DOI: 10.1002/chem.200601634

New Structural Features in Heavy Alkaline Earth-Metal Chemistry — Molecular Heterobimetallic Group 1, Ba Complexes

Maria Felisa Zuniga,[a] Glen B. Deacon,[b] and Karin Ruhlandt-Senge*[a, b]

Abstract: The preparation of heterobimetallic complexes consisting of alkali and heavy alkaline earth metals remains a challenge due to limited available synthetic strategies. Here we present a new class of group 1, Ba compounds of the type $[M_n\{Ba(Odpp)_{2+n}\}]$ (M = Na(n=1) (**1**), K(n=1) (**2**), Cs(n=1) (**3**), Li(n=2) (**4**); HOdpp = 2,6-diphenylphenol) and the Lewis base adducts $[Li_2(thf)_2\{Ba(Odpp)_4\}]\cdot PhMe$ (**5**) and $[K\{Ba(Odpp)_3(diglyme)\}]$ (**6**) (diglyme = [bis(2-methoxy)ethyl ether]) as the first representatives of heterobimetallic group 1, Ba species of low nuclearity. The compounds display a significant degree of metal–arene interaction, believed to be a key factor in stabilizing these highly reactive species. Obtained by solid-state direct metalation, the target compounds are available without further work-up.

Keywords: alkali metals • barium • metalation • O donors • phenoxides • pi interactions

Introduction

Heterobimetallic complexes of magnesium have received significant attention as polymerization initiators,[1] reagents for selective alkylation,[2] deprotonation and metalation,[3] and halogen–magnesium exchange reactions.[4] In contrast, simple heterobimetallic compounds involving the heavier alkaline earth metals remain one of the least explored areas in group 2 chemistry. Aside from a handful of calcium compounds,[5] structurally characterized heterobimetallic complexes involving alkali metals and the heaviest congener, barium, are scarce; examples are limited to the multinuclear $[K\{Ba_2(OSiPh_3)_5(dme)_2\}]$,[6] $[(Li_3Ba_6O_2)^{11+}(OtBu)_{11}(thf)_3]$,[7] $[Na_2Ba\{p\text{-}tBu\text{-calix}[4](OC_5H_9)_2(O)_2\}_2]$,[8] and $[IBa(LiOtBu)_4(OH)(thf)_4]$.[9] The rational preparation of a family of simple complexes composed of alkali and heavy alkaline earth metals will advance the understanding of metal–ligand interactions by illuminating a) the principle of solvation versus ligation, b) structural trends within groups 1 and 2, and c) the detailed correlation between heavy alkaline earth and divalent rare-earth metals. Moreover, this new class of compounds may provide exciting alternatives to the well-established magnesium analogues.[10] Preliminary studies have also indicated their potential as precursors for heavy alkaline earth-metal-containing solids, such as high-temperature superconductors.[11]

A possible reason for the absence of simple heterobimetallic complexes is the failure of conventional metathesis, in contrast to the successful preparation of the rare-earth “ate” analogues.[12] Synthetic attempts involving group 2 reagents typically afford only homometallic species,[5d] a result also confirmed in our group.[13] We now present solid-state direct metalation for the preparation of simple heterobimetallic group 1, Ba complexes. Developed for rare-earth complexes,[14] this synthetic route shows great promise in alkaline earth-metal chemistry.[15]

Our choice of ligand, 2,6-diphenylphenol (HOdpp), is based on recent results, from our laboratory and others,[16] expressing the stabilizing effect of metal–π interactions. Examples include the dinuclear, homoleptic $[M_2(Odpp)_4]$ (Ca, **7**; Sr, **8**; Ba, **9**)[15a] and the anionic aryloxolanthanoidates $[K\{Ln(Odpp)_4\}]$ (Ln = La, Nd)[16a] and $[Na\{Ln(Odpp)_4\}]$ (Ln = Nd, Er).[16b] Here, we aim to explore the significance of such secondary interactions in the structural features of the heterobimetallic-aryloxo complexes of group 1 elements Li, Na, K, and Cs, accompanied by the heavy alkaline earth metal barium in the solid state and in the presence of Lewis bases.

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[a] M. F. Zuniga, Prof. Dr. K. Ruhlandt-Senge
Department of Chemistry
1-014 Center for Science and Technology
Syracuse University, Syracuse, NY 13244-4100 (USA)
Fax: (+1) 315-443-4070
E-mail: kruhland@syr.edu

[b] Prof. Dr. G. B. Deacon, Prof. Dr. K. Ruhlandt-Senge
School of Chemistry
Monash University, Victoria 3800 (Australia)

Results and Discussion

The reaction of elemental barium, 2,6-diphenylphenol (HOdpp), and alkali-metal phenolate in the non-coordinating medium 1,3,5-tri-*tert*-butylbenzene (Mes*H) in an evacuated Carius tube at 225–250 °C affords the target compounds [Eq. (1)] either after crystallization from toluene ($[Na\{Ba(Odpp)_3\}]\cdot PhMe$, **1**; $[K\{Ba(Odpp)_3\}]\cdot PhMe$, **2**; $[Cs\{Ba(Odpp)_3\}]\cdot PhMe$, **3**), directly from the tube ($[Li_2\{Ba(Odpp)_4\}]$, **4**), or after addition of THF to **4** to give $[Li_2(thf)_2Ba(Odpp)_4]\cdot PhMe$, **5**; or diglyme to **2** affording $[K\{Ba(Odpp)_3(diglyme)\}]$, **6**. The synthesis of these species proceeds with good yields and excellent purity in the absence of mercury activation, which is frequently necessary in syntheses that use rare-earth and alkaline-earth metals.[14c,d,15a] In solid-state metalation the flux agent, Mes*H, offers easy and economical scale-up possibilities as it can be recovered and reused. The absence of any volatile solvents in the procedure adds to the attractive and environmentally conscious nature of the process.

$$\begin{aligned}&Ba(s) + n\,MOdpp(s) + 2\,HOdpp\\&\qquad \rightarrow [M_nBa(Odpp)_{2+n}] + H_2\ (\mathbf{1}-\mathbf{4})\end{aligned}\tag{1}$$

1:M = Na, $n=1$; **2**:M = K, $n=1$; **3**:M = Cs, $n=1$; **4**:M = Li, $n=2$

In a variation of the synthetic procedure, the exposure of a mixture of the metals to the alcohol (HOdpp) was successful for the preparation of compound **1** [Eq. (2)]. This approach makes the synthetic procedure more convenient as no air-sensitive reagents need to be prepared. Alkaline-earth and rare-earth metals differ in that heterobimetallic compounds of the latter are available by high-temperature reactions of the metal chlorides and alkali-metal 2,6-diphenylphenolates[16b] or 3,5-di-*tert*-butylpyrazolates.[17] In addition, the preparation of $[K\{Ln(Odpp)_4\}]$(Ln=La, Nd)[16a] involves the use of rare-earth-metal aryloxides as the metal source.

$$Ba(s) + Na(s) + 3\,HOdpp \rightarrow [NaBa(Odpp)_3](\mathbf{1}) + 1.5\,H_2 \tag{2}$$

Although metalation procedures to prepare alkaline-earth-metal aryloxides or amides are not new, previous schemes require the presence of donor solvents such as THF, HMPA (hexamethylphosphoramide), or NH_3, with the resulting compounds occurring as adducts of these bases.[18] Use of these solvents involves the added inconvenience of drying procedures. The removal of water from THF and HMPA utilizes standard procedures, whereas NH_3 involves condensation over sodium, and the added safety risk of working with a condensed gas. We believe that solid-state, high-temperature metalation offers a very attractive synthetic approach by providing a low-maintenance, facile alternative. Current work in our laboratory focuses on expanding the solid-state methods towards other ligand systems.

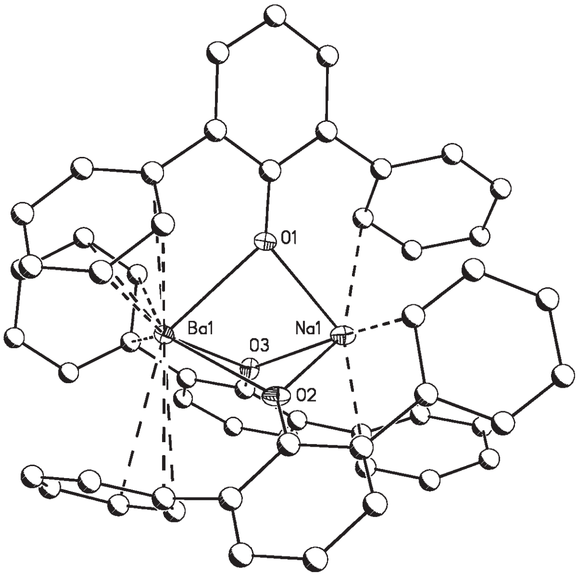

Figure 1. Structure of $[Na\{Ba(Odpp)_3\}]\cdot PhMe$, **1**. For clarity, the hydrogen atoms and toluene solvate are not shown.

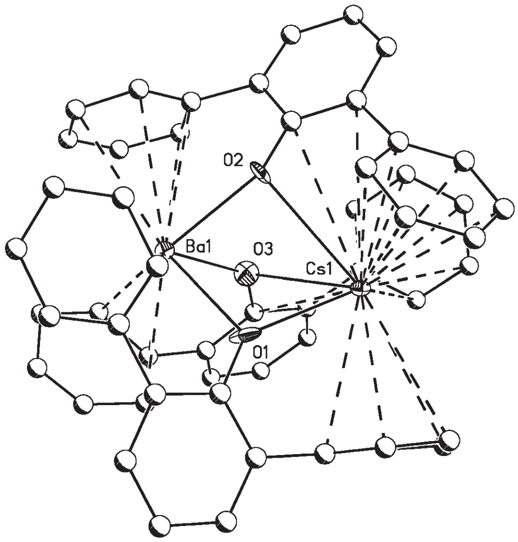

Figure 2. Structure of $[Cs\{Ba(Odpp)_3\}]\cdot PhMe$, **3**. For clarity, the hydrogen atoms and toluene solvate are not shown.

Compounds **1**–**3** share many critical structural features, as shown in Figures 1 and 2. Pertinent bond lengths and angles are summarized in Table 1. In these compounds, three aryloxides bridge the alkali metals and barium, giving a pyramidal MO_3 core for each metal. This unusual structural motif that contains solely bridging-oxygen atoms is closely related to the $[Yb_2(Odpp)_3]^+$ cation[19] and a series of heterobimetallic group 14 species $[Li\{Sn(Odpp)_3\}]$[16c] and $[M\{Ge(Odpp)_3\}]$ (M = Li, Na, K, Cs, Rb).[16d] The structural similarities between the group 2 and divalent group 14 elements are surprising considering the vast difference in their metal diameters.[20] A related core structure is also found in dimeric **9**, which contains a fourth aryloxide located in a ter-

Table 1. Selected bond lengths [Å] and angles [°] in [Na{Ba(Odpp)$_3$}]·PhMe (**1**), [K{Ba(Odpp)$_3$}]·PhMe (**2**), and [Cs{Ba(Odpp)$_3$}]·PhMe (**3**).

	1(M=Na)	**2**(M=K)	**3**(M=Cs)
bond lengths			
Ba1−O1	2.547(2)	2.570(7)	2.678(6)
Ba1−O2	2.599(2)	2.710(6)	2.570(4)
Ba1−O3	2.542(2)	2.523(6)	2.513(5)
M1−O1	2.338(2)	2.618(7)	2.773(5)
M1−O2	2.326(2)	2.527(5)	3.102(6)
M1−O3	2.335(2)	2.742(6)	3.044(6)
bond angles			
O1-Ba1-O2	72.13(6)	75.0(2)	76.5(2)
O1-Ba1-O3	74.69(6)	77.4(2)	81.9(2)
O2-Ba1-O3	73.32(6)	71.0(2)	80.2(2)
O1-M1-O2	81.02(8)	77.4(2)	66.9(1)
O1-M1-O3	82.69(7)	70.4(2)	71.5(2)
O2-M1-O3	82.39(8)	72.9(2)	64.3(1)
Ba1-O1-M1	87.36(6)	92.8(2)	95.0(2)
Ba1-O2-M1	86.38(6)	91.6(2)	89.7(2)
Ba1-O3-M1	87.52(6)	91.0(2)	92.1(2)
Ba1-O1-C11	135.9(2)	139.6(5)	121.0(5)
Ba1-O2-C21	136.0(2)	112.9(4)	138.2(4)
Ba1-O3-C31	137.1(2)	140.2(4)	140.0(4)
M1-O1-C11	136.7(2)	125.8(6)	138.6(4)
M1-O2-C21	137.6(2)	139.8(4)	103.3(4)
M1-O3-C31	135.2(2)	109.9(4)	111.1(5)

minal position. In contrast, previous monoanionic amido calciates[5a,d] and magnesiates[3,21] display one of three ligands in a terminal position, probably an expression of the smaller alkaline-earth metal size.

The Ba−O bond lengths in **1** fall within a small range (av 2.563(2) Å) and are comparable to the bridging Ba−O bond lengths in the three-(oxygen)coordinate Ba center of **9** (2.588(2) Å).[15a] The Na−O bond lengths of **1** are in a narrow range (av 2.333(2) Å) and compare favorably to [Na{Ge(Odpp)$_3$}] (av 2.306(2) Å),[16d] but are significantly shorter than in [NaNd(Odpp)$_4$] (2.343(6)–2.722(5) Å),[16b] in which sodium has a higher formal coordination number. The close range of O-Ba-O, O-Na-O, and Ba-O-Na angles in **1** result in approximate C_3 symmetry around the metal centers. Compound **2** exhibits 50/50 disorder over the two metal sites, an observation completely consistent with the very similar ionic radii (Ba^{2+} (CN6) = 1.49 Å; K^+ (CN6) = 1.52 Å; CN = coordination number). As such, metal–oxygen distances carry a slightly higher degree of uncertainty, with differences in Ba−O and K−O bond lengths of up to ca. 0.2 Å. In general, a larger range of metal-oxygen bond lengths are observed for the heavier alkali-metal derivatives, a trend consistent with structural features in germanates, in which large deviations were observed in the Cs species.[16d] Analogously, **3** displays a relatively wide range of Ba−O bond lengths (2.513(5)–2.678(6) Å), as well as significant disparities in the Cs−O contacts, with one short bond (2.773(5) Å) and two longer interactions (3.102(6) and 3.044(6) Å). The differences in bond lengths and angles are associated with increased structural flexibility, as well as increased capacity for π-arene interactions.[16a]

With their simple framework and close metal–oxygen contacts, **1**–**3** represent the first examples of molecular cage-like structures for alkali (Na, K, or Cs)/barium complexes. The rational synthesis and the unassociated structural motif of these compounds are significant because heterobimetallic complexes involving alkali and heavy alkaline earth metals are usually based on multinuclear arrangements.[6–9]

In contrast to the 1:1 alkali (Na, K, Cs)/Ba formulation of **1**–**3**, use of lithium aryloxide in a 1:1 reaction with barium gives **4**, a compound with a 2:1 lithium/barium ratio (Figure 3, Table 2). With a theoretical yield of 50 %, **4** was then prepared rationally by introducing two equivalents of lithium aryloxide. In **4** the barium center is in a severely distorted tetrahedral environment created by four aryloxides. The O−Ba−O angles of **4** range from 65.34(4)–146.76(4)°; the narrow angles that involve barium bridge two oxygen atoms that are linked to one lithium center. To reduce steric

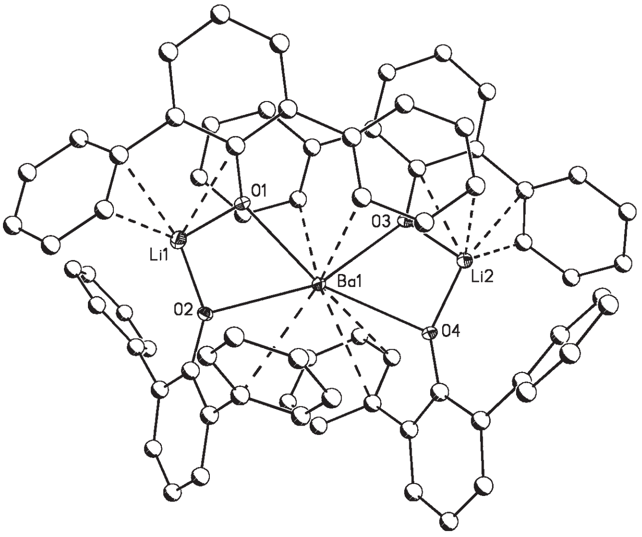

Figure 3. Structure of [Li$_2${Ba(Odpp)$_4$}], **4**. For clarity, the hydrogen atoms are not shown.

Table 2. Selected bond lengths [Å] and angles [°] in [Li$_2${Ba(Odpp)$_4$}] (**4**).

bond lengths			
Ba1−O1	2.625(1)	Li1−O1	1.872(4)
Ba1−O2	2.640(1)	Li1−O2	1.777(4)
Ba1−O3	2.627(1)	Li2−O3	1.888(4)
Ba1−O4	2.701(1)	Li2−O4	1.804(2)
bond angles			
O1-Ba1-O2	65.75(4)	O1-Li1-O2	103.1(2)
O1-Ba1-O3	104.88(4)	O3-Li2-O4	102.4(2)
O1-Ba1-O4	142.08(4)	Ba1-O1-Li1	91.7(1)
O2-Ba1-O3	146.76(4)	Ba1-O2-Li1	93.4(1)
O2-Ba1-O4	141.61(4)	Ba1-O3-Li2	91.9(1)
O3-Ba1-O4	65.34(4)	Ba1-O4-Li2	91.4(1)
Ba1-O1-C11	145.5(2)	Li1-O1-C11	119.7(2)
Ba1-O2-C21	119.5(1)	Li1-O2-C21	145.6(2)
Ba1-O3-C31	141.4(1)	Li2-O3-C31	118.1(2)
Ba1-O4-C41	123.3(1)	Li2-O4-C41	144.5(2)

strain and allow a maximum of intramolecular π interactions, the three metal centers are arranged in a nonlinear fashion with a Li1-Ba-Li2 angle of 153.1(1)° and the two LiO_2Ba rings tilted by 53.2°. The phenyl substituents in **4** are tilted relative to the phenoxide unit (at C2 40.9°, at C6 54.0°) to further maximize π interactions. The two four-membered rings, aside from displaying similar geometrical features, are non-planar (sum of endocyclic angles = 354 and 351°).

As rationalized by the core structure of **4**, the Ba–O bond lengths are slightly longer than in **1**, but closely resemble the bridging distances in the hexameric $[Ba_6(OPh)_{12}(TMEDA)_4]$ (TMEDA = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine) (2.619(3)–2.676(3) Å).[22] Li–O bond lengths in **4** (1.777(2)–1.888(4) Å) are shorter than in solvated magnesiates, including $[Li_2(TMEDA)_2Mg(2\text{-}Me\text{-}C_6H_4O)_4]$ (1.917(5)–1.964(5) Å),[23] despite a higher formal coordination number in **4** (CN = 5 (Li1); 6 (Li2).

Table 3. Metal–carbon distances [Å] of π-phenyl–metal interactions in **1**–**6**, in which *n* = *xyz* *x* indicates the oxygen number of the ligand, *y* indicates the 2- or 6- positions of phenyl substituents, and *z* indicates the carbon number in phenyl substituents.

1		**2**		**3**		**4**		**5**		**6**	
Ba1–C*n*		Ba1–C*n*		Ba1–C*n*		Ba1–C*n*		Ba1–C*n*		Ba1–C*n*	
121	3.282(3)	121	3.373(8)	121	3.293(6)	12	3.267(2)	326	3.396(2)	226	3.400(2)
122	3.203(3)	122	3.374(9)	126	3.371(7)	25	3.439(2)				
123	3.320(3)	21	3.436(7)	221	3.322(5)	54	3.273(2)	Li2–C*n*		K1–C*n*	
221	3.328(3)	261	3.235(7)	222	3.324(7)	67	3.430(2)	31	2.756(4)	161	3.035(2)
222	3.249(3)	262	3.419(7)	223	3.474(7)	68	3.444(2)	41	2.732(4)	162	3.248(2)
223	3.359(3)	266	3.381(7)	226	3.475(7)					166	3.179(2)
321	3.308(3)	321	3.287(6)	321	3.32(1)	Li1–C*n*				21	3.433(2)
325	3.394(3)	322	3.271(8)	322	3.313(9)	11	2.776(5)			261	3.044(2)
326	3.178(3)	323	3.40(1)	326	3.37(1)	161	2.491(5)			262	3.295(3)
		326	4.349(7)			166	2.482(5)			266	3.217(2)
Na1–C*n*				Cs1–C*n*						31	3.412(2)
166	2.849(3)	K1–C*n*		161	3.449(6)	Li1–C*n*				361	3.068(2)
262	2.896(3)	161	3.320(7)	162	3.500(8)	124	2.718(5)			362	3.416(2)
366	2.913(3)	166	3.376(6)	163	3.596(6)	31	2.766(4)			365	3.135(2)
		221	3.279(6)	164	3.620(9)	321	2.588(4)				
		222	3.290(8)	165	3.577(7)	326	2.643(5)				
		223	3.421(7)	166	3.474(9)						
		226	3.376(7)	21	3.639(9)						
		31	3.417(7)	26	3.774(9)						
		361	3.174(7)	261	3.302(6)						
		362	3.341(7)	262	3.517(6)						
		366	3.383(7)	263	3.776(6)						
				265	3.670(6)						
				266	3.415(6)						
				31	3.756(9)						
				361	3.405(8)						
				362	3.507(8)						
				363	3.716(8)						
				364	3.790(8)						
				365	3.698(9)						
				366	3.509(9)						

In contrast to **4**, lithium germanates and stannates have the composition $[Li\{E(Odpp)_3\}]$ (E = Ge, Sn),[16c,d] although dianionic complexes are well recognized in magnesiates, $[Li_2(MgR_4)]$ (R = alkyl, aryl, amide, aryloxide).[21b,23,24] The tendency to form a $[M_2Ae(OR)_4]$ (M = Li, Ae = Ba, R = aryl) species for lithium versus the cage-like motif for **1**–**3** may be due to the small metal size of lithium, disfavoring the rare triply bridging motif.

A significant structural feature in **1**–**4** is the stabilization of the metals through π-arene interactions from the neutral phenyl substituents (Table 3). Although the role of π coordination in alkaline-earth-metal chemistry has been well established for cyclopentadienides and cyclooctadienides,[5f,25,26] the involvement of neutral arenes as part of larger ligand systems is only now being realized as a major structure-determining force.[15,27] The extent of metal–arene interaction depends on the metal diameter, in **1** the barium interacts with the three phenyl substituents in a $\eta^3:\eta^3:\eta^3$ fashion (upper limit ≤ 3.48 Å);[15a] the shortest distance is 3.178(2) Å. The smaller sodium center displays a $\eta^1:\eta^1:\eta^1$ binding mode to three phenyl substituents with Na–π Ar contacts in the range of 2.849(3)–2.913(3) Å (upper limit 3.01 Å).[16b,17] In **2**, both metal centers (K/Ba, 50/50 disorder) exhibit a $\eta^2:\eta^3:\eta^4:\eta^1$ binding mode that involves interactions from both phenyl substituents and the *ipso* carbon of the phenoxide unit. As the metal diameter increases, metal–arene interactions become more prominent, as seen in **3**, in which the large cesium metal (Cs^+ (CN6) = 1.81 Å) exhibits a $\eta^6:\eta^5:\eta^6$ coordination to three pendant phenyl rings and an additional $\eta^2:\eta^1$ binding mode involving the *ipso* and *ortho* carbons of the phenoxide units, with Cs–C distances ranging from 3.302(6) to 3.776(6) Å. The sum of the Ba–arene interactions ($\eta^2:\eta^4:\eta^2$) in **3** compares to those of **1** and **2**, with only minor variations with regards to the π contributions from the individual phenyl rings.

In **4**, the addition of a fourth aryloxide ligand increases the steric congestion around the barium center, resulting in a decreased amount of π bonding ($\eta^1:\eta^1:\eta^1:\eta^2$) relative to **1**–**3**. The lithium centers are also stabilized through π interactions originating from the phenyl substituents as well as *ipso* carbons of the phenoxide units (Li1: $\eta^2:\eta^1$; Li2: $\eta^1:\eta^2:\eta^1$; Li–C distances 2.482(5)–2.776(5) Å). The extensive π interactions in **1**–**4** are in contrast to the aryloxomagnesiate $[Li_2(TMEDA)_2Mg(2\text{-}Me\text{-}C_6H_4O)_4]$ and several other magnesiates with a 2:1 or 1:1 Li/Mg ratio, albeit secondary interactions have been shown to stabilize some of these compounds.[23]

The importance of π interactions that increase the stabilization of the target compounds is further demonstrated in the unsuccessful preparation of heterobimetallic compounds by using the bulky ligand 2,6-tBu$_2$-4-MeC$_6$H$_2$OH (HBHT).[28] Despite repeated attempts to prepare the target compounds by using solid-state and solution chemistry in various solvents, only the homometallic compounds were isolated. In contrast, **1** can be reproduced in excellent yield (93 %) by solution chemistry involving the homometallic species [Ba$_2$(Odpp)(μ-Odpp)$_3$] (**9**) and sodium phenolate in toluene [Eq. (3)]. A possible pathway for the formation of **1** may include the spontaneous dissociation of the dimeric barium species and association with sodium phenolate to form the metal-arene stabilized heterobimetallic complex.

$$[\mathrm{Ba_2(Odpp)(\mu\text{-}Odpp)_3}] + 2\,\mathrm{NaOdpp} \rightarrow 2\,[\mathrm{NaBa(Odpp)_3}](\mathbf{1}) \qquad (3)$$

Experiments focusing on the addition of the oxygen-donor THF were conducted to explore the significance of metal–arene interactions. Remarkably, adduct formation was observed with **4**, whereas the molecular cages, **1**–**3**, remained donor-free. The addition of THF to **4** led to the coordination of the Lewis base donor to the lithium centers to afford **5**. The [Li$_2$Ba(OR)$_4$] core is maintained in the THF solvate **5** (Figure 4) in which the Ba–O (av 2.626(2) Å) and bridging Li–O (av 1.854(4) Å) bond lengths are comparable to the distances in **4** (Table 4). The Li–O(thf) bond lengths (1.912(4) and 1.869(4) Å) are in good agreement with literature values.[5i] The solvation in **5** led to a significant reduction of lithium-arene interactions relative to **4;** only Li2 exhibited π bonding (η^1:η^1) to the *ipso* carbon of two phenoxide units of O3 and O4. Moreover, the minimal amount of π interactions allows the LiO$_2$Ba rings to tilt further away from each other (tilt angle = 79°), with an approximate linear arrangement of the metal centers (Li1-Ba1-Li2 angle = 177°). The orientation of the fused-rings enhances the steric saturation of the barium center, which displays only one close Ba–C contact (3.400(2) Å). The distorted-tetrahedral geometry around barium observed in **4** is also evident in **5**, in which the two narrow O-Ba-O angles of both compounds are quite similar (ca. 65°). However, all other O-Ba-O angles in **5** are relatively more acute than in **4**, rendering more planar LiO$_2$Ba rings in **5** (sum of endocyclic angles = 360 and 359°).

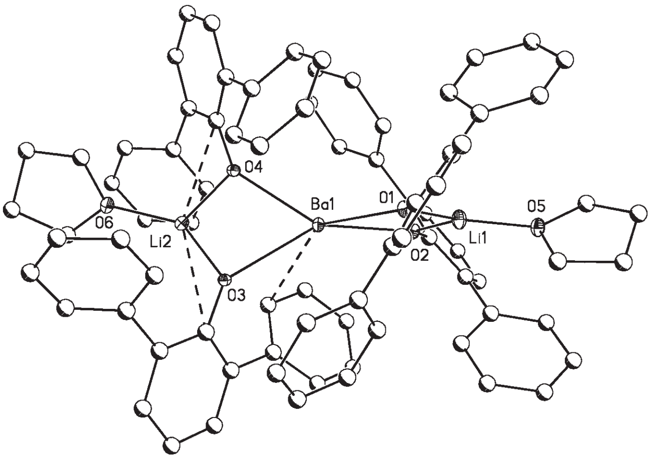

Figure 4. Structure of [Li$_2$(thf)$_2${Ba(Odpp)$_4$}]·PhMe, **5**. For clarity, the hydrogen atoms and toluene solvate are not shown.

Table 4. Selected bond distances [Å] and angles [°] in [Li$_2$ (thf)$_2${Ba-(Odpp)$_4$}]·PhMe (**5**).

bond lengths			
Ba1–O1	2.612(2)	Li1–O1	1.868(4)
Ba1–O2	2.631(2)	Li1–O2	1.862(4)
Ba1–O3	2.618(2)	Li1–O5	1.912(4)
Ba1–O4	2.602(2)	Li2–O3	1.835(4)
		Li2–O4	1.850(4)
		Li2–O6	1.869(4)
bond angles			
O1-Ba1-O2	66.14(4)	O1-Li1-O2	100.2(2)
O1-Ba1-O3	131.48(5)	O1-Li1-O5	119.2(2)
O1-Ba1-O4	137.25(5)	O2-Li1-O5	139.5(2)
O2-Ba1-O3	141.48(5)	O3-Li2-O4	101.7(2)
O2-Ba1-O4	128.19(5)	O3-Li2-O6	137.1(2)
O3-Ba1-O4	66.37(5)	O4-Li2-O6	119.7(2)
Ba1-O1-C11	137.5(1)	Ba1-O1-Li1	97.1(1)
Ba1-O2-C21	136.8(1)	Ba1-O2-Li1	96.6(1)
Ba1-O3-C31	139.9(1)	Ba1-O3-Li2	95.9(1)
Ba1-O4-C41	141.5(1)	Ba1-O4-Li2	96.0(1)
		Li1-O1-C11	124.9(2)
		Li1-O2-C21	126.5(2)
		Li2-O3-C31	120.5(2)
		Li2-O4-C41	117.7(2)

Illustrating further the competition between solvation and intramolecular stabilization involving metal–π arene interactions, one equivalent of diglyme coordinates to barium in **2** to afford **6**. Notably, the coordination of diglyme to barium in **6** (Figure 5) contrasts the THF coordination in **5** wherein

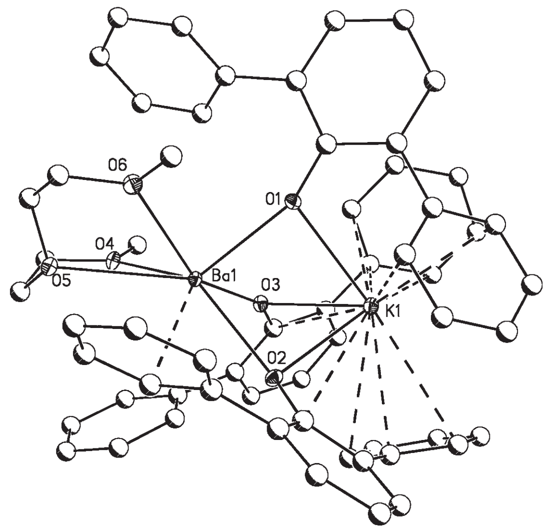

Figure 5. Structure of [K{Ba(Odpp)$_3$(diglyme)}], **6**. For clarity the hydrogen atoms are not shown.

the solvent bonds preferentially to the smaller lithium metals. The overall structural features of donor-free **2** and solvated **6**, including the three bridging aryloxides and asymmetric pyramidal geometry at the metal centers (Table 5), are similar. The bridging Ba–O bond lengths (av 2.564(2) Å) and K–O distances (av 2.779(2) Å) in **6** are slightly longer than those in **2**, and the terminal Ba–O(diglyme) bond lengths are longer (av 2.848(2) Å) than the bridging distances. The O-K-O angles in **6** are in good agreement with those in **2**, however, the O-Ba-O angles in **6** are approximately 10° wider as a consequence of a significant reduction in π interactions with the bridging ligands. The π stabilization on barium decreased to an η^1 binding mode (Ba–C distance = 3.396(2) Å), but not surprisingly, the K–π arene interactions (η^3:η^4:η^4) are rather similar to those in **2**. The subtle differences between lanthanoids and alkaline-earth metals are demonstrated by the reactions of diglyme with either [Na{Ln(Odpp)$_4$}] (Ln = Nd, Er) or compound **2**. Although the former affords separated ions [Na(diglyme)$_2$][Ln(Odpp)$_4$] (Ln = Nd, Er),[16b] complex **6** is observed for the later by using a relatively smaller amount of the donor, a result explained by the weaker metal–ligand/donor bonds. The addition of a large excess of diglyme to **2**, as carried out in the lanthanoids experiments, resulted in the homometallic donor adduct, [Ba(Odpp)$_2$(diglyme)$_2$].[13]

Table 5. Selected bond lengths [Å] and angles [°] in [K{Ba(Odpp)$_3$-(diglyme)}] (**6**).

bond lengths			
Ba1–O1	2.530(2)	K1–O1	2.826(2)
Ba1–O2	2.620(2)	K1–O2	2.766(2)
Ba1–O3	2.542(2)	K1–O3	2.745(2)
Ba1–O4	2.856(2)		
Ba1–O5	2.910(2)		
Ba1–O6	2.777(2)		
bond angles			
O1-Ba1-O2	85.65(5)	O1-K1-O2	77.50(5)
O1-Ba1-O3	83.98(5)	O1-K1-O3	72.53(5)
O2-Ba1-O3	78.33(5)	O2-K1-O3	74.93(5)
O1-Ba1-O4	124.94(5)	Ba1-O1-K1	85.26(5)
O1-Ba1-O5	132.98(5)	Ba1-O2-K1	84.81(5)
O1-Ba1-O6	77.90(5)	Ba1-O3-K1	86.75(5)
O2-Ba1-O4	135.89(5)	Ba1-O1-C11	158.6(2)
O2-Ba1-O5	127.83(5)	Ba1-O2-C21	153.9(2)
O2-Ba1-O6	121.58(5)	Ba1-O3-C31	158.5(2)
O3-Ba1-O4	74.02(5)	K1-O1-C11	114.0(1)
O3-Ba1-O5	129.61(5)	K1-O2-C21	109.5(1)
O3-Ba1-O6	151.29(5)	K1-O3-C31	109.3(1)
O4-Ba1-O5	57.40(5)		
O4-Ba1-O6	98.05(5)		
O5-Ba1-O6	57.17(5)		

Upon gentle heating of **5** and **6**, THF and diglyme are released, presumably leading to the formation of **4** and **2**, respectively. Thermogravimetric analysis (TGA) studies show loss of THF from **5** beginning at 100 °C, and being complete at 150 °C. In the case of **6**, diglyme is lost upon heating to 116 °C, with its complete loss at 140 °C. These observations are further supported by variable temperature (VT) powder diffraction data, in which different powder patterns were observed at temperatures above 140 °C.

To gain further insight into the solution-state constitution of compounds **1**–**6**, room-temperature ^{1}H NMR spectra in C_6D_6 were obtained. In addition to chemical shifts for toluene, THF, and diglyme if appropriate, each compound shows a single set of signals for the Odpp ligand with slight differences in the chemical shifts for **1**–**3** and **6.** However, more upfield resonances (ca. 0.2 ppm) of the doublets representing *ortho* hydrogens are seen in **4** and **5**. These observations indicate that the distinct structural features of the compounds are maintained in solution, consistent with the cage-like motif of **1**–**3** and the fused-rings core of **4** as seen in the solid state. It is important to note that the identification of metal–π phenyl interactions in solution is not possible due to the propensity for metal–C_6D_6 coordination.

Conclusion

The synthesis of heterobimetallic group 1, Ba complexes demonstrates the potential of the solid-state metalation route for the preparation of alkaline-earth-metal species. The target compounds allowed detailed analysis of strategies to achieve steric saturation. Moreover, these species highlight the importance of secondary interactions through π bonding in stabilizing the highly reactive metal centers, a principle that will guide future developments in alkaline-earth-metal compounds and potential synthetic and materials applications. The preliminary data suggests the related calcium derivative can be utilized as a metal–organic chemical vapor deposition (MOCVD) precursor.[13] Consequently, current work is concerned with solution studies as well as the correlation of metal combinations with thermal stability and volatility. Furthermore, solid-state metalation is currently being explored as an alternative synthetic method for other families of alkaline-earth-metal compounds.

Experimental Section

The compounds described herein are extremely air and moisture sensitive, consequently, all manipulations are to be carried out under an inert-gas atmosphere. 2,6-Diphenylphenol (HOdpp) was purchased from Aldrich and used as received. MOdpp (M = Li, Na, K, Cs) was prepared according to literature procedures.[29] All other reagents and solvents were purified under standard procedures. ^{1}H NMR spectra were recorded by using a Bruker DPX 300 spectrometer. IR spectra (4000–650 cm^{-1}) were recorded as Nujol mulls between NaCl plates by using a Nicolet IR200 spectrometer. Metal analyses were determined by Complete Analysis Laboratories, Parsippany, NJ, USA. Carius tubes were charged with the starting materials then sealed under vacuum (50 mtorr) and heated in a furnace. The tubes were cooled to RT and placed in the glove box, in which the crude product was transferred to a Schlenk flask and washed with hexane (2 × 30 mL) to remove 1,3,5-tBu$_3$C$_6$H$_3$. Crystals of **1, 2**, and **3**, suitable for X-ray diffraction, were obtained by recrystallization from toluene. In the case of **4**, crystalline material was collected from a deposit from the top of the tube. Crystallization of **5** and **6** is described below.

Crystallographic analyses for compounds **1**–**6** were conducted as described.[30,31]

[Na{Ba(Odpp)$_3$}]·PhMe, **1**

Method A: Ba (0.69 g, 5.0 mmol), HOdpp (0.50 g, 2.0 mmol), NaOdpp (0.27 g, 1 mmol), and 1,3,5-tBu$_3$C$_6$H$_3$ (1.0 g, 4 mmol) were heated to 225 °C for 5 days. Yield: 0.58 g (62 %).

Method B: Ba (0.41 g, 3.0 mmol), Na (0.023, 1.0 mmol), HOdpp (0.74 g, 3.0 mmol), and 1,3,5-tBu$_3$C$_6$H$_3$ (1.0 g, 4 mmol) were heated to 225 °C for 7 days. Yield: 0.20 g (21 %).

Method C: [Ba$_2$(Odpp)(μ-Odpp)$_3$] (0.55 g, 0.44 mmol) (prepared according to literature procedures, but without the addition of mercury)[15a] was dissolved in 30 mL toluene then added to NaOdpp (0.27 g, 1.0 mmol). The solution was stirred overnight, warmed to 80 °C, then cooled to RT to give colorless crystals after 2 days. Yield: 0.76 g (93 %).

M.p. (sealed tube/N$_2$): 270–274 °C; ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 7.46 (d, 12 H; o-H(Ph)), 7.33 (d, 6 H; m-aryl-H), 7.15 (m, 2.5 H; aryl-PhMe), 6.84 (t, 12 H; m-H(Ph)), 6.78 (t, 3 H; p-aryl-H), 6.73 (t, 6 H; p-H(Ph)), 2.11 ppm (s, 1.5 H; CH$_3$-PhMe); IR (Nujol): $\tilde{\nu}$ = 2921 (s), 1957 (w), 1892 (w), 1827 (w), 1592 (m), 1581 (m), 1551 (m), 1494 (m), 1451 (s), 1411 (s), 1295 (s), 1254 (s), 1172 (m), 1154 (w), 1106 (w), 1068 (m), 1025 (w), 1009 (m), 990 (m), 917 (s), 849 (s), 813 (w), 799 (w), 766 (m), 754 (s), 730 (w), 704 (s), 623 cm^{-1} (w); metal analysis calcd (%) for C$_{54}$H$_{39}$BaNaO$_3$ (896.32) (toluene lost by exposure to vac.): Na 2.57, Ba 15.32; found: Na 2.77, Ba 15.40.

1: C$_{54}$H$_{39}$BaNaO$_3$·PhMe; M_r = 988.32; monoclinic $P2_1/c$; a = 15.258(1), b = 16.934(1), c = 18.393(2) Å; $\alpha = \gamma$ = 90, β = 94.325(2)°; V = 4738.8(7) Å^3; T = 97 K; Z = 4; μ = 0.894 mm^{-1} (Mo$_{K\alpha}$); yellow block 0.32 × 0.30 × 0.16 mm^3; 8345 independent reflections, $3.6 \leq 2\theta \geq 50.0$; R_1 = 0.0313, wR_2 = 0.0767 for data [$I > 2\theta(I)$] and R_1 = 0.0351, wR_2 = 0.0796 for all data. Disorder in one of the phenyl groups was handled by introducing 50:50 split positions.

[K{Ba(Odpp)$_3$}]·PhMe, 2: Ba (0.41 g, 3.0 mmol), HOdpp (0.50 g, 2.0 mmol), KOdpp (0.28 g, 1 mmol), and 1,3,5-tBu$_3$C$_6$H$_3$ (0.5 g, 2 mmol) were heated to 245 °C for 7 days. Yield: 0.36 g (26 %). M.p. (sealed tube/N$_2$): 284–287 °C; ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 7.42 (d, 12 H; o-H(Ph)), 7.30 (d, 6 H; m-aryl-H), 7.15 (m, 5 H; aryl-PhMe), 6.86 (t, 12 H; m-H(Ph)), 6.75 (m, 9 H; p-aryl-H, p-H(Ph)), 2.11 ppm (s, 3 H; CH$_3$-PhMe); IR (Nujol): $\tilde{\nu}$ = 2910 (s), 2723 (m), 1950 (w), 1878 (w), 1681 (w), 1667 (w), 1650 (w), 1644 (w), 1589 (m), 1547 (m), 1455 (s), 1410 (s), 1294 (s), 1258 (s), 1170 (m), 1153 (m), 1106 (m), 1074 (m), 1064 (m), 1025 (w), 1009 (m), 989 (m), 916 (s), 848 (s), 801 (w), 768 (w), 757 (s), 737 (s), 703 (s), 665 (w), 624 cm^{-1} (w).

2: C$_{54}$H$_{39}$BaKO$_3$·PhMe; M_r = 1004.43; monoclinic $P2_1$; a = 12.487(2), b = 12.712(2), c = 15.380(2) Å; $\alpha = \gamma$ = 90, β = 108.632(2)°; V = 2313.4(6) Å^3; Z = 2; μ = 0.997 mm^{-1} (Mo$_{K\alpha}$); colorless block 0.42 × 0.30 × 0.20 mm^3; 11207 independent reflections, $2.8 \leq 2\theta \geq 56.7$; R_1 = 0.0724, wR_2 = 0.1643 for data [$I > 2\theta(I)$] and R_1 = 0.0746, wR_2 = 0.1655 for all data.

[Cs{Ba(Odpp)$_3$}]·PhMe, 3: Ba (0.41 g, 3.0 mmol), HOdpp (0.50 g, 2 mmol), CsOdpp (0.38 g, 1 mmol), and 1,3,5-tBu$_3$C$_6$H$_3$ (0.50 g, 2 mmol) were heated to 235 °C for 5 days. Yield: 0.47 g (43 %). M.p. (sealed tube/N$_2$): 290–294 °C; ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 7.52 (d, 12 H; o-H(Ph)), 7.32 (d, 6 H; m-aryl-H), 7.15 (m, 5 H; aryl-PhMe), 6.89 (t, 12 H; m-H(Ph)), 6.80 (m, 9 H; p-aryl-H), p-H(Ph)), 2.11 ppm (s, 3 H; CH$_3$-PhMe); IR (Nujol): $\tilde{\nu}$ = 3047 (s), 2961 (s), 2851 (s), 1952 (w), 1887 (w), 1821 (w), 1600 (s), 1539 (s), 1494 (s), 1449 (s), 1404 (s), 1290 (s), 1257 (s), 1175 (w), 1151 (w), 1110 (m), 1065 (s), 1028 (m), 983 (m), 910 (m), 853 (s), 808 (m), 763 (s), 747 (s), 693 (s), 587 cm^{-1} (s).

3: C$_{54}$H$_{39}$BaCsO$_3$·PhMe; M_r = 1098.24; monoclinic $P2_1$; a = 15.635(2), b = 12.817(2), c = 12.540(2) Å; $\alpha = \gamma$ = 90, β = 71.257(3)°; V = 2379.6(6) Å^3; T = 98 K; Z = 2; μ = 1.635 mm^{-1} (Mo$_{K\alpha}$); colorless block 0.24 × 0.10 × 0.08 mm^3; 11796 independent reflections, $2.8 \leq 2\theta \geq 56.8$; R_1 = 0.0544, wR_2 = 0.1335 for data [$I > 2\theta(I)$] and R_1 = 0.0571, wR_2 = 0.1359 for all data. Disorder in one of the phenyl groups has been handled by introducing 60:40 split positions.

[Li$_2${Ba(Odpp)$_4$}], 4: Ba (0.41 g, 3.0 mmol), HOdpp (0.50 g, 2 mmol), LiOdpp (0.52 g, 2 mmol), and 1,3,5-tBu$_3$C$_6$H$_3$ (0.50 g, 2 mmol) were heated to 245 °C for 5 days. Yield: for 1:1 Li/Ba: 0.11 g (18 %), for 2:1 Li/Ba: 0.37 g (33 %). M.p. (sealed tube/N$_2$): 246–251 °C; ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 7.24 (d, 16 H; o-H(Ph)), 7.14 (d, 8 H; m-aryl-H), 6.99 (t, 16 H; m-H(Ph)), 6.89 (t, 8 H; p-H(Ph)), 6.73 ppm (t, 4 H; p-aryl-H); IR (Nujol): $\tilde{\nu}$ = 2923 (s), 1958 (w), 1892 (w), 1922 (w), 1731 (w), 1592 (m), 1582 (m), 1492 (s), 1449 (s), 1407 (s), 1305 (m), 1287 (s), 1268 (s), 1251 (s), 1175 (w), 1155 (w), 1108 (w), 1083 (s), 1069 (s), 1024 (m), 1010 (m), 993 (m), 919 (m), 847 (s), 803 (s), 754 (s), 707 (s), 666 (w), 618 cm^{-1} (w); metal analysis calcd (%) for C$_{72}$H$_{52}$BaLi$_2$O$_4$ (1132.32): Ba 12.13; found: Ba 11.87.

4: C$_{72}$H$_{52}$BaLi$_2$O$_4$; M_r = 1132.36; monoclinic $P2_1/c$; a = 18.867(1), b = 10.8852(7), c = 26.682(2) Å; $\alpha = \gamma$ = 90, β = 97.560(1)°; V = 5432.1(6) Å^3; T = 94 K; Z = 4; μ = 0.784 mm^{-1} (Mo$_{K\alpha}$); yellow block 0.36 × 0.28 × 0.10 mm^3; 13534 independent reflections $3.5 \leq 2\theta \geq 56.6$; R_1 = 0.0355, wR_2 = 0.0823 for data [$I > 2\theta(I)$] and R_1 = 0.0431, wR_2 = 0.0861 for all data.

[Li$_2$(thf)$_2${Ba(Odpp)$_4$}]·PhMe, 5: Complex **5** was obtained by addition of THF to **4**. Work up with toluene and layering the solution with THF (2 mL) and hexane (5 mL) gave colorless crystals after 3 days at 0 °C. Yield: 0.39 g(57 %). M.p. (sealed tube/N$_2$): 122 °C (1st), 251–256 °C (2nd); ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 7.30 (d, 16 H; o-H(Ph)), 7.21 (d, 8 H; m-aryl-H), 7.15 (m, 5 H; aryl-PhMe), 7.03 (t, 16 H; m-H(Ph)), 6.87 (t, 8 H; p-H(Ph)), 6.75 (t, 4 H; p-aryl-H), 3.23 (m, 8 H; THF) 2.11 (s, 3 H; CH$_3$-PhMe) 1.26 ppm (m, 8 H; THF); IR (Nujol): $\tilde{\nu}$ = 3047 (s), 2973 (s), 2847 (s), 1940 (w), 1874 (w), 1800 (w), 1760 (w), 1670 (w), 1584 (s), 1552 (s), 1498 (s), 1457 (s), 1408 (s), 1319 (m), 1277 (s), 1266 (s), 1179 (m), 1143 (m), 1065 (s), 1032 (s), 1004 (m), 922 (m), 890 (s), 849 (s), 762 (s), 710 (s), 616 cm^{-1} (s).

5: C$_{80}$H$_{68}$BaLi$_2$O$_6$·PhMe; M_r = 1368.70; monoclinic $P2_1/c$; a = 13.081(2), b = 21.094(3), c = 25.168(3)Å; $\alpha = \gamma$ = 90, β = 100.399(2)°; V = 6830(2) Å^3; T = 100 K; Z = 4; μ = 0.638 mm^{-1} (Mo$_{K\alpha}$); colorless block 0.40 × 0.40 × 0.38 mm^3; 17077 independent reflections, $2.5 \leq 2\theta \geq 56.8$; R_1 = 0.0397, wR_2 = 0.0916 for data [$I > 2\theta(I)$] and R_1 = 0.0485, wR_2 = 0.0966 for all data.

[K{Ba(Odpp)$_3$(diglyme)}]·PhMe, 6: Compound **6** was obtained by addition of diglyme to **2**. Work up with toluene and addition of diglyme (0.30 mL, 2 mmol) gave yellow crystals after 2 days at 0 °C. Yield: 0.65 g (62 %). M.p. (sealed tube/N$_2$): 146 °C (1st), 280–285 °C (2nd); ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C) (sample for ^{1}H NMR recrystallized from toluene): δ = 7.46 (d, 12 H; o-H(Ph)), 7.31 (d, 6 H; m-aryl-H), 7.15 (m, 2.5 H; aryl-PhMe), 6.88 (t, 12 H; m-H(Ph)), 6.80 (m, 9 H; p-H(Ph), p-aryl-H), 3.31 (t, 4 H; CH$_2$-diglyme), 3.2 (t, 4 H; CH$_2$-diglyme), 3.05 (s, 6 H; CH$_3$-diglyme), 2.11 ppm (s, 1.5 H; CH$_3$-PhMe); IR (Nujol): $\tilde{\nu}$ = 2921 (m), 1960 (w), 1885 (w), 1836 (w), 1593 (s), 1549 (s), 1493 (s), 1453 (s), 1361 (s), 1312 (s), 1289 (s), 1247 (s), 1210 (m), 1174 (m), 1154 (m), 1123 (w), 1100 (s), 1069 (s), 1026 (s), 1012 (s), 967 (m), 943 (w), 920 (s), 860 (s), 846 (s), 803 (s), 769 (s), 747 (s), 705 (s), 683 (s); metal analysis calcd (%) for C$_{60}$H$_{53}$BaKO$_6$·0.5PhMe (1092.25): Ba 12.57; found: Ba 12.81.

6: C$_{60}$H$_{53}$BaKO$_6$; M_r = 1046.46; orthorhombic $P2_12_12_1$; a = 15.1884(9), b = 16.0355(9), c = 20.435(1) Å; $\alpha = \beta = \gamma$ = 90°; V = 4976.9(5) Å^3; Z = 4; μ = 0.934 mm^{-1} (Mo$_{K\alpha}$); yellow block 0.4 × 0.28 × 0.24 mm^3; 12356 independent reflections, $3.2 \leq 2\theta \geq 56.6$; R_1 = 0.0267, wR_2 = 0.0653 for data [$I > 2\theta(I)$] and R_1 = 0.0287, wR_2 = 0.0662 for all data.

Acknowledgements

We gratefully acknowledge support from the National Science Foundation (CHE-0505863) and the Australian Research Council. Purchase of the X-ray diffraction equipment was made possible with grants from the National Science Foundation (CHE-9527858, and CHE-0234912), Syracuse University, and the W. M. Keck Foundation.

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[1] a) H. L. Hsieh, I. W. Wang, *Macromolecules* **1986**, *19*, 299–304; b) T. A. Antkowiak, J. E. Hall (Bridgestone Corporation, Japan), EP 0747405 A1, **1996**, p. 20.

[2] a) J. Farkas, Jr., S. J. Stoudt, E. M. Hanawalt, A. D. Pajerski, H. G. Richey, Jr., *Organometallics* **2004**, *23*, 423–427; b) H. G. Richey, Jr., J. Farkas, Jr., *Organometallics* **1990**, *9*, 1778–1784.

[3] R. E. Mulvey, *Organometallics* **2006**, *25*, 1060–1075.

[4] A. Inoue, K. Kitagawa, H. Shinokubo, K. Oshima, *J. Org. Chem.* **2001**, *66*, 4333–4339.

[5] a) A. R. Kennedy, R. E. Mulvey, R. B. Rowlings, *J. Organomet. Chem.* **2002**, *648*, 288–292; b) X. He, B. C. Noll, A. Beatty, R. E. Mulvey, K. W. Henderson, *J. Am. Chem. Soc.* **2004**, *126*, 7444–7445; c) P. B. Hitchcock, A. V. Khvostov, M. F. Lappert, *J. Organomet. Chem.* **2002**, *663*, 263–268; d) R. P. Davies, *Inorg. Chem. Commun.* **2000**, *3*, 13–15; e) V. Knapp, G. Muller, *Angew. Chem.* **2001**, *113*, 187–190; *Angew. Chem. Int. Ed.* **2001**, *40*, 183–186; f) S. A. Kinsley, A. Streitwieser, Jr., A. Zalkin, *Organometallics* **1985**, *4*, 52–57; g) P. B. Hitchcock, M. F. Lappert, X. H. Wei, *Dalton Trans.* **2006**, 1181–1187; h) L. Bonomo, E. Solari, R. Scopelliti, C. Floriani, *Chem. Eur. J.* **2001**, *7*, 1322–1332; i) W. Maudez, D. Haussinger, K. M. Fromm, *Z. Anorg. Allg. Chem.* **2006**, *632*, 2295–2298.

[6] P. S. Coan, W. E. Streib, K. G. Caulton, *Inorg. Chem.* **1991**, *30*, 5019–5023.

[7] H. Bock, T. Hauck, C. Naether, N. Roesch, M. Staufer, O. D. Haeberlen, *Angew. Chem.* **1995**, *107*, 1439–1441; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1353–1355.

[8] G. Guillemot, E. Solari, C. Rizolli, C. Floriani, *Chem. Eur. J.* **2002**, *8*, 2072–2080.

[9] a) K. M. Fromm, *Dalton Trans.* **2006**, 5103–5112; b) K. M. Fromm, E. D. Gueneau, H. Goesmann, *Chem. Commun.* **2000**, 2187–2188.

[10] J. S. Alexander, M. F. Zuniga, M. Guino-o, R. Hahn, K. Ruhlandt-Senge, *Encyclopedia of Inorganic Chemistry, Vol. 2*, 2nd ed. (Ed.: D. A. Atwood), Wiley, Germany, **2006**, pp 116-147.

[11] a) L. G. Hubert-Pfalzgraf, *Inorg. Chem. Commun.* **2003**, *6*, 102–120; b) D. C. Bradley, *Chem. Rev.* **1989**, *89*, 1317–1322.

[12] a) D. C. Bradley, R. C. Mehrotra, I. P. Rothwell, A. Singh, *Alkoxo and Aryloxo Derivatives of Metals*, Academic Press, San Diego, **2001**; b) S. A. Cotton in *Comp. Coord. Chem. II* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier, Oxford, **2004**, *Vol. 3*, Chapter 3.2; c) M. Ma, X. Xu, Y. Yao, Y. Zhang, Q. Shen, *J. Mol. Struct.* **2005**, *740*, 69–74.

[13] M. F. Zuniga, G. B. Deacon, K. Ruhlandt-Senge, unpublished results.

[14] a) G. B. Deacon, C. M. Forsyth in *Inorganic Chemistry Highlights* (Eds.: G. Meyer, D. Naumann, L. Wesemann), Wiley-VCH, Weinheim, **2002**, Chapter 7; b) K. Muller-Buschbaum, *Z. Anorg. Allg. Chem.* **2005**, *631*, 811–828; c) G. B. Deacon, C. M. Forsyth, R. Harika, P. C. Junk, J. W. Ziller, W. J. Evans, *J. Mater. Chem.* **2004**, *14*, 3144–3149; d) G. B. Deacon, C. M. Forsyth, A. Gitlits, B. W. Skelton, A. H. White, *Dalton Trans.* **2004**, 1239–1247.

[15] a) G. B. Deacon, C. M. Forsyth, P. C. Junk, *J. Organomet. Chem.* **2000**, *607*, 112–119; b) J. Hitzbleck, G. B. Deacon, K. Ruhlandt-Senge, *Angew. Chem.* **2004**, *116*, 5330–5332; *Angew. Chem. Int. Ed.* **2004**, *43*, 5218–5220.

[16] a) G. B. Deacon, A. Gitlits, P. C. Junk, B. W. Skelton, A. H. White, *Z. Anorg. Allg. Chem.* **2005**, *631*, 861–865; b) G. B. Deacon, T. Feng, P. C. Junk, B. W. Skelton, A. H. White, *J. Chem. Soc. Dalton Trans.* **1997**, 1181–1186; c) G. D. Smith, P. E. Fanwick, I. P. Rothwell, *Inorg. Chem.* **1989**, *28*, 618; d) C. S. Weinert, P. E. Fanwick, I. P. Rothwell, *Dalton Trans.* **2003**, 1795.

[17] G. B. Deacon, E. E. Delbridge, D. J. Evans, R. Harika, P. C. Junk, B. W. Skelton, *Chem. Eur. J.* **2004**, *10*, 1193–1204, and references therein.

[18] a) K. G. Caulton, M. H. Chisholm, S. R. Drake, K. Folting, J. C. Huffman, *Inorg. Chem.* **1993**, *32*, 816–820; b) K. G. Caulton, M. H. Chisholm, S. R. Drake, K. Folting, *J. Chem. Soc. Chem. Commun.* **1990**, 1349–1351; c) K. G. Caulton, M. H. Chisholm, S. R. Drake, K. Folting, *Inorg. Chem.* **1991**, *30*, 1500–1503.

[19] G. B. Deacon, C. M. Forsyth, P. C. Junk, B. W. Skelton, A. H. White, *Chem. Eur. J.* **1999**, *5*, 1452–1459.

[20] a) R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751–767; b) N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Butterworth-Heinemann, London, **2002**.

[21] a) A. R. Kennedy, R. E. Mulvey, R. B. Rowlings, *J. Am. Chem. Soc.* **1998**, *120*, 7816–7824; b) W. Clegg, K. W. Henderson, R. E. Mulvey, P. A. O'Neil, *J. Chem. Soc. Chem. Commun.* **1994**, 769–770; c) G. C. Forbes, A. R. Kennedy, R. E. Mulvey, P. J. A. Rodger, R. B. Rowlings, *J. Chem. Soc. Dalton Trans.* **2001**, 1477–1484.

[22] K. G. Caulton, M. H. Chisholm, S. R. Drake, K. Folting, J. C. Huffman, W. E. Streib, *Inorg. Chem.* **1993**, *32*, 1970–1976.

[23] R. E. Mulvey, *Chem. Commun.* **2001**, 1049–1056, and references therein.

[24] M. F. Zuniga, G. B. Deacon, K. Ruhlandt-Senge, unpublished results.

[25] M. D. Walter, G. Wolmershaeuser, H. Sitzmann, *J. Am. Chem. Soc.* **2005**, *127*, 17494–17503, and references therein.

[26] T. P. Hanusa, *Organometallics* **2002**, *21*, 2559–2571, and references therein.

[27] S. O. Hauber, F. Lissner, G. B. Deacon, M. Niemeyer, *Angew. Chem.* **2005**, *117*, 6021–6025; *Angew. Chem. Int. Ed.* **2005**, *44*, 5871–5875, and references therein.

[28] M. F. Zuniga, G. B. Deacon, K. Ruhlandt-Senge, unpublished results.

[29] C. S. Weinert, P. E. Fanwick, I. P. Rothwell, *Inorg. Chem.* **2003**, *42*, 6089–6094.

[30] CCDC-616023–616025 (**1**,**4**,**6**), 621430 (**2**), 624273 (**3**), 624274 (**5**) contain(s) the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

[31] K. Ruhlandt-Senge, U. Englich, *Chem. Eur. J.* **2000**, *6*, 4063–4070.

Received: November 14, 2006