A unique heterobimetallic benzyl calciate—an organometallic mixed-metal species involving a heavy alkaline-earth metal†

Marites A. Guino-o,[a] Charles F. Campana[b] and Karin Ruhlandt-Senge*[a]

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A co-complexation reaction utilizing homometallic benzylcalcium and benzyllithium affords a rare example of a heterobimetallic benzyl calciate.

While the first heterobimetallic "ate" complexes involving combinations of lithium and magnesium were reported more than 50 years ago,[1] their synthetic potential was only fully recognized in 2000 in halogen–magnesium exchange reactions utilizing lithium magnesiates, $LiMgR_3$.[2] Since then, this area of chemistry has seen continuous growth, involving preparative aspects as well as the evaluation of the target compounds in polymer initiation and functionalization,[3] deprotonation and metalation,[1] and selective alkylation.[4] Among the growing list of alkali/alkaline-earth heterobimetallics, the vast majority of compounds involve amido and/or alkoxo/aryloxo ligands, with most of the alkaline-earth metal centers limited to magnesium.[5] Likewise, heterobimetallic heteroleptic compounds are mainly based on magnesium, utilizing amido/alkoxo ligand combinations, as seen in $[MMg\{N(iPr)_2\}_2OR]_2$ (where M = Li, R = *n*Oct; M = Na, R = *n*Bu or *n*Oct).[6] Alkyl and aryl complexes of this type focussed mainly on lithium magnesiates[7a] or inverse crown ethers.[7b]

Heterobimetallic compounds involving heavier alkaline-earth metals are almost exclusively limited to amides including $Li(thf)(\mu\text{-}NCH_2tBu)_2\text{-}1,2\text{-}C_6H_4)(\mu\text{-}I)Ca(thf)$, $Li(thf)Ca[NR_2]_3$, $Li[\eta\text{-}NR_2]_2Ca[NR_2]$, and $KCa[NR_2]_3{\cdot}THF$ (where R = $SiMe_3$).[8] This list of compounds was recently supplemented by a family of aryloxides of the form $Li_2Ba(OR)_4$ and $MBa(OR)_3$ (M = Na, K, Rb, Cs; R = 2,6-diphenylphenol) published by this group,[8e] other alkali/alkaline-earth heterobimetallic aryloxides are aggregates,[8f–j] including two recent K/Ca based enolates.[8d]

Less explored are heterobimetallic compounds involving alkyl/aryl ligands,[9a–f] well characterized examples include a intramolecularly coordinated benzyl calciate $[(OEt_2)Na]\text{-}[Ca(2\text{-}MeOC_6H_4CHPPh_2')_3]$ (Ph′ = *p*-tolyl),[9g] and a sole unsubstituted benzylate $[Li(tmeda)_2][(tmeda)Li(\mu\text{-}CH_2Ph)_2\text{-}Mg(CH_2Ph)_2]$ (tmeda = N',N',N'',N''-tetramethylethylenediamine), **2**.[10]

To shed light onto the structure and function relationship of "ate" derivatives, we here report on the synthesis and characterization of a unique, benzyl lithium calciate, $(tmeda)_2Li_2Ca(CH_2Ph)_4{\cdot}PhMe$, **1** (Fig. 1). We were especially interested in evaluating the degree of delocalization in the benzyl moiety, as this would provide important information towards metal–ligand bond characteristics. Detailed data on homometallic benzyl species are available for both lithium and calcium, so a direct comparison is possible.[11,12]

Further, equilibria between the homometallic compounds and their heterobimetallic aggregates pose important synthetic questions for metathesis reactions, an example being the formation of intractable reaction mixtures from a calcium based transamination reaction in diethyl ether for the preparation of dibenzylcalcium.[13] Compound **1** was obtained by treating $Ca(CH_2Ph)_2(thf)_4$, **3a** with two equivalents of $Li(CH_2Ph)(tmeda)$, **4**, in toluene at room temperature (eqn (1)).‡

$$\begin{array}{c} Ca(CH_2Ph)_2(thf)_4 \\ +\ 2\ Li(CH_2Ph)(tmeda) \end{array} \xrightleftharpoons{\text{toluene, rt}} \begin{array}{c} tmeda_2Li_2Ca(CH_2Ph)_4 \\ \mathbf{(1)} \end{array} \qquad (1)$$

Compound **1** is only moderately soluble in toluene with a slight increase of solubility in benzene. Attempts to increase solubility by addition of a drop of $[D_8]THF$ to the toluene solution at room temperature to facilitate NMR spectroscopic studies resulted in immediate decomposition under ether cleavage and formation of enolate (as identified by NMR

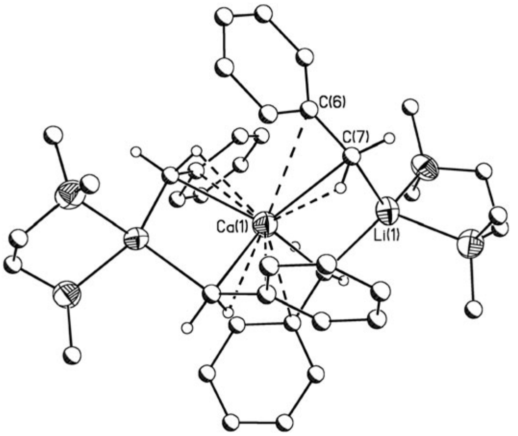

Fig. 1 Representation of **1** (tetragonal, $I\bar{4}2d$ (no. 122)). Hydrogen atoms except those involved in π- or agostic-interactions are omitted for clarity.

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[a] *Department of Chemistry, 1-014 Center for Science and Technology, Syracuse University, Syracuse, NY 13244-4100, USA. E-mail: kruhland@syr.edu; Fax: (+1)315-443-4070*
[b] *Bruker AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373, USA*

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analysis), among other unidentified decomposition products. In contrast, the homometallic $Ca(CH_2Ph)_2(thf)_4$, **3a** and $Ca(CH_2\text{-}4\text{-}tBuC_6H_4)_2(thf)_4$, **3b** appear to be stable in THF, as indicated by their synthesis *via* salt metathesis in THF at room temperature.[11] The immediate decomposition of **1** upon addition of a small quantity of THF at room is remarkable, considering that **3a** contains four THF donors. However, we believe compound **1** could be isolated, albeit in low yields, by maintaining low-temperature conditions. It is important to note that ether cleavage is a well-described phenomenon in the chemistry of heavy alkaline-earth organometallics.[14]

Compound **1** can also be obtained in low yields in a mixture with **3a** by treating $Ca[N(SiMe_3)_2]_2(thf)_2$ with two equivalents of **4** in toluene. Aside from an oily, toluene insoluble residue identified as **3a**, the bright orange supernatant affords **1** after storage at −23 °C, suggesting that the initial transamination reaction was incomplete.

^1H NMR analysis of **1** in [D$_6$]benzene indicates the reproducible presence of a small quantity of **3a**, suggesting a solution-dependent equilibrium between **1** and the homometallic **3a** and **4**. Addition of a slight excess of **4** results in the clean formation of **1**. These results might provide the rationale for the difficulties encountered while isolating dibenzylcalcium and strontium from a transamination regime in diethyl ether, a route that provided clean dibenzylbarium.[13] Similar observations while preparing heterobimetallic amides $R_2NMg\{\mu\text{-}NR_2\}_2CaNR_2$ (where R = $SiMe_3$) led to the isolation of clean product after addition of an excess of magnesium amide.[15]

NMR spectroscopy was utilized to determine if **1** is retained in solution and to obtain insight into the delocalization of the benzylic moiety. The $^1J(^{13}C, {}^1H)$ coupling constant on C_α is affected by the hybridization of the benzylic carbon, while the chemical shifts of the *para* hydrogen and carbon atoms are influenced by π-electron density.[16] Table 1 summarizes these values for **1** along with the homometallic **3a** and **4**.

The chemical shift for the *para*-hydrogen in **1** is slightly upfield from **3a**, but downfield from **4**. Chemical shifts for the *para*-carbon atoms in **1**, **3a** and **4**, a measure of π electron density in the aromatic ring, point to similar values for **1** and **3a**. $^1J(^{13}C, {}^1H)$ coupling constants have been used to evaluate delocalization in $M(CH_2Ph)$ (M = Li, K and Rb),[15a] with expected values for a tetrahedral (sp^3) CH_2 moiety of 125 Hz, and 167 Hz for a planar (sp^2) CH_2 unit.[15a] Conforming to these results, the $^1J(^{13}C, {}^1H)$ constant for **1** is comparable to **4** with that of **3a** being lower, suggesting that charge delocalization in **1** may predominantly be affected by the lithium center in the heterobimetallic compound. Since only one set of benzylic signals was observed, NMR data suggest that **1** is retained in solution. The alternative scenario, rapid exchange between the homo- and heterobimetallic compounds is unlikely, but can not be excluded since VT-NMR studies are prevented by the poor solubility of **1** in toluene and rapid decomposition upon addition of THF.

Table 1 Selected NMR parameters (δ/ppm, *J*/Hz)

	1 (C_6D_6)	**3a**[11] (C_6D_6–[D$_8$]THF)	**4**[12] [D$_8$]THF
$\delta(^1H_{para})$	6.14	6.29	5.46
$\delta(^{13}C_{para})$	109.0	109.6	104.7
$^1J(C_\alpha\text{–}H)$	137	125	135

The limited degree of delocalization identified in the NMR spectra was also confirmed in the solid state by slightly shortened C_α–C_{ipso} bonds (Table 2). The C_α–C_{ipso} distances in **1** (1.445(8) Å) are comparable to those in **3a** (1.425(3)$_{av}$ Å) and **4** (1.420(4) Å), despite higher C_α coordination numbers in **1**. Accordingly, solution and solid-state data support that the charge delocalization in **1** is comparable to the homometallic species.

A further test for the degree of delocalization would be the analysis of deformation in the aromatic ring and the relative shortening of the C_α–C_{ipso} moiety. Deviations would further involve an elongation for C_{ipso}–C_{ortho} and C_{meta}–C_{para}, and shortening of the C_{ortho}–C_{meta} bonds.[16c] Likewise, angles on C_{ipso} and C_{para} would be less than 120°, while the C_{ortho} and C_{meta} angles should be wider.[16c] Further supporting our previous arguments, all compounds display quite similar deviations from ideal geometry, suggesting comparable degrees of delocalization.

Compound **1** is a toluene solvate that crystallizes in the rare tetragonal space group $I\bar{4}2d$ with the calcium metal located on the $\bar{4}$ axis that influenced the Li···Ca···Li angle of 180° (Fig. 1 and 2).§ The asymmetric unit consists of a calcium center bridged by one benzylate moiety to the TMEDA bound lithium. Not surprisingly, Ca–C_α (2.610(5) Å) and Li–C_α distances (2.283(7) Å) in **1** are longer than in the homometallic **3a** (Ca–C_α 2.2568(5)–2.595(5) Å)[11] and **4** (Li–C_α 2.210(5) Å)[12] likely the consequence of the bridging nature of C_α. The coordination sphere of the larger calcium is supplemented by several secondary interactions, including π-interactions to the *ipso* carbon on the phenyl ring (η^1-Ca–C6 2.972(5) Å), in addition to an agostic interactions involving a benzylic hydrogen atom (Ca–H7a 2.33 Å) (Fig. 2). Agostic interactions are recently being recognized as a major stabilizing factor in the coordination chemistry of the heavy alkaline-earth metals. These contacts are frequently observed in compounds with low formal coordination numbers as obtained in the presence of sterically demanding ligands.[8e,17] A noteworthy structural feature is the Li···Ca···Li separation of 180°. As shown earlier

Table 2 Selected bond lengths (Å) and angles (°)

	1	**2**[10]	**3a**[11]	**4**[12]
Ca/Mg–C_α	2.610(5)	2.313(9)–2.322(1)[a]	2.568(5)–2.595(5)	—
Li–C_α	2.283(7)	2.229(2)–2.272(2)	—	2.210(5)
C_α–C_{ipso}	1.445(8)	1.483(2)–1.485(1)	1.411(8) − 1.436(7)	1.420(4)
Li–C_α–Ca/Mg	46.97(1)	72.6(6)–73.5(5)	—	—
C_{ortho}–C_{ipso}–C_{ortho}[b]	114.9	117.6	114.5	114.4

[a] Two bridging benzyl ligands. [b] Esds not included.

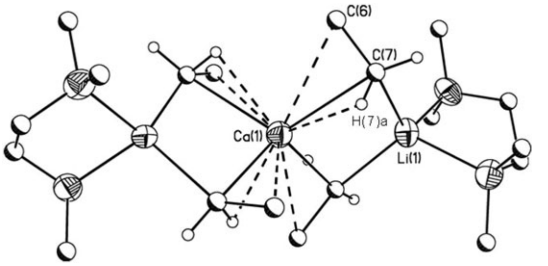

Fig. 2 Graphical representation of **1** showing in detail the secondary interactions, π- (η^1-Ca–C6 2.970(4) Å) and agostic (Ca–H7a 2.33 Å).

in families of lithium magnesiates and bariates significant deviations from this linear arrangement have been observed due to steric effects or allow for the maximization of secondary interactions.[18]

The combination of two homometallic benzyl reagents afforded a rare heterobimetallic lithium calciate that decomposes in THF at room temperature. NMR and crystallographic data suggest similar benzylic features for the homo- and heterobimetallic compounds, which do not provide a rationale for the increased reactivity of the heterobimetallic compound. Future studies will expand this work to the strontium and barium analogs, including detailed studies into structure and function relations and their use in polymerization and metallation reactions.

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Notes and references

‡ All reactions were carried out with careful exclusion of water and oxygen with the aid of a Braun Labmaster 100 drybox and/or modified Schlenk-line techniques. The high reactivity of the compound prevented elemental analysis as decomposition in less than 24 h inside a freshly regenerated dry box is observed upon removal of mother-liquor. **1**: (a) Li(CH_2Ph)(tmeda) and Ca(CH_2Ph)$_2$(thf)$_4$ were combined in toluene at room temperature. (b) Ca(N($SiMe_3$)$_2$)$_2$(thf)$_2$ was combined with Li(CH_2Ph)(tmeda) at room temperature. Analytical and crystallographic data obtained from (a) and (b) are identical. Further experimental data are available in the ESI.†

§ *Crystal structure* analyses for **1**: $CaLi_2N_4C_{47}H_{68}$, M_r = 743.02, tetragonal, space group $I\bar{4}2d$ (no. 122), $a = b$ = 13.6240(7), c = 28.4840(1) Å, $\alpha = \beta = \gamma = 90°$, V = 5287.0(5) Å, T = 100(2) K, Z = 4, μ = 0.142 mm (Mo-Kα radiation); yellow blocks 0.50 × 0.50 × 0.50 mm; 1738 independent reflections (5.10 ≤ Θ ≤ 44.98°); R_1 = 0.0656 ($I > 2\sigma(I)$), wR_2 = 0.1837 (all data). CCDC 663415. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b715701k

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