Not Just Heavy "Grignards": Recent Advances in the Organometallic Chemistry of the Alkaline Earth Metals Calcium, Strontium and Barium

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Keywords: Calcium / Strontium / Barium / σ-bound organometallics / Synthesis / Structural characterization

Since their initial development in the early 1900's, Grignard reagents have proven to be immensely useful and are among the most common organometallic reagents. The nature of the reagents in solution is complex and depends on substituents, solvent, concentration and temperature. Despite continuing questions about their solid state and solution composition and conformation, organomagnesium reagents find new applications continually. In contrast, little information about the heavier alkaline earth organometallic compounds RMX and R_2M (R = alkyl, aryl; M = Ca, Sr, Ba, X = halide) exists. High reactivity due to the predominantly ionic character of the metal-ligand bond and increased lability complicates synthetic access. Recent interest in the organometallic chemistry of the alkaline earth metals calcium, strontium and barium has been sparked by the realization that heavy alkaline earth metal organometallics play unique roles in synthetic applications, such as polymerization initiators and as reagents to modify polymers. As a result, the organometallic chemistry of calcium, strontium and barium has received significant attention over the last few years. This article summarizes recent results in this emerging area of chemistry.

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Karin Ruhlandt-Senge studied chemistry at the Gutenberg University in Mainz (Germany) and the Philipps University in Marburg, Germany. She received her doctorate in 1991 working with Ulrich Müller (Marburg) on transition metal chemistry and crystallography, and with Philip P. Power and Håkon Hope at the University of California, Davis (U.S.A.) where she was concerned with main group III chemistry and crystallography. After her return to Davis for postdoctoral work in P.P. Power's group (1992−1993), she started her independent career in fall 1993 at Syracuse University (U.S.A.). Her current research interests focus on various aspects of alkali and alkaline earth metal chemistry.

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1. Introduction

The organometallic chemistry of the heavy alkaline earth metals dates back to the early 1900's, with the intent to synthesize highly reactive "Grignard analogs" for synthetic applications.[1] The assumption that the organometallic chemistry of these metals roughly resembles that of the lighter congener, magnesium, prompted attempts to synthesize candidate molecules bearing small organic ligands. However, the formation of either unstable and/or sparsely soluble compounds with little opportunity to be utilized for synthesis discouraged further efforts. These compounds continued to be viewed as obscure, and rather recently a popular organometallic textbook remarked: "Since the heavier alkaline earth organometallics do not offer any advantages over Grignard reagents, their chemistry has not been studied extensively [..]."[2] In consideration of the recent prominence organometallic calcium, strontium, and barium derivatives have received, this view is now changing. Still, most applications rely on the preparation of reagents in situ, and little information exists with regard to the reactive species.

Organometallic derivatives of the heavy alkaline earth metals have been most intensely studied for cyclopentadienyl systems, dating back to 1956 with the preparation of $(C_5H_5)_2Ca$.[3] Since then, many related derivatives have been prepared due to the unique capability of this system to stabilize the alkaline earth metal centers both sterically and electronically.[4−6] Similar work has been extended to fluorenyl, indenyl and related π-ligand systems.[7−10]

This progress did not however extend towards σ-bonded ligand systems and, aside from the early studies mentioned above and some activity in the latter part of the last century,[9,11−21] little attention has been devoted to them. High reactivity and low solubility complicated the isolation and detailed characterization of these systems, resulting in reports of the in situ preparation of the candidate molecules, whose identity was predominantly verified by the products from chemical reactions.

Examples of well-characterized σ-bonded organometallic calcium, strontium, and barium derivatives are heavily based on heteroleptic compounds, incorporating cyclopentadienyl (Cp) ligation in addition to a σ-bonded organometallic ligand system, taking advantage of the stabilizing effect provided by the Cp ligand.[4−6,22] Well-characterized organometallic compounds relying purely on σ-bonded ligands remain scarce, the original examples being the now familiar $[Ca\{CH(SiMe_3)_2\}_2(1,4\text{-dioxane})_2]$,[23] available by co-condensation of metal and ligand at 77 K, and $Ca[C(SiMe_3)_3]_2$, prepared by treatment of CaI_2 with two equivalents of $KC(SiMe_3)_3$.[24] Treatment of the latter with diethyl ether results in immediate ether scission and formation of the parent hydrocarbon and $Ca(OEt)_2$, illustrating the problems associated with the organometallic chemistry of these elements: severe limitation of synthetic variables due to high reactivity, low solubility caused by the high ionic character of the metal-ligand bond, high lability, and a prominent tendency towards the formation of oligomeric or polymeric species associated with a dramatic reduction of solubility.

The ability to reproducibly and cleanly prepare organometallic derivatives in good yield and purity and analyze their structure and function is critical for the progress of this emerging area of chemistry. Several recent studies have provided much needed information to improve the performance and utility of existing applications while establishing a new branch of organometallic chemistry with room for considerable growth.

2. Scope of This Microreview

This review examines recent examples of structurally characterized σ-bound and charge-separated organometallic complexes of calcium, strontium and barium with a focus on synthetic access strategies and structural features. Compounds of magnesium and beryllium will not be addressed. Numerous π-bound calcium, strontium and barium derivatives are now known, such as the families of cyclopentadienyl-, fluorenyl- and indenyl-stabilized organometallics; with a few exceptions these lie outside of the chemistry reviewed here. Similarly, allyl or vinyl systems will not be discussed; instead we refer to the several excellent review articles on these subjects.[4−6,25]

3. Synthetic Strategies

Multiple synthetic strategies towards the target compounds have been explored; among the most successful are transamination, direct metallation, alkane/arene elimination and transmetallation.

3.1 Transamination

The ready availability of the alkaline earth metal amides $M[N(SiMe_3)_2]_2$,[26] their solubility in many different solvent systems, and the easy removal of $HN(SiMe_3)_2$ make this an attractive route for the synthesis of alkaline earth metal organometallics [Equation (1)].[27]

$$M[N(SiMe_3)_2]_2 + 2\,HR \longrightarrow MR_2 + 2\,HN(SiMe_3)_2 \qquad R = \text{alkyl, aryl} \quad M = Ca, Sr, Ba \tag{1}$$

A limiting factor in this reaction is the pK_a range of hydrocarbon sources: only those with a higher acidity than $HN(SiMe_3)_2$ can be utilized. Highly acidic substrates, however, induce a competing side reaction involving protonation of the liberated secondary amine and formation of the silane [Equation (2)].

$$HN(SiMe_3)_2 + HR \longrightarrow Me_3SiR + 2\,H_2NSiMe_3 \qquad R = \text{alkyl, aryl} \tag{2}$$

This side reaction may be suppressed by careful and dilute addition of the acid.[28] An additional complication stems from the basic amide starting material promoting ether cleavage. This may be avoided using low temperature conditions.

3.2 Direct Metallation

The ease of the reaction and ready availability of precursors adds to the attractive nature of this route [Equation (3)].

$$2\,HR + M_{act} \longrightarrow MR_2 + H_2$$

R = alkyl, aryl, Act.= activated, M = Ca, Sr, Ba (3)

Necessary requirements for this reaction include the presence of highly active and pure alkaline earth metal. Activation methods include the distillation or sublimation of the metals,[29] the reduction of metal iodides with alkali metals,[30] or by dissolving the metals in anhydrous, deoxygenated liquid ammonia.[31] The reactivity of the metals plays a major role: barium will react smoothly, while the less reactive strontium and calcium generally require reflux conditions in liquid ammonia.

Problems associated with the ammonia route focus on difficulties in evolving a viable solvent system. Often, cosolvent systems are necessary along with the ammonia, but the sparse solubility of many organometallic complexes upon removal of NH_3 precludes crystallographic and spectroscopic characterization, and, more importantly, use of the target compound as a soluble precursor. If the system allows, this obstacle may be overcome by using donor systems in addition to the ammonia.

3.3 Arene Elimination

Until recently, this method was not applicable for the synthesis of heavy alkaline earth organometallics due to the unavailability of suitable precursor materials. The widely known and easily available cyclopentadienyl (Cp) complexes as basic substrates are not suitable due to the inherent stability of the Cp^- anion. In addition, the tendency of liberated C_5H_6 to dimerize causes significant difficulties in separation and purification. Fortunately, during the last few years several dibenzyl derivatives of calcium,[32,33] strontium[34] and barium[35] have become available, making arene elimination an attractive route. This method takes advantage of the strong thermodynamic drive towards the formation of toluene (and/or substituted phenylmethanes), resulting in the facile metallation of a variety of acidic hydrocarbons [Equation (4)].[52]

$$M(C_7H_7)_2(THF)_2 + 2HR \longrightarrow MR_2 + 2C_7H_8$$

R = alkyl, aryl M = Ca, Sr, Ba (4)

This method is particularly attractive as it forms simple hydrocarbons as the reaction products that can be easily removed from the reaction mixture. Again, similar pK_a limitations as discussed above apply (see section 3.1), as well as the lack of flexibility in solvent selection for some of the heavier analogs. Particularly for the heavier metal congeners, the high ionic character of the complexes precludes solvation in all but the most polar solvents, such as THF. This limitation makes the separation of the two solid reaction products difficult due to the lack of differentiation in solubility. In addition, great care must be applied to choose the appropriate reaction conditions as alkaline earth metal arene systems are extremely basic and will readily promote ether scission.

3.4 Transmetallation/Metal Exchange

Several possible variations of these schemes may be considered: the use of organomercury reagents in conjunction with activated alkaline earth metals [Equation (5)], or the reaction of organolithium compounds with alkaline earth metal alkoxides, aryloxides [Equation (6)], or amides [Equation (7)]. The chemistry as successfully employed in Equation (6) and (7) has been applied in the synthesis of dibenzylcalcium, -strontium and -barium derivatives [Equation (8)],[32−35] whereas organomercury chemistry [Equation (5)] has been employed to prepare the related organolanthanides.[36]

$$HgR_2 + M_{act} \longrightarrow MR_2 + Hg \qquad (5)$$

$$2LiR + M(OR)_2 \longrightarrow MR_2 + 2LiOR \qquad (6)$$

$$M[N(SiMe_3)_2]_2 + 2\,LiR \longrightarrow MR_2 + 2\,LiN(SiMe_3)_2 \qquad (7)$$

$$M[N(SiMe_3)_2]_2 + 2\,LiCH_2Ph \longrightarrow M(CH_2Ph)_2 + 2LiN(SiMe_3)_2$$

R = alkyl, aryl M = Ca, Sr, Ba (8)

Although these reactions often proceed smoothly and with few side products, the toxicity of mercury and its compounds make this route less attractive, and have therefore not been applied extensively towards the alkaline earth metal systems. In the case of the reactions shown in Equation (6) and (7), the separation of the two solid reaction products remains the key challenge. Necessary for successful separation are sufficient differences in the solubility of the products, sometimes achievable by careful choice of ligands or by addition of donors.[37]

4. Historical Examples

Successful structurally authenticated investigations into the area of σ-bonded organometallic compounds of the heavy alkaline earth metals opened in 1991 with the now-familiar isolation and structural characterization of $[Ca\{CH(SiMe_3)_2\}_2(C_4H_8O_2)_2]$ (**1**).[23] This four-coordinate complex arose from a co-condensation of calcium vapor and bis(trimethylsilyl)bromomethane in THF at 77 K, presumably to give $RCaBr(THF)_n$, with subsequent formation of the target compound via a Schlenk-type equilibrium. This calcium compound was a starting point for observing

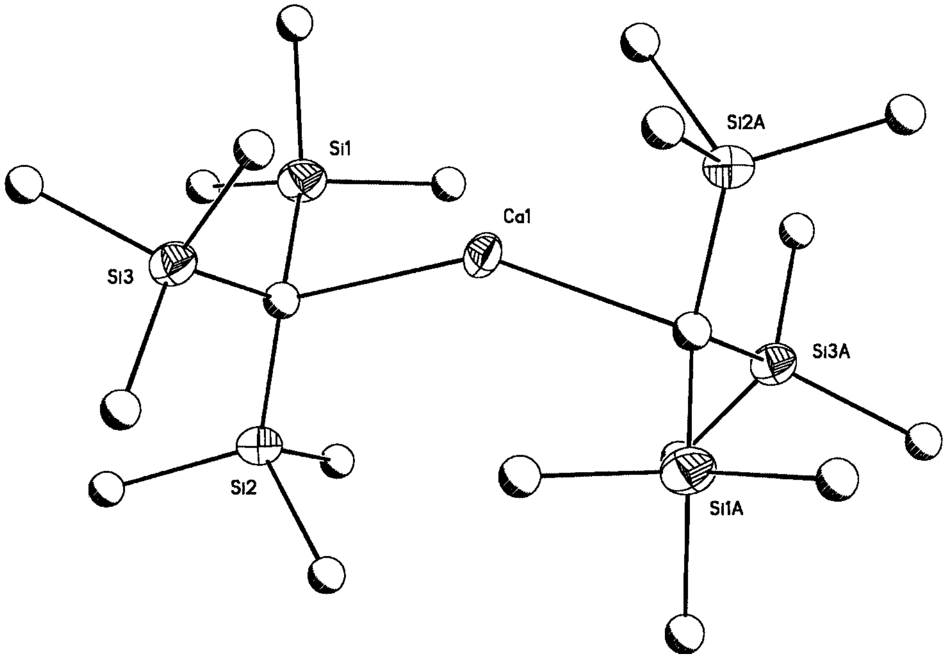

Figure 1. Molecular structure of **2**; heavy atoms displayed anisotropically with ellipsoids at 30% probability; hydrogen atoms have been omitted for clarity

σ-type alkaline earth metal-carbon interactions in Group 2 organometallics.

The first, and to date only, example of an unsolvated, two-coordinate complex of a heavy Grignard analog came with the report of the remarkable calcium bis(tristrimethylsilyl)methanide (**2**; Figure 1).[24] Reaction of the potassium methanide with calcium iodide in benzene over extended periods of time, followed by recrystallization from benzene/heptane, led to the isolation of extremely thin plates suitable for X-ray diffraction. While considerable disorder exists in the structure, the structural information is reliable and agrees well with other σ-bonded alkaline earth organometallics. Interestingly, there is little evidence for strong agostic interactions, although the compound still adopts the bent geometry predicted for compounds of this type.[38]

5. Dibenzyl Derivatives of the Heavy Alkaline Earth Compounds

Early studies on alkaline earth metal benzyl derivatives focussed on the use of organomercury reagents; the reaction products were solely characterized by NMR studies and no definitive structural information exists. Very recently, a facile synthesis of homoleptic dibenzylbarium became available by treatment of barium bis[bis(trimethylsilyl)]amide or barium *tert*-butoxide with two equivalents of the TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) adduct of benzyllithium in diethyl ether.[35] This promising result, coupled with the known activity of dibenzylbarium as a polymerization initiator, led to intense efforts to provide a wider array of derivatives of this type, as summarized in Table 1. Major impediments in this chemistry lie in the relative insolubility of dibenzylbarium in hydrocarbons, in addition to difficulties separating pure compounds for the lighter metals, calcium and strontium, from a mixture of reaction products of varying solubility. These problems were addressed by altering the substitution pattern of the benzyl moiety in an attempt to tune the solubility of the resulting compounds.

As a result, the first benzylcalcium complex (**3**; Figure 2) was reported from the reaction of the potassium salt of an α,α-bis(trimethylsilyl)-substituted toluene derivative with calcium iodide.[32] This compound crystallizes as the bis-THF adduct with a four-coordinate metal center with some additional weak π-contacts to the attendant phenyl rings. Interestingly, beyond these contacts (2.89−2.95 Å) no agostic interactions to the trimethylsilyl moieties are seen, probably as a result of the THF-metal interaction.

A related approach improved the solubility properties with intramolecular stabilization by means of a tethered dimethylamino moiety to give the diastereomeric benzylcalcium complex as its bis-THF adduct (**4**; Figure 3).[33] This benzene soluble derivative exhibits a six-coordinate distorted octahedral metal center with slightly shorter $Ca-C_\alpha$ distances than the α,α-disubstituted benzylide **3** as well as mixed hybridization of the α-carbons, with angles summing to 342(1)° and 346(1)°. Unlike **3**, this bidentate compound shows no additional aryl interactions. In solution, a temperature- and concentration-dependant exchange between diastereomers is observed; the addition of THF assists this exchange.

The first example of a heteroleptic benzylcalcium derivative displays fluorenyl stabilization with a distorted η^5 coordination (**5**).[39] One additional THF completes the coordination sphere of the metal. The metal-C_α distance of 2.50 Å is noticeably shorter than the purely σ-bound species **3**

Table 1. Details of dibenzylcalcium, -strontium and -barium derivatives

Compound	Aggr.	CN	M−C [Å]	D	M−D [Å]	ref.
$[Ca\{C_7H_5(SiMe_3)_2\}_2(THF)_2]$ (**3**)	1	4	2.65	THF	2.38	32
$[Ca\{C_8H_{10}N(SiMe_3)\}(THF)_2]_2$ (**4**)	1	6	2.64, 2.62	THF NMe_2	2.44, 2.37 2.56, 2.63	33
$[Ca\{C_8H_{10}N(SiMe_3)(C_{13}H_8SiMe_3)\}(THF)]$ (**5**)	1	3+5[a]	2.50, 2.69−2.78	THF NMe_2	2.30, 2.46	39
$[Na(OEt_2)][Ca(2\text{-}MeO\text{-}C_6H_4CHPPh'_2)_3]$ (**7**)[b]	1	6	2.53−2.57	OMe	2.42−2.44	40
$[Ca(2\text{-}O\text{-}C_6H_4CHPPh'_2)(THF)]_4$ (**8**)[b]	4	6	2.59	$Ph-O^-$ PPh'_2	2.34−2.43, 2.99	40
$[Sr\{C_8H_{10}N(SiMe_3)\}(THF)_2]_2$ (**6**)	1	6	2.77, 2.79	THF NMe_2	2.53, 2.56 2.76, 2.78	34
$[Ba\{Ph_2P(CH_2C_6H_4\text{-}4\text{-}Me)_2\}_2]$ (**9**)	1	6+4[c]	2.98−4.07	PPh_2	3.71, 3.94	41

[a] Fluorenyl stabilized. [b] Ph′ = *p*-tolyl. [c] Two η^3- and two η^2-metal-carbon interactions.

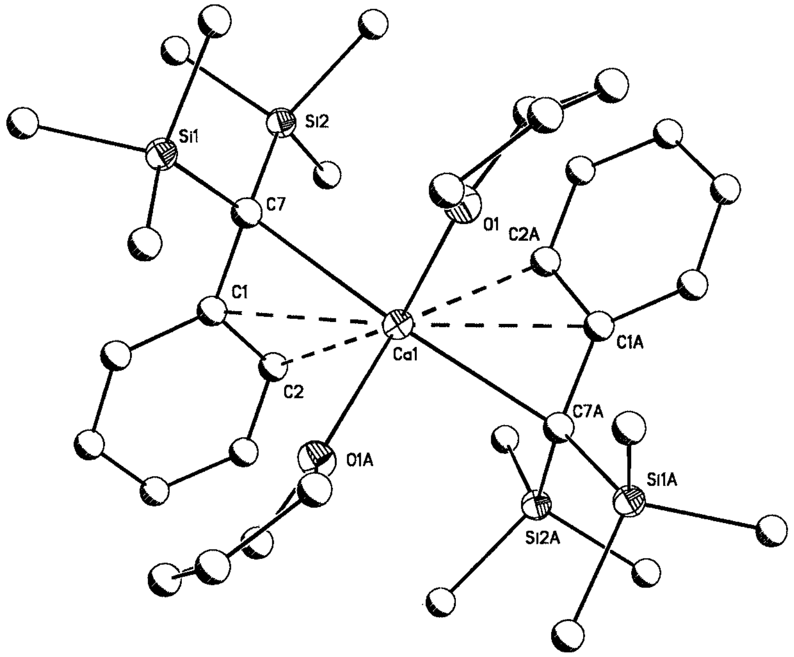

Figure 2. Molecular structure of **3**; heavy atoms displayed anisotropically with ellipsoids at 30% probability; hydrogen atoms have been omitted for clarity

and **4**, and is rationalized as a result of the π-stabilization afforded by the fluorenyl system.

Currently, the only example of a simple homoleptic dibenzylstrontium complex is the well-defined bis[(2-dimethylamino-α-trimethylsilyl)benzyl]strontium (**6**).[34] Like the calcium congener, this internally stabilized compound crystallizes as the bis-THF adduct. Unlike the calcium compound, however, there are several close contacts to the aryl rings, which may indicate an η^3-interaction. The geometry around the metal is strongly distorted, and takes up a nearly trigonal prismatic arrangement, with a bridging $C_\alpha-Sr-C_\alpha'$ angle of 143.5°, versus 157.5° for the calcium congener. This compound also crystallizes as a set of diastereomers, and shows slow exchange from the heterochiral to the homochiral orientation similar to that of the calcium compound. As in that example, the extra intramolecular stabilization afforded by the NMe_2 ligation and the added bulk of the $SiMe_3$ moiety result in a low coordination number at the metal center and good solubility, although apparently at the expense of the efficacy of the compound as a polymerization initiator. There appears to be a clear connection between the steric bulk and the reactivity of these compounds for polymerization; for detailed discussions on this topic we refer the reader to the original literature.[32−35]

The concept of internal stabilization and modification of the benzyl group was also utilized in the synthesis of two closely related organometallic complexes of calcium.[40] The first uses the stabilization of PPh_2' (Ph′ = *p*-tolyl) on the α-carbon along with internal coordination from a methoxy substituent on the benzyl ring to afford an example of a benzylcalcium complex (**7**; Figure 4). The parent hydrocarbon was lithiated in Et_2O, then transmetallated with sodium *tert*-butoxide followed by salt elimination with CaI_2. This compound assumes a coordination number of six, with the geometry around the metal lying between octahedral and trigonal prismatic. There are several agostic interactions be-

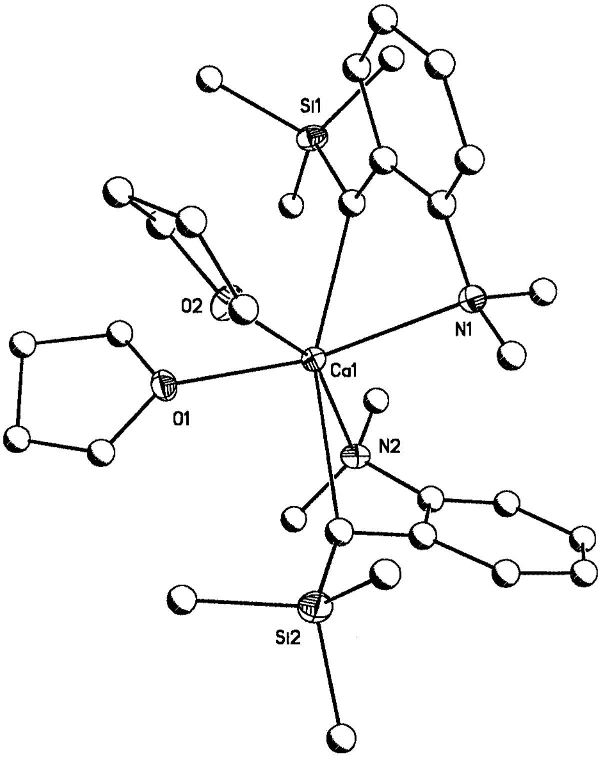

Figure 3. Molecular structure of **4**; heavy atoms displayed anisotropically with ellipsoids at 30% probability; hydrogen atoms have been omitted for clarity

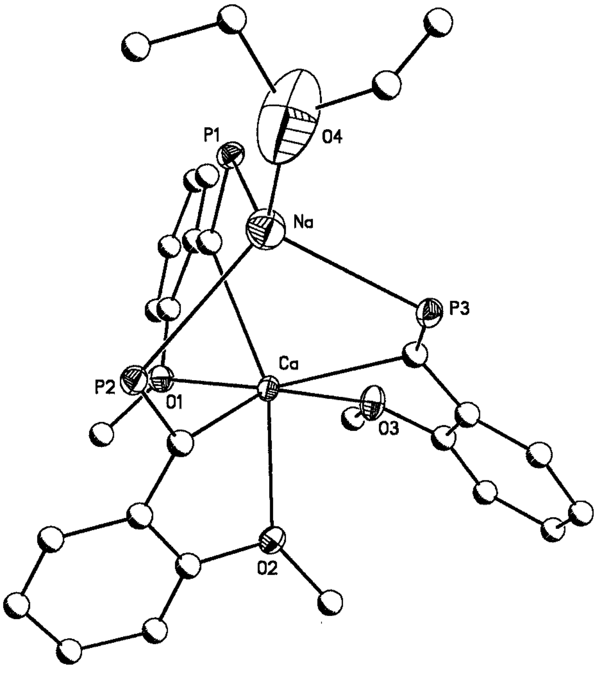

Figure 4. Molecular structure of **7**; heavy atoms displayed anisotropically with ellipsoids at 30% probability; hydrogen atoms and *p*-tolyl groups have been omitted for clarity

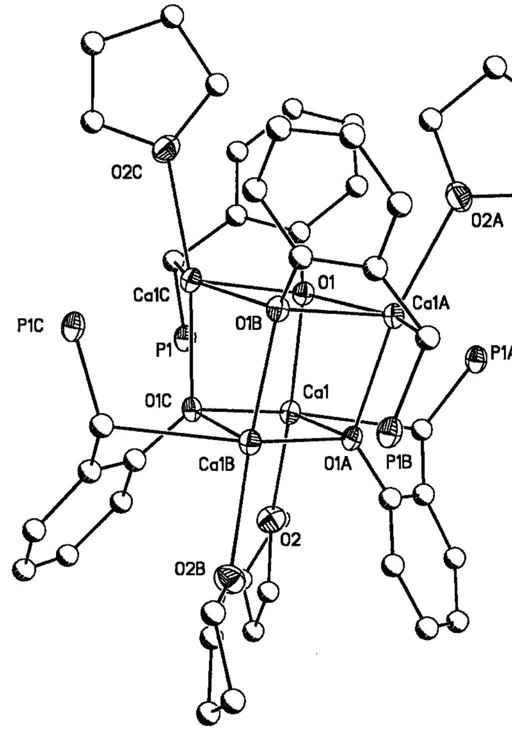

Figure 5. Molecular structure of **8**; heavy atoms displayed anisotropically with ellipsoids at 30% probability; hydrogen atoms and *p*-tolyl groups have been omitted for clarity

tween H_α and the metal center of 2.41 Å, possibly as a consequence of the calcium being situated out of the plane of the π-bound benzyl moieties. The phosphanyl groups do not coordinate to the calcium, but rather to the sodium counterion.

If the salt elimination reaction is instead carried out in THF, an ether cleavage occurs on the methoxy substituent leading to the formation of a tetrameric benzyl alkoxide derivative (**8**; Figure 5) in very low yield. The mechanism is explained by nucleophilic attack of the iodide ion at the carbon of the calcium-coordinated methoxy group. The resulting compound displays a distorted cuboidal structure with the oxygen atoms at alternate corners. This reaction illustrates one of the most prevalent problems in the organometallic chemistry of the heavy group 2 metals: ether cleavage is a common occurrence, limiting solvent and donor choices.

Another example of the use of phosphorus-bearing substituents is observed in barium phosphonium dibenzylide (**9**; Figure 6).[41] This example of a heavy organoalkaline earth metal compound is accessible through the reduction of the phosphonium ylide bromide with potassium amide followed by addition of 0.5 equivalents of barium amide. The ylidic ligand easily fills the coordination sphere of barium with numerous η^2- and η^3-interactions; the added bulk of the substituents affords a complex which is readily soluble in toluene, benzene and THF. The benzyl planes occupy four different orientations with respect to the metal, and the contact distances vary. For all four ylidic carbons, the angles add up to perfectly planar sp^2-bonding geometries.

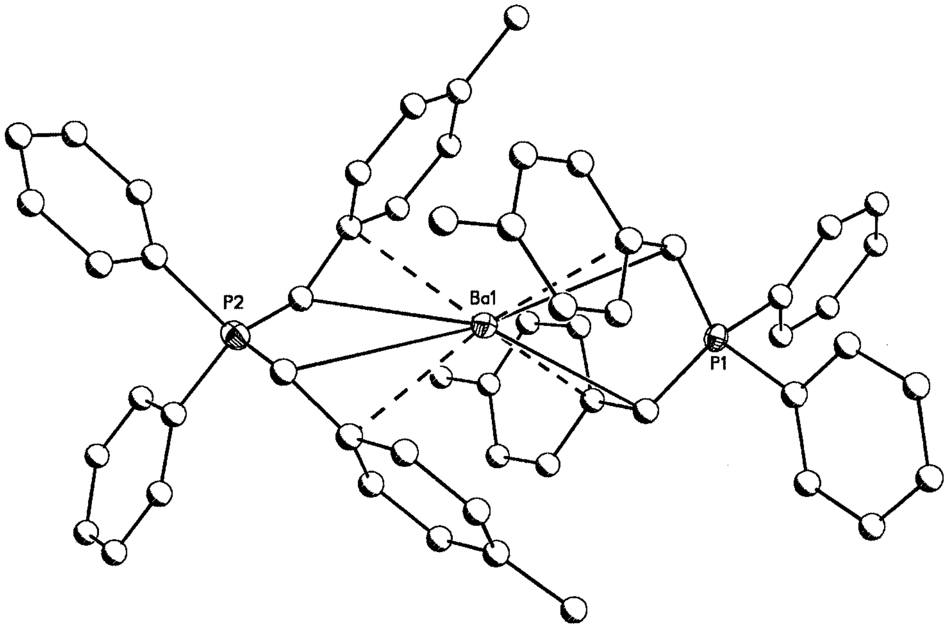

Figure 6. Molecular structure of **9**; heavy atoms displayed anisotropically with ellipsoids at 30% probability; hydrogen atoms have been omitted for clarity

The solubility of the dibenzyl derivatives can be adjusted by a careful choice of substituents, allowing for increased utility of these organometallics in an array of synthetic applications. The internal stabilization appears to play a key role in isolation and characterization.

6. "Ate" Complexes of Calcium, Strontium and Barium

The structural chemistry of "ate" complexes of the alkaline earth metals has been mostly limited to compounds of magnesium and beryllium.[42] There are many examples of anionic transition and main group organometallic compounds with beryllium and magnesium counterions, usually with a coordinating donor, but rarely in these cases do the metals display metal-carbon contacts. Several recent examples of such complexes involving heavy alkaline earth cations displaying metal-carbon bonds have been reported, as summarized in Table 2.

The addition of tris(trimethylsilylmethyl)alane and unsolvated calcium bis[bis(trimethylsilyl)amide] in a 2:1 molar ratio in toluene affords the dimeric calcium bis(trimethylsilyl)amide-tetrakis(trimethylsilylmethyl) aluminate (**10**; Figure 7).[43] The central Ca_2N_2 core of the complex is planar. The complex exhibits calcium-carbon distances of 2.68 and 2.64 Å. The close calcium-aluminum contact (3.25 Å) and the small Ca−C−Al angles (85.5° and 86.3°) might indicate the presence of three-center, two-electron bonding. There are several agostic interactions from the methylene hydrogens, also explaining the short Ca−Al contacts.

Several "ate" complexes have been obtained by the reaction of bis[(trimethylsilyl)methyl]zinc with freshly distilled alkaline earth metals with extrusion of elemental zinc. Utilizing this route, the reaction of freshly distilled strontium metal with bis[(trimethylsilyl)methyl]zinc in THF at room temperature over 24 hours yielded the strontium zincate (**11**; Figure 8).[44] This complex assumes a coordination number of six at the strontium center in a slightly distorted octahedral geometry as a result of the small chelation angle

Table 2. Details of -ate complexes of calcium, strontium and barium

Compound	Aggr.	CN	M−C [Å]	D	M−D [Å]	ref.
$Ca_2[Al(CH_2(SiMe_3)_4]_2[N(SiMe_3)_2]_2$ (**10**)	2	4	2.68, 2.63			43
$Sr(THF)_2[Zn(SiMe_3)(CH_2SiMe_3)_2]_2$ (**11**)	1	6	2.08, 2.02 2.10	THF	2.53	44
$Ba(THF)_4[Zn(SiMe_3)(CH_2SiMe_3)_2]_2$ (**12**)	1	8	3.09, 3.23 3.18, 3.17	THF	2.78−2.87	44
$Ba(Tol)_2[Zn(SiMe_3)(CH_2SiMe_3)_2]_2$ (**13**)	1	6	3.03, 3.05	Tol	3.37−3.41	44
$[Ba(THF)_3OZn_2(CH_2SiMe_3)_2(SiMe_2)]_2$ (**14**)	2	7	3.18, 3.24	O THF	2.51, 2.57 2.79−2.86	44
$Ba_4[Zn_6(CH_2SiMe_3)_4(CHSiMe_3)_3]_2$ (**15**)	2	5, 6	2.83−3.20			45

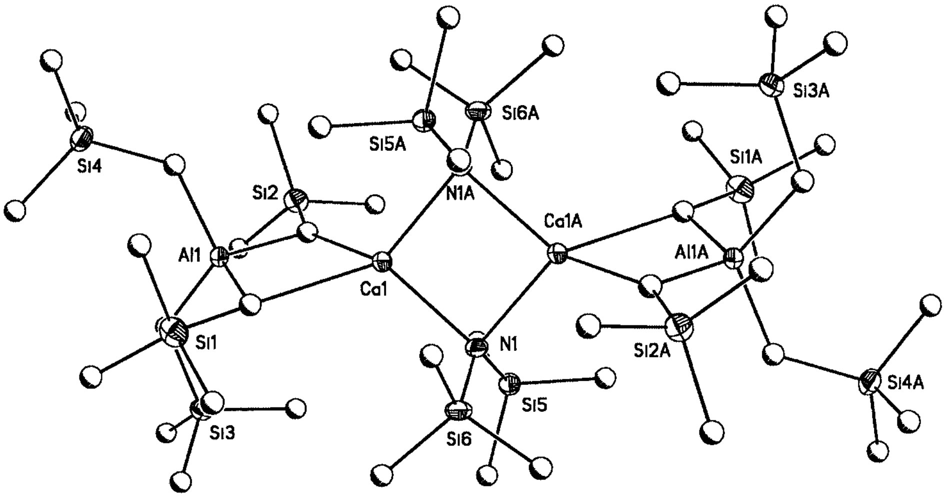

Figure 7. Molecular structure of **10**; heavy atoms displayed anisotropically with ellipsoids at 30% probability; hydrogen atoms have been omitted for clarity

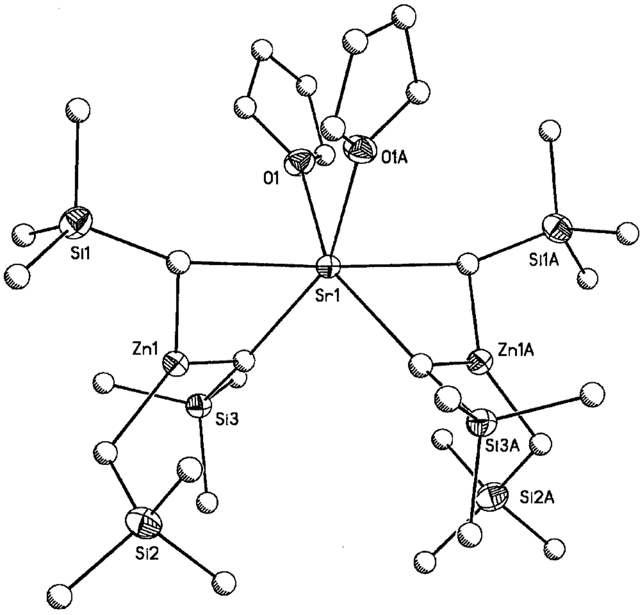

Figure 8. Molecular structure of **11**; heavy atoms displayed anisotropically with ellipsoids at 30% probability; hydrogen atoms have been omitted for clarity

afforded by the anion. The somewhat longer strontium-carbon contacts, as compared to other organostrontium compounds, are probably the result of the higher coordination number of the strontium as well as the result of a proposed Sr−C−Zn three-center, two-electron bonding mode through the core of the complex.

An analogous reaction between freshly distilled barium metal and a dialkylzinc derivative in THF affords the barium congener (**12**).[44] The larger radius of barium allows for an expanded coordination sphere filled by two additional THF donor molecules. Overall, the barium center possesses a coordination number of eight in a rather irregular geometry. As a result, the barium-carbon contacts are considerably longer than those of the strontium congener.

Repeating the reaction in toluene affords the bis-toluene adduct (**13**) of the zincate, with the toluene molecules π-bound to the barium metal center.[44] If each toluene is counted as filling one coordination site, then the coordination number of the barium is six, allowing a slightly distorted octahedral metal environment. This low coordination state, coupled with the steric shielding provided by the closely coordinated toluene donors also allows for shorter metal-carbon contacts than in the THF adduct (3.05 vs. 3.23 Å).

An attempt to obtain donor-free derivatives by using *n*-heptane as the solvent did not lead to a crystalline product. However, dropwise addition of THF to the reaction mixture led to a barium zincate/oxide (**14**; Figure 9).[44] This barium complex features a dimeric barium oxide with numerous contacts to THF donors and silyl substituents. An apparent rearrangement and elimination leads to the concurrent formation of a zinc silanide in situ, indicating the possibility of water or oxygen contamination causing the unexpected side reactions. The low coordinate zinc centers exhibit very short contacts to the oxygen atoms, while the barium-carbon distances are extremely long due to the lack of anionic charge located in these carbon centers.

A complex reaction of barium bis[tris(trimethylsilylmethyl)zincate] with excess barium, with extrusion of zinc metal, leads to the formation of a proposed alkylbarium moiety in situ. This highly reactive substrate reacts immediately with subsequently added metal and excess zincate to form the unique barium cubane (**15**; Figure 10) with extrusion of tetramethylsilane.[45] This distorted, face-sharing double cube possesses agostic interactions between the methylene groups and the nearby barium centers, in addition to metal-carbon σ-bonds within the range observed for other σ-bonded compounds.

In addition, this complex shows carbon ligands in the unusual coordination state of six, resulting in rather long contacts to the nearly trigonal planar environments of the zinc centers.

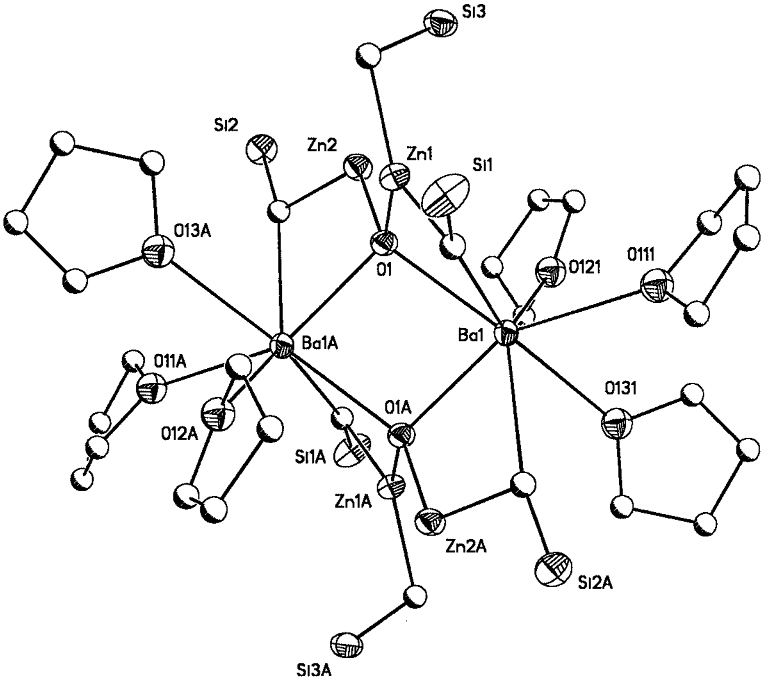

Figure 9. Molecular structure of **14**; heavy atoms displayed anisotropically with ellipsoids at 30% probability; hydrogen atoms and methyl groups have been omitted for clarity

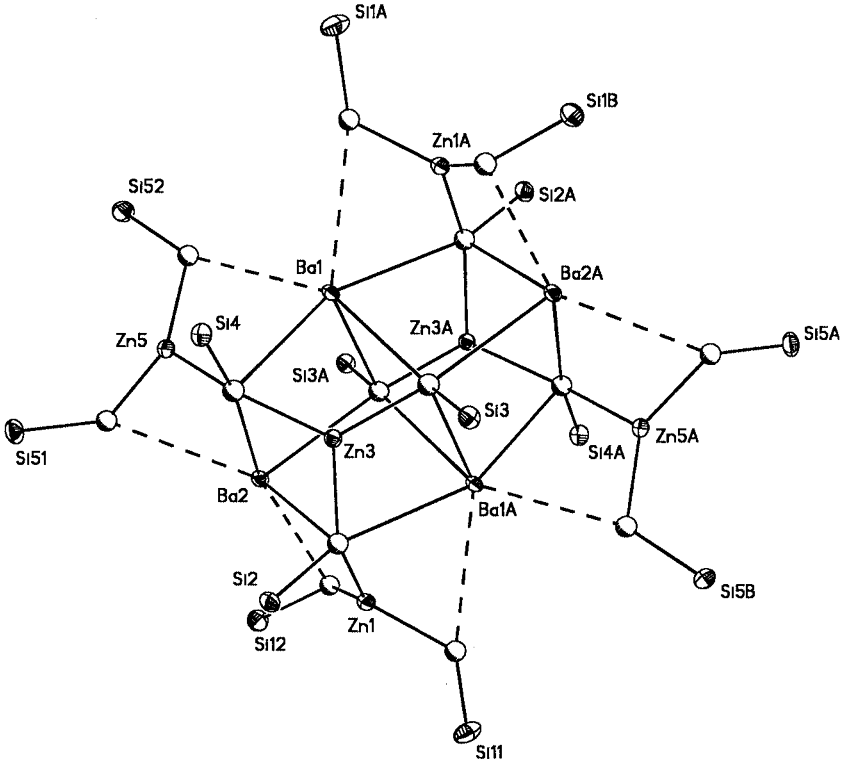

Figure 10. Molecular structure of **15**; heavy atoms displayed anisotropically with ellipsoids at 30% probability; hydrogen atoms and methyl groups have been omitted for clarity

Table 3. Details of σ-bonded complexes of the heavy alkaline earth metals

Compound	CN	M−C [Å]	C−M−C [°]	$M-C_{ipso}-C$ [°]	ref.
$[Ca\{CH(SiMe_3)_2\}_2(C_4H_8O_2)_2]$ (**1**)	4	2.48	133.7		23
$[Ca\{C(SiMe_3)_3\}_2]$ (**2**)	2	2.46	149.7		24
$[Ca(CCSiMe_3)_2$(18-crown-6)] (**16**)	6	2.52, 2.56	168.7	162.4, 164.0	46
$[Sr(CCSiMe_3)_2$(18-crown-6)] (**17**)	6	2.69, 2.72	166.0	158.9, 159.7	46
[Sr(CCPh*t*Bu)$_2$(18-crown-6)] (**19**)	6	2.69, 2.71[a]	180, 180[a]	166.4,167.0	48
$[Ba(CCSiMe_3)_2$(18-crown-6)] (**18**)	6	2.85	162.7	126.6, 141.3	46
[Ba(CCPh*t*Bu)$_2$(18-crown-6)] (**20**)	6	2.86	180	115.8−145.7[b]	48

[a] Two independent molecules. [b] Acetylide ligands disordered over three positions.

7. Acetylides of the Heavy Group 2 Metals

The first examples of homoleptic heavy alkaline earth metal acetylides were reported recently;[46] these examples are summarized in Table 3.

The heavy Group 2 acetylides were prepared by transamination: reacting triphenylsilylethyne with a metal amide in THF at −78 °C with the addition of 18-crown-6. The geometry of these acetylides (**16**−**18**; the structure of **18** is shown in Figure 11) can be envisioned as distorted, pseudo-octahedral with the crown ether occupying the equatorial plane and the ligands filling the axial positions. The presence of the crown ether is critical for the formation of the acetylides. The complexes react with trace amounts of water to form siloxides and acetylene.[47]

The structural composition of the calcium, strontium and barium derivatives reveals a number of interesting trends, beginning with a smooth increase of metal-C_α distances with increasing size of the metal. Of particular note is an unexpected bend angle through the presumably sp-hybridized *ipso*-carbon, with a value of 168° for the calcium congener decreasing to 127° for the barium complex. This unexpected geometry led to several suggestions to explain the surprising results, including a lack of directionality in the ethyne sp orbital and subsequent freedom of motion. Other possibilities include the potential for partial rehybridization of the acetylide moiety, a possible side-on π-interaction of the ligand with the heavier metals, or crystal packing effects.

To further probe these trends, the effects of the ligands on the structural features were examined with the synthesis of less sterically demanding acetylides. Utilization of the same transamination pathway with *para*-*tert*-butylphenylethyne led to the formation of the strontium and barium acetylides (**19**; Figure 12) and **20**.[48] It was expected that the smaller phenyl substituents would experience a reduced steric repulsion with the crown ether ring and allow for more flexibility and perhaps an even closer approach of the ligand to the crown ether than in the bulkier triphenylsilyl analogs.

Intriguingly, very similar geometrical features were observed for both groups of acetylides, suggesting that simple steric models do not satisfactorily explain the unexpected geometry. DFT calculations to shed further light on this topic are currently underway.[49]

8. Di- and Triphenylmethanides

Organometallic di- and triphenylmethanide complexes of the alkali metals are well-known.[50] In contrast, such compounds of the heavier alkaline earth metals are rare; only the compounds shown in Table 4 have been structurally characterized.[51] Of particular interest in these systems is the structural geometry about the methyl carbon, as the

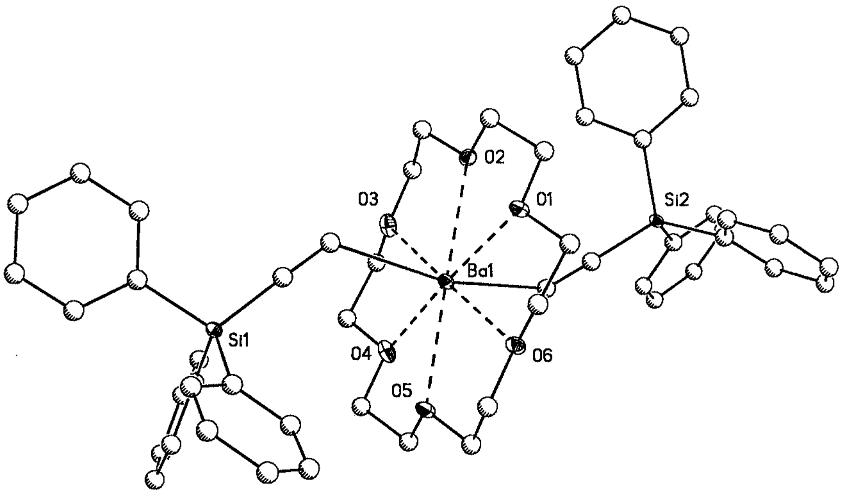

Figure 11. Molecular structure of **18**; heavy atoms displayed anisotropically with ellipsoids at 30% probability; hydrogen atoms have been omitted for clarity

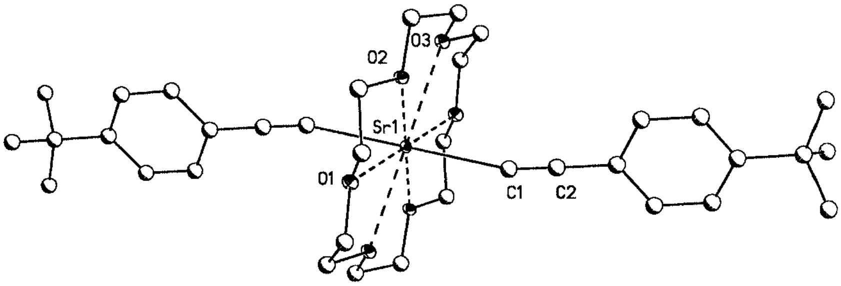

Figure 12. Molecular structure of **19**; heavy atoms displayed anisotropically with ellipsoids at 30% probability; hydrogen atoms have been omitted for clarity

Table 4. Di- and triphenylmethanes, contact and ion pairs

Compound	CN	M−R [Å]	D	M−D [Å]	ref.
$[Sr(CPh_3)_2(HMPA)_2(18\text{-crown-6})]$ (**24**)[a]	6		HMPA 18-c-6	2.41 2.68−2.72	53
$[Sr\{N(SiMe_3)_2\}]_2(C_{12}H_{23}O_2)$ (**23**)	7	2.57[b]	O^-[c] 18-c-6[d]	2.47, 2.42 2.72−2.88	53
$[Ba(CPh_3)_2(HMPA)_2(18\text{-crown-6})]$ (**22**)	6		HMPA 18-c-6	2.59 2.78−2.79	52
$[Ba\{N(SiMe_3)_2\}(C_{12}H_{23}O_2)]_2$ (**21**)	7	2.71[b]	O^-[c] 18-c-6[d]	2.57, 2.61 2.61−2.95	52
$[Ba(HCPh_2)_2(18\text{-crown-6})]$ (**25**)	7	3.07, 3.10 3.39[e]	18-c-6	2.75−2.80	54
$[Ba\{\eta^5\text{-}PhCH(C_5H_4N)\}(THF)(diglyme)]$ (**26**)	4 + 5[f]	2.76−3.30	THF Diglyme	2.82 2.77−2.86	56

[a] HMPA = Hexamethylphosphoramide. [b] Metal-amide distance. [c] Bridging alkoxy anion. [d] Cleaved crown ether distances. [e] Close phenyl contact. [f] Two η^5-metal-carbon interactions.

level of resonance through the phenyl rings can be derived from studies of this type.

Early attempts to synthesize group 2 triphenylmethanides focussed on the transamination route employed successfully to prepare the acetylides (**16−20**). Reaction of triphenylmethane and barium bis[bis(trimethylsilyl)]amide in the presence of 18-crown-6 in THF at low temperature did not afford the desired product; instead, cleavage of the crown ether and subsequent elimination of free amine led to the formation of the heteroleptic vinyl ether amide (**21**; Figure 13).[52]

This heteroleptic barium amide exists as a dimer, with two slightly asymmetrically bridging alkoxide moieties connecting the two metal centers. The opposite face is filled by an amide ligand, and the vinyl ether wraps around the equator of the barium atom giving four additional metal-oxygen interactions for a total coordination number of seven. This reproducible product continued to form even with the switch to an arene elimination route utilizing dibenzylbarium. It was not until the addition of HMPA (HMPA = hexamethylphosphoramide) in conjunction with the arene elimination route that charge separation was induced and the desired product observed.

The barium triphenylmethanide crystallizes as a separated ion pair, with the metal center occupying a center of symmetry (**22**; Figure 14). The crown ether fills the equatorial plane, while two HMPA molecules occupy the axial sites. The metal lies almost directly at the center of the crown ether ring, at an average M−O distance of 2.78 Å. The triphenylmethanide anions exhibit a "propeller" geometry, with the center of the anion fully planarized, suggesting considerable resonance through the phenyl rings. The rings are too sterically demanding to be coplanar and so twist out of the plane by an average of 31.1°. One of the phenyl substituents exhibits a slightly longer bond length to the methyl center; this ring possesses the greatest twist angle, reducing the possible orbital overlap and subsequent resonance stabilization. It is noteworthy that the crown ether is cleaved rather than the THF solvent.

Similarly, the strontium congeners (**23**) and (**24**) of these complexes can be prepared.[53] Reaction of triphenylmethane with strontium bis[bis(trimethylsilyl)]amide with 18-crown-6 in THF at low temperatures leads to the heteroleptic vinyl ether amide (**23**). This compound adopts the same basic geometry as the barium congener, with a similar bridged dimeric structure. As expected, the bonds in the strontium complex overall are slightly shorter than those in the barium compound. The metal centers are still seven coordinate with the cleaved ether wrapping around to complete the coordination sphere.

The strontium triphenylmethanide can be synthesized analogously to the barium congener.[53] Preparation via arene elimination with dibenzylstrontium in the presence of triphenylmethane and HMPA in THF at low temperature

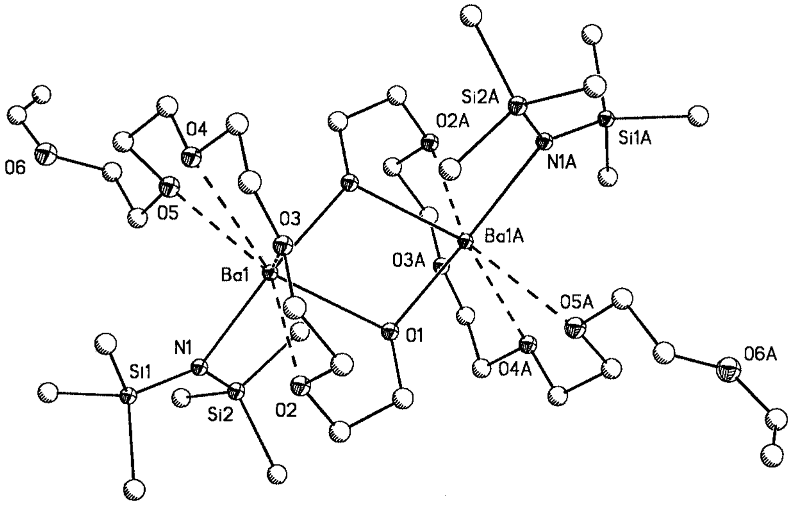

Figure 13. Molecular structure of **21**; heavy atoms displayed anisotropically with ellipsoids at 30% probability; hydrogen atoms have been omitted for clarity

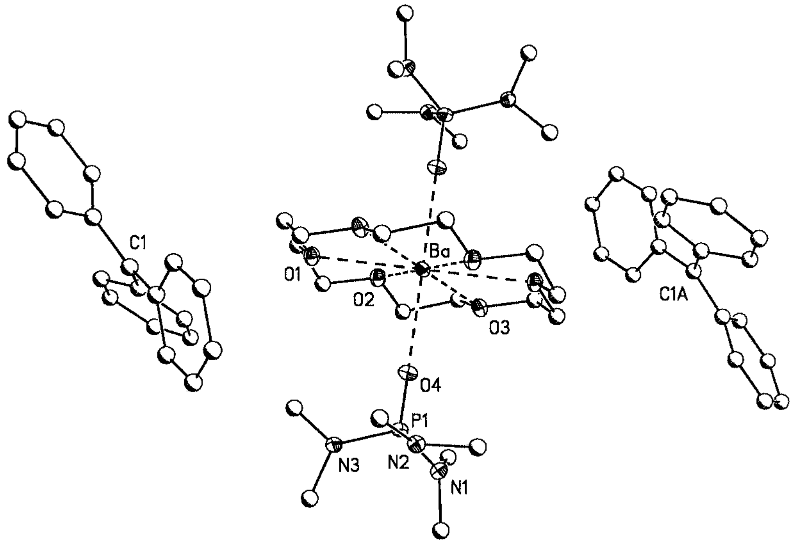

Figure 14. Molecular structure of **22**; heavy atoms displayed anisotropically with ellipsoids at 30% probability; hydrogen atoms have been omitted for clarity

leads to the charge-separated strontium triphenylmethanide (**24**). This complex adopts a structure analogous to the barium congener, with the anions exhibiting a "propeller" geometry. The methyl center is planar, and the phenyl rings twist out of the plane by an average of 30.6°. The ring showing the greatest twist angle leads to the longest C-C distance. If dibenzylbarium is treated with diphenylmethane in the presence of 18-crown-6, the contact barium diphenylmethanide (**25**; Figure 15) stabilized by 18-crown-6 is observed.[54]

Compound **25** crystallizes out of warm THF as a nine-coordinate distorted pseudo-octahedron with the methanide anions capping the axial positions over the crown ether encapsulated metal. The α-carbons in the ligand are slightly pyramidal. The phenyl rings are not coplanar, and are twisted slightly away from the methyl center by an average of 5.5°. Curiously, this compound is stable enough in THF to allow for recrystallization without any of the ether cleavage reactions observed for the triphenylmethanide system. It is possible that the lower steric demand of the diphenylmethanide anion plays a key role. Similar chemistry using dibenzylbarium, diphenylmethane and six equivalents of HMPA led to a charge-separated diphenylmethanide compound with six HMPA donors stabilizing the barium cation. Insufficient crystal quality has thus far prevented a satisfactory structure elucidation.[55]

An earlier example of a heavy alkaline earth dibenzyl system comes with the metallation of 2-pyridylphenylmethane in liquid NH_3/THF with barium and the addition of diglyme (**26**; Figure 16).[56] This "open metallocene" has the potential to add stabilization through coordination of the pyridyl moiety. The metal center is saturated with two η^3-contacts, two pyridyl contacts, one diglyme and one THF molecule. Although the ligands show conjugation through

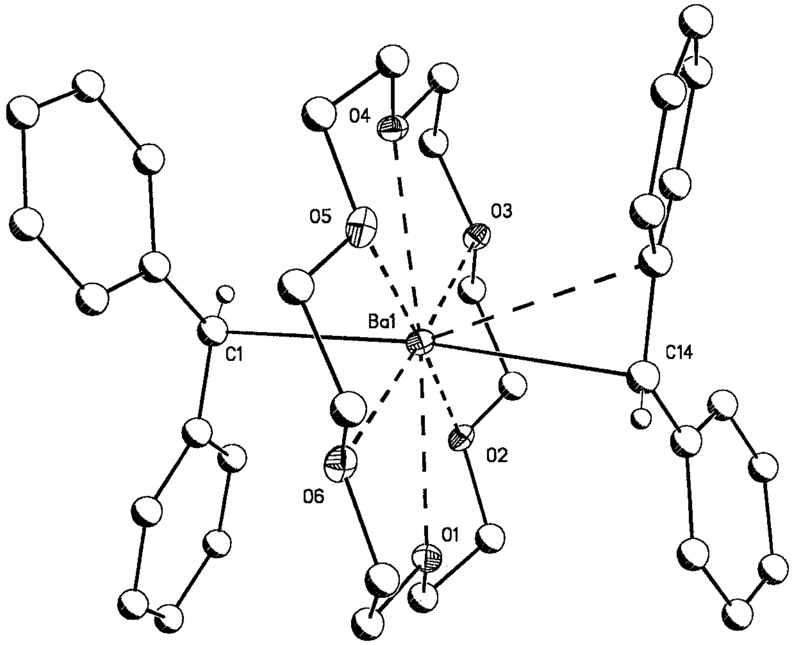

Figure 15. Molecular structure of **25**; heavy atoms displayed anisotropically with ellipsoids at 30% probability; hydrogen atoms except those on the *ipso* carbons have been omitted for clarity

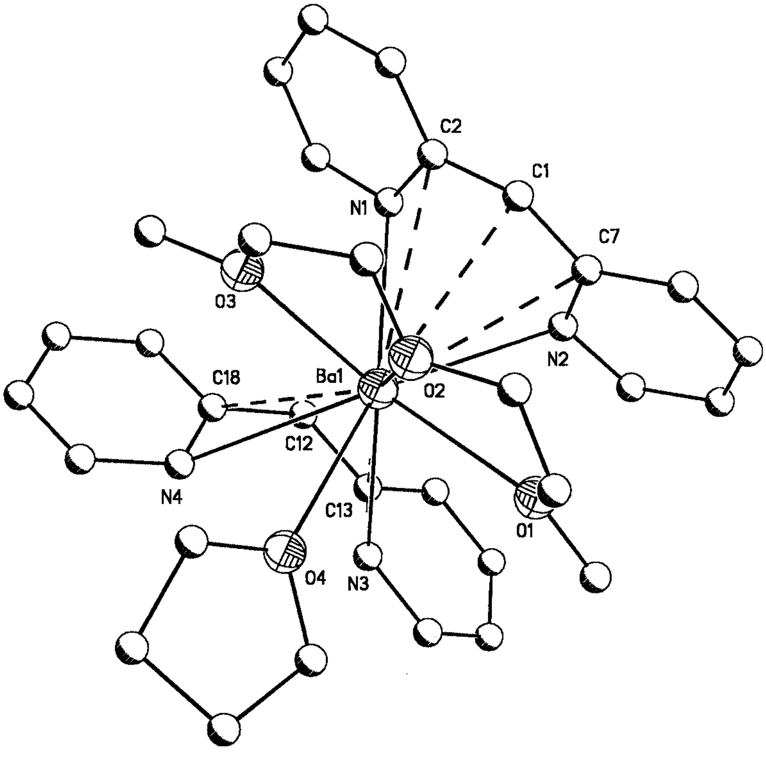

Figure 16. Molecular structure of **26**; heavy atoms displayed anisotropically with ellipsoids at 30% probability; hydrogen atoms have been omitted for clarity

the *ipso*-carbons ($C_{ipso}-C$ distances of 1.41−1.43 Å) the rings are tilted away from the metal center (dihedral angles of 16.0°, 21.8°). Interestingly, the steric bulk of the ligands appears to be of little consequence, as they are pushed quite near each other by the approach of the donor.

9. Conclusions

With the advent of new synthetic methods and an array of possible applications the once sparsely investigated organometallic chemistry of calcium, strontium and barium is coming to the forefront of main group chemistry. A wide variety of compounds once thought inaccessible are now being prepared simply and efficiently, and the interesting structural features of these complexes and the questions they raise demand further examination. With the synthesis and structural characterization of new targets, information on the relationship between structure and reactivity is slowly becoming clear. This will have a profound effect on the possible applications of the target molecules. Future investigations will extend to new ligand systems and alternative synthetic pathways to probe the fascinating geometry, unusual chemical properties and various applications exhibited by this exciting new collection of compounds.

Note added in proof (July 24, 2002): After submission of this article we became aware of two publications which are of importance to this review.[57,58]

Acknowledgments

We are deeply indebted to Professor Dr. Matthias Westerhausen and Priv. Doz. Dr. Sjoerd Harder for sharing information prior to publication. We are also grateful to Dr. Jesse Taylor for his assistance in designing illustrations.

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Received March 21, 2002
[I02148]