Alkali and Alkaline-Earth Metal Ketyl Complexes: Isolation, Structural Diversity, and Hydrogenation/Protonation Reactions

Zhaomin Hou,*[a] Xueshun Jia,[a] Akira Fujita,[b] Hiroaki Tezuka,[b] Hiroshi Yamazaki,[b] and Yasuo Wakatsuki*[a]

Abstract: The use of hexamethylphosphoric triamide (HMPA) as a stabilizing ligand allowed successful isolation of a series of structurally characterizable alkali metal and calcium ketyl complexes. Reaction of lithium and sodium with one equivalent of fluorenone and reaction of sodium with one equivalent of benzophenone in THF, followed by addition of two equivalents of HMPA, yielded the corresponding ketyl complexes **1**, **2**, and **11**, respectively, as μ-ketyl-bridged dimers. If one equivalent of HMPA was used in the reaction of sodium with fluorenone, a further aggregated complex, the μ_3-ketyl-bridged tetramer **3**, was isolated, whereas analogous reaction of benzophenone with sodium afforded the trimeric ketyl complex **13**, rather than a simple benzophenone analogue of **3**. In the reaction of potassium with fluorenone, the use of two equivalents of HMPA gave the tetramer **4**, rather than a dimeric complex analogous to **1** or **2**. Compared to the tetrameric sodium complex **3**, there is an extra HMPA ligand that bridges two of the four K atoms in **4**. When 0.5 equiv of HMPA was used in the above reaction, complex **5**, a THF-bridged analogue of **4**, was isolated. In the absence of HMPA, the reaction of sodium with an *excess* of fluorenone yielded the tetrameric ketyl complex **6**, in which two of the four Na atoms are each terminally coordinated by a fluorenone ligand, and the other two Na atoms are coordinated by a THF ligand. Two bridging THF ligands are also observed in **6**. Reaction of 1,2-bis(biphenyl-2,2′-diyl)ethane-1,2-diol (**7**) with two equivalents of $LiN(SiMe_3)_2$ or $NaN(SiMe_3)_2$ in the presence of four equivalents of HMPA easily afforded **1** or **2**, respectively, via C–C bond cleavage of a 1,2-diolate intermediate. The reaction of calcium with two equivalents of fluorenone or benzophenone in the presence of HMPA gave the corresponding complexes that bear two independent ketyl ligands per metal ion. In the presence of 3 or four equivalents of HMPA, the fluorenone ketyl complex was isolated in a six-coordinate octahedral form (**10**), while the benzophenone ketyl complex was obtained as a five-coordinate trigonal bipyramid (**13**). The radical carbon atoms in both benzophenone ketyl and fluorenone ketyl complexes are still in an sp^2-hybrid state. However, in contrast with the planar configuration of the whole fluorenone ketyl unit, the radical carbon atom in a benzophenone ketyl species is not coplanar with any of the phenyl groups; this explains why benzophenone ketyl is more reactive than fluorenone ketyl. Hydrolysis of **2** or **11** with 2 N HCl yielded the corresponding pinacol-coupling product, while treatment of **2** or **11** with 2-propanol, followed by hydrolysis, gave the pairs fluorenone and fluorenol or benzophenone and benzhydrol, respectively. A possible mechanism for these reactions is proposed.

Keywords: alkali metals · calcium · ketones · radical anions · reductions

Introduction

Metal ketyl species, formed by one-electron reduction of ketones or aldehydes with reducing metals, represent one of the most important kinds of intermediates in organic chemistry.[1, 2] These highly reactive and synthetically useful species have received continuous attention from a broad range of chemists since their discovery more than 100 years ago. Although extensive studies have been carried out so far in this area, structurally characterized examples of metal ketyls remain rare owing to their extremely high reactivity, which makes them difficult to isolate.[3] Isolation and structural characterization of new metal ketyl complexes continue to be of great importance and interest for understanding the nature of this important class of species.

Alkali and alkaline-earth metal ketyls are among the best known and most widely used ketyls.[1, 2f,g, 3c, 4] Because they are so well known and synthetically very useful, we carried out a

---

[a] Dr. Z. Hou, Dr. Y. Wakatsuki, Dr. X. Jia
RIKEN (The Institute of Physical and Chemical Research)
Hirosawa 2-1, Wako, Saitama 351-0198 (Japan)
Fax: (+48) 462-4665
E-mail: houz@postman.riken.go.jp

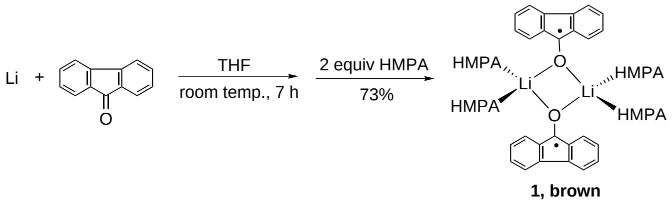
[b] A. Fujita, H. Tezuka, Prof. Dr. H. Yamazaki
Department of Applied Chemistry, Chuo University
Kasuga 1-13-27, Bunkyo, Tokyo 112-0003 (Japan)

0947-6539/00/0616-2994 $ 17.50+.50/0

systematic study on the isolation and structures of a series of alkali and alkaline-earth metal ketyl complexes, as part of our recent research project on structurally well-defined metal–ketyl complexes.[3a–e,h–j] Herein, we report on lithium, sodium, potassium, and calcium benzophenone and fluorenone ketyl complexes (benzophenone ketyl = diphenyl ketyl, fluorenone ketyl = biphenyl-2,2′-diyl ketyl). X-ray analyses of these complexes have revealed unprecedented structural features of metal ketyl complexes. Hydrogenation/protonation of some of these ketyl complexes have shed new light on the mechanistic aspects of the reduction of ketones with dissolving metals. A portion of this work has been communicated previously.[3e,i]

Results and Discussion

Alkali metal fluorenone ketyl complexes: Reaction of one equivalent of lithium chips with fluorenone in THF, followed by addition of two equivalents of hexamethylphosphoric triamide (HMPA), easily afforded the lithium fluorenone ketyl complex **1** as brown crystals (Scheme 1).[5] An X-ray analysis has shown that **1** adopts a centrosymmetric dimeric structure, in which the two Li atoms are bridged by two identical fluorenone ketyl ligands and each of the two Li atoms is also coordinated by two HMPA ligands (Figure 1 and Table 1). This dimeric structure seemed to be the most favorable form for the HMPA-coordinated lithium fluorenone ketyl complex. The use of one equivalent of HMPA also yielded the bis(HMPA)-coordinated dimeric complex **1** as the only isolable product, while further addition of HMPA to a THF solution of **1** did not give a monomeric complex. The C(1)–O(1) bond length in **1** (1.288(8) Å) is in the 1.27–1.32 Å range of the C–O (ketyl) bond lengths found in other metal ketyl complexes,[3] which is longer than the C–O double bond of free fluorenone (1.220(4) Å)[6] and shorter than the C–O single bond found in a samarium fluorenoxide complex, $[Sm(OC_{13}H_9)(OC_6H_2tBu_2\text{-}2,6\text{-}Me\text{-}4)_2(HMPA)_2]$ (1.404(8) Å).[7]



Scheme 1. Isolation of the dimeric lithium fluorenone ketyl complex **1**.

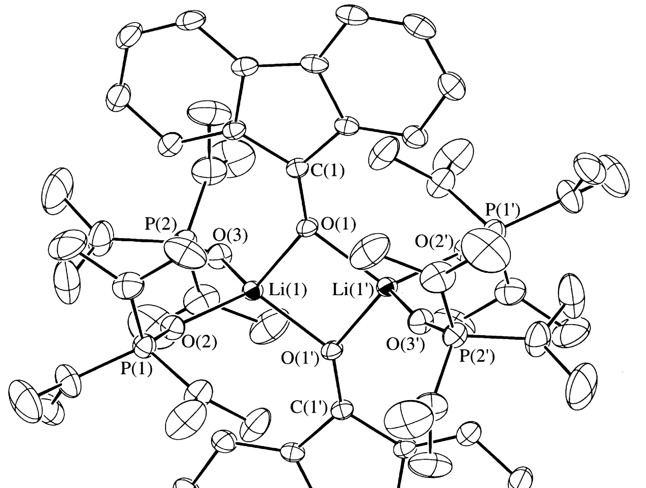
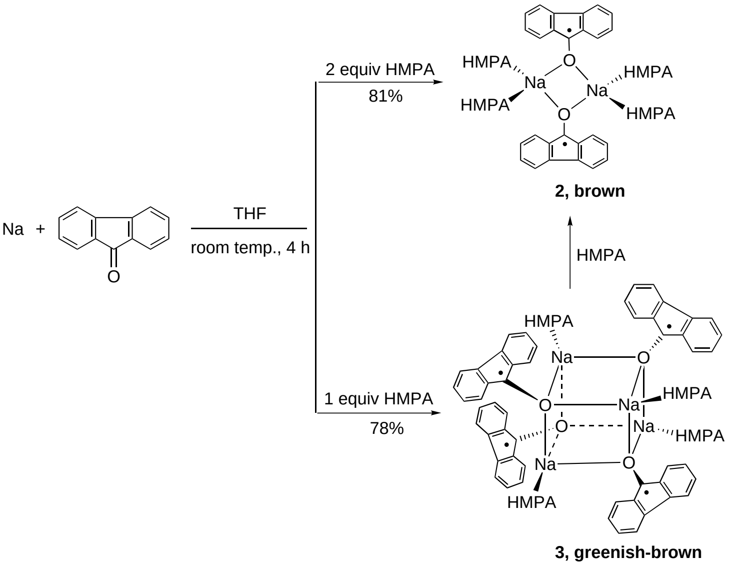


Figure 1. X-ray crystal structure of **1** (with 30 % thermal ellipsoids).

Table 1. Selected bond lengths [Å] and angles [°] of **1**.

Li(1)–O(1)	1.953(12)	Li(1)–O(1′)	1.976(12)
Li(1)–O(2)	1.972(12)	Li(1)–O(3)	1.925(12)
O(1)–C(1)	1.288(8)		
O(1)-Li(1)-O(1′)	90.6(5)	O(1)-Li(1)-O(2)	114.4(6)
O(1)-Li(1)-O(3)	114.0(6)	O(1′)-Li(1)-O(2)	115.6(6)
O(1′)-Li(1)-O(3)	114.1(6)	O(2)-Li(1)-O(3)	107.7(6)
Li(1)-O(1)-Li(1′)	89.4(5)	Li(1)-O(1)-C(1)	134.3(6)
Li(1′)-O(1)-C(1)	135.7(6)	Li(1)-O(2)-P(1)	146.2(5)
Li(1)-O(3)-P(2)	168.1(5)		

Similar reaction of sodium chips with one equivalent of fluorenone and two equivalents of HMPA yielded the analogous dimeric sodium fluorenone ketyl complex **2** as brown crystals (Scheme 2), which is isostructural with the lithium complex **1** (Figure 2 and Table 2). When one equivalent of HMPA was used in this reaction, the tetrameric, μ_3-ketyl-bridged sodium complex **3** was isolated as greenish-brown crystals in 78 % yield (Scheme 2). Complex **3** possesses an Na_4O_4 cubane core, in which each Na atom is coordinated by one terminal HMPA ligand (Figure 3 and Table 3). The formation of **3** can formally be viewed as dimerization of two molecules of **2** by removal of one of the two HMPA ligands on



Scheme 2. Isolation of dimeric (**2**) and tetrameric (**3**) sodium fluorenone ketyl complexes.

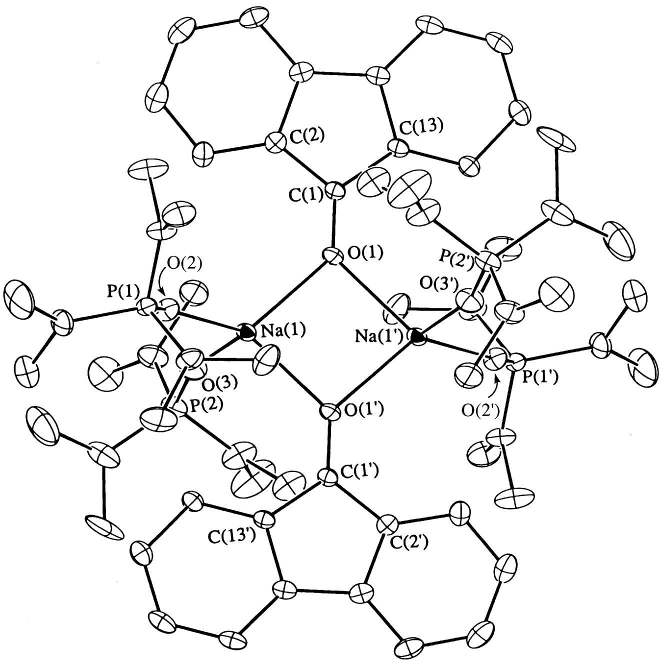


Figure 2. X-ray crystal structure of **2** (with 30% thermal ellipsoids).

Table 2. Selected bond lengths [Å] and angles [°] of **2**.

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)	Na(1) -O(2)-P(1)	151.5(3)
Na(1)-O(3)-P(3)	163.0(4)		

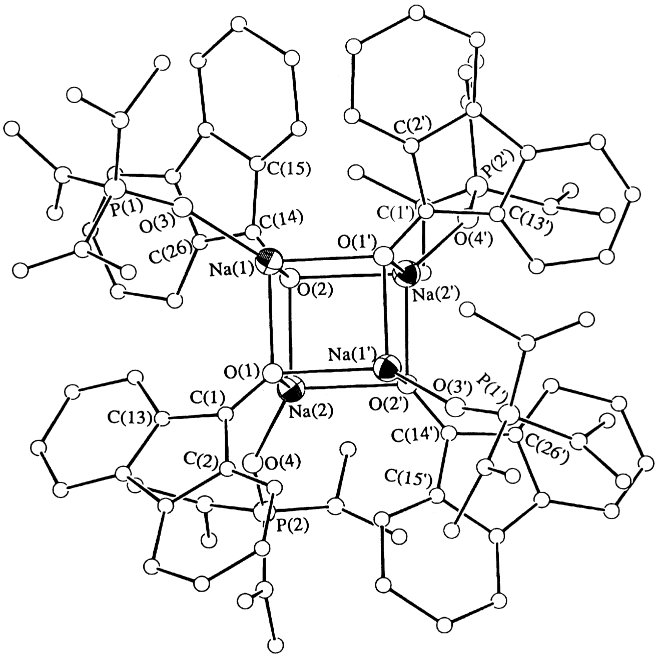


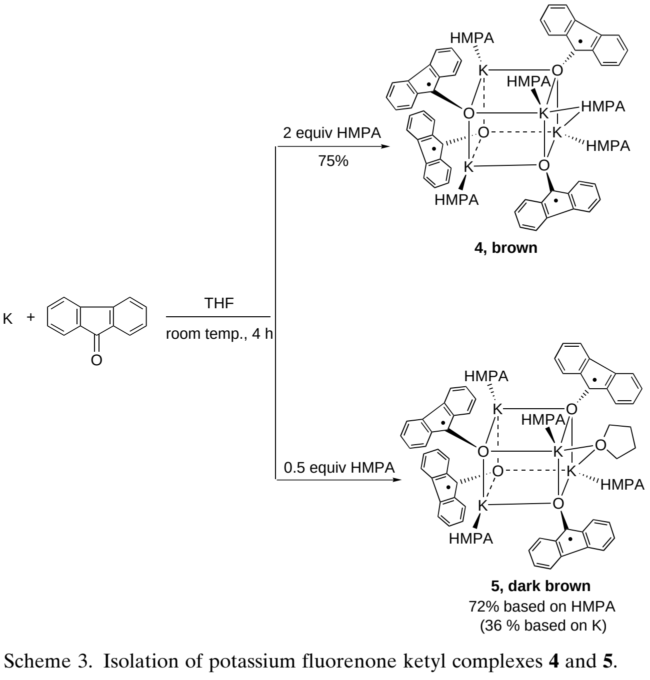
Figure 3. X-ray crystal structure of **3**.

Table 3. Selected bond lengths [Å] and angles [°] of **3**.

Na(1)–O(1)	2.290(14)	Na(1)–O(1′)	2.315(15)
Na(1)–O(2)	2.418(17)	Na(1)–O(3)	2.129(19)
Na(2)–O(1)	2.453(18)	Na(2)–O(2)	2.328(15)
Na(2)–O(2′)	2.290(16)	Na(2)–O(4)	2.171(19)
O(1)–C(1)	1.27(3)	O(2)–C(14)	1.30(3)
O(1)-Na(1)-O(1′)	89.6(5)	O(1)-Na(1)-O(2)	90.0(6)
O(1)-Na(1)-O(3)	135.7(7)	O(1′)-Na(1)-O(2)	90.0(6)
O(1′)-Na(1)-O(3)	119.5(7)	O(2)-Na(1)-O(3)	120.0(7)
O(1)-Na(2)-O(2)	88.3(6)	O(1)-Na(2)-O(2′)	89.8(6)
O(1)-Na(2)-O(4)	130.7(7)	O(2)-Na(2)-O(2′)	89.7(6)
O(2)-Na(2)-O(4)	118.7(7)	O(2′)-Na(2)-O(4)	127.4(7)
Na(1)-O(1)-Na(1′)	90.4(5)	Na(1)-O(1)-Na(2)	90.9(6)
Na(1′)-O(1)-Na(2)	89.4(6)	Na(2)-O(2)-Na(2′)	90.3(6)
Na(1)-O(2)-Na(2)	90.8(6)	Na(1′)-O(2)-Na(2)	90.8(6)
Na(1)-O(1)-C(1)	136.3(12)	Na(1′)-O(1)-C(1)	131.3(12)
Na(2)-O(1)-C(1)	100.7(13)	Na(1)-O(2)-C(14)	102.2(12)
Na(2)-O(2)-C(14)	126.0(12)	Na(2′)-O(2)-C(14)	140.5(12)
Na(1)-O(3)-P(1)	163.5(12)	Na(2)-O(4)-P(2)	150.1(11)

each Na atom. It is noteworthy that this dimerization is not pinacol-coupling of the ketyls[3d,j] but further aggregation of the ketyls through Na–O(ketyl) interactions. Addition of four equivalents of HMPA to the tetrameric complex **3** in THF easily gave the dimeric complex **2**. But further addition of HMPA to a THF solution of **2** did not afford a monomeric ketyl complex. The HMPA-dependence of the reaction, leading to formation of either dimeric complex **2** or tetrameric complex **3**, is in sharp contrast with what was observed in the case of lithium fluorenone ketyl. This difference may result from the different ion sizes of lithium and sodium.

In contrast with lithium and sodium fluorenone ketyls, potassium fluorenone ketyl always adopted a tetrameric structure. A bis(HMPA)-coordinated dimeric potassium complex analogous to **1** and **2** was not obtained when two equivalents of HMPA was added to a THF solution of potassium fluorenone ketyl, but instead the tetrameric complex **4**, which bears one terminal HMPA ligand on each K atom, was isolated in 75% yield (Scheme 3). Furthermore,



Scheme 3. Isolation of potassium fluorenone ketyl complexes **4** and **5**.

reflecting the larger ion size of potassium, an additional bridging HMPA ligand is also bonded to two of the four potassium atoms, and the K_4O_4 cubane core in **4** is thus more distorted than the Na_4O_4 core in **3** (Figure 4 and Table 4). This K_4O_4 cubic skeleton was obtained even when less than one equivalent of HMPA was employed. As shown in Scheme 3, addition of 0.5 equiv of HMPA to a THF solution of potassium fluorenone ketyl afforded **5**, a THF-bridged analogue of **4** (Figure 5 and Table 5), whereas formation of a further aggregated complex was not observed.

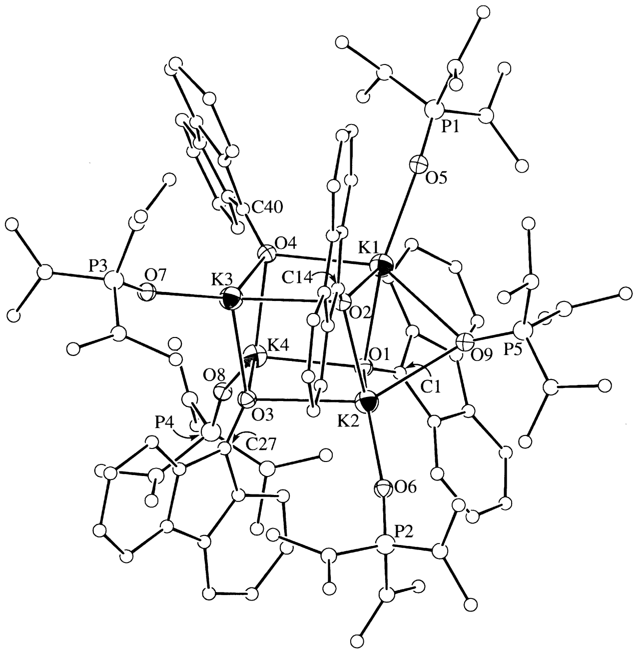


Figure 4. X-ray crystal structure of **4**.

Although the use of HMPA as a stabilizing ligand was essential to isolate a structurally characterizable metal ketyl complex in most of the above reactions, single crystals of the HMPA-free, tetrameric ketyl complex **6** could also be isolated when an excess of fluorenone was employed in the reaction with sodium in THF (Scheme 4). In contrast to the HMPA-coordinatedtetrameric complexes **3**–**5**, two of the four Na atoms in **6** are each terminally coordinated by a fluorenone and the other two Na atoms are coordinated by a THF ligand (Figure 6 and Table 6). In addition, the Na atoms in **6** are also bridged in pairs by a THF ligand whose oxygen atom is sitting on a crystallographic C_2 axis. As far as we are aware, complex **6** represents the first example of a ketone-coordinated ketyl complex, and is also a rare example of a complex bearing bridging THF ligands.[8]

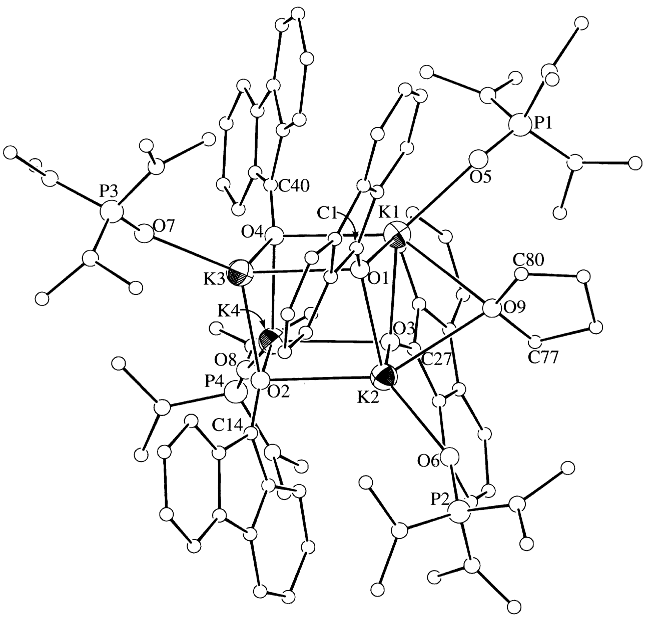


Figure 5. X-ray crystal structure of **5**.

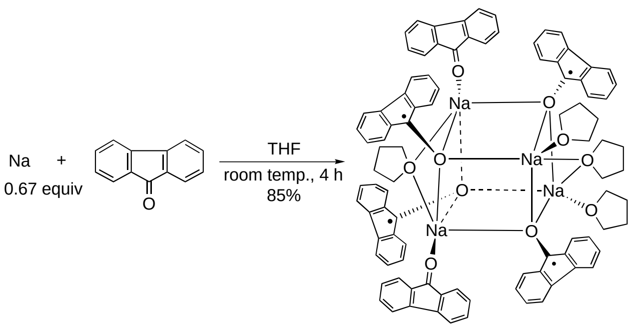
Deprotonation of an appropriate 1,2-diol, followed by C–C bond cleavage of the resultant diolate, the reverse process of a normal pinacol-coupling reaction,[3d,j] could also be used for the synthesis of a ketyl complex. As shown in Scheme 5, reaction of 1,2-bis(biphenyl-2,2′-diyl)ethane-1,2-diol (**7**) with two equivalents of $LiN(SiMe_3)_2$ or $NaN(SiMe_3)_2$ in the presence of four equivalents of HMPA easily afforded the ketyl complex **1** or **2**, respectively, through C–C bond cleavage of the 1,2-diolate intermediate **8**.[3d,j] Although this

Table 4. Selected bond lengths [Å] and angles [°] of **4**.

K1–O1	2.837(10)	K1–O2	2.715(9)	K1–O4	2.785(10)	K1–O5	2.576(11)	K1–O9	2.778(10)	K2–O1	2.714(10)
K2–O2	2.740(9)	K2–O3	2.830(10)	K2–O6	2.574(10)	K2–O9	2.744(10)	K3–O2	2.678(10)	K3–O3	2.629(10)
K3–O4	2.774(10)	K3–O7	2.541(11)	K4–O1	2.587(10)	K4–O3	2.727(10)				
K4–O4	2.688(11)	K4–O8	2.511(11)	O1–C1	1.276(16)	O2–C14	1.278(16)				
O3–C27	1.286(16)	O4–C40	1.285(16)								
O1-K1-O2	96.3(3)	O1-K1-O4	80.0(3)	O1-K1-O5	142.8(4)	O1-K1-O9	70.4(3)	O2-K1-O4	85.6(3)		
O2-K1-O5	120.9(4)	O2-K1-O9	78.2(3)	O4-K1-O5	101.7(3)	O4-K1-O9	144.1(3)	O5-K1-O9	114.1(4)		
O1-K2-O2	98.7(3)	O1-K2-O3	79.6(3)	O1-K2-O6	142.6(4)	O1-K2-O9	72.8(3)	O2-K2-O3	80.7(3)		
O2-K2-O6	118.8(4)	O2-K2-O9	78.4(3)	O3-K2-O6	105.0(4)	O3-K2-O9	142.1(3)	O6-K2-O9	112.7(4)		
O2-K3-O4	86.5(3)	O2-K3-O7	126.5(4)	O3-K3-O4	89.0(3)	O2-K3-O3	85.7(3)	O3-K3-O7	113.7(4)		
O4-K3-O7	139.4(4)	O1-K4-O3	83.8(3)	O1-K4-O4	86.4(3)	O1-K4-O8	112.6(4)	O3-K4-O4	88.8(3)		
O3-K4-O8	132.7(4)	O4-K4-O8	134.1(4)	K1-O1-K2	77.8(3)	K1-O1-K4	97.1(3)	K2-O1-K4	101.2(4)		
K1-O2-K2	79.4(3)	K1-O2-K3	95.7(3)	K2-O2-K3	97.1(3)	K2-O3-K3	96.0(3)	K2-O3-K4	95.0(3)		
K3-O3-K4	90.5(3)	K1-O4-K3	92.0(3)	K1-O4-K4	96.0(4)	K3-O4-K4	88.3(3)	K1-O9-K2	78.3(3)		
K1-O5-P1	164.1(7)	K1-O1-C1	111.0(8)	K2-O1-C1	131.5(9)	K4-O1-C1	123.5(8)	K1-O2-C14	143.4(9)		
K2-O2-C14	131.1(8)	K3-O2-C14	98.9(8)	K2-O3-C27	112.3(8)	K3-O3-C27	141.0(8)	K4-O3-C27	112.1(8)		
K1-O4-C40	125.9(9)	K3-O4-C40	119.2(9)	K4-O4-C40	125.3(9)	K2-O6-P2	168.0(7)	K3-O7-P3	160.2(7)		
K4-O8-P4	158.5(8)	K1-O9-P5	127.7(6)	K2-O9-P5	144.9(6)						

Table 5. Selected bond lengths [Å] and angles [°] of **5**.

K1−O1	2.643(10)	K1−O3	2.776(11)	K1−O4	2.839(10)	K1−O5	2.539(12)	K1−O9	3.007(15)	K2−O1	2.758(10)
K2−O2	2.804(10)	K2−O3	2.687(10)	K2−O6	2.547(13)	K2−O9	2.922(15)	K3−O1	2.769(10)	K3−O2	2.656(10)
K3−O4	2.668(10)	K3−O7	2.566(11)	K4−O2	2.726(10)	K4−O3	2.678(9)	K4−O4	2.618(10)	K4−O8	2.511(11)
O1−C1	1.291(16)	O2−C14	1.285(17)	O3−C27	1.281(16)	O4−C40	1.299(17)				
O1-K1-O3	96.1(4)	O1-K1-O4	84.3(3)	O1-K1-O5	119.4(4)	O1-K1-O9	71.8(4)	O3-K1-O4	80.3(3)		
O3-K1-O5	128.9(4)	O3-K1-O9	73.3(4)	O4-K1-O5	134.4(4)	O4-K1-O9	141.8(4)	O5-K1-O9	83.7(4)		
O1-K2-O2	83.3(3)	O1-K2-O3	95.5(4)	O1-K2-O6	129.1(4)	O1-K2-O9	71.7(4)	O2-K2-O3	85.4(3)		
O2-K2-O6	127.7(4)	O2-K2-O9	146.9(4)	O3-K2-O6	122.7(4)	O3-K2-O9	76.0(4)	O6-K2-O9	85.4(4)		
O1-K3-O2	85.9(3)	O1-K3-O4	85.2(3)	O1-K3-O7	134.8(4)	O2-K3-O4	88.6(3	O2-K3-O7	127.2(4)		
O4-K3-O7	120.6(4)	O2-K4-O3	87.2(3)	O2-K4-O4	88.2(3)	O2-K4-O8	140.1(4)	O3-K4-O4	86.2(3)		
O3-K4-O8	111.8(4)	O4-K4-O8	126.3(4)	K1-O1-K2	82.7(3)	K1-O1-K3	96.4(3)	K2-O1-K3	94.4(3)		
K2-O2-K3	95.9(4)	K2-O2-K4	91.8(3)	K3-O2-K4	89.4(3)	K1-O3-K2	81.6(3)	K1-O3-K4	96.7(3)		
K2-O3-K4	95.5(3)	K1-O4-K3	94.2(3)	K1-O4-K4	96.5(3)	K3-O4-K4	91.5(4)	K1-O9-K2	74.0(4)		
K1-O1-C1	137.5(9)	K2-O1-C1	134.4(9)	K3-O1-C1	99.6(8)	K2-O2-C14	98.8(8)	K3-O2-C14	141.1(9)		
K4-O2-C14	125.7(9)	K1-O3-C27	118.9(9)	K2-O3-C27	147.2(9)	K4-O3-C27	106.1(8)	K1-O4-C40	99.0(8)		
K3-O4-C40	130.7(8)	K4-O4-C40	133.2(9)	K1-O5-P1	151.3(7)	K2-O6-P2	153.1(8)	K3-O7-P3	150.6(7)		
K4-O8-P4	173.5(8)	K1-O9-C77	125.5(13)	K1-O9-C80	107.5(14)	K2-O9-C77	106.4(13)	K2-O9-C80	131.0(13)		



6, dark-green

Scheme 4. Isolation of an HMPA-free sodium fluorenone ketyl complex **6**.

approach does not offer an advantage over the reduction method for the synthesis of an alkali metal ketyl complex such as **1** or **2**, it may provide a particularly useful route to metal ketyls whose metal species are not good electron-transfer agents but are available as deprotonation agents (or bases).[3c]

Calcium fluorenone ketyl complexes: In contrast to the one-electron reducing alkali metals, the reaction of calcium metal, a two-electron transfer agent, with two equivalents of fluorenone and two equivalents of HMPA in THF gave the monomeric bis(ketyl) complex **9** in 79% yield (Scheme 6).

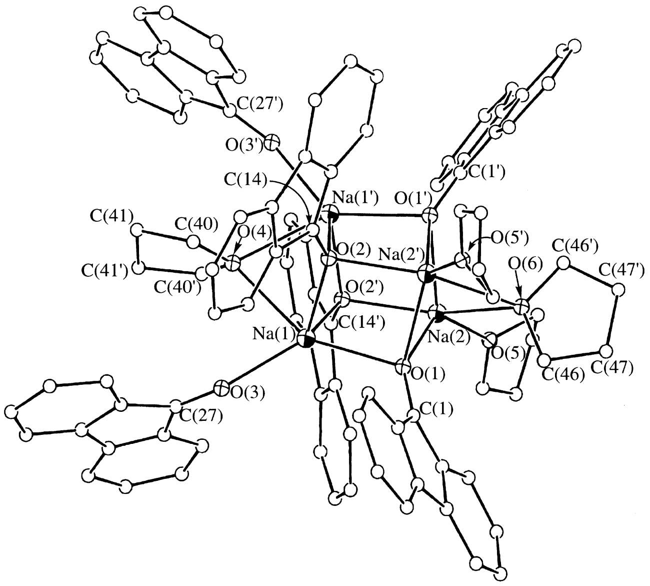


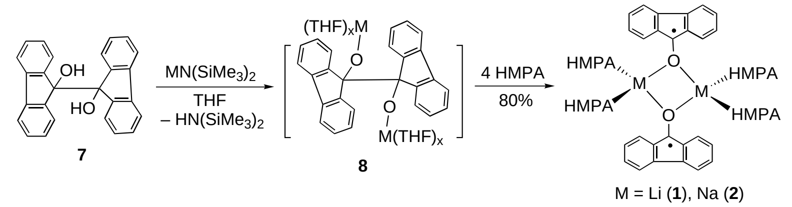
Figure 6. X-ray crystal structure of **6** (the lattice solvent C_6H_6 is omitted for clarity).

Complex **9** possesses an octahedral structure, in which the central Ca^{II} ion is coordinated in *trans* form by two fluorenone ketyl, two THF, and two HMPA ligands (Figure 7 and

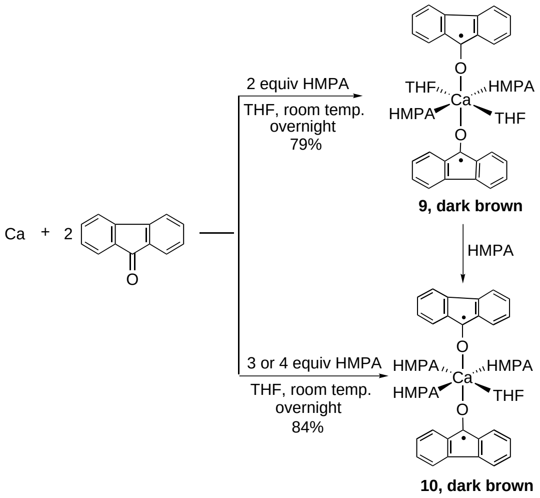
Table 6. Selected bond lengths [Å] and angles [°] of **6**.

Na(1)−O(1)	2.413(10)	Na(1)−O(2)	2.298(10)	Na(1)−O(2′)	2.434(10)	Na(1)−O(3)	2.335(11)
Na(1)−O(4)	2.556(11)	Na(2)−O(1)	2.327(10)	Na(2)−O(1′)	2.452(10)	Na(2)−O(2′)	2.376(10)
Na(2)−O(5)	2.330(15)	Na(2)−O(6)	2.667(14)				
O(1)−C(1)	1.286(17)	O(2)−C(14)	1.294(18)	O(3)−C(27)	1.22(3)		
O(1)-Na(1)-O(2)	86.4(4)	O(1)-Na(1)-O(2′)	82.3(4)	O(1)-Na(1)-O(3)	131.1(4)	O(1)-Na(1)-O(4)	150.2(4)
O(2)-Na(1)-O(2′)	97.0(4)	O(2)-Na(1)-O(3)	116.6(4)	O(2)-Na(1)-O(4)	77.5(3)	O(2′)-Na(1)-O(3)	131.1(4)
O(2′)-Na(1)-O(4)	75.1(3)	O(3)-Na(1)-O(4)	78.7(4)	O(1)-Na(2)-O(1′)	97.6(4)	O(1)-Na(2)-O(2′)	85.4(4)
O(1)-Na(2)-O(5)	131.5(5)	O(1)-Na(2)-O(6)	77.5(3)	O(1)-Na(2′)-O(2)	83.9(4)	O(1′)-Na(2)-O(5)	128.4(5)
O(1′)-Na(2)-O(6)	75.4(3)	O(2′)-Na(2)-O(5)	110.9(5)	O(2′)-Na(2)-O(6)	150.9(4)	O(5)-Na(2)-O(6)	98.0(5)
Na(1)-O(1)-Na(2)	96.1(4)	Na(1)-O(1)-Na(2′)	91.8(4)	Na(2)-O(1)-Na(2′)	79.4(4)	Na(1)-O(2)-Na(1′)	79.4(3)
Na(1)-O(2)-Na(2′)	96.8(4)	Na(1)-O(4)-Na(1′)	72.6(4)	Na(2)-O(6)-Na(2′)	69.9(4)	Na(1)-O(1)-C(1)	118.0(8)
Na(2)-O(1)-C(1)	139.8(8)	Na(2′)-O(1)-C(1)	117.3(8)	Na(1)-O(2)-C(14)	142.9(9)	Na(1′)-O(2)-Na(2′)	94.3(4)
Na(1′)-O(2)-C(14)	122.1(9)	Na(1)-O(3)-C(27)	146.0(11)				
Na(1)-O(4)-C(40)	116.1(7)	Na(1)-O(4)-C(40′)	118.2(7)	Na(2)-O(5)-C(42)	129.9(16)	Na(2)-O(5)-C(45)	127.7(18)
Na(2)-O(6)-C(46)	120.8(12)	Na(2)-O(6)-C(46′)	114.0(12)				

0947-6539/00/0616-2998 $ 17.50+.50/0



Scheme 5. Formation of ketyl complexes **1** and **2** by C–C bond cleavage of the pinacol compound **7** via **8**.



Scheme 6. Isolation of calcium complexes **9** and **10** bearing two independent fluorenone ketyl ligands.

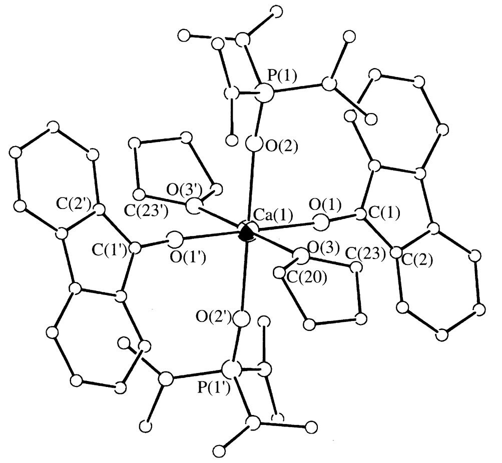


Figure 7. X-ray crystal structure of **9** (only one of the two independent molecules is shown for clarity)

Table 7). Upon further reaction with HMPA, one of the two THF ligands in **9** was replaced by an HMPA ligand, leading to formation of **10** (Scheme 6, Figure 8 and Table 8). Complex **10** could also be prepared in 84% yield by direct reaction of calcium with two equivalents of fluorenone and three equivalents of HMPA in THF. Further replacement of the THF ligand in **10** by HMPA did not occur when four or more equiv of HMPA was used, apparently owing to steric hindrance of the HMPA ligand.[9]

Benzophenone ketyl complexes: The reaction of benzophenone with one equivalent of sodium and two equivalents of HMPA yielded the sodium benzophenone ketyl complex **11** as blue crystals; it adopts a dimeric structure similar to its fluorenone analogue **2** (Scheme 7, Figure 9 and Table 9). However, when one equivalent of HMPA was used in this reaction, the trimeric complex **12**, rather than a simple benzophenone analogue of the tetrameric complex **3**, was obtained (Scheme 7 and Figure 10).[10] Similarly, the reaction of calcium with two equivalents of benzophenone in the presence of 3 or four equivalents of HMPA in THF yielded the five-coordinate trigonal bipyramidal complex **13** (Scheme 8, Figure 11 and Table 10), instead of a simple benzophenone analogue of the octahedral complex **9** or **10**. The radical carbon atoms in **11** and **13** are still in an sp^2-hybrid state, as in fluorenone ketyl complexes.[3d] However, the CO groups in **11** and **13** are not coplanar with any of the phenyl rings (Tables 9 and 10). The structural differences between **12** and **3** and between **13** and **10**

Table 7. Selected bond lengths [Å] and angles [°] of **9**.

Ca(1)–O(1)	2.208(15)	Ca(1)–O(2)	2.323(15)
Ca(1)–O(3)	2.447(18)	Ca(2)–O(4)	2.221(16)
O(1)–C(1)	1.33(3)		
O(1)-Ca(1)-O(1′)	180.0	O(1)-Ca(1)-O(2)	89.2(6)
O(1)-Ca(1)-O(2′)	90.8(6)	O(1)-Ca(1)-O(3)	88.7(6)
O(1)-Ca(1)-O(3′)	91.3(6)	O(2)-Ca(1)-O(2′)	180.0
O(2)-Ca(1)-O(3)	89.2(6)	O(2)-Ca(1)-O(3′)	90.8(6)
O(3)-Ca(1)-O(3′)	180.0	Ca(1)-O(1)-C(1)	171.9(13)
Ca(1)-O(2)-P(1)	165.7(10)	Ca(1)-O(3)-C(20)	125.1(17)
Ca(1)-O(3)-C(23)	121.2(18)		

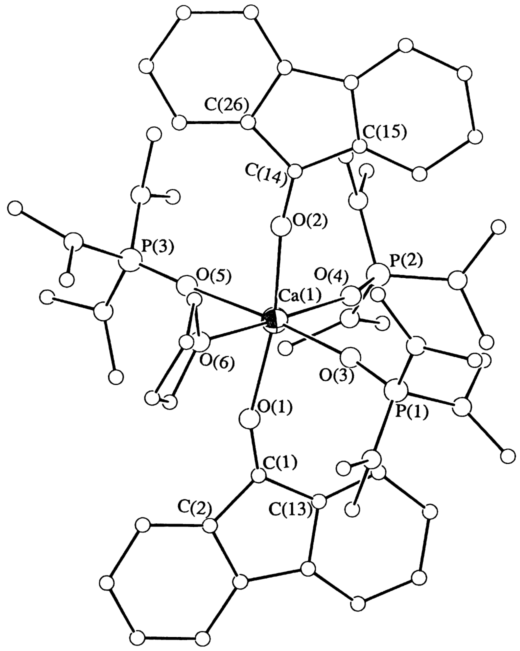


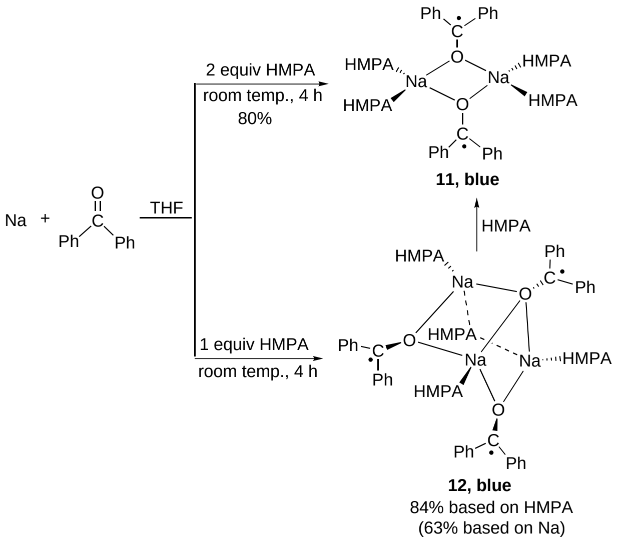
Figure 8. X-ray crystal structure of **10**.

Table 8. Selected bond lengths [Å] and angles [°] of **10**.

Ca(1)-O(1)	2.281(10)	Ca(1)-O(2)	2.234(11)
Ca(1)-O(3)	2.324(10)	Ca(1)-O(4)	2.328(8)
Ca(1)-O(5)	2.334(10)	Ca(1)-O(6)	2.487(11)
O(1)-C(1)	1.286(17)	O(2)-C(14)	1.280(18)
O(1)-Ca(1)-O(2)	168.5(4)	O(1)-Ca(1)-O(3)	92.6(4)
O(1)-Ca(1)-O(4)	97.6(4)	O(1)-Ca(1)-O(5)	86.6(4)
O(1)-Ca(1)-O(6)	86.5(4)	O(2)-Ca(1)-O(3)	89.6(4)
O(2)-Ca(1)-O(4)	93.5(4)	O(2)-Ca(1)-O(5)	89.7(4)
O(2)-Ca(1)-O(6)	82.6(4)	O(3)-Ca(1)-O(4)	92.9(4)
O(3)-Ca(1)-O(5)	172.1(4)	O(3)-Ca(1)-O(6)	82.7(4)
O(4)-Ca(1)-O(5)	95.0(4)	O(4)-Ca(1)-O(6)	174.1(4)
O(5)-Ca(1)-O(6)	89.4(4)	Ca(1)-O(1)-C(1)	158.4(10)
Ca(1)-O(2)-C(14)	169.7(10)	Ca(1)-O(3)-P(1)	171.4(7)
Ca(1)-O(4)-P(2)	159.3(6)	Ca(1)-O(5)-P(3)	174.5(6)
Ca(1)-O(6)-C(45)	122.0(9)	Ca(1)-O(6)-C(48)	123.3(11)

Table 9. Selected bond lengths [Å] and angles [°] of **11**.

Na(1)−O(1)	2.317(6)	Na(1)−O(1′)	2.269(6)
Na(1)−O(2)	2.260(6)	Na(1)−O(3)	2.261(8)
O(1)−C(1)	1.299(10)		
O(1)-Na(1)-O(1′)	87.8(2)	O(1)-Na(1)-O(2)	123.2(3)
O(1)-Na(1)-O(3)	110.3(3)	O(1′)-Na(1)-O(2)	121.3(3)
O(1′)-Na(1)-O(3)	115.7(3)	O(2)-Na(1)-O(3)	99.4(3)
Na(1)-O(1)-Na(1′)	92.2(2)	Na(1)-O(1)-C(1)	131.8(5)
Na(1′)-O(1)-C(1)	135.8(5)	Na(1)-O(2)-P(1)	150.8(4)
Na(1)-O(3)-P(2)	165.6(5)		
O(1)-C(1)-C(2)-C(8)/Ph(C_{2-7}) dihedral angle: 24			
O(1)-C(1)-C(2)-C(8)/Ph(C_{8-13}) dihedral angle: 15			



11, blue

12, blue
84% based on HMPA
(63% based on Na)

Scheme 7. Isolation of sodium benzophenone ketyl complexes **11** and **12**.

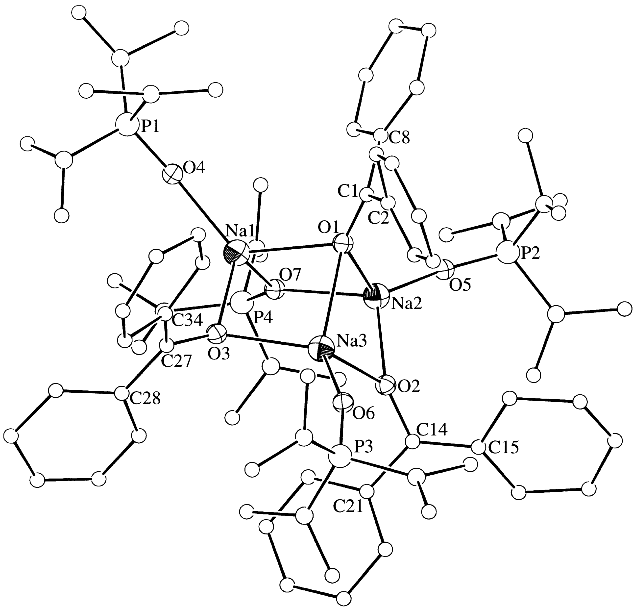


Figure 10. X-ray crystal structure of **12**.

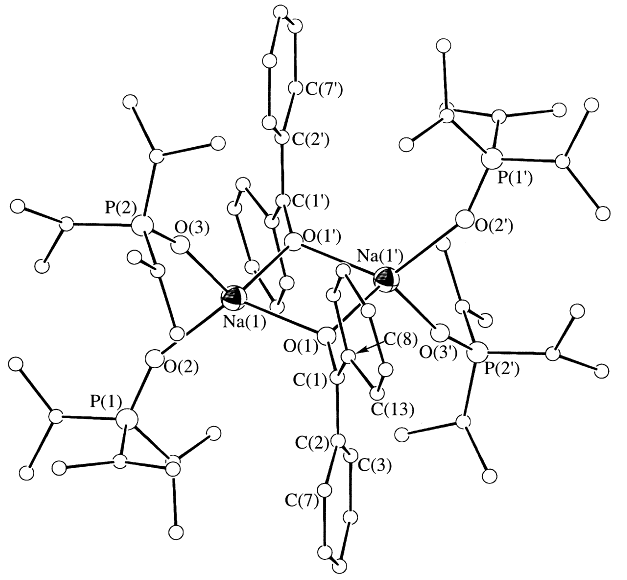
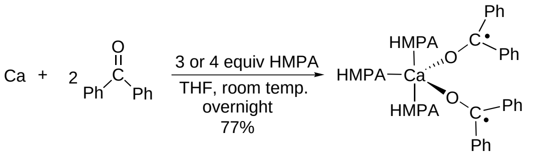


Figure 9. X-ray crystal structure of **11**.



13, blue

Scheme 8. Isolation of the calcium complex **13** bearing two independent benzophenone ketyl ligands.

must result from the structural difference between benzophenone ketyl and fluorenone ketyl; because the phenyl groups in a benzophenone ketyl unit can rotate, this unit may become sterically more demanding than a fluorenone ketyl unit. On the other hand, the lack of planarity in the whole benzophenone ketyl unit also explains why benzophenone ketyl is more reactive than fluorenone ketyl:[3d] stabilization of the radical through $p_z-\pi$ orbital interactions with the phenyl groups becomes more difficult in benzophenone ketyl than in the planar fluorenone ketyl.

Hydrogenation/protonation of ketyl complexes: The reactions of sodium fluorenone ketyl complex **2** and benzophenone ketyl complex **11** with 2-propanol and aqueous HCl were investigated, so that information on the elemental steps of the reduction of ketones by dissolving metals could be obtained.[2f] The typical reactivity of a ketyl species is reflected in the treatment of **2** with 2 N HCl which yielded

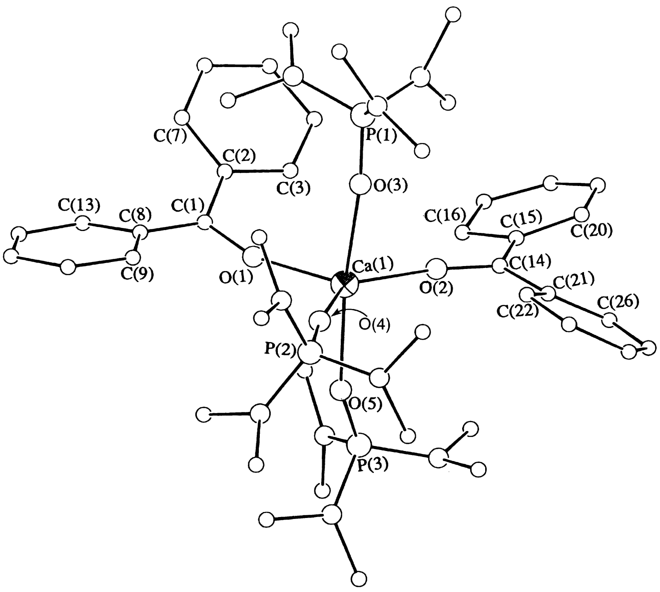
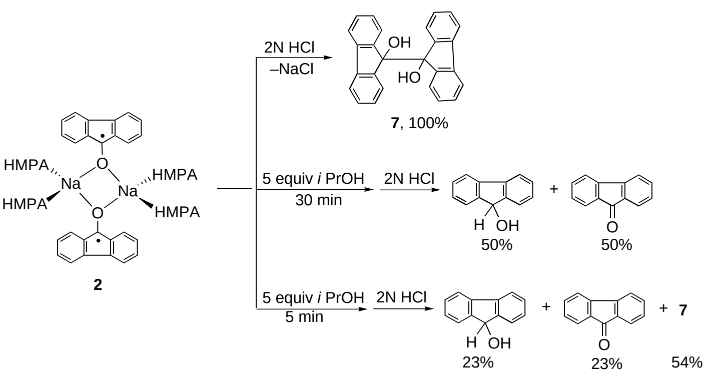


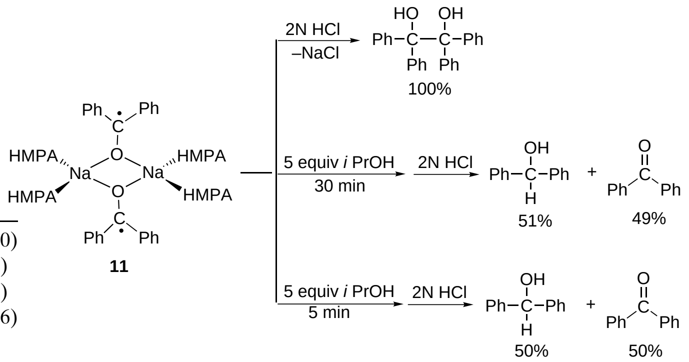
Figure 11. X-ray crystal structure of **13**.



Scheme 9. Hydrogenation/protonation of sodium fluorenone ketyl complex **2**.

Table 10. Selected bond lengths [Å] and angles [°] of **13**.

Ca(1)-O(1)	2.187(9)	Ca(1)-O(2)	2.206(10)
Ca(1)-O(3)	2.315(9)	Ca(1)-O(4)	2.286(8)
Ca(1)-O(5)	2.314(10)	P(1)-O(3)	1.446(9)
O(1)-C(1)	1.313(14)	O(2)-C(14)	1.308(16)
O(1)-Ca(1)-O(2)	114.2(4)	O(1)-Ca(1)-O(3)	95.0(4)
O(1)-Ca(1)-O(4)	110.2(4)	O(1)-Ca(1)-O(5)	94.5(4)
O(2)-Ca(1)-O(3)	89.4(4)	O(2)-Ca(1)-O(4)	135.6(4)
O(2)-Ca(1)-O(5)	90.0(4)	O(3)-Ca(1)-O(4)	86.2(3)
O(3)-Ca(1)-O(5)	169.8(4)	O(4)-Ca(1)-O(5)	87.1(4)
Ca(1)-O(1)-C(1)	162.5(8)	Ca(1)-O(2)-C(14)	160.0(10)
Ca(1)-O(3)-P(1)	165.6(6)	Ca(1)-O(4)-P(2)	171.9(7)
Ca(1)-O(5)-P(3)	154.3(6)		
O(1)-C(1)-C(2)-C(8)/Ph(C$_{2-7}$) dihedral angle:	16		
O(1)-C(1)-C(2)-C(8)/Ph(C$_{8-13}$) dihedral angle:	30		
O(2)-C(14)-C(15)-C(21)/Ph(C$_{15-20}$) dihedral angle:	20		
O(2)-C(14)-C(15)-C(21)/Ph(C$_{21-26}$) dihedral angle:	30		

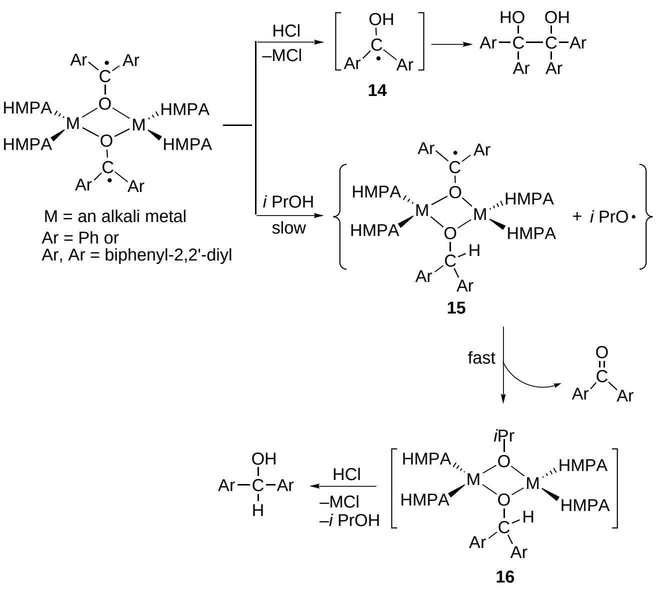


Scheme 10. Hydrogenation/protonation of sodium benzophenone ketyl complex **11**.

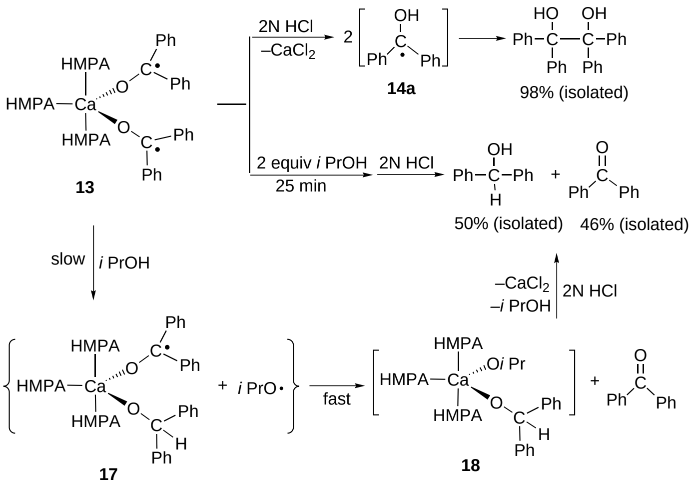
quantitatively the pinacol-coupling product **7** (Scheme 9). However, when **2** was stirred with 5 equiv of 2-propanol in THF for 30 min and then hydrolyzed with 2N HCl, fluorenol and fluorenone were obtained in a 1:1 molar ratio, whereas **7** did not form (Scheme 9). Similarly, hydrolysis of **11** afforded only benzopinacol, while the reaction of **11** with 2-propanol followed by hydrolysis with 2N HCl exclusively yielded benzhydrol and benzophenone in a 1:1 molar ratio (Scheme 10). If the reaction of fluorenone ketylcomplex **2** with 2-propanol was carried out for a shorter time (5 min), followed by hydrolysis with 2N HCl, a mixture of fluorenol, fluorenone, and **7** was obtained, in which the molar ratio of fluorenol to fluorenone was still 1:1 (Scheme 9). The higher reactivity of benzophenone ketyl is reflected in the analogous reaction of **11** with 2-propanol under the same conditions (5 min) which afforded only benzhydrol and benzophenone without formation of a coupling product (Scheme 10). These results suggest that the first step in the pinacol-coupling reaction of **2** or **11** is that of a proton (H^+) attacking the oxygen anion (O^-) of the ketyl unit, leading to formation of a hydroxymethyl radical species such as **14** (Scheme 11). Subsequent rapid dimerization of the hydroxymethyl radical yields the final 1,2-diol product. On the other hand, the formation of benzhydrol or fluorenol must proceed through hydrogen radical abstraction from 2-propanol by a ketyl radical species,[3d,h] while the formation of benzophenone or fluorenone obviously requires oxidation of the corresponding ketyl species. As shown in Scheme 11, hydrogen radical abstraction from 2-propanol by one of the two ketyl radicals in a dimeric ketyl complex such as **11** or **2** would yield the mixed ketyl/diarylmethoxide **15** and the *i*PrO• radical. Subsequent oxidation of the ketyl unit in **15** by the inner-sphere radical *i*PrO• could afford the ketone (benzophenone or fluorenone) and **16**, which, after hydrolysis, gives the alcohol (benzhydrol or fluorenol). The formation of benzophenone and benzhydrol, as well as that of fluorenone and fluorenol, in an approximately 1:1 molar ratio strongly suggests that the oxidation of the ketyl radical species in **15** by the inner-sphere radical *i*PrO• should be much faster than the hydrogen radical abstraction from 2-propanol by a ketyl radical species. Similarly, the reaction of the calcium bis(benzophenone ketyl) complex **13** with 2-propanol, followed by hydrolysis with 2N HCl, afforded benzhydrol and benzophenone, possibly through the intermediates **17** and **18**, as shown in Scheme 12.

Conclusion

By using HMPA as a stabilizing ligand, we successfully isolated and structurally characterized a series of alkali and alkaline-earth metal ketyl complexes, including those of the



Scheme 11. A plausible mechanism for the hydrogenation/protonation of dimeric ketyl complexes.



Scheme 12. Hydrogenation/protonation of bis(benzophenone ketyl) complex **13**.

well-known sodium benzophenone ketyl. The structures of these ketyl complexes are dependent on both the ion size of the metals and the structure of the ketones. Lithium fluorenone ketyl favors a dimeric structure (**1**), while potassium fluorenone ketyl prefers to form tetrameric aggregations (**4** and **5**). In the case of sodium, both dimeric (**2**) and tetrameric (**3**) fluorenone ketyl complexes can be isolated through adjustment of the ligand-to-substrate ratios. For sodium benzophenone ketyl, a trimeric complex (**12**), rather than a simple benzophenone analogue of the tetrameric **3**, is preferred, while a dimeric complex (**11**) is also isolable. In contrast to the one-electron reducing alkali metals, which yield ketyl complexes bearing one ketyl ligand per metal ion, the reactions of calcium metal with two equivalents of ketones afford the corresponding bis(ketyl) complexes, in which two independent ketyl ligands are bonded to one metal ion. Calcium fluorenone ketyl tends to form six-coordinated, octahedral structures (**9** and **10**), while calcium benzophenone ketyl favors a five-coordinate, trigonal-bipyramidal form (**13**). On the other hand, the formation of the ketyl complexes **1** and **2** from the 1,2-diol **7** demonstrates that deprotonation of a pinacol followed by C – C bond cleavage of the resultant pinacolate can constitute a new method for the synthesis of metal ketyls. The reactions of the ketyl complexes **2**, **11**, and **13** with 2-propanol and/or aqueous HCl have provided unprecedented insights into the elemental steps of the reduction of ketones by dissolving metals.

Experimental Section

General methods: All reactions were carried out under a dry and oxygen-free argon atmosphere by Schlenk techniques or under a nitrogen atmosphere in an Mbraun glovebox. The argon was purified by being passed through a Dryclean column (4-Å molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves (4 Å) catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer (Mbraun) to ensure both were always below 1 ppm. Samples for spectroscopic studies were prepared in the glovebox, and J. Young valve cells were used for measurements. UV/Vis spectra were recorded on a Shimadzu UV-2400PC spectrometer. ESR spectra were obtained on a Jeol JES FE 3AX X-band spectrometer and the *g* value was calibrated with DPPH (2,2-diphenyl-1-picrylhydrazyl). Elemental analyses were performed by the Chemical Analysis Laboratory of RIKEN. Solvents were distilled from sodium/benzophenone ketyl, degassed by the freeze – thaw method (three times) and dried over fresh Na chips in the glovebox. HMPA was distilled from sodium chips under reduced pressure, degassed by the freeze – thaw method (three times) and dried over molecular sieves (4 Å). 2-Propanol was degassed by the freeze – thaw method (three times) and dried over molecular sieves (4 Å). Benzophenone and fluorenone were purchased from Tokyo Kasei Co. and recrystallized from MeOH.

[Li($C_{13}H_8O$)(HMPA)$_2$]$_2$ (1): A solution of fluorenone (366 mg, 2.03 mmol) in THF (20 mL) was added to lithium shots (4 – 16 mesh, 14 mg, 2.03 mmol). A brown mixture was initially obtained, which changed to dark green after being stirred at room temperature for 7 h. Addition of HMPA (0.71 mL, 4.06 mmol) yielded a dark brown solution, which was then stirred for 20 min. After filtration and concentration under reduced pressure, diethyl ether was layered, to give **1** as brown crystals (808 mg, 0.74 mmol, 73 %). Reaction of **7** with two equivalents of $LiN(SiMe_3)_2$ in THF, followed by addition of four equivalents of HMPA, also afforded **1** in 75 % yield. UV/Vis (THF, 22 °C): $\lambda = 453$ nm ($\varepsilon = 6.3 \times 10^3$ cm^{-1}M^{-1}), 500 nm ($\varepsilon = 4.6 \times 10^3$ cm^{-1}M^{-1}), 518 nm ($\varepsilon = 4.7 \times 10^3$ cm^{-1}M^{-1}); ESR (THF, 22 °C): $g = 2.0030$; elemental analysis calcd (%) for $C_{50}H_{88}N_{12}O_6P_4Li_2$: C 55.04, H 8.13, N 15.40; found: C 55.08, H 8.20, N 15.58.

[Na($C_{13}H_8O$)(HMPA)$_2$]$_2$ (2): A solution of fluorenone (360 mg, 2.00 mmol) in THF (20 mL) was added to fresh sodium chips (46 mg, 2.00 mmol). The color of the mixture changed immediately to brown and finally to dark green after being stirred at room temperature for 4 h. Addition of HMPA (0.70 mL, 4.02 mmol) yielded a red-brown solution, which was then stirred for 20 min. After filtration and concentration under reduced pressure, hexane was layered to give **2** as brown crystals (910 mg, 0.81 mmol, 81 %). Reaction of 1,2-bis(biphenyl-2,2′-diyl)ethane-1,2-diol (**7**) with two equivalents of $NaN(SiMe_3)_2$ in THF followed by addition of four equivalents of HMPA also afforded **2** in 80 % yield. UV/Vis (THF, 22 °C): $\lambda = 460$ nm ($\varepsilon = 4.4 \times 10^3$ cm^{-1}M^{-1}), 530 nm ($\varepsilon = 6.1 \times 10^3$ cm^{-1}M^{-1}); ESR (THF, 22 °C): $g = 2.0030$; elemental analysis calcd (%) for $C_{50}H_{88}N_{12}O_6P_4Na_2$: C 53.47, H 7.90, N 14.96; found: C 53.00, H 8.06, N 14.78.

[Na($C_{13}H_8O$)(HMPA)]$_4$ (3): A solution of fluorenone (360 mg, 2.00 mmol) in THF (20 mL) was added to fresh sodium chips (46 mg, 2.00 mmol). The color of the mixture changed immediately to brown and finally to dark green after being stirred at room temperature for 4 h. Addition of HMPA (0.35 mL, 2.01 mmol) yielded a brown solution, which was then stirred for 20 min. After filtration and concentration under reduced pressure, hexane was layered to give **3** as greenish-brown crystals (597 mg, 0.39 mmol, 78 %). UV/Vis (THF, 22 °C): $\lambda = 460$ nm ($\varepsilon = 10.2 \times 10^3$ cm^{-1}M^{-1}), 530 nm ($\varepsilon = 16.0 \times 10^3$ cm^{-1}M^{-1}); ESR (THF, 22 °C): $g = 2.0030$; elemental analysis calcd (%) for $C_{76}H_{104}N_{12}O_8P_4Na_4$: C 59.68, H 6.85, N 10.99; found: C 58.82, H 6.89, N 10.59.

[K($C_{13}H_8O$)(HMPA)]$_4$(μ-HMPA) (4): A solution of fluorenone (180 mg, 1.00 mmol) in THF (15 mL) was added to fresh potassium chips (39 mg, 1.00 mmol). The resultant brown mixture was stirred at room temperature for 4 h, and HMPA (0.35 mL, 2.01 mmol) was then added. After being stirred for 20 min, the red-brown solution was filtered and concentrated under reduced pressure. Layering of diethyl ether and hexane yielded **4** as brown crystals (332 mg, 0.19 mmol, 75 %). UV/Vis (THF, 22 °C): $\lambda = 465$ nm ($\varepsilon = 10.2 \times 10^3$ cm^{-1}M^{-1}), 535 nm ($\varepsilon = 19.6 \times 10^3$ cm^{-1}M^{-1}); ESR (THF, 22 °C): $g = 2.0032$; elemental analysis calcd (%) for $C_{82}H_{122}N_{15}O_9P_5K_4$: C 55.54, H 6.93, N 11.85; found: C 55.07, H 6.99, N 11.65.

[K($C_{13}H_8O$)(HMPA)]$_4$(μ-THF) (5): A solution of fluorenone (184 mg, 1.02 mmol) in THF was added to fresh potassium chips (40 mg, 1.02 mmol). The resultant brown mixture was stirred at room temperature for 4 h, and HMPA (0.089 mL, 0.51 mmol) was then added. After being stirred for 20 min, the brown solution was filtered and concentrated under reduced pressure. Layering of hexane yielded **5** as dark brown crystals (152 mg, 0.09 mmol; 36 % based on K, 72 % based on HMPA). UV/Vis (THF, 22 °C): $\lambda = 465$ nm ($\varepsilon = 7.3 \times 10^3$ cm^{-1}M^{-1}), 535 nm ($\varepsilon = 13.0 \times 10^3$ cm^{-1}M^{-1}); ESR (THF, 22 °C): $g = 2.0032$; elemental analysis calcd (%) for $C_{80}H_{112}N_{12}O_9P_4K_4$: C 57.67, H 6.78, N 10.09; found: C 56.89, H 6.81, N 10.31.

$Na_4(\mu_3$-$C_{13}H_8O)_4(C_{13}H_8O)_2(THF)_2(\mu$-$THF)_2$ (6): A solution of fluorenone (400 mg, 2.22 mmol) in THF was added to fresh sodium chips (34 mg, 1.48 mmol). The color of the mixture changed immediately to brown and finally to dark-green after being stirred at room temperature for 4 h. After filtration, the solvent was evaporated to give a green crystalline product which after recrystallization from diethyl ether afforded **6** as green crystals (460 mg, 0.31 mmol, 85 %). UV/Vis (THF, 22 °C): $\lambda = 460$ nm ($\varepsilon = 13.6 \times 10^3$ cm^{-1}M^{-1}), 530 nm ($\varepsilon = 16.0 \times 10^3$ cm^{-1}M^{-1}); ESR (THF, 22 °C): $g = 2.0030$; IR (THF, 22 °C): $\tilde{\nu}_{CO} = 1720$ cm^{-1}; elemental analysis calcd (%) for $C_{94}H_{80}O_{10}Na_4$: C 77.25, H 5.52; found C 77.46, H 5.75.

$Ca(C_{13}H_8O)_2(HMPA)_2(THF)_2$ (9): CH_2I_2 (2 % mol) in THF (1 mL) was added to calcium chips (31 mg, 0.77 mmol). After the mixture was stirred for 2 h at room temperature to activate the metal surface, HMPA (0.27 mL, 1.54 mmol) was added. Addition of a solution of fluorenone (279 mg, 1.4 mmol) in (10 mL) yielded a brown mixture within a few minutes. After being stirred at room temperature overnight, the brown solution was filtered and concentrated under reduced pressure. Addition of hexane precipitated **9** (549 mg, 0.61 mmol, 79 %) as dark brown blocks. UV/Vis (THF, 22 °C): $\lambda = 453$ nm ($\varepsilon = 4.5 \times 10^3$ cm^{-1}M^{-1}), 490 nm ($\varepsilon = 2.6 \times 10^3$ cm^{-1}M^{-1}); ESR (THF, 22 °C): $g = 2.0030$; elemental analysis calcd (%) for $C_{46}H_{68}N_6O_6P_2Ca$: C 61.18, H 7.59, N 9.31; found C 60.65, H 7.53, N 9.76.

$Ca(C_{13}H_8O)_2(HMPA)_3(THF)$ (10): CH_2I_2 (2 % mol) in THF (1 mL) was added to calcium chips (21 mg, 0.52 mmol). After the mixture was stirred for 2 h at room temperature (to activate the metal surface), HMPA (0.36 mL, 2.08 mmol) was added. Addition of a solution of fluorenone (189 mg, 1.05 mmol) in THF (10 mL) yielded a brown mixture within a few minutes. After being stirred at room temperature overnight, the brown solution was filtered and concentrated under reduced pressure. Addition of hexane precipitated **10** (440 mg, 0.44 mmol, 84 %) as dark brown blocks. UV/Vis (THF, 22 °C): $\lambda = 453$ nm ($\varepsilon = 4.2 \times 10^3$ cm^{-1}M^{-1}), 490 nm ($\varepsilon = 2.4 \times 10^3$ cm^{-1}M^{-1}); ESR (THF, 22 °C): $g = 2.0030$; elemental analysis calcd (%) for $C_{48}H_{78}N_9O_6P_3Ca$: C 57.07, H 7.78, N 12.48; found: C 56.94, H 7.82, N 12.73.

[Na($C_{13}H_{10}O$)(HMPA)$_2$]$_2$ (11): HMPA (0.42 mL, 2.42 mmol) and a solution of benzophenone (221 mg, 1.21 mmol) in THF (10 mL) were successively added to fresh sodium chips (28 mg, 1.21 mmol). The resultant blue mixture was stirred at room temperature for 4 h, during which all sodium chips disappeared. After filtration and concentration under reduced pressure, hexane was layered to give **11** as blue blocks (545 mg, 0.48 mmol, 80 %). UV/Vis (THF, 22 °C): $\lambda = 675$ nm ($\varepsilon = 5.7 \times 10^3$ cm^{-1}M^{-1}); ESR (THF, 22 °C): $g = 2.0030$; elemental analysis calcd (%) for $C_{50}H_{92}N_{12}O_6P_4Na_2$: C 53.28, H 8.23, N 14.91; found: C 53.01, H 8.29, N 15.17.

$Na_3(C_{13}H_{10}O)_3(HMPA)_4$ (12): HMPA (0.15 mL, 0.87 mmol) and a solution of benzophenone (158 mg, 0.87 mmol) in THF (10 mL) were successively added to fresh sodium chips (20 mg, 0.87 mmol). The resultant blue mixture was stirred at room temperature for 4 h, during which all sodium chips disappeared. After filtration and concentration under reduced pressure, hexane was layered to yield **12** as blue blocks (242 mg, 0.18 mmol, 63 % based on Na, 84 % based on HMPA). UV/Vis (THF, 22 °C): $\lambda = 675$ nm ($\varepsilon = 6.5 \times 10^3$ cm^{-1}M^{-1}); ESR (THF, 22 °C): $g = 2.0030$; elemental analysis calcd (%) for $C_{63}H_{102}N_{12}O_7P_4Na_3$: C 56.79, H 7.72, N 12.61; found: C 56.40, H 7.93, N 12.68.

$Ca(C_{13}H_{10}O)_2(HMPA)_3$ (13): CH_2I_2 (2 % mol) in THF (1 mL) was added to calcium chips (28 mg, 0.7 mmol). After the mixture was stirred for 2 h at room temperature to activate the metal surface, HMPA (0.36 mL, 2.08 mmol) was added. Addition of a solution of benzophenone (255 mg, 1.40 mmol) in THF (10 mL) yielded a blue mixture within a few minutes. After being stirred at room temperature overnight, the blue solution was filtered and concentrated under reduced pressure. Addition of hexane precipitated **13** as blue blocks (510 mg, 0.54 mmol, 77 %). UV/Vis (THF, 22 °C): $\lambda = 635$ nm ($\varepsilon = 3.8 \times 10^3$ cm^{-1}M^{-1}); ESR (THF, 22 °C): $g = 2.0028$; elemental analysis calcd (%) for $C_{44}H_{74}N_9O_5P_3Ca$: C 56.09, H 7.92, N 13.38; found: C 55.81, H 8.03, N 13.33.

A typical procedure for alcoholysis/hydrolysis of ketyls: To a solution of a ketyl complex in THF was added 2–5 equivalents of 2-propanol. Usually, the typical color of a ketyl species faded gradually. then 2 N HCl was added. The mixture was extracted with diethyl ether and dried over Na_2SO_4. The organic products were separated by chromatography (silica gel) and identified by ^{1}H NMR comparison with authentic samples. The ^{1}H NMR spectra of the product mixture could also be easily assigned by comparison with authentic samples.

X-ray crystallographic studies: Crystals for X-ray analyses were obtained as described in the preparations. The crystals were manipulated in the glovebox under a microscope mounted on the glovebox window, and were sealed in thin-walled glass capillaries. Data were collected on a Mac Science MXC3 K diffractometer (20 °C, $Mo_{K\alpha}$ radiation, graphite monochromator, $\lambda = 0.71073$ Å, ω-2θ scan), and were corrected for Lorentzian and polarization effects and X-ray absorption effects. Lattice constants and orientation matrices were obtained by least-squares refinement of 25 reflections with $25° \leq 2\theta \leq 35°$. Three reflections were monitored periodically as a check for crystal decomposition or movement; no significant decay or movement was observed. The observed systematic absences were consistent with the space groups given in Table 11. The structures were solved by direct methods with SIR92 in the Crystan-GM software package. Hydrogen atoms in **1** and **2** were either located from the difference Fourier maps, or placed at calculated positions. Attempts to locate the hydrogen atoms in other complexes were not made. Refinements against $|F|$ were performed anisotropically for non-hydrogen atoms and isotropically for hydrogen atoms by the block-diagonal least-squares method. Neutral atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*.[11] The residual electron densities (< 1e Å^{-3}) were of no chemical significance. Crystal data, data collection and processing parameters are given in Table 11. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-139185–CCDC-139194. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was partly supported by a grant-in-aid from the Ministry of Education of Japan. We are grateful to Drs. M. Hoshino and Q. Meng for ESR measurements.

---

[1] For early examples of the formation of ketyl species, see: a) F. Bechman, T. Paul, *Justus Liebigs Ann. Chem.* **1891**, *266*, 1; b) W. Schlenk, T. Weichel, *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 1182; c) W. Schlenk, A. Thal, *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 2840.

[2] For recent reviews on metal ketyl-mediated organic synthesis, see: a) G. A. Molander, *Acc. Chem. Res.* **1998**, *31*, 603; b) T. Skrydstrup,

Table 11. Summary of crystallographic data for **1–6**, **9–11**, and **13**.

	1	**2**	**3**	**4**	**5**
formula	$C_{50}H_{88}N_{12}O_6P_4Li_2$	$C_{50}H_{88}N_{12}O_6P_4Na_2$	$C_{76}H_{104}N_{12}O_8P_4Na_4$	$C_{82}H_{122}N_{15}O_9P_5K_4$	$C_{80}H_{112}N_{12}O_9P_4K_4$
f_w	1091.11	1123.21	1529.61	1773.24	1666.15
cryst syst	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)	$P2_1/a$ (no. 14)
a [Å]	10.929(1)	11.152(5)	29.195(7)	18.428(5)	22.010(5)
b [Å]	11.480(3)	12.398(2)	11.938(4)	24.208(7)	24.275(5)
c [Å]	13.799(2)	12.492(2)	27.942(7)	23.894(8)	17.462(4)
α [°]	113.38(1)	107.56(1)			
β [°]	102.68(1)	103.11(2)	117.99(2)	112.64(2)	102.19(2)
γ [°]	87.01(2)	95.53(2)			
V [Å^3]	1549.2(5)	1598.1(7)	8599(4)	9838(5)	9120(4)
Z	1	1	4	4	4
ρ_{calcd} [g cm^{-3}]1.17	1.17	1.18	1.20	1.21	
2θ range [°]	3–55	3–55	3–55	3–55	3–55
μ [m^{-1}]	1.688	1.774	1.585	3.374	3.150
no. of reflns collcd	6903	10413	8404	18639	17448
no. of unique reflns	6395	7351	7581	17192	16055
no. of reflns for refinement ($I_o \geq x\,\sigma(I_o)$)	3061 ($x=3$)	3864 ($x=3$)	1640 ($x=3$)	8284 ($x=3$)	7061 ($x=2$)
no. of variables	447	366	267	1036	982
R_{int}	0.03	0.07	0.10	0.08	0.08
R [%]	5.60	6.64	10.49	7.93	8.58
R_w [%]	5.64	6.68	11.79	8.59	9.39
	6 · C_6H_6	2[**9**]	**10**	**11**	**13**
formula	$C_{100}H_{86}O_{10}Na_4$	$C_{92}H_{136}N_{12}O_{12}P_4Ca_2$	$C_{48}H_{78}N_9O_6P_3Ca$	$C_{50}H_{92}N_{12}O_6P_4Na_2$	$C_{44}H_{74}N_9O_5P_3Ca$
f_w	1539.75	1806.24	1010.22	1127.24	942.14
cryst syst	monoclinic	triclinic	monoclinic	triclinic	triclinic
space group	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a [Å]	20.279(5)	10.248(2)	18.771(4)	10.960(2)	10.953(2)
b [Å]	18.718(5)	13.846(8)	13.876(3)	12.867(3)	11.812(2)
c [Å]	21.814(6)	18.268(6)	21.883(5)	13.416(5)	22.360(5)
α [°]		94.33(4)		113.95(3)	93.09(2)
β [°]	93.33(2)	97.73(2)	90.22(2)	107.96(2)	93.36(2)
γ [°]		93.96(3)		73.04(2)	108.92(2)
V [Å^3]	8266(4)	2553(2)	5700(2)	1614.3(9)	2724
Z	4	1	4	1	2
ρ_{calcd} [g cm^{-3}]	1.24	1.18	1.18	1.16	1.15
2θ range [°]	3–55	3–55	3–55	3–50	3–55
μ [cm^{-1}]	0.908	2.149	2.628	1.758	2.432
no. of reflns collcd	8003	9690	11126	6112	10383
no. of unique reflns	5529	8994	10046	4387	9566
no. of reflns for refinement ($I_o \geq x\,\sigma(I_o)$)	3556 ($x=2$)	3114 ($x=2$)	4269 ($x=2.5$)	2731 ($x=3$)	3929 ($x=2$)
no. of variables	510	448	604	334	559
R_{int}	0.06	0.10	0.08	0.05	0.06
R [%]	8.71	11.57	7.76	8.40	8.67
R_w [%]	9.70	12.86	8.53	9.11	8.90

Angew. Chem. Int. Ed. Engl. **1997**, *36*, 345. *Angew. Chem.* **1997**, *109*, 355; c) G. A. Molander, C. R. Harris, *Chem. Rev.*, **1996**, *96*, 307; d) T. Wirth, *Angew. Chem. Int. Ed. Engl.*, **1996**, *35*, 61; e) A. Fürstner, *Angew. Chem. Int. Ed. Engl.*, **1993**, *32*, 164. *Angew. Chem.* **1993**, *105*, 171. f) J. W. Huffman in *Comprehensive Organic Synthesis, Vol. 8* (Eds.: B. M. Trost, I. Fleming), Pergamon, New York, **1991**, chapter 1.4; g) G. M. Robertson in *Comprehensive Organic Synthesis*, *Vol. 3* (Eds.: B. M. Trost, I. Fleming), Pergamon, New York, **1991**, chapter 2.6; h) J. E. McMurry, *Chem. Rev.* **1989**, *89*, 1513.

[3] For structurally characterized ketyl complexes, see: a) Z. Hou, Y. Wakatsuki, *Chem. Eur. J.* **1997**, *3*, 1005; b) Z. Hou, Y. Wakatsuki, *Top. Organomet. Chem.* **1999**, *2*, 233; c) Z. Hou, A. Fujita, T. Koizumi, H. Yamazaki, Y. Wakatsuki, *Organometallics* **1999**, *18*, 1979; d) Z. Hou, A. Fujita, Y. Zhang, T. Miyano, H. Yamazaki, Y. Wakatsuki, *J. Am. Chem. Soc.* **1998**, *120*, 754; e) Z. Hou, X. Jia, Y. Wakatsuki, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1292; *Angew. Chem.* **1997**, *109*, 1348; f) W. Clegg, C. Eaborn, K. Izod, P. O'Shaughnessy, J. D. Smith, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2815; *Angew. Chem.* **1997**, *109*, 2925; g) J. Takats, *J. Alloys Compd.* **1997**, *249*, 51; h) Z. Hou, A. Fujita, H. Yamazaki, Y. Wakatsuki, *J. Am. Chem. Soc.* **1996**, *118*, 7843; i) Z. Hou, A. Fujita, H. Yamazaki, Y. Wakatsuki, *J. Am. Chem. Soc.* **1996**, *118*, 2503; j) Z. Hou, T. Miyano, H. Yamazaki, Y. Wakatsuki, *J. Am. Chem. Soc.* **1995**, *117*, 4421; k) H. Bock, H. -F. Herrmann, D. Fenske, H. Goesmann, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1067; *Angew. Chem.* **1988**, *100*, 1125.

[4] For example, sodium benzophenone ketyl is familiar to almost every chemist for its use in dehydration and deoxygenation of ethereal solvents.

[5] All alkali and alkaline-earth metal ketyl complexes reported in this paper showed well-resolved *X*-band ESR spectra and UV/Vis spectra (see Experimental Section), which were similar to those previously reported for the corresponding ketyl species generated in situ. For examples of spectroscopic studies on alkali and alkaline-earth metal ketyl species, see: a) P. H. Rieger, G. K. Fraenkel, *J. Chem. Phys.* **1962**,

37, 2811; b) N. Hirota, S. I. Weissman, *J. Am. Chem. Soc.* **1964**, *86*, 2538; c) N. Hirota, *J. Am. Chem. Soc.* **1967**, *89*, 32; d) K. Nakamura, N. Hirota, *Chem. Phys. Lett.* **1969**, *3*, 134; e) S. W. Mao, N. Hirota, *Chem. Phys. Lett.* **1973**, *22*, 26; f) S. W. Mao, K. Nakamura, N. Hirota, *J. Am. Chem. Soc.* **1974**, *96*, 5341.

[6] H. R. Luss, D. L. Smith, *Acta Crystallogr. Sect. B* **1972**, *28*, 884.

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

[8] For previous examples of complexes bearing bridging THF ligands, see: a) Z. Hou, A. Fujita, H. Yamazaki, Y. Wakatsuki, *Chem. Commun.* **1998**, 669; b) S. Brooker, F. T. Edelmann, T. Kottke, H. W. Roesky, G. M. Scheldrick, D. Stalke, K. H. Whitmire, *J. Chem. Soc. Chem. Commun.* **1991**, 144; c) Q. Shen, M. Qi, Y. Lin, *J. Organomet. Chem.* **1990**, *399*, 247.

[9] a) Z. Hou, Y. Wakatsuki, *J. Chem. Soc., Chem. Commun.* **1994**, 1205; b) Z. Hou, Y. Zhang, Y. Wakatsuki, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 149.

[10] Crystal data for **12**: $C_{63}H_{102}N_{12}O_7P_4Na_3$, $F_w = 1332.46$, monoclinic, space group $P2_1/c$ (No. 14), $a = 12.2681(6)$, $b = 25.389(2)$, $c = 25.032(1)$ Å, $\beta = 93.445(4)^\circ$, $V = 7782.9(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.14\,g\,cm^{-3}$. Since the crystal was very small, the diffraction data (collected on an Enraf-Nonius CAD4 diffractometer with a rotating Cu anode) were not good enough for satisfactory full refinement of the structure. Nevertheless, the connectivity of the whole molecule was unequivocally determined.

[11] D. T. Cromer, J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch, Birmingham, **1974**.

Received: January 24, 2000 [F2257]