

# More Arrows in the Quiver: New Pathways and Old Problems with Heavy Alkaline Earth Metal Diphenylmethanides

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**Abstract:** Progress in the field of  $\sigma$ -bonded alkaline earth organometallics has been handicapped by numerous complications, such as high reactivity, low solubility, and the limited availability of suitable starting materials. Here we present two synthetic methods, hydrocarbon elimination and desilylation, as alternative routes into this chemistry. A novel barium diphenylmethanide was prepared using these routes delineating that both methods provide a powerful, versatile synthetic access route to an extended library of organometallic alkaline earth derivatives.

**Keywords:** alkaline earth metals · arene ligands · ether cleavage · organometallics · structure elucidation

## Introduction

The chemistry of  $\sigma$ -bonded organometallic compounds of the heavy alkaline earth metals calcium, strontium, and barium has been the subject of considerable recent attention.<sup>[1]</sup> This is a result of the wide range of applications for these previously ignored compounds, and what was a scarcely investigated field even a decade ago is now being approached with significant interest. The number of well-characterized compounds is increasing steadily; a particular success has been the stabilization of these metal centers using cyclopentadienyl ligands.<sup>[2,3]</sup> In contrast,  $\sigma$ -bonded compounds remain scarce, owing largely to the synthetic difficulties encountered, most notably their high reactivity and sparse solubility in common aprotic solvents. Because of these challenges, we are interested in broadening the available synthetic pathways to these compounds.

Several possible synthetic techniques are available for the preparation of alkaline earth organometallics. Examples include direct metallation, salt elimination, and transamination. Direct metallation necessitates highly active and pure alkaline earth metals [Eq. (1)], in which R = alkyl, aryl; act = activated; and M = Ca, Sr, Ba.



Activation methods include the distillation of the metals,<sup>[4]</sup> the reduction of metal iodides with alkali metals,<sup>[5]</sup> or by dissolving the metals in anhydrous, deoxygenated liquid ammonia.<sup>[6]</sup> The difficulty in employing direct metallation is not just limited to the activation of the metal; very often the reaction products are insoluble without careful choice of a co-solvent or donor system, and the use of a sterically demanding ligand system. While this route has not yet led to structurally authenticated organometallic species, it has been employed with some success.<sup>[7,8]</sup>

By far the most commonly employed route in the preparation of alkaline earth organometallics is salt elimination. Usually the potassium salt of the desired ligand is utilized in conjunction with an alkaline earth metal iodide to afford the desired product [Eq. (2)], in which R = alkyl, aryl; M = Ca, Sr, Ba; A = Na, K.

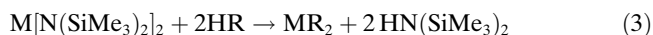


This method, while powerful, has the drawback that the final product may be potentially contaminated with alkali metal halides. This can be minimized with careful choice of solvent, alkali metal, and halide, but the separation of products and consequent purity remains a concern. In addition, the preparation of most potassium salts involves the use of “superbase” chemistry, which employs an *n*BuLi/KOtBu mixture that may leave residual lithium alkoxide to interfere with later reactions.<sup>[9]</sup> Also, the high reactivity of the potassium salts limits the solvent choice, since ether cleavage chemistry is a frequent occurrence.

Transamination chemistry has also been employed successfully. The ready availability of the alkaline earth metal amides  $\text{M}(\text{N}(\text{SiMe}_3)_2)_2$  [M = Ca, Sr, Ba],<sup>[10–12]</sup> their solubility in a host of different solvent systems, and the easy removal

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of  $\text{HN}(\text{SiMe}_3)_2$  make this an attractive route [Eq. (3)], in which  $\text{R} = \text{alkyl, aryl}$  and  $\text{M} = \text{Ca, Sr, Ba}$ .<sup>[13]</sup>



A limiting factor in this reaction is the  $\text{p}K_a$  range of the hydrocarbon sources: only those with a higher acidity than  $\text{HN}(\text{SiMe}_3)_2$  can be used. Highly acidic substrates, however, induce a competing side reaction involving protonation of the liberated secondary amine under formation of the silylated hydrocarbon and primary amine [Eq. (4)], in which  $\text{R} = \text{alkyl, aryl}$ .

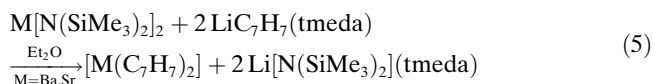


This side reaction may be suppressed by careful and dilute addition of the acid.<sup>[14]</sup> An additional complication stems from the basic properties of the amide starting material that may promote ether cleavage. This may be avoided by using low-temperature conditions. Finally, the relatively low  $\text{p}K_a$  for the amines is close to those of many ligand systems currently under investigation. The resulting slow metallation rate may allow for the formation of undesired side products.<sup>[1,15]</sup>

With a vested interest in broadening the number of synthetic strategies available to the alkaline earth metal chemist, we endeavored to make available alternative methodologies for the clean, facile preparation of organometallic complexes of calcium, strontium, and barium. Here we present two powerful entries into this field of chemistry, namely an arene elimination route with strontium and barium dibenzyl derivatives, and a desilylation pathway based on recent success with related alkali metal systems. An examination of the strengths and shortcomings of these new synthetic routes is included. We present four new alkaline earth metal diphenylmethanides resulting from these reactions and explore their structural characteristics.

## Results

**Synthetic aspects:** The development of a facile synthesis of dibenzylbarium by Harder and co-workers provides a potent reagent for the metallation of an array of acidic ligands<sup>[16]</sup> [Eq. (5)].



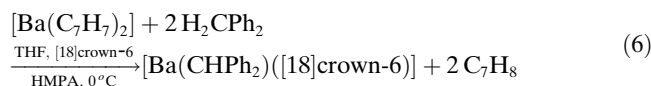
Although dibenzylbarium may also be prepared through treatment of alkoxides with benzylolithium,<sup>[16]</sup> the method shown in Equation (5) is preferred due to the formation of the highly soluble lithium amide, which is more easily separated from the dibenzyl target compound than lithium alkoxide. This straightforward preparation cleanly affords strontium and barium dibenzyl derivatives. Although the original reference reports that no single product is isolable for the strontium and calcium congeners,<sup>[16]</sup> we had no diffi-

culty in preparing clean dibenzyl strontium. While the homoleptic, unsubstituted calcium system still eludes isolation, there are several examples of fully characterized substituted dibenzyl systems that show great promise and flexibility, and it is likely these could be applied in similar reaction schemes.<sup>[17–19]</sup>

While previous work regarding dibenzyl alkaline earth metal compounds was concerned with their function as polymerization initiators,<sup>[16,18–21]</sup> this class of compounds is ideally suited to be starting materials for the preparation of a variety of organometallic strontium and barium compounds. Due to the high basicity of the starting material ( $\text{p}K_a(\text{toluene}) \cong 43$ ), a wide array of ligand systems can be easily metallated. The resulting large  $\text{p}K_a$  differences between toluene and the proton source should drive the reaction and help prevent undesirable side reactions. However, care must be taken in selecting reaction conditions, as ether scission side reactions are commonly observed.<sup>[22,23]</sup> The drawback of this reaction route includes the lack of flexibility in solvent choice, as the dibenzyl reagents are only soluble in THF, a solvent well known to suffer from ether cleavage reactions with strongly basic anions. Because of this, careful monitoring of the reaction conditions is necessary.

Previous work applying hydrocarbon elimination afforded the clean, high-yield preparation of triphenylmethanides  $[\text{M}(\text{CPh}_3)_2([\text{18}]\text{crown-6})(\text{hmpa})_2]$  (HMPA = Hexamethylphosphoramide) and acetylides  $[\text{M}(\text{CC-4}t\text{BuC}_6\text{H}_4)_2([\text{18}]\text{crown-6})]$   $[\text{M} = \text{Sr, Ba}]$ ,<sup>[15,22]</sup> prompting us to extend these studies towards the less acidic diphenylmethanide system.

Treatment of two equivalents of diphenylmethane with dibenzylbarium in THF at 0°C under addition of a complexing crown ether led to the contact ion pair  $[\text{Ba}(\text{CHPh}_2)_2([\text{18}]\text{crown-6})]$  [**1**; Eq. (6)], a rare example of a compound displaying a  $\sigma$ -type bond between the metal and ligand.



This desirable result was unexpected for several reasons. First, the existence of such a contact structure, while proposed earlier, was deemed too reactive in the case of the trityl anion to exist in close proximity to the crown ether; ether cleavage chemistry resulting in vinyl ethers was reported in all instances.<sup>[22]</sup> While no contact structure exists for the heavy alkaline earth metal trityl systems, the lower steric demand and higher negative charge on the  $\alpha$ -carbon atom of the diphenylmethanide ligand as compared to the trityl is responsible for the different ion association. Also noteworthy was the fact that crystals suitable for X-ray diffraction studies could be obtained only after recrystallization from *hot* THF. No indication of ether cleavage chemistry under the formation of enolate was observed.

If this reaction is carried out in the presence of HMPA and crown ether, separated cations and anions are observed ( $[\text{Ba}(\text{hmpa})_6][\text{CHPh}_2]_2$  **2**). The barium cation is stabilized by the presence of six HMPA molecules, and no crown ether coordination is observed due to the presence of the strong

donor HMPA. This type of charge separation utilizing either HMPA or crown ether/HMPA combinations is well established for cations of this type and complexes containing the  $[M(\text{hmpa})_6]^{2+}$  or  $[M(\text{hmpa})_2([18]\text{crown-6})]^{2+}$  ( $M = \text{Sr}, \text{Ba}$ ) ions have been observed.<sup>[22,24–26]</sup> While no satisfactory refinement of the X-ray crystal structure was possible due to repeatedly poor crystal quality, a preliminary crystallographic analysis in conjunction with  $^1\text{H}$  and  $^{13}\text{C}$  spectroscopic data leaves no doubt as to the overall geometry and composition of the complex (Figure 1).

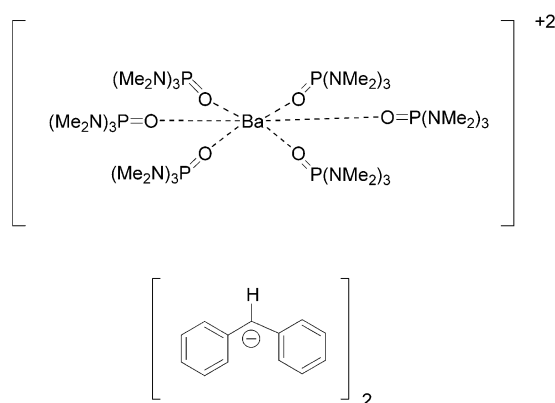
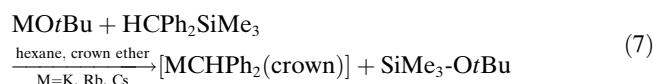


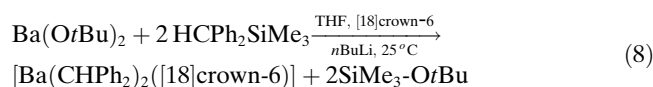
Figure 1. Schematic representation of compound 2.

Recent results on alkali metal diphenylmethanides suggested a synthetic pathway which might avoid the strongly basic conditions that exist in the hydrocarbon elimination reaction.<sup>[15]</sup> Reactions between heavy alkali metal *tert*-butoxides and trimethylsilyl-substituted diphenylmethane led to the elimination of silyl ether and concomitant formation of alkali diphenylmethanide in the presence of coordinating donors [Eq. (7)].<sup>[15]</sup>



This scheme was derived from the previously reported preparation of potassium silanides or phosphides, which are available by treatment of trimethylsilyl-substituted silanes and phosphines with potassium *tert*-butoxide.<sup>[27,28]</sup> This suggests that similar chemistry might be possible for the alkaline earth metals, thus providing access to a milder, more selective method towards the alkaline earth metal target compounds.

Utilizing this reaction scheme initially did not lead to the desired products; it was not until the addition of *n*BuLi that the reaction proceeded smoothly [Eq. (8)].

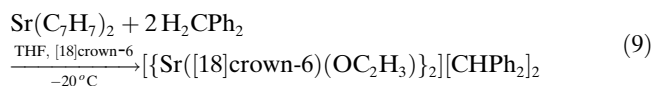


The exact role of the lithium reagent remains uncertain, but two different reaction mechanisms can be discussed.

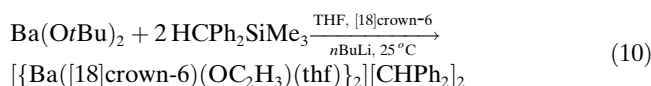
The first is desilylation, which would afford the target compounds **1** and **2** in conjunction with silyl ether, as identified in the  $^1\text{H}$  NMR analysis of the reaction products. However, this scheme does not explain the necessary presence of *n*BuLi. In addition, the formation of lithium *tert*-butoxide, which was also identified in the  $^1\text{H}$  NMR spectra of the reaction products cannot be rationalized. A second pathway, transmetalation, would involve the formation of dibutylbarium or the heteroleptic butylbarium *tert*-butoxide from the reaction of barium *tert*-butoxide with *n*BuLi. The butylbarium would then react with the silylated diphenylmethane under formation of the silylated dibenzyl organometallic and butane. This reaction scheme would explain the formation of lithium *tert*-butoxide, but would not allow for the formation of compounds **1** and **2** and the silyl ether.

Current work in the laboratory is focused on these mechanistic questions and an exploration of the general utility of this synthetic route towards other primary or secondary alkaline earth organometallics.

Attempts to synthesize the strontium analogue to the contact barium structure **1** by the hydrocarbon elimination route did not yield a crystalline product, and concentration of the mother liquor to approximately 5 mL led to an ether cleavage product by attack of the THF solvent, even at the storage temperature of  $-20^\circ\text{C}$ . The dimeric heteroleptic enolate  $[\{\text{Sr}([18]\text{crown-6})(\text{OC}_2\text{H}_5)_2\}]_2[\text{CHPh}_2]_2$  (**3**) is obtained reproducibly in reasonable yield [Eq. (9)].



While the reaction of barium *tert*-butoxide with the silylated diphenylmethane and butyllithium afforded compound **1** in good yield and purity, the same reaction affords the ether-cleaved product **4** if the reaction solution is concentrated significantly to initialize crystallization, yielding the barium enolate  $[\{\text{Ba}([18]\text{crown-6})(\text{OC}_2\text{H}_5)(\text{thf})\}]_2[\text{CHPh}_2]_2$  (**4**) [Eq. (10)].



Despite different starting materials, the fact that both ether-cleavage products adopt the same structure might suggest that a common intermediate species is responsible for the attack on the solvent. It is believed that in the hydrocarbon elimination route, a fast reaction between the dibenzyl reagent and the ligand takes place, followed by the slower ether cleavage initiated by the diphenylmethanide anion. In the desilylation strategy, the first reaction most likely entails the removal of the trimethylsilyl moiety, then over time and under more concentrated conditions attack by the diphenylmethanide occurs in a manner similar to the previous example **3**.

**Structural aspects:** The crystal structures for these compounds display a common motif based on conformational disorder in the diphenylmethanide anion. In this “50/50 flip” disorder, the anion adopts two separate orientations

that may or may not involve a center of symmetry (Figure 2).

This disorder is manifest particularly in charge-separated structures. Generally, the disorder was modeled by treating each orientation of the anion (one with the methylene

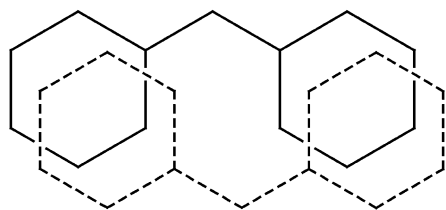


Figure 2. Representation of the anion disorder.

pointing “up” and one “down”) as a whole, and allowing the respective occupancy of each orientation to refine freely. These were typically centered very close to 50/50, with the largest outliers preferring one orientation in the crystal with a 60/40 ratio. While similar in appearance, the two orientations are not exactly identical. However, they follow the same trends with only minor deviations, and only one orientation is listed in the tables.

In compound **1**, shown in Figure 3 and Table 1, the cation takes up a slightly distorted pseudo-octahedral geometry with the crown ether occupying the equatorial plane with an average Ba–O length of 2.778(2) Å. The two diphenyl ligands, located in the axial positions exhibit Ba–C lengths of

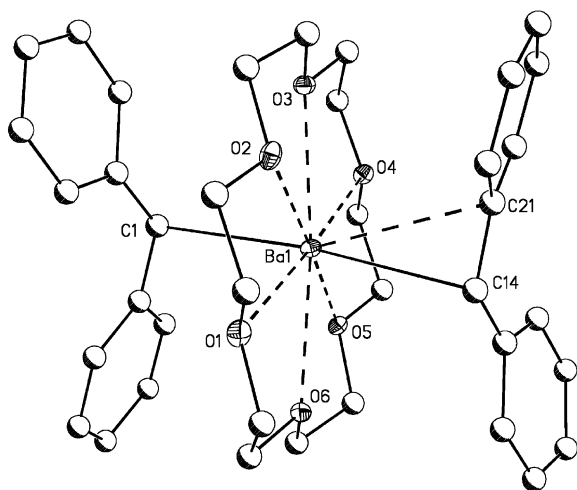


Figure 3. Crystal structure of **1**. Non-carbon atoms shown as thermal ellipsoids at 30% probability. Hydrogen atoms have been removed for clarity.

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

Ba1–O4	2.750(2)	Ba1–C1	3.096(3)
Ba1–O1	2.763(3)	Ba1–C21	3.389(3)
Ba1–O2	2.764(2)		
Ba1–O5	2.790(3)	C14–Ba1–C1	174.69(10)
Ba1–O3	2.797(2)	C8–C1–C2	129.7(4)
Ba1–O6	2.802(3)	C21–C14–C15	129.2(4)
Ba1–C14	3.065(3)		

3.096(3) Å and 3.065(3) Å and a slightly bent C1–Ba–C14 unit with an angle of 174.69(10)°.

A close contact between the metal center and one of the rings exists at C21 of 3.389(3) Å. While rather long, evidence for this interaction is provided by the elongated aromatic C–C bond lengths around the contact area. The anion geometry is slightly different than in the separated lithium diphenylmethanide reported by Power and co-workers. In compound **1** the two phenyl rings exhibit slightly different geometry. Ligand **1** does not exhibit  $\pi$ -interactions with the metal center; in this ligand the environment around the *ipso* carbon is nearly planar and the rings are twisted away from the plane defined by the *ipso* hydrogen, central carbon, and two carbon atoms of the phenyl ring by about 5°. In the separated [Li([12]crown-4)<sub>2</sub>][HCPPh<sub>2</sub>] the phenyl rings are coplanar.<sup>[29]</sup> This difference in geometry might be explained by the metal–ligand contact, which introduces additional steric strain on the anion, preventing a perfectly planar geometry with coplanar phenyl substituents. The second ligand exhibits an additional close contact to the metal, resulting in significantly different geometry. The C15 ring exhibits a ring twist of more than 10°; in contrast, ring C21 displaying the metal– $\pi$  contact, is almost coplanar with a twist of only 1°. Overall, the anion geometry is determined by steric repulsion between the phenyl moieties, resulting in a widening of the phenyl–C–phenyl angles to 127.9(4)° and 129.2(4)°. This is slightly less than seen in the alkali congeners which generally observe an angle of approximately 132°.<sup>[15]</sup>

It is instructive to observe that compound **1** compares well with a related “open metallocene” [Ba(2-pyridylphenylmethane)(triglyme)(thf)].<sup>[30]</sup> In this compound, the lower steric demands of the donors afford an asymmetric bonding scheme, which allows the ligands to take up a more involved bonding orientation; both ligands exhibit Ba–C contacts in an  $\eta^5$  fashion with bond lengths ranging from 2.9–3.3 Å. Here, however, the larger crown ether ring pushes the ligands to a more symmetric orientation, preventing additional  $\pi$  interactions.

Interestingly, the structure of the anion does not agree well with those of the related alkali diphenylmethanides. In these compounds, the anion geometry is mostly independent of the cation, regardless of whether contact molecules or separated ions are observed.<sup>[15]</sup>

Compound **1** is a rare example of a compound with a Ba–C  $\sigma$ -bond. Only one other example exhibiting a non-bridging Ba–C ( $sp^3$ ) contact has been communicated, namely [Ba{(Me<sub>3</sub>Si)<sub>2</sub>(MeOMe<sub>2</sub>Si)C<sub>2</sub>(MeOCH<sub>2</sub>CH<sub>2</sub>OMe)}].<sup>[31]</sup> Barium–carbon separations in the alkyl complex (3.036(2) and 3.049(2) Å) compare favorably with those in compound **1** (3.096(3) Å). The slightly longer bond in **1** might be explained by the higher metal coordination number.

Compound **3**, shown in Figure 4 and Table 2, crystallizes as a doubly enolate-bridged strontium diphenylmethanide dimer. The structure adopts a very irregular geometry with each metal center adopting a coordination number of nine.

The crown ether macrocycles are quite folded as a result of the proximity of the metal centers (3.746(7) Å), and form a snug envelope coordination with metal–oxygen distances exhibiting little variation at 2.654–2.680(4) Å. There is some

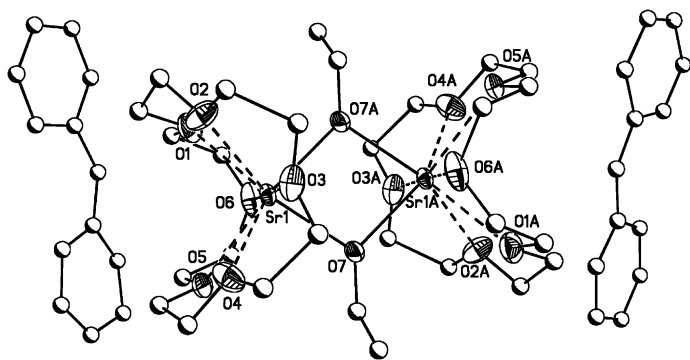


Figure 4. Crystal structure of **3**. Non-carbon atoms shown as thermal ellipsoids at 30% probability. Hydrogen atoms have been removed for clarity.

Table 2. Selected bond lengths [Å] and angles [°] of **3**.

Sr1–O7a	2.395(3)	Sr1–O6	2.680(5)
Sr1–O7	2.399(3)	Sr1–O3	2.701(3)
Sr1–O1	2.654(4)	C1–C2	1.395(5)
Sr1–O2	2.667(3)		
Sr1–O5	2.669(7)	O7a–Sr1–O7	77.22(10)
Sr1–O4	2.674(6)	Sr1a–O7–Sr1	102.78(10)

disorder in the crown rings; this was modeled by restraining bond lengths to appropriate distances. The folding of the two crown ethers opens the inner face of the dimer to allow for the bridging enolate moieties. A crystallographic center of symmetry located between the metal centers imposes restrictions that necessitate a symmetric structure. The enolate oxygens neatly bridge the cations with Sr1–O7 and Sr1–O7a lengths of 2.399(3) and 2.395(3) Å. The angle through the bridging oxo groups Sr1–O7–Sr1a is 102.78(10)°. No apparent metal interaction with the alkene carbons is indicated, nor is any metal–metal interaction likely. One noncoordinating THF molecule is present in the structure as a solvent of crystallization. The O–M–O angle is much larger than in the barium congener, with an angle of 77.22(10)°. The enolate C–C bond length is unexceptional at 1.422(9) Å. The diphenylmethanide anion is similar to those seen earlier, and exhibits the “50/50 flip” disorder.<sup>[15]</sup>

Compound **4**, seen in Figure 5 and Tables 3 and 4, consists of a doubly enolate-bridged barium diphenylmethanide dimer.

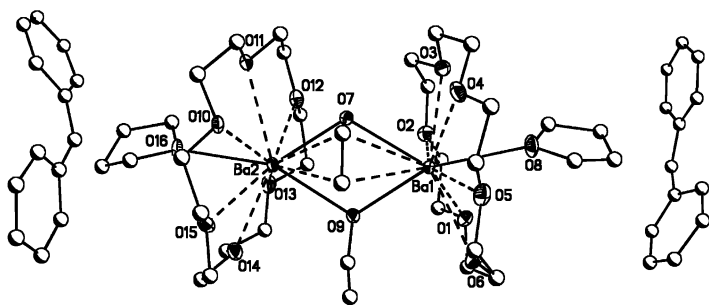


Figure 5. Crystal structure of **4**. Non-carbon atoms shown as thermal ellipsoids at 30% probability. Hydrogen atoms have been removed for clarity.

Table 3. Selected bond lengths [Å] and angles [°] of **4**.

Ba1–O9	2.655(3)	Ba2–O13	2.856(3)
Ba1–O7	2.716(3)	Ba2–O12	2.872(3)
Ba1–O6	2.803(4)	Ba2–O10	2.897(3)
Ba1–O3	2.844(3)	Ba2–O11	2.921(3)
Ba1–O2	2.851(3)	C15–C16	1.287(10)
Ba1–O5	2.857(3)	C73–C74	1.453(9)
Ba1–O8	2.882(3)	C73–C80	1.462(9)
Ba1–O1	2.908(3)	C86–C87	1.458(9)
Ba1–O4	2.938(4)	C87–C92	1.372(11)
Ba1–C13	3.166(5)		
Ba1–C14	3.342(5)	O9–Ba1–O7	71.00(9)
C13–C14	1.345(7)	Ba2–O7–Ba1	108.06(10)
C13–Ba2	3.195(5)	Ba1–O9–Ba2	109.17(11)
C14–Ba2	3.426(5)	O7–Ba2–O9	71.12(9)
Ba2–O15	2.821(3)	C74–C73–C80	132.8(6)
Ba2–O16	2.848(3)	C93–C86–C87	135.2(7)
Ba2–O14	2.855(3)		

Table 4. Crystal data for compounds **1**, **3**, and **4**.

	<b>1</b>	<b>3</b>	<b>4</b>
formula	BaC <sub>46</sub> H <sub>62</sub> O <sub>8</sub>	Sr <sub>2</sub> C <sub>51</sub> H <sub>82</sub> O <sub>16</sub>	Ba <sub>2</sub> C <sub>62</sub> H <sub>91</sub> O <sub>16</sub>
<i>M<sub>r</sub></i>	880.3	1126.37	1366.52
crystal size [mm]	0.40 × 0.30 × 0.05	0.20 × 0.20 × 0.15	0.20 × 0.20 × 0.20
space group	<i>P</i> <sub>2</sub> <sub>1</sub> <sub>2</sub> <sub>1</sub>	<i>P</i> $\bar{1}$	<i>P</i> <i>n</i>
<i>a</i> [Å]	13.4969(7)	9.8673(5)	11.3423(8)
<i>b</i> [Å]	15.3439(8)	13.5007(7)	20.0218(14)
<i>c</i> [Å]	20.129(1)	13.7253(7)	28.0425(19)
$\alpha$ [°]	90	68.3230(10)	90
$\beta$ [°]	90	76.4370(10)	92.0820(10)
$\gamma$ [°]	90	82.6140(10)	90
<i>V</i> [Å <sup>3</sup> ]	4168.6(4)	1649.95(15)	6364.1(8)
<i>Z</i>	4	1	8
$\mu$ [mm <sup>-1</sup> ]	1.005	1.67	1.294
2 $\theta$ range [°]	3.5–56.58	3.5–56.58	3.5–50
unique reflections	10011	7536	22390
<i>R</i> 1 [ <i>F</i> > 4 $\sigma$ ( <i>F</i> )]	0.0412	0.0628	0.0356
<i>wR</i> 2 (all data)	0.0806	0.1879	0.0813

Two closely related independent molecules are present in the asymmetric unit, with each metal center adopting a coordination number of 11, which includes additional contacts to the enolate  $\pi$ -system. This is not surprising considering the known propensity of larger alkaline earth metals for increased acceptance of  $\pi$ -type coordination. The metal ions lie considerably above the plane of the crown macrocycles with metal–oxygen distances of 2.803(4)–2.938(4) Å. The two crown ethers are tipped towards each other on one face to allow for insertion of the enolate moieties. The large size of barium allows for additional THF coordination, and M–O(THF) lengths of 2.848(3) and 2.882(3) Å are observed. The enolates are more symmetrically bound between the two metal centers than in the related crown-ether-derived vinyl ether complexes.<sup>[22]</sup> The enolate oxygen atoms bridge the two metal centers with Ba–O lengths between 2.665(3) and 2.716(3) Å. The angles through the bridging oxo groups are Ba1–O7–Ba2 108.06(10)° and Ba1–O9–Ba2 109.17(11)°. There are close contacts between the metal centers and one of the two enolate groups, with possible  $\pi$ -interactions with lengths of Ba1–C13 and Ba1–C14 of 3.166(5) and 3.342(5) Å, respectively, and similar distances from Ba2 to those atoms of 3.195(5) and 3.426(5) Å, respec-

tively. The other enolate group shows no such interaction. The angle described though the metal centers between the two bridging oxo groups is quite narrow, with values of 71.00(9)° (O7-Ba1-O9) and 71.12(9)° (O7-Ba2-O9). The enolate C–C bond lengths are somewhat shorter than typical (1.287(10) Å), though the moiety showing metal coordination is noticeably longer at 1.345(7) Å. This interaction has only a slight effect on the enolate geometry, with O–C–C angles of 126.65(9)° for the  $\pi$ -interaction moiety and 129.12(9)° for the uncoordinated. Each diphenylmethanide anion is similar to those observed typically, exhibiting the “50/50 flip” disorder model.<sup>[15]</sup>

When comparing the two enolate structures **3** and **4**, it is immediately apparent that they comprise an excellent example of cation-directed geometry. The smaller strontium cation has its coordination sphere comfortably filled by the folded crown ether and bridging oxo groups, and no further interactions are necessary. The larger barium congener, with its higher tendency towards  $\pi$ -bonding requires considerably more ligand and donor interactions to sterically saturate the cation. As a result, compound **3** does not display the additional enolate coordination exhibited by **4**, nor is any solvent interaction necessary to fill the metal sphere. The clear steric differences between the two compounds, including the smooth change in metal–oxygen separations, O–M–O bite angles, and bridging enol M–O–M angles are all related to the differences in cation radius between strontium and barium.

## Conclusion

Two synthetic routes, hydrocarbon elimination and desilylation, were utilized to prepare two novel barium diphenylmethanides, one a contact molecule, the other displaying separated ions. The contact molecule provides a rare example of barium ( $sp^3$ )– $\sigma$  bound to an organic ligand. While both routes provided the target compounds in good yield and purity, the frequent occurrence of ether cleavage reactions, as evidenced through the isolation of two different enolate derivatives, indicates that the high reactivity of the target compounds will remain a challenge. While the mechanism of the desilylation pathway is still under scrutiny, it appears that this synthetic route will allow access to a larger group of primary and secondary alkali and alkaline earth organometallics.

## Experimental Section

All reactions were performed with vigorous exclusion of water and oxygen. The compounds  $Ba(C_7H_7)_2$ ,  $Sr(C_7H_7)_2$ , and  $HCPPh_2SiMe_3$  were prepared by literature methods.<sup>[16,32]</sup> All other reagents and solvents were purified by standard procedures. Due to the highly reactive nature of alkaline earth organometallics, elemental analysis, and IR spectra could not be obtained. This is a well-known problem in alkaline earth chemistry.<sup>[1]</sup>  $^1H$  and  $^{13}C$  NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer. The crystals were mounted on the diffractometer as described previously.<sup>[33]</sup> The data were collected using a Bruker SMART system, complete with three-circle goniometer and CCD detec-

tor as described earlier.<sup>[34]</sup> The crystal structures were solved using direct or Patterson methods and were refined by full-matrix least-squares refinement on  $F^2$ .<sup>[35]</sup> All non-hydrogen atoms were refined anisotropically. CCDC-215610, CCDC-215611, and CCDC-215612 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

**[Ba(HCPh<sub>2</sub>)<sub>2</sub>][18]crown-6] (1a):** Solutions of  $Ba(C_7H_7)_2$  (0.43 g, 1.0 mmol) and [18]crown-6 (0.4 g, 1.54 mmol) in THF (15 mL) were prepared. The benzylbarium solution was subsequently cooled to 0°C and diphenylmethane (0.4 mL, 2.2 mmol) was added dropwise. Then the crown ether solution was added dropwise and the resulting reaction mixture was stirred at 0°C for 2 h, during which time a yellow precipitate slowly developed. The solution was allowed to warm to room temperature, then heated gently to redissolve the precipitate. The resulting dark brown solution was then stored at –20°C. Yellow-orange crystals formed overnight. M.p. 138–141°C; yield: 0.64 g, (72.7%).

**[Ba(HCPh<sub>2</sub>)<sub>2</sub>][18]crown-6] (1b):** Solutions of  $Ba(OrBu)_2$  (0.56 g, 2.0 mmol),  $SiMe_3HCPPh_2$  (0.5 g, 4.0 mmol), and [18]crown-6 (0.52 g, 2 mmol) in THF (10 mL) were prepared. The acid and crown ether solutions were added to the barium mixture, followed by *n*BuLi (2.6 mL, 4.17 mmol) giving a deep orange, slightly turbid solution. This solution was stirred at 25°C for 4 h, warmed gently to dissolve all solids, filtered, and the volume reduced to approximately 10 mL prior to slow cooling to –20°C. Yellow crystals formed over 24 h. M.p. 138–141°C; yield: 0.64 g, (72.7%).

**[Ba(HCPh<sub>2</sub>)<sub>2</sub>][18]crown-6] (1a,b):**  $^1H$  NMR (25°C, [D<sub>8</sub>]THF):  $\delta$  = 1.65 (t; THF) 3.49 (t; [18]crown-6 and THF), 4.20 (s; *HCPPh<sub>2</sub>*), 5.66–7.05 (m; phenyl);  $^{13}C$  NMR (25°C, [D<sub>8</sub>]THF):  $\delta$  = 42.02 (*CHPh<sub>2</sub>*), 71.26 ([18]crown-6), 125.94, 126.31, 128.30, 128.70, 129.05, 129.27 (phenyl); crystal data for **1** are given in Table 4.

**[Ba(hmpa)<sub>6</sub>][CHPh<sub>2</sub>]<sub>2</sub> (2):** Solutions of  $Ba(C_7H_7)_2$  (0.40 g, 1.0 mmol) and HMPA (1.05 mL, 6.0 mmol) in THF (15 mL) were prepared. The benzylbarium solution was subsequently cooled to –78°C and diphenylmethane (0.35 mL, 2.0 mmol) added dropwise. The HMPA was also added dropwise, and the solution was stirred at –78°C for 3 h, during which time a deep orange precipitate slowly developed. The solution was allowed to warm to room temperature, and then was heated gently to redissolve the precipitate. The resulting dark reddish-brown solution was then stored at –20°C. Yellow-orange crystals formed overnight. M.p. 135–138°C; yield: 0.60 g, (38.7%);  $^1H$  NMR (25°C, [D<sub>8</sub>]THF):  $\delta$  = 1.78 (t; THF), 2.58 (m; HMPA), 3.59 (t; THF), 4.25 (s; *HCPPh<sub>2</sub>*), 5.66 (m; phenyl), 6.50 (m; phenyl), 7.19 (m; phenyl);  $^{13}C$  NMR (300 MHz, 25°C, [D<sub>8</sub>]THF):  $\delta$  = 26.55 (HMPA), 37.27 (*CHPh<sub>2</sub>*), 107.75, 117.94, 129.27, 147.27 (phenyl).

**[[Sr][18]crown-6(OC<sub>2</sub>H<sub>3</sub>)<sub>2</sub>][HCPPh<sub>2</sub>]<sub>2</sub> (3):** Solutions of  $Sr(C_7H_7)_2$  (0.28 g, 1.0 mmol), and [18]crown-6 (0.24 g, 1.0 mmol) in THF (15 mL) were prepared. The benzylstrontium solution was subsequently cooled to –78°C and diphenylmethane (0.35 mL, 2.0 mmol) was added dropwise. The resulting solution was stirred at –78°C for 3 h, after which the crown ether solution was slowly added. The reaction mixture was then allowed to warm to 25°C, and was stirred for a further hour at this temperature. The solution was then filtered and the volume concentrated to approximately 5 mL. Yellow-orange crystals formed overnight: M.p. 130–135°C; yield: 0.20 g, (17.8%);  $^1H$  NMR (25°C, [D<sub>8</sub>]THF):  $\delta$  = 3.47 (s; [18]crown-6), 3.95 (s; *HCPPh<sub>2</sub>*), 4.8 (d; enolate), 7.02–7.14 (m; phenyl), 7.35 (dd; enolate);  $^{13}C$  NMR (25°C, [D<sub>8</sub>]THF):  $\delta$  = 46.48 (*CHPh<sub>2</sub>*), 71.26 (crown), 125.41, 128.31, 129.27, 143.51 (phenyl), 126.31 (enolate), 141.55 (enolate); crystal data for **3** are given in Table 4.

**[[Ba][18]crown-6(OC<sub>2</sub>H<sub>3</sub>)(thf)<sub>2</sub>][HCPPh<sub>2</sub>]<sub>2</sub> (4):** Solutions of  $Ba_6(OrBu)_{12}$  (0.95 g, 0.5 mmol),  $HCPPh_2SiMe_3$  (1.5 g, 6 mmol), and [18]crown-6 (1.5 g, 6.0 mmol) in THF (15 mL) were prepared. *n*BuLi (3.4 mL, 5.44 mmol) was added to the acid solution yielding a deep orange-red color. The acid/lithium solution was added to the alkoxide suspension, causing an instant dissolution of all solids. The crown ether solution was added, and the mixture allowed to stir at 25°C for 1 h. The resulting solution was then filtered, the volume concentrated to approximately 5 mL, and the resulting oily solution stored at –20°C. Yellow-orange crystals formed overnight. M.p. 120–122°C; yield: 1.12 g, (30.5%);  $^1H$  NMR (25°C, [D<sub>8</sub>]THF):  $\delta$  = 1.73 (m; THF), 3.47 (m; [18]crown-6), 3.59 (m; THF), 3.95

(s;  $HCPPh_2$ ), 4.70 (d; enolate), 5.52 (m; phenyl), 6.45 (m; phenyl), 7.15 (m; phenyl), 7.42 (dd; enolate);  $^{13}C$  NMR (25°C,  $[D_6]THF$ ):  $\delta$  = 42.76 ( $CHPh_2$ ), 71.73 (crown), 126.86, 129.26, 129.82, 142.25 (phenyl); enolate peaks could not be located in the  $^{13}C$  NMR due to solubility issues; crystal data for **4** are given in Table 4.

**Note added in proof:** A recent publication reports on the preparation of dibenzylcalcium and its use in hydrocarbon elimination chemistry.<sup>[36]</sup>

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