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Probing the Salt-Metathesis Route to Bis(aryl)calcium Compounds: Structure of an Arylcalcate Complex

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Dedicated to Professor Rudi van Eldik on the occasion of his 70th birthday

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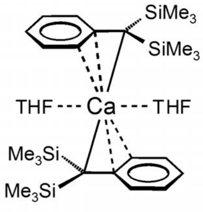
1,3-Diisopropoxybenzene can be selectively metalated by *n*BuLi or by the superbase mixtures *n*BuLi/NaOC(Me)$_2$Et or *n*BuLi/KOC(Me)$_2$Et to give 2,6-diisopropoxyphenyllithium (71 %), 2,6-diisopropoxyphenylsodium (61 %), or 2,6-diisopropoxyphenylpotassium (59 %) as isolated products. The attempted synthesis of bis(2,6-diisopropoxyphenyl)calcium by the salt metathesis route using 2,6-diisopropoxyphenylsodium and CaI$_2$ gave an undefined mixture of products, whereas the attempted synthesis of bis(2,6-diisopropoxyphenyl)calcium by the same approach using 2,6-diisopropoxyphenylpotassium and CaI$_2$ gave the calcate complex [{(*i*PrO)$_2$C$_6$H$_3$}$_3$Ca]$^-$K$^+$, which is the first arylcalcate complex to have been structurally characterized. The trend in the ^{13}C NMR chemical shifts of the aryl C$_{ipso}$ atoms shows that the calcate complex displays an aryl–metal bond polarity (nucleophilicity/basicity) similar to that in arylsodium compounds.

Introduction

Although the discovery and widespread application of Grignard reagents is more than a century old,[1] notable development of the organometallic chemistry of the heavier alkaline-earth metals (Ca, Sr, Ba) only started a few decades ago.[2] Organocalcium chemistry, in particular, has seen major breakthroughs[3] with applications as initiators in polymer chemistry,[4,5] the exploitation of their lanthanide-like properties in homogeneous catalysis[6] and their use in chemical vapour deposition.[7]

Application of organocalcium complexes in stereoselective styrene polymerization[4] initiated the challenging goal of developing highly reactive and nucleophilic organocalcium reagents. As historically known cyclopentadienyl,[8] tris(trimethylsilyl)methyl[9] and 1,3-bis(trimethylsilyl)allyl[10] complexes of calcium were not suitable as initiators for styrene polymerization, benzylcalcium complexes of increasing reactivity have been developed ($\mathbf{1}$[4a] < $\mathbf{2}$[4b] < $\mathbf{3}$[4f] < $\mathbf{4}$[11]). Routes to benzyl complexes of the heavier alkaline-earth metals have also recently been reported.[12] Subsequently, unsubstituted bis(allyl)calcium was found to be a potent precursor in organocalcium chemistry.[13] The growing variety of reactive heavier alkaline-earth metal complexes has been extended further to [(Me$_3$Si)$_2$CH]M·(thf)$_x$ (M/x = Ca/2, Sr/3, Ba/3)[14] and complexes with the phenyl-substituted carbanions Ph$_3$C$^-$ and Ph$_2$CH$^-$.[11,15]



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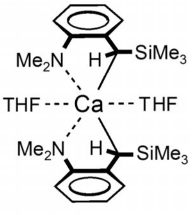

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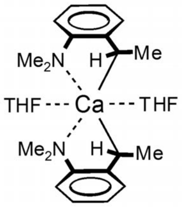

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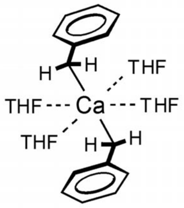

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The most reactive organocalcium compounds are undoubtedly the "heavy" arylcalcium Grignard complexes.[13] It was not until 2005 that well-defined arylcalcium complexes appeared in the literature: three groups independently reported the synthesis and crystal structures of arylcalcium complexes.[16] Niemeyer and co-workers treated the in situ prepared (C$_6$F$_5$)$_2$Ca with a triazene ligand to obtain

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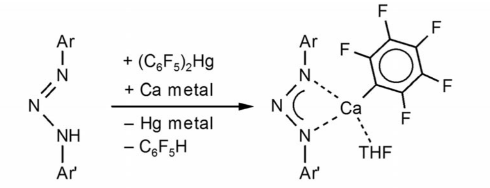
the first well-defined heteroleptic arylcalcium compound [Equation (1)].[16a] Our attempts to synthesize a homoleptic bis(aryl)calcium complex with tamed reactivity through a salt-metathesis route led to a tetrameric cluster with incorporated O^{2-} [Equation (2)].[16b] Careful analysis of first structural data of the arylcalcium moiety showed aryl ring distortions typical of polar arylmetal compounds.[17] As the extent of this distortion is dependent on the polarity of the metal–carbon bond, it could be concluded that C–Ca and C–Li bonds have approximately similar polarity. Westerhausen and co-workers[16c] reported a similar tetrameric arylcalcium cluster, $Ph_3Ca_4I_3O$, with incorporated O^{2-}, which was synthesized by the Grignard method [Equation (3)]. The incorporated O^{2-} could originate from oxidation by traces of air[16b] or by ether cleavage,[16c] which is a well-established process in polar organometallic chemistry.[18]



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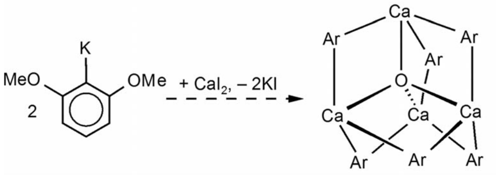

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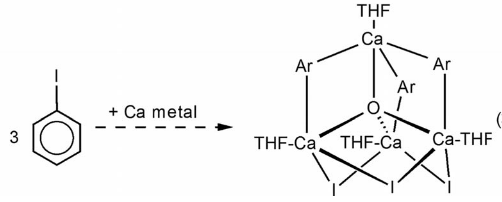


(3)

Westerhausen and co-workers achieved a major breakthrough by showing that careful activation of Ca and synthesis at low temperatures could give arylcalcium iodide compounds by the Grignard route. The isolated complexes could be obtained in crystalline purity and the first crystal structure of a Ca Grignard, MesCaI·(thf)$_4$, was obtained.[19] This set the stage for a decade of "heavy" Grignard chemistry.[3c–3h] It was immediately clear that these post-Grignard reagents are highly reactive and first reports mention thf cleavage at temperatures as low as –30 °C.[20] However, a recent detailed investigation showed that Ca Grignard reagents are more stable than initially expected[21] and this certainly widens the scope for the application of these potent reagents. Their stability in ethereal solvents is dependent on temperature, concentration and solvent, but can also be influenced by the second anionic ligand on Ca^{2+}.

Ca Grignard reagents are important building blocks for the synthesis of bis(aryl)calcium compounds. Although the first bis(aryl)calcium complexes were obtained in poor yields by tedious fractional crystallization of a Ca Grignard mixture,[22] the Schlenk equilibrium [Equation (4)] can be simply shifted by the addition of KO*t*Bu.[23] In this case the intermediate ArCaO*t*Bu is in equilibrium with $CaAr_2$ and $Ca(OtBu)_2$, and precipitation of the insoluble $[Ca(OtBu)_2]_\infty$ drives the equilibrium to the homoleptic $CaAr_2$ [Equation (5)].

$$2\,\mathrm{ArCaI} \rightleftharpoons \mathrm{Ar_2Ca} + \mathrm{CaI_2} \tag{4}$$

$$\Big\downarrow\ {+\,2\,\mathrm{KOtBu} \atop -\,2\,\mathrm{KI}}$$

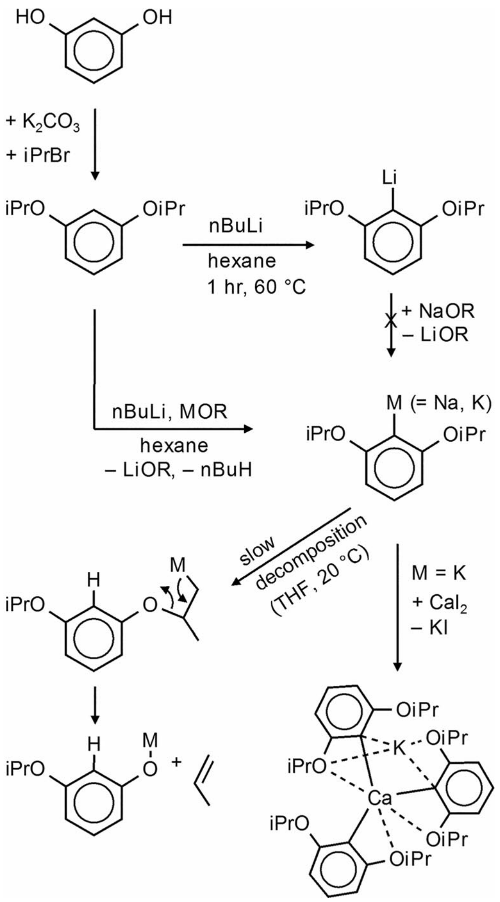
$$2\,\mathrm{ArCaOtBu} \rightleftharpoons \mathrm{Ar_2Ca} + \mathrm{Ca(OtBu)_2}\downarrow \tag{5}$$

$$2\,\mathrm{ArM} + \mathrm{CaI_2} \longrightarrow \mathrm{Ar_2Ca} + 2\,\mathrm{MI} \tag{6}$$

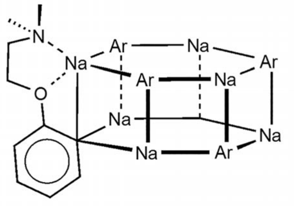
Following our earlier synthetic protocol, we report herein our attempts to synthesize a bis(aryl)calcium complex by the salt-metathesis route, which is most efficient for CaI_2 precursors partially dissolved in a polar solvent like thf and with M = K or Na [Equation (6)]. The driving force for the reaction is the insolubility of KI or NaI. Because arylsodium and -potassium compounds generally show high reactivity towards polar solvents like thf, we used an aryl anion of tamed reactivity and with increased steric bulk. We describe the synthesis and isolation of the precursors 2,6-(iPrO)$_2$-phenyllithium, 2,6-(iPrO)$_2$-phenylsodium and 2,6-(iPrO)$_2$-phenylpotassium. The crystal structure of the tetrameric aggregate [2,6-(iPrO)$_2$-phenylsodium]$_4$ presents one of the few structures of a solvent-free arylsodium complex. Further reaction of these reagents with CaI_2 did not lead to the anticipated bis(aryl)calcium compound, but instead, the first example of an arylcalcate complex was isolated: $[Ar_3Ca]^-K^+$. In addition, we describe the structure of an accidental oxidation product, ArOCaI·(thf), obtained from the metathesis reaction.

Results and Discussion

The bulky 1,3-diisopropoxybenzene, (iPrO)$_2$C$_6$H$_4$, was prepared in 75% yield according to the procedure of Yasuda and co-workers (Scheme 1).[24] In contrast to the literature procedure, in which (iPrO)$_2$C$_6$H$_4$ was lithiated in situ by *n*BuLi in thf to give 2,6-diisopropoxyphenyllithium and subsequently converted,[24] we aimed to isolate a solvent-free product. Therefore we performed the lithiation in hexane at reflux and isolated the pure product (iPrO)$_2$-C$_6$H$_3$Li in 29% yield. The low yield of this "directed orthometallation" reflects the steric pressure of the two *i*PrO substituents: the analogous lithiation of the less bulky 1,3-dimethoxybenzene to 2,6-dimethoxyphenyllithium is a straightforward procedure (yield: 95%).[25] Attempts to convert 2,6-diisopropoxyphenyllithium into 2,6-diisopropoxyphenylsodium and -potassium by transmetallation with NaOC(Me)$_2$Et and KOC(Me)$_2$Et in hexane, benzene or thf, respectively, failed. In all cases, the starting material (iPrO)$_2$C$_6$H$_3$Li was isolated. This is likely due to the fact that this lithium compound is quite insoluble even in thf. However, the corresponding sodium and potassium compounds could be obtained by direct metallation of 1,3-diisopropoxybenzene with the superbase mixtures, *n*BuLi/NaOC(Me)$_2$Et and *n*BuLi/KOC(Me)$_2$Et, respectively, in hexane, with the products precipitating from solution. The solvent-free sodium compound (*i*PrO)$_2$C$_6$H$_3$Na is remarkably soluble in hexane and could even be obtained in the form of large well-defined crystals by the slow cooling of a hexane solution. Because the literature describes only two crystal structures of solvent-free arylsodium compounds (**5**[26] and **6**[27]) and a handful of tmeda-solvated arylsodium dimers (**7**[28–31]), we determined the structure of (*i*PrO)$_2$C$_6$H$_3$Na by single-crystal X-ray diffraction.



Scheme 1.



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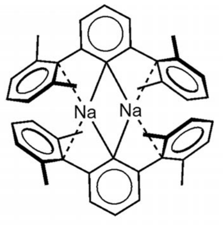

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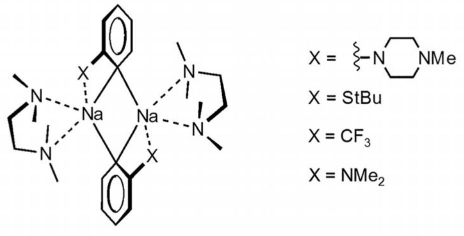

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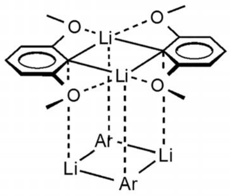

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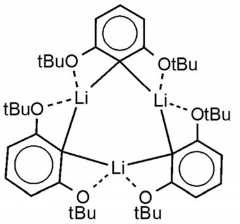

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(*i*PrO)$_2$C$_6$H$_3$Na crystallizes in the tetragonal space group $P\text{-}42_1c$ with two tetrameric aggregates in the unit cell (Figure 1, Table 1). The structure of [(*i*PrO)$_2$C$_6$H$_3$Na]$_4$ shows very high crystallographic S_4 symmetry. The tetramer can be described as a distorted cube consisting of four Na$^+$ ions and the four C$_{ipso}$ atoms of the aryl anions, a structure type typical of organolithium tetramers. The C$_{ipso}$ atoms can be envisaged to be involved in 4-centre–2-electron bonding. Although the terminology "4-centre–2-electron bonding" implies a covalent bonding model, it should be noted that bonding in organoalkalimetal complexes is largely ionic.[32] However, the bonding geometry is quite clearly defined by such terminology and therefore we chose to use this description. The remaining coordination sites on Na$^+$ are occupied by the two chelating *i*PrO arms. One of the *i*PrO arms bridges two Na$^+$ ions, and therefore the total coordination number of each Na$^+$ ion is six. The C–Na distances are in the relatively narrow range of 2.6267(8)–2.7268(9) Å, and considerably longer than those in **5** [2.523(5)–2.579(5) Å] or **6** [2.572(2)–2.609(2) Å]. This is likely due to the much higher coordination number of six for Na in the structure of (*i*PrO)$_2$C$_6$H$_3$Na (cf. Na in **5** is five-coordinate and Na in **6** is four-coordinate). There are two types of Na–O bonds in [(*i*PrO)$_2$C$_6$H$_3$Na]$_4$: the bridging *i*PrO substituents show much longer Na–O bonds [2.5143(6)–2.6861(8) Å] than the *i*PrO groups that are coordinated to a single Na$^+$ ion [2.2908(7) Å].

It is of interest to compare the structure of [(*i*PrO)$_2$C$_6$H$_3$Na]$_4$ with those of similar aryllithium compounds. 2,6-Dimethoxyphenyllithium (**8**) also crystallizes as a tetramer, but displays a completely different structure that could be envisaged to consist of two stacked dimers in which the C$_{ipso}$ atoms are involved in 3-centre–2-electron bonding.[17d] The Li atoms within the dimeric subunits interact with the C sp^2 orbital, whereas contacts between the dimeric subunits are formed by interaction along the C p orbital. This view is apparent from the significantly shorter C–Li bonds within the dimer compared with those between dimers and from their different ^{13}C–^{6}Li magnetic coupling constants. Thus, the tetramer **8** is constructed of two loosely bound dimeric subunits. The subunit itself has attracted considerable interest for formally containing a planar four-coordinate carbon atom. The difference between the Li and Na structures originates from the much larger ionic radius of Na$^+$ compared with Li$^+$ (1.02 vs. 0.74 Å, six-coordinate).[33]

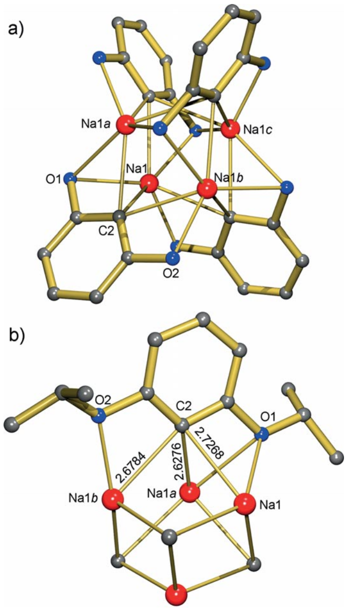

Figure 1. a) Crystal structure of $[(i\text{PrO})_2\text{C}_6\text{H}_3\text{Na}]_4$. Hydrogen atoms and *i*Pr substituents are not shown for clarity. b) Graphical presentation of the partial structure showing the geometry of the distorted C_4Na_4 cube and the C–Na/O–Na bonding geometry.

Table 1. Selected bond lengths for $[(i\text{PrO})_2\text{C}_6\text{H}_3\text{Na}]_4$, $\{[(i\text{PrO})_2\text{C}_6\text{H}_3\text{O}]\text{CaI·thf}\}_2$ and $[\{(i\text{PrO})_2\text{C}_6\text{H}_3\}_3\text{Ca}]^-\text{K}^+$.

Bond	Bond length [Å]	Bond	Bond length [Å]
$[(i\text{PrO})_2\text{C}_6\text{H}_3\text{Na}]_4$			
Na1–C2	2.7268(9)	Na1–O1	2.6861(8)
Na1a–C2	2.6267(8)	Na1a–O1	2.5143(6)
Na1b–C2	2.6784(8)	Na1b–O2	2.2908(7)
$\{[(i\text{PrO})_2\text{C}_6\text{H}_3\text{O}]\text{CaI·thf}\}_2$			
Ca–O1	2.2457(12)	Ca–I	3.0702(4)
Ca–O2	2.5657(13)	Ca–O1′	2.2508(12)
Ca–O4	2.3686(13)	Ca–O2′	2.5544(12)
$[\{(i\text{PrO})_2\text{C}_6\text{H}_3\}_3\text{Ca}]^-\text{K}^+$			
Ca–C2	2.5498(15)	K–C2	3.0607(15)
Ca–C14	2.5352(13)	K–C26	2.9914(14)
Ca–C26	2.5416(14)	K–O2	3.0523(12)
Ca–O2	2.4258(11)	K–O6	2.6784(12)
Ca–O4	2.4566(12)	K–O3′′	2.8442(11)
Ca–O5	2.4348(11)		

This allows for 4-centre–2-electron bonding and the higher coordination number of six in the arylsodium structure. The crystal structure of 2,6-di-*tert*-butoxyphenyllithium (**9**) shows a completely different structure type: in this case an unusual trimeric aggregate is formed that has no resemblance to the structure of $[(i\text{PrO})_2\text{C}_6\text{H}_3\text{Na}]_4$.[34]

The sodium compound $(i\text{PrO})_2\text{C}_6\text{H}_3\text{Na}$ shows good solubility in benzene and even dissolves in hexane, but the potassium compound $(i\text{PrO})_2\text{C}_6\text{H}_3\text{K}$ only dissolves in thf. We were unable to grow single crystals of $(i\text{PrO})_2\text{C}_6\text{H}_3\text{K}$, but based on its insolubility in aromatic solvents and the much larger ionic radius for K^+ (1.38 Å, six-coordinate),[33] it is likely a coordination polymer. The ^{1}H and ^{13}C NMR spectra of the aryllithium, -sodium and -potassium precursors all show a single set of signals (see the Exp. Sect.). Although a thf solution of $(i\text{PrO})_2\text{C}_6\text{H}_3\text{Li}$ is stable, the heavier alkali metal compounds $(i\text{PrO})_2\text{C}_6\text{H}_3\text{Na}$ and $(i\text{PrO})_2\text{C}_6\text{H}_3\text{K}$ both slowly decompose in solution. ^{1}H NMR monitoring shows continuous growth of a set of signals that can be assigned to propene (which was also independently detected by a GC–MS analysis).[35] Therefore, decomposition is not due to a reaction with thf, but caused by an intramolecular rearrangement: the intramolecular deprotonation of the Me substituent of *i*Pr leads to an immediate Wittig-type rearrangement giving propene and presumably a phenolate complex (Scheme 1).

As the decomposition of the Na and K compounds is relatively slow (half-life about 2 days), we continued to target the synthesis of the bis(aryl)calcium compound by a salt-metathesis reaction with CaI_2. The driving force in this reaction is the formation and precipitation of the very stable, insoluble salt $(\text{NaI})_\infty$ or $(\text{KI})_\infty$ (due to the good solubility of LiI in thf, use of the Li precursor would be disadvantageous).

After many attempts, the reaction of 2 equivalents of $(i\text{PrO})_2\text{C}_6\text{H}_3\text{Na}$ with anhydrous CaI_2 in thf did not give pure or crystalline products that could be identified as the desired product $[(i\text{PrO})_2\text{C}_6\text{H}_3]_2\text{Ca}$. In one case we isolated a small batch of colourless well-defined crystals (yield $< 10\,\%$) that were identified as $[(i\text{PrO})_2\text{C}_6\text{H}_3\text{O}]\text{CaI·thf}$, likely formed after partial oxidation by O_2 from traces of air (ether-substituted phenyl anions are oxidation-sensitive).[16b] The decomposition product crystallized as a centrosymmetric dimer in the monoclinic space group $P2_1/c$ (Figure 2, Table 1). Two aryloxide anions bridge two Ca^{2+} ions in such a way that both *i*PrO substituents can form intramolecular Ca–O bonds. *O,O′,O′′*-Chelation of the 2,6-di-*i*PrO-phenoxy ligands leads to a nearly planar $(\text{ArOCa})_2$ framework in which the Ca^{2+} ions lie only 0.237(1) Å out of the ArO least-squares plane. The coordination spheres of both Ca^{2+} ions are completed by iodide and thf ligands. The terminal Ca–I bond of 3.0702(4) Å is significantly shorter than that in $(p\text{-tolyl})\text{CaI·(thf)}_4$

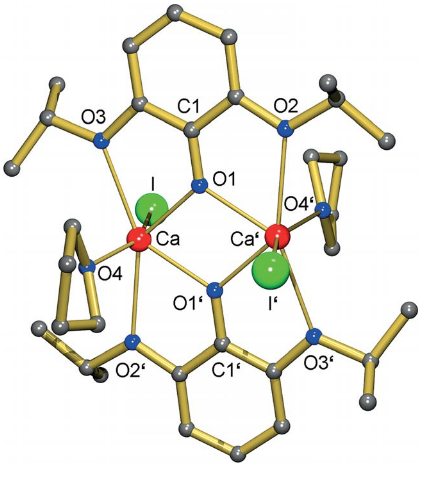

Figure 2. Crystal structure of the dimer $\{[(i\text{PrO})_2\text{C}_6\text{H}_3\text{O}]\text{CaI·thf}\}_2$. Hydrogen atoms are not shown for clarity.

[3.172(1) Å],[20] which also features a hexacoordinate Ca^{2+} ion. This may be explained by the unusual coordination geometry of Ca in $[(iPrO)_2C_6H_3O]CaI·thf$, in which a large part of the coordination sphere is not occupied by ligands but shielded by *i*Pr groups. As $[(iPrO)_2C_6H_3O]CaI·thf$ is an accidental product, the development of a high-yielding synthetic route and further analysis was not pursued.

Failure of the salt-metathesis route using $(iPrO)_2C_6H_3Na$ may be due to the partial decomposition of the precursor (see above) or insufficient precipitation of NaI resulting in a mixture of products. Salt metathesis using $(iPrO)_2C_6H_3K$ may be advantageous on account of the lower solubility of KI. The reaction of 2 equivalents of $(iPrO)_2C_6H_3K$ with anhydrous CaI_2 in thf, followed by evaporation of all solvents and extraction with benzene gave, after crystallization, a batch of colourless crystals that were identified as a rare calcate complex, $[\{(iPrO)_2C_6H_3\}_3Ca]^-K^+$, by single-crystal X-ray diffraction. The use of different $(iPrO)_2C_6H_3K/CaI_2$ ratios either led to complex reaction mixtures or isolation of the calcate complex. The crystallized yield of 12% is low, but likely due to the partial decomposition of the potassium precursor and the presence of other products in the reaction mixture.

The complex $[\{(iPrO)_2C_6H_3\}_3Ca]^-K^+$ crystallizes in the monoclinic space group $P2_1/c$ (Figure 3, Table 1). The central Ca^{2+} ion is surrounded by three Ar anions each of which chelate the metal in a bidentate bonding mode through the C_{ipso} atom and one of the *i*PrO oxygen atoms. This results in quite an unusual ligand–metal bonding geometry with very narrow C–Ca–O bite angles [55.38(5)–55.83(5)°]. The K^+ ion is less strongly bound at the fringe of the calcate anion by two *C*,*O*-chelating aryl anions and a K–O3 contact to a neighbouring calcate anion. This arrangement results in a linear coordination polymer in which K^+ ions bridge the calcate units. The C_{ipso} atoms C2 and C26 bridge the Ca^{2+} and K^+ ions. The Ca–C bond lengths do not show much variation and its average value of 2.542(1) Å is considerably shorter than the average Ca–C bond length of 2.749(4) Å in Ar_6Ca_4O [see Equation (2)] in which the C_{ipso} atom also bridges two Ca^{2+} ions.[16b] The average Ca–C bond is similar in length to the terminal Ca–C_{ipso} bond in (*p*-tolyl)$CaI·(thf)_4$ (2.556 Å).[20]

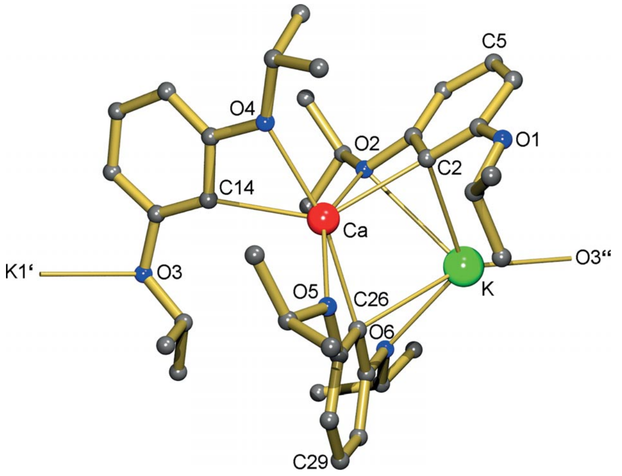

Figure 3. Crystal structure of the calcate complex $[\{(iPrO)_2C_6H_3\}_3Ca]^-K^+$ (linear coordination polymer). Hydrogen atoms are not shown for clarity.

Although there are examples of arylpotassium compounds embedded in mixed-metal "ate" complexes,[36] no crystal structure has been reported of a "pure" arylpotassium compound that does not contain other metal cations. However, there are some examples of structurally characterized alkyl,[37] benzyl[38] and acetylide[39] potassium complexes. The C–K bond lengths vary between 2.90–3.10 Å, which means that the C–K bonds in the current calcate complex are of similar length to those in regular organopotassium compounds. As primary (stronger) bonds should be formed with the higher charged, more electronegative Ca, this may seem counterintuitive. However, one should also consider the directionality of the C_{ipso}–metal bond. The more compact C_{ipso} sp^2 lone pair forms shorter C–metal bonds than the extended perpendicular p-type orbital. For this reason, the structures of mixed-metal "ate" complexes often show that the harder, smaller and higher charged cations are aligned along the sp^2 lone pair whereas the softer and larger alkali metal cations are bound by the p-type orbital. Indeed, the "ate" complex $(tmp)_2PhMgK$ (tmp = tetramethylpiperidide) with incorporated PhK units[36a] shows bonding of Mg^{2+} along the C_{ipso} sp^2 lone pair and bonding of K^+ along the p-type orbital. Its average C–K bond length of 3.046(5) Å is similar to that in the current calcate structure.

Other evidence for the primary bond to Ca^{2+} in the current structure is found in the directionality of the sp^2 lone pairs, which point more towards Ca^{2+} than to K^+. The angles C5···C2–Ca1 (146.62°) and C29···C26–Ca (145.70°) are considerably larger than the angles C5···C2–K (99.67°) and C29···C26–K (128.64°). It is also interesting to note that the sp^2 lone pair at C14, which does not bridge cations but forms a terminal Ca–C bond, is not directed towards the metal. The shift of Ca^{2+} away from the sp^2 axis is due to the strong intramolecular coordination of the *i*PrO substituent through a strained four-membered Ca–C–C–O ring. In the current calcate structure, these observations point to a primary bond between the aryl C_{ipso} atoms and Ca^{2+} and to a much weaker bond between C_{ipso} and K^+.

Although there is precedent for C–Ca bonded organocalcate complexes,[37b,40] the complex $[\{(iPrO)_2C_6H_3\}_3Ca]^-K^+$ is the first example of an arylcalcate complex of type $[Ar_3Ca]^-M^+$. As one can control the nucleophilicity/basicity of the carbanion through the nature of the second metal cation, "ate" complexes are of interest as superbases, mixed-metal reagents or TURBO Grignards.[41] On account of the negative charge on Ar_3Ca^-, the Ar–Ca bond should be more ionic than that in neutral Ar_2Ca and ArCaI complexes. One parameter to probe aryl–metal bond ionicity is the deformation of the aryl ring.[17] Although the aryl ring in the calcate complex $[\{(iPrO)_2C_6H_3\}_3Ca]^-K^+$ shows an unusually acute C–C–C angle at C_{ipso} [average: 113.0(1)°], changes in this parameter are also influenced by other substituents and are not accurate enough for a strong conclusion on bond ionicity. There is, however, another parameter that can be linked to the charge localization at C_{ipso} and C_{ipso}–M bond ionicity. The ^{13}C NMR chemical shift of C_{ipso} in a metallated phenyl ring is very sensitive to charge localization. Compared with the neutral aromatic ligand, an enormous downfield shift is observed. This is caused by increased σ-electron density and decreased π-electron density at the metallated carbon atom and can be used to evaluate aggregation numbers in aryllithium chemistry: the downfield shift increases with decreasing aggregation.[42] In the series of $(iPrO)_2C_6H_3M$ complexes introduced in this work, we also find a distinct influence of the metal on the ^{13}C chemical shift of C_{ipso}: Li (152.2) < Na (154.6) < K (161.8 ppm). The downfield shift increases with the polarity of the C–M bond. Because the chemical shift of the C_{ipso} atom is also strongly influenced by *ortho*-alkoxy substituents, only direct comparisons with similar lead structures are possible. The dinuclear complex $[(MeO)_2C_6H_3]_3Ca_2I\cdot(tmeda)_2$ shows a chemical shift of 152.0 ppm[22] and for the cluster $[(MeO)_2C_6H_3]_6Ca_4O$ the C_{ipso} signal is found at $\delta = 150.2$ ppm. This means that the polarity of the aryl–Ca bond compares well with that of aryllithium compounds. The present calcate $[\{(iPrO)_2C_6H_3\}_3Ca]^-K^+$ shows a ^{13}C signal for C_{ipso} at $\delta = 156.3$ ppm, which relates to an average bond polarity similar to that of organosodium compounds. The high nucleophilicity/basicity of calcate complexes is in line with a recent report on a highly active "ate" complex in catalysis.[43]

Conclusions

1,3-Diisopropoxybenzene has been cleanly metallated at the 2-position and the compounds $(iPrO)_2C_6H_3M$ (M = Li, Na, K) have been isolated. The crystal structure of the tetramer $[(iPrO)_2C_6H_3Na]_4$ is a rare example of solvent-free arylsodium complex that is even soluble in hexane. The salt-metathesis reaction between CaI_2 and $(iPrO)_2C_6H_3Na$ only led to complex reaction mixtures. On one occasion, crystals of the oxidation product $\{[(iPrO)_2C_6H_3O]CaI\cdot thf\}_2$ were obtained. The use of $(iPrO)_2C_6H_3K$ in the salt-metathesis reaction gave a well-defined product that could be structurally characterized and represents the first arylcalcate complex $[\{(iPrO)_2C_6H_3\}_3Ca]^-K^+$.

The unintended isolation of the calcate complex illustrates one of the main problems inherent to salt-metathesis reactions. The exchange of different anions and cations may lead to complex mixtures of compounds in which certain combinations might be favoured, or in the case that the product is obtained by crystallization, the least soluble species will be obtained. Similar problems have been encountered in alkylcalcium chemistry: Lappert and co-workers reported that the reaction of CaI_2 with $[(Me_3Si)_2CH]K$ gave the calcate species $[\{(Me_3Si)_2CH\}_3Ca]^-K^+$, irrespective of the reaction stoichiometry.[37b] Hanusa and co-workers showed that $Ca[N(SiMe_3)_2]_2$ prepared from $KN(SiMe_3)_2$ and CaI_2 by the salt-metathesis route can contain considerable amounts of $KN(SiMe_3)_2$ that are not visible in its NMR spectra.[44] The ^1H NMR chemical shift of the $N(SiMe_3)_2$ anion is dependent on the Ca/K ratio and represents an average signal of different species among which is the known calcate complex $[\{(Me_3Si)_2N\}_3Ca]^-K^+$.[45] Salt metathesis is therefore not the method of choice for the synthesis of arylcalcium complexes. The direct Grignard route gives less complications due to the presence of only one kind of metal cation.

The ^{13}C NMR chemical shift of the aryl C_{ipso} atom is a good measure of aryl–metal bond polarity. Although arylcalcium compounds show a bond polarity similar to that of aryllithium compounds, the calcate complex displays an aryl–metal bond polarity similar to that of arylsodium compounds. The much higher reactivity (nucleophilicity/basicity) of calcate complexes can be exploited in catalyst design.

Experimental Section

General Methods: Solvents were dried by standard methods and distilled from sodium/benzophenone prior to use. All moisture- and air-sensitive reactions were carried out under argon using standard Schlenk techniques. Samples prepared for NMR measurements, elemental analysis as well as for the reactions were handled in a glovebox.

$NaOC(Me)_2Et$ and $KOC(Me)_2Et$ were prepared by heating a twofold excess of the alcohol $HOC(Me)_2Et$ with metallic Na or K at reflux for 18 h after which excess alcohol was removed under vacuum and the remaining white powder dried at 100 °C under high vacuum. The alcoholates were used without further analysis. *n*BuNa was prepared by the addition of *n*BuLi in hexane to a solution of $NaOC(Me)_2Et$ (20% excess) in hexane at –30 °C after which the suspension was warmed to room temperature and the isolated precipitate was washed with hexane to remove $LiOC(Me)_2Et$. The remaining white powder was dried under high vacuum and used without further analysis. 1,3-$(iPrO)_2C_6H_4$ was prepared according to a literature procedure.[24]

NMR spectra were recorded with a Bruker DPX300 or Avance III HD400 spectrometer. Single crystal structures were determined by X-ray diffraction with a Siemens SMART diffractometer (APEXII detector) or a Supernova diffractometer (Rigaku-Oxford diffractions; AtlasS2 detector). Elemental analyses were performed with a CEInstruments EA1110 elemental analyser (samples were applied to a high vacuum before measurements). On account of the high air-sensitivity of the complexes, the data obtained were not always satisfactory. Propene was detected by GC–MS with a HP quadrupole mass spectrometer (Agilent 5973N MSD) in conjunction with a HP gas chromatograph (Type 6890).

Synthesis of 2,6-$(iPrO)_2C_6H_3Li$: *n*BuLi (9.20 mL, 2.46 M in hexane, 22.6 mmol) was added to a solution of 1,3-$(iPrO)_2C_6H_4$ (4.40 g, 22.6 mmol) in hexane (30 mL). The reaction mixture was heated at reflux for 1 h during which time a fine white precipitate was formed. The mixture was centrifuged and the precipitate washed with hexane (2× 15 mL). Drying under high vacuum (0.01 Torr, 20 °C, 30 min) yielded the product as a white powder (3.16 g, 15.8 mmol, 70%). ^1H NMR ($[D_8]$thf, 300 MHz): $\delta = 1.29$ (d, $J = 6.0$ Hz, 12 H), 4.60 (sept, $J = 6.0$ Hz, 2 H), 6.25 (d, $J = 7.5$ Hz, 2 H), 6.77 (t, $J = 7.5$ Hz, 1 H) ppm. ^{13}C ($[D_8]$thf, 75 MHz): $\delta = 23.0$ (*i*Pr-Me), 68.5 (*i*Pr-CH), 105.0 (Ar-*m*), 126.0 (Ar-*p*), 152.2 (C-Li), 168.1 (Ar-*o*) ppm. $C_{12}H_{17}LiO_2$ (200.21): C 71.99, H 8.56; found C 70.83, H 8.02.

Synthesis of 2,6-(*i*PrO)$_2$C$_6$H$_3$Na: 1,3-(iPrO)$_2$C$_6$H$_4$ (2.60 g, 13.4 mmol) dissolved in hexane (10 mL) was added to a suspension of *n*BuNa (0.97 g, 12.1 mmol) in hexane (10 mL). After complete addition, the precipitate dissolved instantaneously to give a yellow solution. The solution was stirred for 2 h at room temperature and subsequently all solvents were removed under vacuum. The resulting solid was washed with cold hexane (2× 5 mL). Drying under high vacuum (0.01 Torr, 20 °C, 30 min) yielded the product as a white powder (1.60 g, 7.40 mmol, 61 %). The product can also be obtained in a similar yield by slow evaporation of the solvent from a hexane solution. ^{1}H NMR (C_6D_6, 300 MHz): δ = 0.97 (d, J = 6.2 Hz, 12 H), 4.33 (sept, J = 6.2 Hz, 2 H), 6.48 (d, J = 7.5 Hz, 2 H), 7.22 (t, J = 7.5 Hz, 1 H) ppm. ^{13}C (C_6D_6, 75 MHz): δ = 22.4 (*i*Pr-Me), 67.8 (*i*Pr-CH), 104.0 (Ar-*m*), 127.2 (Ar-*p*), 154.6 (C-Na), 167.3 (Ar-*o*) ppm. $C_{12}H_{17}NaO_2$ (216.26): C 66.65, H 7.92; found C 66.29, H 7.98.

Synthesis of 2,6-(*i*PrO)$_2$C$_6$H$_3$K: 1,3-(iPrO)$_2$C$_6$H$_4$ (6.50 g, 33.5 mmol) and KOC(Me)$_2$Et (3.55 g, 28.1 mmol) were dissolved in hexane (40 mL) and the mixture was cooled to –50 °C. Then *n*BuLi (11.4 mL, 2.46 M in hexane, 28.1 mmol) was added slowly and a white precipitate formed immediately. While still in the cooling bath, the reaction mixture was slowly warmed to 5 °C and stirred for a further 2 h at this temperature. Subsequently, the reaction mixture was centrifuged and the precipitate washed with hexane (3× 30 mL). Drying under high vacuum (0.01 Torr, 20 °C, 30 min) yielded the product as a white powder (6.00 g, 25.8 mmol, 92 %). ^{1}H NMR ([D$_8$]thf, 300 MHz): δ = 1.22 (d, J = 6.2 Hz, 12 H), 4.72 (sept, J = 6.2 Hz, 2 H), 6.15 (d, J = 7.5 Hz, 2 H), 6.67 (t, J = 7.5 Hz, 1 H) ppm. ^{13}C ([D$_8$]thf, 75 MHz): δ = 20.7 (*i*Pr-Me), 64.7 (*i*Pr-CH), 102.3 (Ar-*m*), 122.5 (Ar-*p*), 161.8 (C-K), 166.1 (Ar-*o*) ppm. Elemental analysis was troublesome due to the high sensitivity of 2,6-(iPrO)$_2$C$_6$H$_3$K towards traces of air.

Synthesis of [{2,6-(*i*PrO)$_2$C$_6$H$_3$}$_3$Ca]$^-$K$^+$: A suspension of CaI$_2$ (3.05 g, 10.4 mmol) in thf (10 mL) was added to a solution of 2,6-(iPrO)$_2$C$_6$H$_3$K (5.30 g, 22.8 mmol) in thf (30 mL). After stirring for 48 h at room temperature, the solvent was removed in vacuo. The residue was extracted with benzene (3× 15 mL) and the combined benzene layers were concentrated and dried in vacuo. The residue was washed with hexane (2× 15 mL) and crystallized from benzene by slow diffusion of hexane to give the product as large colourless crystalline blocks (600 mg, 0.91 mmol, 12 % relative to the potassium precursor). Variation of the K/Ca ratio did not lead to isolation of [2,6-(iPrO)$_2$C$_6$H$_3$]$_2$Ca or to increased yields of the calcate complex. ^{1}H NMR (C_6D_6/[D$_8$]thf, 400 MHz): δ = 1.12 (d, J = 6.2 Hz, 36 H), 4.60 (sept, J = 6.2 Hz, 6 H), 6.43 (d, J = 7.8 Hz, 6 H), 6.96 (t, J = 7.8 Hz, 3 H) ppm. ^{13}C NMR (C_6D_6/[D$_8$]thf, 100 MHz): δ = 22.3 (*i*Pr-Me), 68.9 (*i*Pr-CH), 107.2 (Ar-*m*), 126.3 (Ar-*p*), 156.3 (C-Ca), 166.6 (Ar-*o*) ppm. $C_{36}H_{51}CaKO_6$ (658.98): C 65.62, H 7.80; found C 65.47, H 7.99.

CCDC-1426805 (for [(iPrO)$_2$C$_6$H$_3$Na]$_4$), -1426806 (for {[(iPrO)$_2$C$_6$H$_3$O]CaI·THF}$_2$) and -1426807 (for {[(iPrO)$_2$C$_6$H$_3$]$_3$Ca$^-$}K$^+$) contain 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.

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