# Synthesis and Preparation of Alkaline-Earth-Metal Triphenylmethanides M(CPh₃)₂(18-crown-6)(HMPA)₂ and the Ether Scission Products [M(C₁₂H₂₃O₆)(N(SiMe₃)₂)]₂ (M = Sr, Ba)

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The emerging organometallic chemistry of the heavy alkaline-earth metals critically requires a diverse selection of target compounds to understand the metal−ligand bond characteristics. Accordingly, we set out to prepare a new series of target compounds involving the triphenylmethanide ligand. By investigating various synthetic strategies, we found that transamination results in crown ether scission with formation of vinyl ether, whereas the use of strontium and barium dibenzyl reagents leads to the desired products in good yield and purity.

## Introduction

The chemistry of the heavy alkaline-earth organometallics has undergone a renaissance in recent years, assisted by the availability of new synthetic methods and increasing applications in a variety of technical applications.[1−6] Specifically, chemistry involving cyclopentadienide, indenyl, and fluorenyl ligands has been well established, as summarized in several excellent review articles.[7,8] In contrast, information on $\sigma$-bonded and charge-separated organometallic species remains scant, owing in large part to problems associated with the low solubility and high reactivity of the target compounds. Considerable efforts have been put forth to circumvent these issues, and steady progress has been made in elucidating synthetic pathways which attempt to minimize these difficulties.[9−11]

Our interests lie in the development of novel synthetic routes toward $\sigma$-bonded alkaline-earth organometallics, with a particular interest in systems exhibiting resonance stabilization of the anion. In this regard, the family of substituted phenylmethanes, beginning with the benzyl systems and culminating with the trityl systems, is of special concern. While Harder et al. have published a variety of structurally characterized alkaline-earth-metal dibenzyl reagents, stabilized both through intramolecular N-coordination[12,13] and through trimethylsilyl substitution,[14] recent work in our group has focused on the diphenyl[15] and triphenylmethanide systems. Only one structurally characterized alkaline-earth-metal triphenylmethanide, Ph₃CMgBr·2Et₂O,[16] was known before we communicated the synthesis of the barium triphenylmethanide Ba(CPh₃)₂(18-crown-6)-(HMPA)₂ (HMPA = hexamethylphosphoramide). Difficulties in establishing a straightforward synthetic route to these complexes were compounded by the extremely high reactivity of some of the starting materials, resulting in ether scission chemistry.[17]

We here report a full account on this work, including the synthesis and characterization of strontium and barium triphenylmethanides obtained by the elimination of toluene, in addition to novel strontium and barium vinyl ether derivatives. These were obtained by transamination chemistry and consequent ring-opening chemistry of crown ether during attempts to prepare the target molecules. The isolation of the ether scission products sheds light on some synthetic difficulties encountered in this area of chemistry and will be of importance in the design of future reaction pathways toward the target compounds.

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## Results and Discussion

**Synthetic Aspects.** A wide variety of synthetic approaches to the preparation of alkaline-earth organometallics are now available. Among those, transamination, a simple acid/base reaction (Scheme 1), involves the reaction of alkaline-earth-metal bis(bis(trimethylsilyl)amides) with an acidic hydrocarbon. This reaction has been used successfully to prepare a family of alkaline-earth-metal derivatives, including thiolates and selenolates[18] and acetylides,[19] among others.

### Scheme 1. Transamination Reaction

$$M(N(SiMe_3)_2)_2 + 2HR \xrightarrow{\text{donor}} MR_2 + 2HN(SiMe_3)_2$$
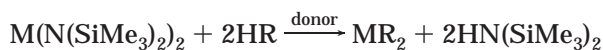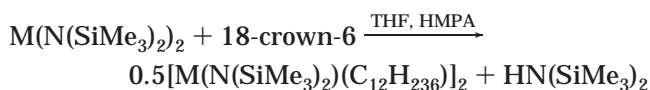
$$R = \text{alkyl, aryl; } M = Ca, Sr, Ba$$

Advantages of this route include the straightforward preparation of the amide starting materials[20] and their high solubility in a wide range of solvents. A necessary requisite for the reaction to proceed smoothly is the difference in $pK_a$ values between the acid substrate and the liberated $HN(SiMe_3)_2$, with the acid being more acidic than the amine. Typically, side reactions occur if the acidity of the substrate is very high. In this case, protonation of the secondary amine with subsequent N−Si bond cleavage and silylation of the acid occurs.[21] This yield-reducing reaction may be avoided if the acid is added very slowly and is dilute.

Given the small but significant difference in $pK_a$ values between $HCPh_3$ and $HN(SiMe_3)_2$, the transamination route seemed feasible. However, the reaction did not proceed as desired, and rather a vinyl ether, as the result of ether cleavage chemistry, was obtained (Scheme 2).

### Scheme 2. Attack of Alkaline-Earth-Metal Amides on Crown Ether

$$M(N(SiMe_3)_2)_2 + \text{18-crown-6} \xrightarrow{\text{THF, HMPA}}$$

$$0.5[M(N(SiMe_3)_2)(C_{12}H_{236})]_2 + HN(SiMe_3)_2$$

$$M = Sr, Ba$$

While the formation of triphenylmethanide derivatives was indicated in the early stages of the reaction by the bright red color of the reaction mixture, the coloration faded within a few hours, yielding a colorless solution and the formation of the heteroleptic vinyl ether bridged compounds **1a** and **1b**. Attempts to isolate the bright red reaction product by changing the solvent or keeping the reaction vessel at low temperature (−80 °C) failed, and in all cases the vinyl ether products were obtained quantitatively.

In an attempt to reduce the basicity of the anion and avoid the ether cleavage, HMPA was added to initiate the formation of separated ions. It was assumed that the combination of 18-crown-6 and HMPA with strontium and barium would yield the stable [M(18-crown-6)(HMPA)$_2$]$^{2+}$ (M = Sr, Ba) dications[18] and separated [CPh$_3$]$^-$ anions. This strategy seemed reasonable, since

the separated triphenylmethanide anion was obtained previously in conjunction with lithium after addition of 2 equiv of 12-crown-4.[22] Since charge separation would induce resonance stabilization by allowing the formation of an anion with a planar core, it was expected that the reduced basicity and resonance stabilization of the anion would allow the preparation of the triphenylmethanide target compounds. However, only the vinyl ether derivatives were obtained. Since compounds **1a** and **1b** were observed in all transamination attempts, a different synthetic strategy, in which the $pK_a$ difference between the substrate and the liberated product would be larger, was needed.

Crown ether cleavage chemistry with formation of vinyl ether derivatives was observed previously when alkaline-earth-metal amides M(N(SiMe$_3$)$_2$)$_2$(THF)$_2$ (M = Ca, Sr, Ba) were treated with various crown ethers.[23] As evidenced by $^1$H NMR studies, treatment of the amides with crown ether proceeds with the elimination of HN(SiMe$_3$)$_2$ and subsequent vinyl ether formation. A mechanism was suggested involving proton abstraction from the macrocycle by the silylamide anion, followed by C−O bond cleavage and formation of vinyl ether. In this study, an analogous mechanism is plausible, since the small difference in $pK_a$ values does not allow a smooth reaction between the amide and the triphenylmethane. This view is further supported by the repeated formation of the vinyl ether products **1a** and **1b**, regardless of reaction conditions and the presence of donors.

It was not until the utilization of strontium and barium dibenzyl derivatives in the presence of both crown ether and HMPA that the desired triphenylmethanide derivatives **2a** and **2b** were obtained (Scheme 3). In this instance, the difference in $pK_a$ values between triphenylmethane and toluene is much larger, and the drive to afford the desired product is significantly increased.

### Scheme 3. Arene Elimination Scheme for Preparation of Alkaline-Earth Triphenylmethanide

$$M(C_7H_7)_2 + 2HCPh_3 \xrightarrow[\text{HMPA, THF}]{\text{18-crown-6}}$$

$$M(CPh_3)_2(\text{18-crown-6})(HMPA)_2 + 2C_7H_8$$
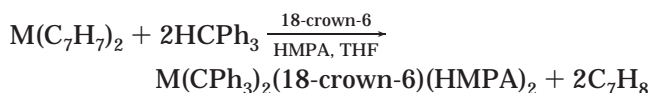
$$M = Sr, Ba$$

While the preparation of dibenzylbarium was reported in the literature, Harder and co-workers reported the formation of inseparable reaction mixtures while attempting to isolate the strontium analogue from a reaction mixture of strontium amide and benzyllithium.[24] By slightly altering the reaction conditions, such as the use of toluene as a solvent, we were able to cleanly prepare in good yields and purity the dibenzylstrontium derivative.

Again, the principle of ion separation and consequent resonance stabilization of the anion through addition of crown ether and HMPA was utilized. In the presence

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**Table 1.  Selected Bond Lengths (Å) and Angles (deg) of 1a**

| | | | |
|---|---|---|---|
| Sr(1)−O(1) | 2.465(2) | Sr(1)−O(3) | 2.741(3) |
| Sr(1)−O(1)′ | 2.417(2) | Sr(1)−O(4) | 2.809(3) |
| Sr(1)−N(1) | 2.574(3) | Sr(1)−O(5) | 2.882(3) |
| Sr(1)−O(2) | 2.719(3) | C(11)−C(12) | 1.308(7) |
| | | | |
| O(1)′−Sr(1)−O(1) | 72.80(9) | Sr(1)′−O(1)−Sr(1) | 107.20(9) |

of the dibenzyl derivatives, which are more powerful metalation reagents, we were able to isolate the target compounds in excellent yield and purity.

The low solubility of the benzyl reagents in hydrocarbon solvents and diethyl ether render the use of THF necessary. Since the dibenzyl reagents will attack THF at temperatures above −40 °C, the reaction needs to be carried out at low temperatures.

Attempts to isolate the corresponding calcium derivatives proved difficult, due to the inability to prepare the dibenzylcalcium starting material in good quality. Commonly, the preparation of the benzyl derivatives is accomplished via metal exchange by treating either the amides $M(N(SiMe_3)_2)_2(THF)_2$ (M = Ca, Sr, Ba) or the *tert*-butoxide with benzyllithium, but the inability to separate the two solid reaction products in case of the calcium reaction made it impossible to obtain pure starting material. In an attempt to show that calcium triphenylmethanide can be obtained, a one-pot reaction was carried out in which calcium amide was treated with a mixture of benzyllithium and triphenylmethane. As expected, a complex reaction mixture was obtained, but we were able to crystallize the charge-separated calcium triphenylmethanide derivative and identify the target species through a preliminary X-ray crystal structure, indicating that separated ions analogous to **2a** and **2b** were obtained. However, poor crystal quality made a full crystallographic analysis impossible. Attempts to fully characterize the reaction product by NMR spectroscopy failed, due to the complex mixture of products. Furthermore, the low solubility and high reactivity of the product made any attempts to purify the calcium target compound by recrystallization impossible.

As would be expected, charge-separated triphenylmethanides are highly air and moisture sensitive and must be handled carefully. Once crystalline, the triphenylmethanides are largely insoluble in aprotic polar solvents and tend to decompose upon heating rather than redissolve. Storage in solution at −20 °C over extended periods of time showed no noticeable decomposition, but the dry crystals were unstable even under nitrogen for more than a few days at room temperature.

**Structural Aspects. Structure Descriptions.** Crystallographic information and data collection parameters for compounds **1a** and **2a** are summarized in Table 3 and the Experimental Section. Details for compounds **1b** and **2b** were communicated previously.[17] Compilations of selected geometrical parameters for compounds **1a** and **2a** are given in Tables 1 and 2, respectively, while Figures 1 and 2 illustrate the structural principles displayed in compounds **1a** and **2a**. An illustration of compound **2a** can be found on the table of contents page. Compounds **1a**,**b** and **2a**,**b** respectively exhibit very similar structural features and will be described and discussed together.

**[M(N(SiMe₃)₂)(C₁₂H₂₃O₆)]₂ (M = Sr, 1a; M = Ba, 1b).** Compounds **1a** (Figure 1) and **1b** are isostructural,
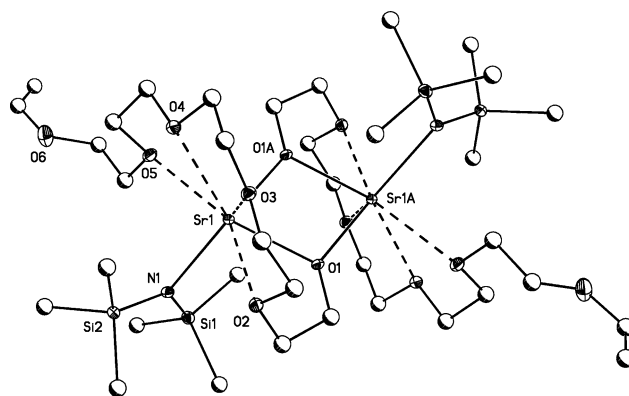


**Figure 1.** Structure of **1a**. Non-carbon atoms are shown as anisotropic ellipsoids at 30% probability. Hydrogen atoms have been removed for clarity.

**Table 2.  Selected Bond Lengths (Å) and Angles (deg) of 2a**

| | | | |
|---|---|---|---|
| Sr(1)−O(4) | 2.4091(17) | C(8)−C(9) | 1.416(3) |
| Sr(1)−O(3) | 2.6844(18) | C(8)−C(13) | 1.417(3) |
| Sr(1)−O(2) | 2.7117(17) | C(9)−C(10) | 1.391(4) |
| Sr(1)−O(1) | 2.7252(17) | C(10)−C(11) | 1.386(4) |
| C(1)−C(2) | 1.461(3) | C(11)−C(12) | 1.389(4) |
| C(1)−C(8) | 1.447(3) | C(12)−C(13) | 1.381(4) |
| C(1)−C(14) | 1.462(3) | C(14)−C(19) | 1.415(4) |
| C(2)−C(7) | 1.414(4) | C(14)−C(15) | 1.417(4) |
| C(2)−C(3) | 1.414(3) | C(15)−C(16) | 1.392(4) |
| C(3)−C(4) | 1.383(4) | C(16)−C(17) | 1.379(5) |
| C(4)−C(5) | 1.383(4) | C(17)−C(18) | 1.376(5) |
| C(5)−C(6) | 1.393(4) | C(18)−C(19) | 1.387(4) |
| C(6)−C(7) | 1.383(4) | | |
| | | | |
| O(1)−Sr(1)−O(1)′ | 180 | C(13)−C(8)−C(1) | 122.9(2) |
| C(8)−C(1)−C(2) | 121.4(2) | C(10)−C(9)−C(8) | 122.7(2) |
| C(8)−C(1)−C(14) | 119.5(2) | C(11)−C(10)−C(9) | 121.4(3) |
| C(2)−C(1)−C(14) | 119.1(2) | C(10)−C(11)−C(12) | 117.3(2) |
| C(7)−C(2)−C(3) | 114.9(2) | C(13)−C(12)−C(11) | 121.5(3) |
| C(7)−C(2)−C(1) | 123.5(2) | C(12)−C(13)−C(8) | 123.1(2) |
| C(3)−C(2)−C(1) | 121.7(2) | C(19)−C(14)−C(15) | 115.0(2) |
| C(4)−C(3)−C(2) | 122.6(2) | C(19)−C(14)−C(1) | 122.1(2) |
| C(3)−C(4)−C(5) | 121.1(3) | C(15)−C(14)−C(1) | 122.9(2) |
| C(4)−C(5)−C(6) | 118.0(3) | C(16)−C(15)−C(14) | 121.4(3) |
| C(7)−C(6)−C(5) | 121.0(3) | C(17)−C(16)−C(15) | 121.4(3) |
| C(6)−C(7)−C(2) | 122.4(3) | C(18)−C(17)−C(16) | 119.2(3) |
| C(9)−C(8)−C(13) | 114.0(2) | C(17)−C(18)−C(19) | 120.0(3) |
| C(9)−C(8)−C(1) | 123.1(2) | C(18)−C(19)−C(14) | 123.1(3) |

**Table 3.  Crystal Data for 1a and 2a**

| | 1a | 2a |
|---|---|---|
| formula | $C_{18}H_{41}NO_6Si_2Sr$ | $C_{70}H_{106}N_6O_{10}P_2Sr$ |
| fw | 511.32 | 1341.17 |
| cryst size (mm) | 0.6 × 0.4 × 0.2 | 0.4 × 0.3 × 0.2 |
| space group | $P\bar{1}$ | $P2_1/n$ |
| $a$ (Å) | 10.0717(13) | 12.9225(10) |
| $b$ (Å) | 11.1738(14) | 21.0331(17) |
| $c$ (Å) | 12.2770(16) | 13.2066(10) |
| $\alpha$ (deg) | 84.404(2) | 90 |
| $\beta$ (deg) | 70.367(2) | 100.439(2) |
| $\gamma$ (deg) | 86.082(2) | 90 |
| $V$ (Å³) | 1294.2(3) | 3530.1(5) |
| $Z$ | 2 | 2 |
| $\mu$ (mm⁻¹) | 2.205 | 0.869 |
| $2\theta$ range (deg) | 3.66−56.74 | 3.74−56.64 |
| no. of rflns measd | 8768 | 23 506 |
| no. of unique rflns | 6007 | 8516 |
| R1 ($F > 4\sigma(F)$) | 0.0504 | 0.0457 |
| wR2 (all data) | 0.1196 | 0.1346 |

with the metal centers located on inversion centers; thus, only half of a molecule is located in each asymmetric unit. The metal cations in this vinyl ether bridged dimer can be described as seven-coordinate,
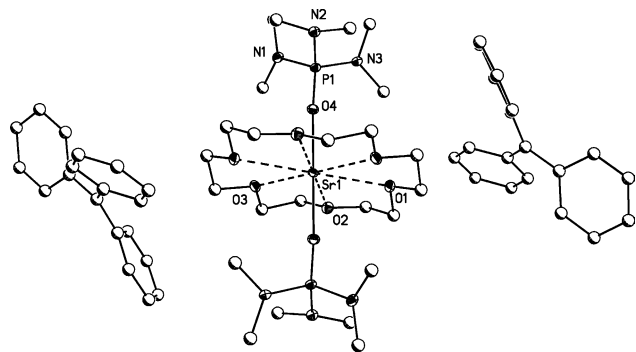
**Figure 2.** Structure of **2a**. Non-carbon atoms are shown as anisotropic ellipsoids at 30% probability. Hydrogen atoms have been removed for clarity.

with the coordination sphere filled by the $\mu_2$-oxo bridges, four oxygens from the cleaved crown ether, and the remaining amide ligand. The ether chains are arranged such that the vinyl "tails" point 180° opposite to each other. The bridging oxygens are slightly asymmetric, with metal–oxo distances reflecting the smaller size of the strontium cation, exhibiting distances of 2.465 and 2.417 Å; these are notably smaller than those of the barium congener (2.611 and 2.573 Å), as would be expected as a result of the smaller cation radius. The Sr1–O1–Sr1′ bridging angle of 107.20° and O1–Sr1–O1′ angle of 72.80° are in accordance with this coordination, and both angles are noticeably different from the barium compound (105.32 and 74.68°), with a wider bite angle for the bridging oxo groups and a subsequent narrowing of the O1–Sr1–O1′ angle as compared to the barium system. The ether–metal bond lengths increase smoothly, moving around the chain away from the bridgehead oxygen within the range of 2.719–2.882 Å, which are, as expected, shorter than in the barium congener (2.860–2.954 Å). The strontium–nitrogen amide distance of 2.574 Å compares well with the 2.714 Å in the barium compound. The C11–C12 vinyl bond length is unaffected by the metal, at 1.308 Å for **1a** and 1.294 Å for **1b**. The metal–metal distances of 3.930 Å (**1a**) and 4.122 Å (**1b**) make any metal–metal interaction unlikely.

**M(CPh$_3$)$_2$(18-crown-6)(HMPA)$_2$ (M = Sr, 2a; M = Ba, 2b).** Compounds **2a** (Figure 2) and **2b** (for an illustration, see the table of contents) are isostructural, with the metal centers located on inversion centers; thus, only a half-molecule is located in each asymmetric unit. Both compounds display charge-separated alkaline-earth-metal triphenylmethanides with considerable (7.169 and 7.196 Å) separation between ions. The dications are coordinated to 18-crown-6 and two HMPA donors, resulting in metal coordination numbers of 8. In compound **2a**, the metal lies in the center of the crown macrocycle at an average of 2.707 Å from the etheral oxygens, shorter than those in the barium compound **2b** (2.785 Å). In both compounds, the HMPA donors are located in trans positions; Sr–O distances of 2.409 Å are observed, as compared to 2.587 Å in **2b**. Of particular interest is the environment around the anionic center. The anions are planar through the methyl carbon, with angles adding up to 360°, indicating resonance stabilization.

The phenyl rings in the strontium compound adopt a propeller geometry, with angles at 35.3, 31.3, and 24.9°

for an average torsion angle of 30.5°. This value agrees fairly well with those reported earlier[22] as well as that predicted by calculations (35 ± 2°).[25] Indeed, in the barium congener very similar torsion angles are observed, with values of 35.6, 32.7, and 24.9° for an average of 31.5°. The bond lengths from the central carbon atom are noteworthy; in **2a**, the C1–C8 distance of 1.447 Å is slightly shorter than the C1–C2 and C1–C14 distance of 1.461 Å, but this is not unexpected, considering this phenyl group is oriented closest to planarity to give maximum orbital overlap through the methyl $\pi$-orbital. This type of contraction is well-known for the triphenylmethanide anion and has been observed in several cases for the alkali-metal salts[26] as well as for the barium congener **2b**.[17]

While the crystal structure of the calcium triphenylmethanide derivative is of poor quality, the chemical composition and overall structural features are reliable. The structure is very similar to those of the strontium and barium derivatives **2a** and **2b**, with crown ether and two HMPA ligands bound to the metal center. The separated anions display planar geometry at carbon, indicating significant resonance.

An examination of the well-established chemistry of the closely related alkali-metal triphenylmethanides is instructive for understanding structural trends. A range of these compounds (Li–Cs) have been prepared and structurally characterized in the solid state, and several key observations can be made. With little exception, the alkali-metal salts can be prepared through application of well-established "superbase" chemistry,[22,26–30] although direct metalation is also an established synthetic option.[31,32] The structures for the alkali-metal salts mainly exist as contact ion pairs isolated with appropriate donors. Two related trends have been demonstrated for these complexes. First, there appears to be a strong drive for lower hapticity in metal coordination as the polarizing power and ionic radius of the cation decreases, as demonstrated in the lithium derivative Li(CPh$_3$)(TMEDA), where the metal is bound to the ipso carbon center of the ligand.[29] For the heavier metals K–Cs, with increasing ionic radius a multihapto metal coordination to the $\pi$-system of the phenyl rings is preferred.[26] An additional trend is the increased tendency for the formation of oligomeric or polymeric complexes. While the lighter congeners tend to be monomeric, the heavier metal derivatives tend to oligomerize with numerous $\pi$-contacts for the rubidium and especially cesium complexes, leading to polymeric zigzag arrangements.[26] In addition, an examination of the central carbon atom of the anion in these compounds reveals a gradual geometric flattening as the bonding becomes more ionic; in the lithium complex the anion is noticeably pyramidal, but the potassium congener is

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nearly planar and the heavier compounds definitely so. This is reflected as well in the charge-separated lithium complex in which the anion is planar, analogous to the alkaline-earth-metal systems reported here.

## Conclusions

Benzyl derivatives of the heavy alkaline-earth metals strontium and barium have considerable utility in the preparation of alkaline-earth organometallics. The strong thermodynamic drive to form toluene establishes them as highly reactive metalating agents, ideal in reactions where slower competing processes might compromise product purity. The target compounds can be isolated as charge-separated ions if 18-crown-6 and HMPA are added to the product mixture. Work is underway to examine the recently prepared diphenyl alkali-metal and alkaline-earth-metal species.[15]

## Experimental Section

**General Procedures.** All reactions were performed using standard procedures under a purified nitrogen atmosphere by utilizing either modified Schlenk techniques and/or a Braun Labmaster 100 drybox. THF, $Et_2O$, and hexamethyldisilazane were distilled prior to use from $CaH_2$ or a Na/K alloy. $M[N(SiMe_3)_2]_2[THF]_2$ (M = Ca, Sr, Ba)[33] and $M(C_7H_7)_2$ (M = Sr, Ba)[24] were prepared by literature methods. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker DPX-300 spectrometer. Spectra were recorded in deuterated THF and referenced to residual solvent resonances. Use of $C_6D_6$ and $CD_3C_6D_5$ as NMR solvents did not allow for the dissolution of the charge-separated compounds, thus precluding the recording of quality spectra. Reliable elemental analyses and IR data could not be obtained, even when glovebox handling was attempted, due to the high moisture and oxygen sensitivity of all compounds reported. This is a well-known problem in alkaline-earth-metal chemistry.[9]

**Standard Procedure for the Synthesis of 1a,b.** Solutions were prepared of $M[N(SiMe_3)_2]_2[THF]_2$ (M = Sr, Ba) (approximately 1 mmol), $Ph_3CH$ (approximately 2 mmol), and 18-crown-6 (approximately 1 mmol) in THF (25 mL). The amide solution was subsequently cooled to −80 °C and the triphenylmethane solution added dropwise. After cooling, the crown ether solution was added dropwise, followed by stirring at −80 °C for 2 h. The resulting pale yellow solution was warmed to room temperature, turning ruby red at ca. 0 °C. The red solution, resulting from some contamination by the vibrant trityl anion, was filtered, the volume was reduced, and the resulting solution was stored at −20 °C. The red color faded quickly during storage, and colorless crystals formed overnight.

**1a**: $Sr[N(SiMe_3)_2]_2[THF]_2$ (0.59 g, 1.1 mmol), $Ph_3CH$ (0.51 g, 2.2 mmol), and 18-crown-6 (0.24 g, 1.0 mmol). Mp: 75−77 °C. Yield: 0.45 g (88.0%); $^1$H NMR (300 MHz, 25 °C, [$D_6$]-benzene): $\delta$ 0.46 (s, 36H, Si$Me_3$) 2.97−4.20, numerous peaks (t, cleaved crown), 3.97 (d, OCH$CH_2$), 6.52 (dd, O$CH$CH$_2$). $^{13}$C NMR (300 MHz, 25 °C, [$D_6$]benzene): $\delta$ 6.82 (Si$Me_3$), 62.98, 66.92, 68.26, 68.30, 69.58, 69.67, 70.24, 71.30, 72.06, 77.22 (cleaved 18-crown-6), 87.10 (OCH$CH_2$), 152.45 (O$CH$CH$_2$).

**1b**: $Ba[N(SiMe_3)_2]_2[THF]_2$ (0.8 g, 1.4 mmol), $Ph_3CH$ (0.72 g, 3.0 mmol), and 18-crown-6 (0.4 g, 1.54 mmol). Mp: 88−89 °C. Yield: 0.32 g (57.0%). $^1$H NMR (300 MHz, 25 °C, [$D_6$]-benzene): $\delta$ 0.45 (s, 36H, Si$Me_3$) 3.0−4.19, numerous peaks (t, cleaved crown), 3.97 (d, OCH$CH_2$), 6.41 (dd, O$CH$CH$_2$). $^{13}$C NMR (300 MHz, 25 °C, [$D_6$]benzene): $\delta$ 6.97 (Si$Me_3$), 63.30,

67.05, 68.10, 69.58, 70.01, 70.17, 70.61, 70.90, 72.06, 77.22 (cleaved 18-crown-6), 87.40 (OCH$CH_2$), 152.24 (O$CH$CH$_2$).

**Standard Procedure for the Synthesis of 2a,b.** Three 100 mL Schlenk flasks were charged with dibenzylstrontium or -barium (typically 1.0 mmol), $Ph_3CH$ (typically 2.0 mmol), and 18-crown-6 (typically 1.0 mmol). After cooling, 15 mL of THF was added to each. The triphenylmethane solution was added slowly to the dibenzylstrontium or -barium solution, followed by addition of HMPA (typically 2.0 mmol), affording a bright red solution. The crown ether solution was added, and the mixture was stirred at −80 °C for 3 h, yielding a fine suspension of the product. The solvent was removed, and 50 mL of fresh THF was added. This solution was gently warmed to dissolve the product;the solution was filtered and its volume reduced and stored at −20 °C. Dark red crystals formed within 12 h.

**2a**: dibenzylstrontium (0.45 g, 1.0 mmol), $Ph_3CH$ (0.50 g, 2.0 mmol), 18-crown-6 (0.27 g, 1.0 mmol), HMPA (0.6 mL, 2.1 mmol). Mp: softens at 135 °C, decomposes at 150 °C. Yield: 0.75 g (56.0%). $^1$H NMR (300 MHz, 25 °C, [$D_8$]THF): $\delta$ 3.46 (m, 32H, 18-crown-6, THF), 1.61 (m, 4H, THF), 3.58 (m, 4H, THF), 2.45−2.48 (d, 36H, HMPA),6.97−7.13 (m, 30H, $Ph_3C$). $^{13}$C NMR (300 MHz, 25 °C, [$D_8$]THF): $\delta$ 36.74 (HMPA), 71.26 (18-crown-6), 126.56 (*p*-C), 128.57 (*m*-C), 129.24 (*o*-C), 129.88 ($C$C$_6$H$_5$), 144.72 (C$_{ipso}$).

**2b**: dibenzylbarium (0.43 g, 1.0 mmol), $Ph_3CH$ (0.48 g, 2.0 mmol), 18-crown-6 (0.27 g, 1.0 mmol), HMPA (0.6 mL, 2.1 mmol). Mp: 158−160 °C. Yield: 0.54 g (35.9%). $^1$H NMR (300 MHz, 25 °C, [$D_8$]THF): $\delta$ 3.42 (m, 32H, 18-crown-6, THF), 1.58 (m, 8H, THF), 2.42 (d, 36H, HMPA), 7.06−7.11 (m, 30H, $Ph_3C$). $^{13}$C NMR (300 MHz, 25 °C, [$D_8$]THF): $\delta$ 37.27 (HMPA), 71.82 (18-crown-6), 127.12 (*p*-C), 129.14 (*m*-C), 130.42 (*o*-C), 132.0 ($C$C$_6$H$_5$), 145.24 (C$_{ipso}$).

**X-ray Diffraction Details.** The crystals were mounted on the diffractometer as described previously.[34] The data were collected using a Bruker SMART system, complete with three-circle goniometer and CCD detector as described earlier.[35] The crystal structures were solved using direct or Patterson methods and were refined by full-matrix least-squares refinement on $F^2$.[36] All non-hydrogen atoms were refined anisotropically. One heavily disordered THF molecule exists in the lattice of **1b** and **2b**, as a solvent of crystallization; this was modeled with restraints on distance for all affected bond lengths and two separate orientations for the molecule, with the occupancies allowed to freely refine. Crystallographic data (excluding structure factors) for the strontium structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication Nos. 212415 and 212416. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

**Supporting Information Available:** X-ray data as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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