonation and C−C bond cleavage of pinacols might constitute a new method for the synthesis of ketyls.

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Supporting Information Available: UV−vis, ESR, and elemental analysis data for **1** and **2** and listings of atomic coordinates, thermal parameters, and bond distances and angles for **1** and **2** (14 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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(10) Crystals suitable for X-ray analysis were not obtained without using HMPA.

(11) For UV−vis and ESR spectra and microelemental analysis data for **1** and **2**, see supporting information.

(12) **1**: triclinic, space group $P\bar{1}$, $a = 11.152(5)$, $b = 12.398(2)$, and $c = 12.492(2)$ Å, $\alpha = 107.56(1)°$, $\beta = 103.11(2)°$, $\gamma = 95.53(2)°$, $V = 1598.1(7)$ Å^3, $Z = 1$, $D_c = 1.17$ g cm^{-3}, $R = 0.0664$ ($R_w = 0.0668$). **2**: monoclinic, space group $C_{2/c}$, $a = 29.195(7)$, $b = 11.938(4)$, and $c = 27.942(7)$ Å, $\beta = 117.99(2)°$, $V = 8599(4)$ Å^3, $Z = 4$, $D_c = 1.18$ g cm^{-3}, $R = 0.1049$ ($R_w = 0.1179$).

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