Arylcalcium Hydrides as Precursors to Alkoxides and Aryloxides of Calcium

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Calcium atoms react with +I-substituted benzene derivatives under cocondensation conditions to yield arylcalcium hydrides. With toluene, *tert*-butylbenzene, and trimethyl(phenyl)silane the reaction showed no selectivity for C–H activation, resulting in the formation of each of the three possible isomers, while with *m*-xylene the reaction resulted in selective activation of the bond *meta* to the CH_3 groups. Treatment of (*tert*-butylphenyl)calcium hydride with di- and trisubstituted phenols such as 2,6-di-*tert*-butylphenol, 2,6-di-*tert*-butyl-4-methylphenol, and 2,4,6-tri-*tert*-butylphenol resulted in the formation of calcium aryloxides in yields > 95%. $[Ca(2,4,6\text{-}tBu_3C_6H_2O)_2(THF)_3]$ crystallises from a THF solution as a distorted trigonal bipyramid, with two THF ligands in the *trans*-axial positions and the third THF ligand and both aryloxide groups in equatorial positions. The $Ca–O_{Aryl}$ bond length was found to average at 2.181(3) Å. The $Ca–O–C_{Aryl}$ angles are almost linear, with Ca1–O1–C1 and Ca1–O2–C19 being 173.9(3)° and 178.8(3)°, respectively, while the O1–Ca1–O2 angle was determined as 152.04(12)°. A reaction between (*tert*-butylphenyl)calcium hydride and triphenylmethanol resulted in the formation of the corresponding monomeric calcium bis(alkoxide) $Ca(OCPh_3)_2(THF)_4$ in 95% yield. The structure was determined as a distorted octahedron with the alkoxide ligands in a *cis*-equatorial arrangement. The Ca–O bond length was determined at 2.1609(17) Å. The $Ca–O–C_{Aryl}$ angle of 177.46(16)° is almost linear, while the O1–Ca1–O1A angle was determined at 110.12(19)°.

Introduction

Until the mid 1980s, complexes of calcium were among the longest known, yet least understood class of compounds. Since the early 1990s, however, there has been renewed interest in this field.[1] The reasons for this slow development have been due to numerous factors. Firstly, calcium complexes have rather poor solubility in hydrocarbon solvents and many are thermally unstable.[1] Secondly, there are only a limited number of starting reagents and preparative techniques for the formation of calcium compounds.[1]

The most popular preparative technique is to use non-elemental forms of calcium (as shown in Figure 1), utilising a salt such as CaI_2 or calcium bis(trimethylsilyl)amide as the source of calcium. Another method is by deprotonation with an activated hydrocarbon, as shown in Equation (C) in Figure 1.

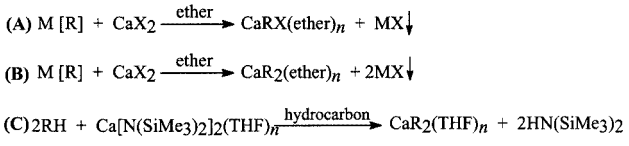

Figure 1. Reactions using non-elemental forms of calcium

Another synthetic method is to use bulk calcium metal for reaction, but a major difficulty encountered with this technique is its relative inertness to reaction. There are a number of different methods to activate the bulk metal, including the formation of an activated powder by displacement of calcium by potassium from a calcium dihalide (Rieke calcium),[2] or by decomposition of alkaline earth metal/anthracene complexes (Bogdanovic method).[3] Alternatively, the metal can be dissolved in liquid ammonia[4] or dispersed in THF.[5]

Metal vapour synthesis (MVS) takes a different approach to the above methods to overcome the inertness of bulk calcium metal. The above procedures are in reality a cleaning of the metal surface. Metal atom techniques are different, in that they utilise the vaporisation enthalpy of calcium as the reaction enthalpy. This technique has received only sporadic attention to date. In the late 1980s, MVS was used to prepare $[Ca(cot)(THF)_n]$[6] and the bis(cyclopentadienyl)-calcium complex $[Ca\{\eta\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_3)_2\}_2(THF)]$,[7] and more recently $[Ca\{CH(SiMe_3)_2\}_2(THF)_3]$,[8] while in the mid 1980s Mochida et al.[9] reported the C−H bond activation of benzene by calcium atoms to form PhCaH, which was not isolated but characterised by its organic products as outlined in Figure 2. In these systems the high reactivity of calcium atoms is stored in the products' highly reactive bonds.

Recently performed theoretical work showed that the molecule "PhCaH" should be able to exist in donor solv-

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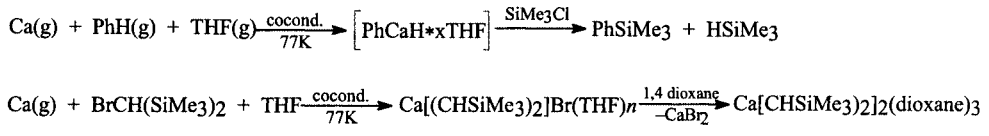


Figure 2. Cocondensation reactions with calcium atoms

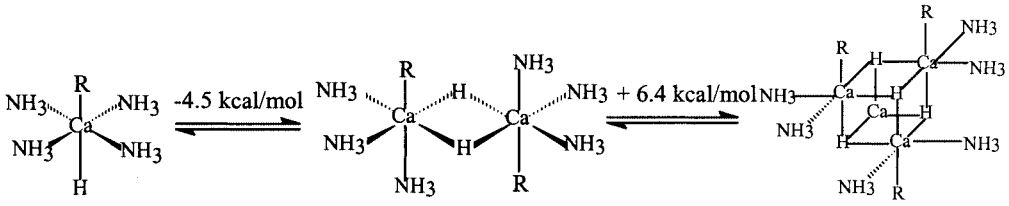


Figure 3. Calculated structures for PhCaH in donor solvents

ents such as THF in different aggregation states.[10] As a means of developing a convenient theoretical model for arylcalcium hydride in donor solvents, ammonia was used to simulate an amine and the elimination of H_2 was suppressed. These calculations show that a concentration-dependent equilibrium exists in donor solvents (as outlined in Figure 3). At low concentrations of "PhCaH", a monomeric species is energetically favoured, while at higher concentrations a tetrameric species with triply bridging hydride ligands exists. However, at average concentrations of "PhCaH" the energetically favoured structure is a dimer.

Calcium alkoxides are used as CVD precursors and for sol-gel synthesis.[1,11] As well as this, alkaline earth metal alkoxides are noted for their rich variety of structures and reactions.[1] This is due to the conformational and bonding flexibility of the alkoxide ligand (e.g., μ^1-, μ^2-, and μ^3-bonding modes are known). Crystallographically identified structural types range from discrete monomeric species such as $[Ca(BHT)_2(THF)_3]$ (BHT = 2,6-*tert*-butyl-4-methylphenolate)[12] to large polynuclear aggregates such as $[Ca_9(OCH_2CH_2OMe)_{18}(HOCH_2CH_2OMe)_2]$.[13]

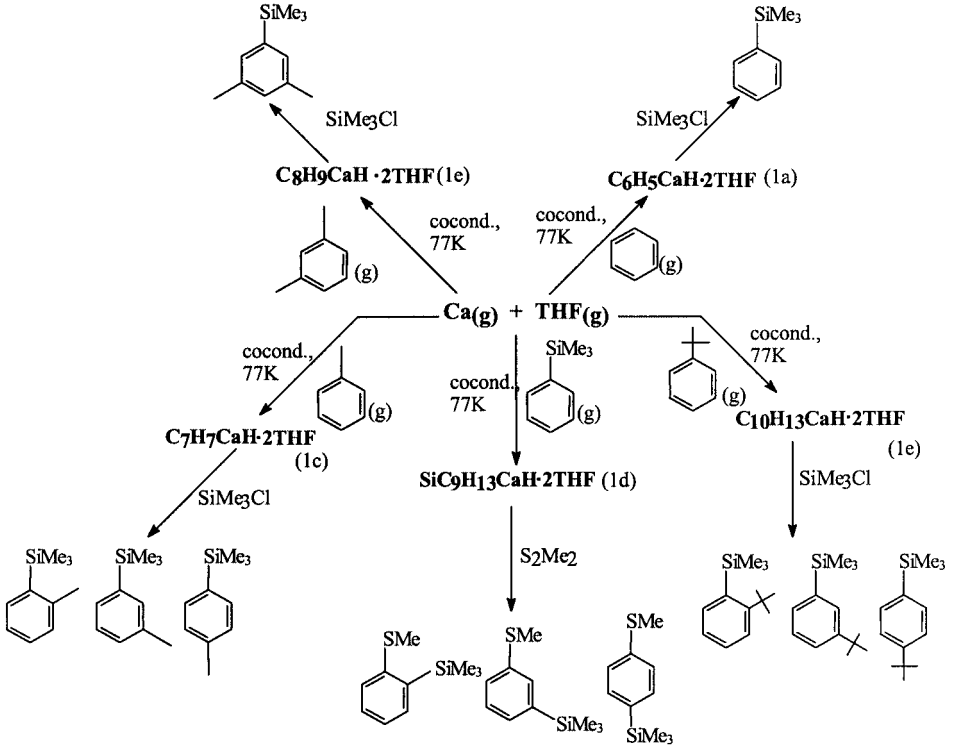
The aim of this work was firstly to use calcium atoms to activate the aromatic C−H bonds of +I-substituted benzene derivatives, thus forming arylcalcium hydrides, and secondly to use these arylcalcium hydrides as starting reagents for the formation of calcium alkoxides and aryloxides. To date, relatively few examples of monomeric alkoxides and aryloxides have been structurally characterised [examples include $[Ca(BHT)_2(THF)_3]$ and $[Ca(cox)_2(THF)_3]$·THF {cox = $C(Ph)_2(CH_2C_6H_4Cl\text{-}4)$}.[12] The reasons for this arise from difficulties in preventing oligomerisation or polymerisation of the calcium alkoxides and their low solubilities in most solvents. For this purpose a series of sterically bulky alcohols and phenols were chosen, in order to prevent oligomerisation and increase solubility in hydrocarbons.

Results

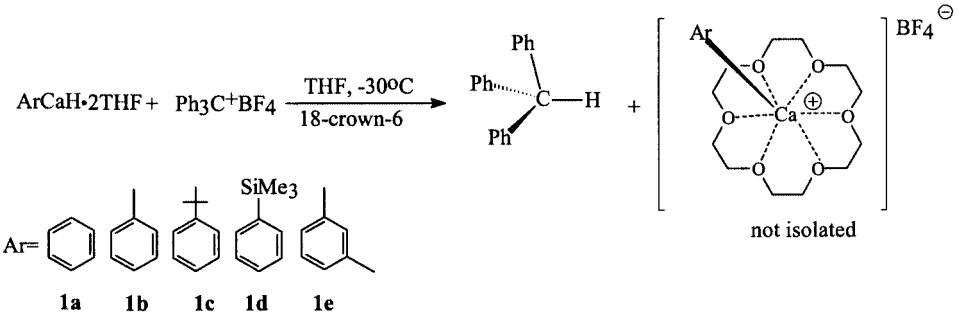
Experimental Study

Under cocondensation conditions, calcium atoms react with +I-substituted benzene derivatives to form extremely air- and moisture-sensitive, dark red solids in yields ranging from 78 to 97%. When calcium atoms were cocondensed with benzene in the presence of THF (as outlined in Scheme 1), a dark red, pyrophoric solid of composition PhCaH·2THF was obtained in a yield of 78%. An IR spectrum in Nujol mull showed a strong vibration at 1094 cm^{-1} and a weaker signal at 1031 cm^{-1}. We assign these as the Ca−H vibration at 1094 cm^{-1} and C−H bond deformations of the phenyl ring at 1031cm^{-1}, based on similar trends seen in our DFT-modelled vibrations. Because of the low solubility of the product in organic solvents and its extremely high sensitivity to air and moisture, however, NMR spectroscopic data were not obtained for this or any other arylcalcium hydride species. Instead, **1a** was treated at −30 °C with $SiMe_3Cl$ (as shown in Scheme 1) and the organic derivative trimethyl(phenyl)silane was identified by GC MS and NMR techniques. Further characterisation to show the presence of the hydride moiety was performed by treatment of **1a** with the hydride-abstracting agent $Ph_3C^+BF_4^-$. The product isolated from this reaction was triphenylmethane, as shown in Scheme 2.

A change of the aromatic compound from benzene to toluene resulted in a higher yield of 97%. The elemental analysis of the solid compound showed that it was composed of a C_7H_7CaH·2THF moiety. As with the benzene cocondensation product, a Ca−H vibration was found at 1092 cm^{-1}. In order to ascertain which C−H bond was activated, **1b** was converted into an organic compound by treating it with chlorotrimethylsilane. In this case, GC MS detected the presence of three different isomers in similar abundances. In conjunction with NMR spectroscopic data,



Scheme 1. Cocondensation of calcium atoms with +I-substituted benzene derivatives in the presence of THF



Scheme 2. Reaction of arylcalcium hydrides with $Ph_3C^+BF_4^-$

these were identified as the *ortho*, *meta*, and *para* isomers of trimethyl(methylphenyl)silane, as outlined in Scheme 1.[14–16] As before, **1b** was treated with $Ph_3C^+BF_4^-$, resulting in the isolation of triphenylmethane as outlined in Scheme 2. No attack at the thermodynamically favoured benzyl position was detected.

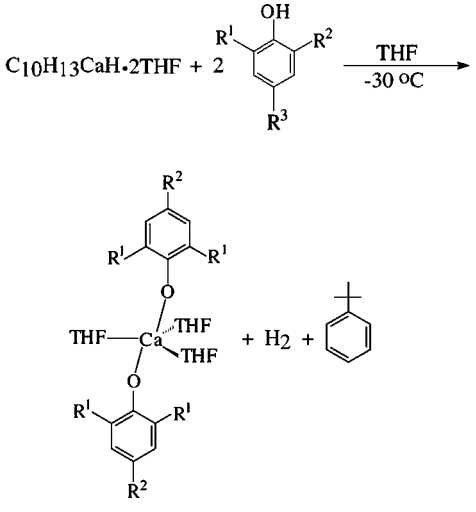
When *tert*-butylbenzene was used instead of toluene (as outlined in Scheme 1), a slightly lower yield of 93% was obtained. Like the previous cocondensation products, elemental analysis showed it to be composed of a $C_{10}H_{13}CaH{\cdot}2THF$ moiety, and a Ca–H vibration was found at 1094 cm^{-1}. As in the toluene cocondensation, **1c** was treated with chlorotrimethylsilane to identify which C–H bonds were activated. As in the case of the toluene reaction product, GC MS and NMR showed the presence of *ortho*, *meta*, and *para* isomers of (*tert*-butylphenyl)trimethylsilane in similar abundances, as outlined in Scheme 1.[17–19] As in the previous cocondensations, **1c** was treated with $Ph_3C^+BF_4^-$ to form triphenylmethane, thus indicating the presence of a hydride ligand, as outlined in Scheme 2.

A change of the +I benzene derivative to *m*-xylene resulted in a lower yield of 85%. As in the previous cocondensation products, elemental analysis shows the product to be of the composition $C_8H_9CaH{\cdot}2THF$, and the Ca–H vibration was detected at 1095 cm^{-1}. To confirm the regiochemistry of this reaction, **1d** was again treated with chlorotrimethylsilane. Unlike in the toluene and *tert*-butylbenzene cocondensations, though, GC MS and NMR showed that a single species had been formed, and this was identified as (3,5-dimethylphenyl)trimethylsilane, as outlined in Scheme 1.[20] Treatment of **1d** with $Ph_3C^+BF_4^-$ as outlined in Scheme 2 confirmed the presence of the hydride ligand.

When trimethyl(phenyl)silane was cocondensed with calcium atoms in the presence of THF, a similar lack of selectivity was observed. The isolated dark red solid (86% yield) had the composition $C_9H_{13}SiCaH{\cdot}2THF$. As in the previous cocondensation products, a Ca–H vibration was found

at 1094 cm^{-1}. For ease of characterisation, **1c** was treated with dimethyl disulfide rather than chlorotrimethylsilane in order to elucidate the selectivity of this reaction. GC MS measurements showed the presence of three different isomers in similar abundances. In conjunction with NMR spectroscopic data, these were identified as the *ortho*, *meta*, and *para* isomers of trimethyl[4-(methylthio)phenyl]silane, as outlined in Scheme 1.[17,19] As in all the previous cocondensations, **1c** was treated with $Ph_3C^+BF_4^-$ (as outlined in Scheme 2) to confirm the presence of a hydride ligand.

These arylcalcium hydrides can be redissolved in THF and utilised as reagents for the formation of new calcium compounds. When arylcalcium hydrides were treated at room temperature with bulky phenols (**3a**−**3c**), the corresponding bis(aryloxides) were formed in excellent yields (all > 95%), as outlined in Scheme 3. IR and NMR techniques identified all species as bis(aryloxides) of calcium. A characteristic ^{13}C NMR signal for the *ipso*-carbon atom (C−O^-) can be seen at δ ≈ 164.4 (for **3a**), 163.9 (for **3b**) and 163.4 ppm (for **3c**). The calcium aryloxides **3b** and **3c** have been reported previously and the NMR and IR data agree with the literature.[12,21] However, no crystal structure for **3c** had been reported in the literature. Integration of the THF signals in the ^1H NMR shows that **3a** has a coordination number of six, while **3b** has the lower coordination number of five.



3a: $R^1 = t$Bu, R^2 = H
3b: $R^1 = t$Bu, $R^2 = CH_3$
3c: $R^1 = t$Bu, $R^2 = t$Bu

Scheme 3. Synthesis of calcium aryloxides using **1c**

A single crystal of **3c** suitable for X-ray diffraction was grown over 5 d at +5 °C in THF. The result of the structure determination is depicted in Figure 4. The coordination number for the calcium is five, with two aryloxide and three THF ligands arranged in a distorted trigonal-bipyramidal coordination polyhedron around the calcium centre. Two and a half further uncoordinated THF molecules could be detected as lattice solvent. Bond lengths and angles are listed in Table 1.

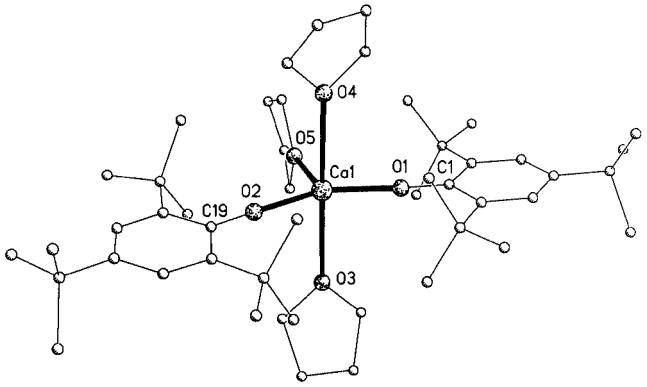


Figure 4. Crystal structure of Ca[2,4,6-tBu$_3$C$_6$H$_2$O]$_2$(THF)$_3$ (**3c**)

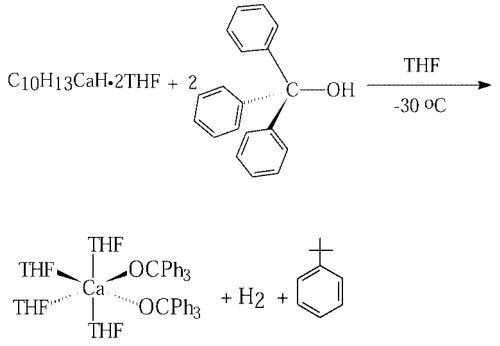
Table 1. Selected bond lengths [Å] and angles [°] for **3c**

Bond	Bond length [Å]	Angle	[°]
Ca1−O1	2.180(3)	O3−Ca1−O4	177.78(12)
Ca1−O2	2.183(3)	O1−Ca1−O2	152.08(12)
Ca1−O3	2.399(3)	O1−Ca1−O5	103.39(10)
Ca1−O4	2.395(3)	O2−Ca1−O5	104.45(11)
Ca1−O5	2.393(3)	C1−O1−Ca1	173.8(3)
O1−C1	1.325(5)	C19−O2−Ca1	178.7(3)
O2−C19	1.336(5)		

The calcium aryloxide **3c** crystallises as a monomer with two aryloxide ligands and a single THF donor molecule in the equatorial plane and two THF donors in axial positions. The Ca atom and three equatorial oxygen atoms are located in a plane with a mean deviation of 0.03 Å. The axial (THF)O−Ca−O(THF) angle of 177.78(12)° is almost linear, but the equatorial ArO−Ca−OAr angle of 152.08(12)° is markedly widened from the expected 120° for an ideal trigonal bipyramid. As a consequence, the angles for the other equatorial ligands are smaller [103.93(10)° for O1−Ca1−O5 and 104.45(11)° for O2−Ca1−O5]. The C_6 planes of the aryl ligands intersect at an angle of 8.2°. The two calcium−oxygen ($^-$OAr) bond lengths of 2.183(3) Å (av.) are almost identical. The Ca−O(THF) bonds are almost invariant at 2.395(3) Å. The carbon−oxygen bonds in the alkoxide ligands are identical within estimated standard deviations [1.324(5) Å for O1−C1 and 1.336(5) Å for O2−C19], and hence considerably shorter than standard C−O single bonds (1.43 Å).[22] In addition, the Ca−O−C angles of 173.8(3)° for Ca1−O1−C1 and 178.7(3)° for Ca1−O2−C19 are almost linear. Similar bond shortening and linearity was found in the analogous complex {[Ca(BHT)$_2$(THF)$_3$]·THF[12] and in the thiolate complex [Ca(SMes)$_2$(THF)$_4$] (Smes = 2,4,6-tBu$_3$C$_6$H$_2$S)}.[23]

The arylcalcium hydride **1c** also reacts with alcohols to form the corresponding bis(alkoxides) of calcium. When triphenylmethanol was allowed to react with **1c**, it produced the previously unrecorded calcium alkoxide **4** in 94% yield, as shown in Scheme 4. A single crystal of **4** was grown for X-ray diffraction over 10 d at +5 °C in THF. The coordina-

tion polyhedron around the central calcium atom is made up of six oxygen atoms, two of the Ph_3CO^- anions in adjacent equatorial positions and four of THF molecules in the remaining equatorial and axial positions (Figure 5). An additional THF molecule is found uncoordinated in the crystal lattice. Bond lengths and angles are described in full in Table 2.



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Scheme 4. Synthesis of **4** using **1c**

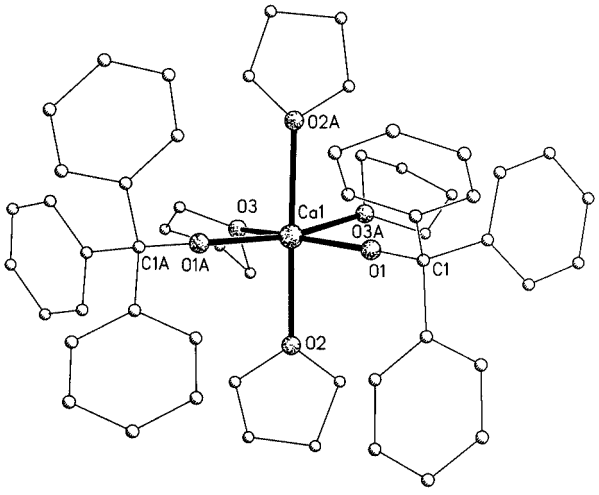

Figure 5. Crystal structure of $Ca[OCPh_3]_2(THF)_4$

Table 2. Selected bond lengths [Å] and angles [°] for **4**

Bond	Bond length [Å]	Angle	[°]
Ca1−O1	2.1609(16)	O1−Ca1−O1A	110.16(9)
Ca1−O2	2.440(2)	O1−Ca1−C3A	87.9(2)
Ca1−O3	2.482(7)	O3−Ca1−O3A	76.3(4)
O1−C1	1.375(2)	O2−Ca1−O2A	166.67(8)
C1−C2	1.565(3)	C1−O1−Ca1	177.47(13)
C1−C8	1.550(3)		
C1−C14	1.565(3)		

The distorted octahedral arrangement is evident from the deviation from linearity of the angle O2−Ca1−O2A, at 166.67(8)°. The calcium atom and four equatorial oxygen atoms are located in a plane with a mean standard deviation of 0.22 Å. The angle O1−Ca1−O1A between the two triphenylmethoxy ligands and the calcium atom is 110.16(9)°, while the angle between the two equatorial THF ligands at the calcium atom is considerably smaller at 76.3(4)°. This deformation in the octahedral geometry can clearly be attributed to the greater steric demand of the alkoxide ligands than of the THF ligands. Both axial THF ligands are bent away from the alkoxide ligands. Again, the angle $Ca-O-C_{Aryl}$, at 177.47(13)°, indicates near linearity. The Ca−O bond length in the alkoxide ligand is 2.1609(16) Å, and hence almost as long as in **3c**. The $O-C_{Aryl}$ single bonds in **4** − at 1.375(2) Å − are slightly longer than in **3c**.

Theoretical Study

In order to gain further insight into the proposed compositions of the arylcalcium hydrides a series of theoretical calculations were performed. As in previous reported theoretical work,[10] the AKR4/6-31g** basis set combination was used. This has proved to give reasonable geometries without greatly increasing the calculation time. As before, ammonia was chosen as a model Lewis base to decrease calculation time.

The aim of this theoretical study was to examine a possible mechanism for this reaction. The first step examined was the direct insertion of calcium atoms into the C−H bond. This is unlikely, since the calculated reaction enthalpy of +10.8 kcal/mol for the formation of PhCaH (**8**) is too large to occur at 77 K (outlined in Figure 6). This would indicate that a highly endothermic reaction is occurring at such a low temperature. The calculated Ca−H bond length for **8** was 2.037 Å and the Ca−C bond length was found to be 2.324 Å. The optimised structure **8** (as shown in detail in Table 3) showed an agostic interaction between the calcium atom and the *ortho* C−H bond of the phenyl ligand. This agostic bond length was calculated as 2.534 Å and the angle between the phenyl ligand, the calcium atom and the hydride ligand (C−Ca−H angle) was found to be 144.8°. This bending of the C−Ca−H angle in conjunction with an agostic C−H bond indicates coordinative unsaturation of the calcium centre in **8**. This is to be expected, since a coordination number of two for calcium is extremely low, particularly in view of the lack of steric bulk in the phenyl and hydride ligands. It would be reasonable to expect that, in the presence of donor solvents such as THF, a higher coordination number would be achieved through the coordination of donor solvent molecules.

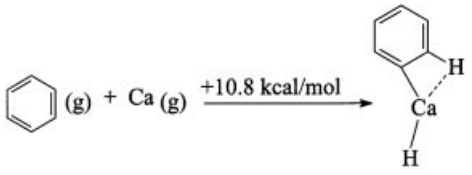

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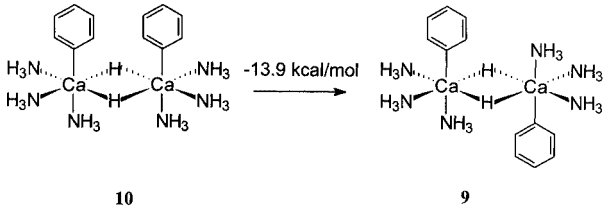
Figure 6. Reaction of calcium atoms with benzene

In a previous theoretical study,[10] it was reported that phenylcalcium hydride exists in donor solvents as a hydride-bridged dimer with a coordination number of six. Here it is extended to show that the *trans* "$PhCaH\cdot3NH_3$" dimer

Table 3. Comparison of bond lengths and IR frequencies in calculated arylcalcium hydride species

	PhCaH	*trans*-PhCaH·3NH$_3$	*cis*-PhCaH·3NH$_3$
Ca−H [Å]	2.037	2.305	2.318
Ca−C [Å]	2.324	2.552	2.528
Ca−N [Å]	N/A	2.569	2.575
Ca−Ca [Å]	N/A	3.461	3.532
ν_s(Ca−H) [cm^{-1}]	N/A	991 (sym)	849 (sym)
ν_{as}(Ca−H) [cm^{-1}]	N/A	1048 (antisym)	930 (antisym)

species **9** has a reaction enthalpy −13.9 kcal/mol lower than that of the *cis* dimer species **10**, as described in Figure 7. For the *trans* species **9**, the calculated Ca−H bond length is 2.305 Å, the Ca−C bond length is 2.552 Å and the Ca−N bond length is 2.569 Å; these values are outlined in Table 3. The Ca−H antisymmetric vibration, which is IR-active, is calculated as 1078 cm^{-1}. Slightly different values (as shown in Table 3) are seen for **10**. The calculated Ca−H bond (2.318 Å) is slightly longer than in **9**, while the Ca−C bond length was found to be 2.528 Å, shorter than in **9**. The Ca−H antisymmetric vibration in **10** is 930 cm^{-1}. This value is lower than that of **9** (1078 cm^{-1}). It should be possible to distinguish whether "solvated PhCaH" exists in either *cis* or *trans* form in solution by IR methods.



10 **9**

Figure 7. Energy difference between *cis* and *trans* isomers of PhCaH·3NH$_3$

Discussion

Composition of Arylcalcium Hydrides

Mochida originally proposed that the product from the reaction between benzene and calcium atoms was "PhCaH",[9] but he failed to isolate this compound. Instead, it was allowed to react with D_2O and $SiMe_3Cl$. On repeating this experiment in THF, we isolated a dark red, air- and moisture-sensitive solid in 78% yield, as shown in Scheme 1. This is an extremely high yield for an MVS experiment, and it appears moreover that the loss in yield stems from a relatively high-melting matrix in the vessel, which hinders collection of the entire sample. In the benzene cocondensation, for example the matrix is a benzene/THF mixture. The melting point of benzene is 5.5 °C and the melting point of THF is −103 °C. However, the toluene cocondensation has a lower melting matrix of toluene/THF (melting point of toluene −95 °C) and hence a higher yield. This reaction type was expanded to include other +I-substituted benzene derivatives, as in the similar lithium atom reaction.[20] Calcium atoms were able to activate the C−H bonds of toluene, *tert*-butylbenzene, trimethyl(phenyl)silane, and *m*-xylene, as outlined in Scheme 1. It is clear from the derivatisation reactions with chlorotrimethylsilane (as shown in Scheme 1) and $Ph_3C^+BF_4^-$ (shown in Scheme 2) that the backbone of **1a** is composed of the anionic ligands Ph^- and H^-. However, the elemental analysis indicates that the composition is (PhCaH·2THF)$_x$: The existence of coordinated Lewis base molecules such as THF is a well-known facet of calcium chemistry.[1]

Theoretical calculations show the tendency towards oligomerisation through hydride bridging and the uptake of THF to fill the coordination sphere of the calcium atom. These calculations showed that the formation of PhCaH is energetically unfavourable by +10.8 kcal/mol and that an aggregated state through hydride bridging is favoured over a monomeric species.[6] These calculations also showed that the favoured coordination number is six and that a solvent-dependent equilibrium exists in donor solvents. The calculations show that the aggregation state can be elucidated from the IR data on the Ca−H vibration. The calculated IR frequency for a terminal hydride ligand (e.g., monomeric PhCaH·4NH$_3$) is 897 cm^{-1}. When the hydride ligand is bridging, as in a dimeric species, the calculated Ca−H vibration is higher, at 1048 cm^{-1}. The calculated data for this dimeric species are in good agreement with the experimentally measured value of 1094 cm^{-1}. However, the possibility of higher aggregates such as tetramers (in which the hydride ligand would be triply bridging) or an oligomeric species through mixed bridging of the phenyl and hydride ligands cannot be gauged from these data.

Selectivity of C−H Activation with Calcium Atoms

Lithium atoms have been reported to activate aromatic C−H bonds of +I-substituted benzene derivatives selectively in the *para* position.[24] By use of an approach similar to Mochida's and by treatment of the "ArCaH" with chlorotrimethylsilane at −30 °C, easy identification of the activated positions on the aromatic ring by NMR and GC MS is possible. On expanding this reaction type to other aromatic compounds [e.g., toluene, *tert*-butylbenzene, trimethyl(phenyl)silane, and *m*-xylene], it was expected that selective C−H bond activation in the *para* position would be observed, in a reaction series analogous to that of lithium atoms.[20] However, this was not observed; instead, a lack of selectively was noted. All benzene derivatives except xylene experienced the activation of the *ortho*, *meta*, and *para* C−H bonds. This lack of selectivity is different to the case of the lithium atom reaction, in which the *para* position was selectively attacked.[24] Another difference was that xylene, which had failed to react with lithium atoms, reacted with calcium atoms. [Calcium atoms react with mesitylene, which does not react with lithium atoms, to yield an extremely pyrophoric, insoluble, red solid.]

One similarity to the lithium atom reaction is that the reaction between calcium atoms and toluene does not result in the activation of the thermodynamically favoured benzyl position. In the case of lithium atoms, it was shown the a key intermediate was the formation of a π complex between

the benzene ring and an Li_2 cluster, which favours the activation of the aromatic C−H bonds.[24]

Reactions of Arylcalcium Hydrides

These arylcalcium hydrides can be redissolved in THF and allowed to react with sterically bulky phenols and alcohols to form bis(aryloxides)/-(alkoxides) of calcium in improved yields (all > 95%).[12]

The structure of **3c** is similar to those of **5** and **7**, which are shown in Figure 8 and have been reported previously.[12,23] It is monomeric, in a distorted trigonal-bipyramidal arrangement, with the Ca−O(phenolate) bond length of 2.182(3) Å av. for **3c** being shorter than that for **5** at 2.197 Å. Like those in **5** and **7**, the aryloxide ligands in **3c** are in the equatorial positions. Another similarity between **3c** and **5** is the almost linear Ca−O−C angle. It is not clear what causes this linearity (and shortened Ca−O bond) in calcium aryloxides.[12] One possible explanation is the steric load on the ligands in both **3c** and **5**; another might lie in π-bonding.[25,26] This is not as unreasonable as it appears, since aryloxides are good π-donor ligands and it has been shown that calcium possesses low-lying d orbitals that influence the structure of molecules.[27−29] It can be very difficult to separate steric and electronic effects.[30] It has been demonstrated that the M−O−C angle has no simple correlation with the degree of π-bonding.[25] A similar comparison can be made between the calcium alkoxide **4** and the previously reported species **6** and **8**.[12,31] There is a pronounced difference between the structures. In **4**, the crystal was grown from THF and crystallised as a monomer of coordination number six, while compounds **6** and **8** were grown from toluene and crystallised as dimers with lower coordination numbers of four and three, respectively. The Ca−O bond length for the terminal alkoxide in **6** is 2.105 Å, shorter than the same Ca−O bond length, of 2.1609(17) Å, in **4** and more akin to the Ca−O bond lengths found in the aryloxide species **3d** [2.182(3) Å] and **8** (2.121 Å). Unlike those in the above species **3c**, **4**, and **5**, the Ca−O−C angle in **6** is bent at 167.4°, while in **4** the Ca−O−C angle is 177.46(14)°. This is almost linear and similar in value to those in the aryloxide species **3c** and **5**.

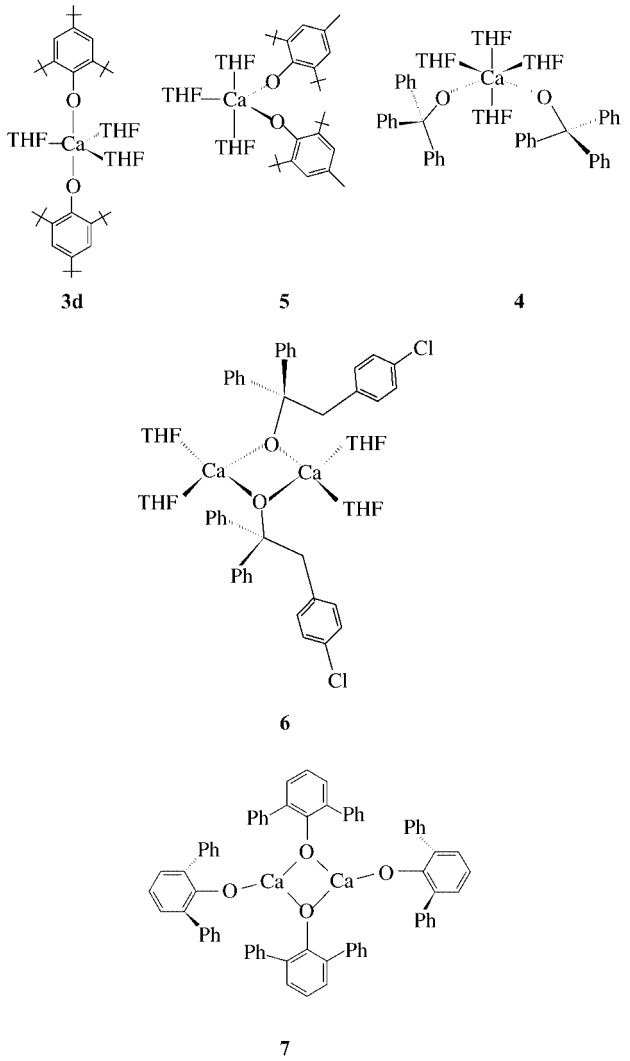


Figure 8. A comparison of some selected group-II bis(alkoxides)

Conclusion

Calcium atoms react unselectively with toluene, *tert*-butylbenzene and trimethyl(phenyl)silane to form the *ortho*, *meta*, and *para* isomers of each arylcalcium hydride. However, when *m*-xylene was cocondensed with calcium atoms in the presence of THF, selective C−H bond activation in the position *meta* to the methyl groups was observed. These arylcalcium hydrides are useful reagents for the formation of calcium bis(alkoxides). The reactions between (*tert*-butylphenyl)calcium hydride and different *tert*-butyl-substituted phenols resulted in the formation of the corresponding aryloxides in high yields. In $Ca(2,4,6\text{-}tBu_3C_6H_2O)_2(THF)_3$ the five oxygen atoms furnish a distorted trigonal-bipyramidal coordination polyhedron with the sterically bulky aryloxide ligands in the equatorial positions. In a similar reaction, triphenylmethanol yielded the alkoxide $[Ca\{OC(C_6H_5)_3\}_2(THF)_4]$ in a similar high yield. This compound shows a distorted octahedron of six oxygen atoms around the central metal atom and the two alkoxide ligands in a *cis* equatorial geometry.

Experimental Section

General: All experimental procedures were performed by use of standard Schlenk techniques under dry argon. Solvents such as THF, benzene, toluene, *m*-xylene, and *tert*-butylbenzene were dried and distilled prior to use from sodium benzophenone ketyl under argon. Trimethyl(phenyl)silane was dried and distilled from calcium dihydride under argon. Pentane was dried and distilled prior to use from sodium/potassium amalgam under argon. The solvents were then degassed by three freeze-pump-thaw cycles. Triphenylcarbenium tetrafluoroborate and 18-crown-6 were purchased from Aldrich and dried under high vacuum for 2 d. Celite was stored in an oven at 120 °C overnight and was dried under vacuum for 3 h before use. Approximately 6 cm of Celite was used for each filtra-

tion. ^{1}H and ^{13}C NMR spectra were obtained with either a Varian 300 MHz or a Varian 500 MHz NMR machine. All chemical shifts are reported in ppm and are referenced to TMS. All the GC MS samples were run as ethyl acetate solutions with a Finnigan Trace GC MS, on a room temp. X-5MS 15-m column. Warwick Analytical Service, Warwick, UK, performed the elemental analysis.

Typical Cocondensation Experiment: Calcium (1.5 g, 0.0375 mol) was vaporised from an alumina crucible over 90 min (5.6 V and 56 A) and cocondensed with a mixture of the aromatic compound (20 mL) and THF (80 mL). The pressure measured at the bottom of the cocondensation vessel was kept below 10^{-5} mbar to avoid gas-phase reactions between the metal atoms and reactants. The apparatus used has been described previously.[24] At the end of the experiment, the frozen matrix was allowed to warm up under argon. The molten mixture flowed through an internal drain into a Schlenk tube. The solution was filtered through 6 cm of Celite and the solvent was evaporated under reduced pressure to yield a dark red, pyrophoric solid $\{(ArCaH{\cdot}2THF)_x\}$ in yields ranging from 78 to 97%.

Cocondensation of Benzene with Calcium Atoms in THF: This cocondensation yielded a dark red, pyrophoric solid $\{(PhCaH{\cdot}2THF)_x\}$(**1a**) in 78% yield. $C_6H_5CaH{\cdot}2THF$ (262.4): calcd. C 64.1, H 8.4, Ca 15.3; found C 63.5, H 7.9, Ca 15.2. IR (Nujol mull; major peaks): $\tilde{\nu}$ = 3369 (s), 1285 (m), 1224 (s), 1094 (vs), 1031 (w), 981 (m), 905 (s), 837 (s), 751 (m), 726 (m), 696 (m) cm^{-1}.

Cocondensation of Toluene with Calcium Atoms in THF: This cocondensation yielded a brown, pyrophoric solid $\{(C_7H_7CaH{\cdot}2THF)_x\}$ (**1b**) in 97% yield. $C_7H_7CaH{\cdot}2THF$ (276.4): calcd. C 65.2, H 8.8, Ca 14.5; found C 64.4, H 8.8, Ca 14.3. IR (Nujol mull; major peaks): $\tilde{\nu}$ = 3368 (s), 1285 (m), 1223 (s), 1093 (vs), 1032 (w), 986 (m), 908 (s), 837.9 (s), 752 (m), 728 (m), 691 (m) cm^{-1}.

Cocondensation of *tert*-Butylbenzene with Calcium Atoms in THF: This cocondensation yielded a dark red, pyrophoric solid $\{(C_{10}H_{13}CaH{\cdot}2THF)_x\}$ (1c) in 93% yield. $C_{10}H_{13}CaH{\cdot}2THF$ (318.5): calcd. C 67.9, H 9.5, Ca 12.6; found C 67.0, H 9.2, Ca 12.3. IR (Nujol mull; major peaks): $\tilde{\nu}$ = 3370 (s), 1264 (s), 1112 (s), 1094 (vs), 1033 (w), 982 (m), 835 (s), 761.6 (m), 723 (m), 697 (m) cm^{-1}.

Cocondensation of *m*-Xylene with Calcium Atoms in THF: This cocondensation yielded a dark red, pyrophoric solid $\{(C_8H_9CaH{\cdot}2THF)_x\}$ (**1d**) in 85% yield. $C_8H_9CaH{\cdot}2THF$ (290.5): calcd. C 66.2, H 9.0, Ca 13.8; found C 65.9, H 8.7, Ca 13.6. IR (Nujol mull; Major peaks): $\tilde{\nu}$ = 3372 (s), 1288 (m), 1220 (s), 1096 (vs), 10323 (w), 989 (m), 912 (s), 838.4 (s), 757 (m), 732 (m), 686 (m)cm^{-1}.

Cocondensation of Trimethyl(phenyl)silane with Calcium Atoms in THF: This cocondensation yielded a dark red, pyrophoric solid $\{(C_9H_{13}CaH{\cdot}2THF)_x\}$ in 86% yield. $C_9H_{13}SiCaH{\cdot}2THF$ (334.6): calcd. C 61.0, H 9.0, Ca 12.0, Si 8.4; found C 59.8 H 8.8, Ca 12.3, Si 8.0. IR (Nujol mull; major peaks): $\tilde{\nu}$ = 3372 (s), 1591 (w), 1306 (w), 1260 (s), 1206 (m), 1114 (m), 1094 (vs), 1034 (m), 1019 (s), 837 (m), 801 (br), 751 (m), 725 (s), 698 (m), 618 (m) cm^{-1}.

Typical Derivatisation of the Arylcalcium Hydride with Chlorotrimethylsilane: Chlorotrimethylsilane (0.06 mL, 0.73 mmol) in THF (5 mL) was added dropwise at −30 °C to a stirred solution of arylcalcium hydride (1.0 g, dissolved in 50 mL of THF). The dark red colour turned yellow over a period of 5 min. After this time, the stirring was continued, while the solution was allowed to warm to room temperature. Water (15 mL) was added to this solution. The organic layer was separated and dried with magnesium sulfate, and the solvent was removed under reduced pressure to yield the corresponding substituted silane as a dark red oil.

Derivatisation of 1b with Chlorotrimethylsilane: All three possible trimethyl(methylphenyl)silane isomers were detected by GC MS ([M$^+$]: *m*/*z* = 164.1). Trimethyl(2-methylphenyl)silane: ^{1}H and ^{13}C NMR spectroscopic data agree with literature values.[14] Trimethyl(3-methylphenyl)silane: ^{1}H and ^{13}C NMR spectroscopic data agree with literature values.[15] Trimethyl(4-methylphenyl)silane: ^{1}H and ^{13}C NMR spectroscopic data agree with literature values.[16]

Treatment of 1c with Chlorotrimethylsilane. All three possible (*tert*-butylphenyl)trimethylsilane isomers were detected by GC MS ([M$^+$]: *m*/*z* = 206.4). (2-*tert*-Butylphenyl)trimethylsilane: ^{1}H and ^{13}C NMR spectroscopic data agree with literature values.[17] (3-*tert*-Butylphenyl)trimethylsilane: ^{1}H and ^{13}C NMR spectroscopic data agree with literature values.[18] (4-*tert*-Butylphenyl)trimethylsilane: ^{1}H and ^{13}C NMR spectroscopic data agree with literature values.[19]

Treatment of 1e with Chlorotrimethylsilane: Only one compound was detected by GC MS ([M$^+$]: *m*/*z* = 178.4), corresponding to (3,5-dimethylphenyl)trimethylsilane as identified by ^{1}H and ^{13}C NMR data.[20]

Treatment of 1d with Dimethyl Disulfide: Dimethyl disulfide (0.07 mL, 0.73 mmol) in THF (5 ml) was added dropwise at −30 °C to a stirred solution of **1d** (1.0 g, 0.091 mmol, dissolved in 50 mL of THF). The workup was performed as for the derivatisation above. All three isomers of trimethyl[(methylthio)phenyl]-silane were detected by GC MS ([M$^+$]: *m*/*z* = 196.4). Trimethyl[2-(methylthio)phenyl]silane: ^{1}H NMR ($CDCl_3$): δ = 0.33 (s, 9 H, $SiMe_3$), 2.52 (s, 3 H, SCH_3), 7.31 (2 H, Ar-H), 7.5 (2 H, ArH) ppm.^{13}C NMR ($CDCl_3$): δ = −1.1 ($SiMe_3$), 15.6 (SCH_3), 124.4 ($C_{meta'}$), 125.9 (C_{meta}), 129.0 (C_{para}), 132.5 ($C_{ortho'}$), 138.1 (C_{ipso} $CSiMe_3$), 144.1 (C_{ortho} CSMe). Trimethyl[3-(methylthio)phenyl]silane: ^{1}H and ^{13}C NMR spectroscopic data agree with literature values.[17] Trimethyl[4-(methylthio)phenyl]silane: ^{1}H and ^{13}C NMR spectroscopic data agree with literature values.[19]

Typical Hydride Abstraction Reaction of the Arylcalcium Hydride with Ph_3CBF_4: The appropriate arylcalcium hydride (0.52 g, 1.9 mmol) was dissolved in toluene (30 mL) and 18-crown-6 (0.5 g, 1.9 mmol) and placed in a pressure-equalising dropping funnel. This solution was added slowly at −30 °C and with vigorous stirring to a suspension of triphenylcarbenium tetrafluoroborate (0.65 g, 1.9 mmol) in toluene (20 mL). After completion of the addition, the dark red solution was stirred at −30 °C for 1 h. Any unchanged solid was removed by filtration and the toluene solvent was removed in vacuo to yield triphenylmethane.

Typical Synthesis of Calcium Bis(alkoxides) by Use of 1c: Compound **1c** (1.27 g, 0.001 mol) was dissolved in THF (150 mL). The substituted alcohol or phenol (0.008 mol), dissolved in THF (50 mL), was added dropwise to this solution over 15 min at −30 °C. The solution was kept at −30 °C with vigorous stirring until the evolution of H_2 had ceased. The solution was then allowed to warm up slowly to room temperature. The solvent was removed under vacuum to yield a beige, moisture-sensitive solid. This was washed twice with pentane and the remaining solid was dried under vacuum to yield the corresponding bis(alkoxide) of calcium in high yields ranging from 95 to 98%.

Synthesis of $[Ca(2,6\text{-}tBu_2C_6H_2O)_2(THF)_3]$ (3a): This reaction yielded 0.53 g (96% yield) of **3a** as an off-white solid. ^{1}H NMR

(500 MHz, C_6H_6) δ = 7.3 (d, 4 H), 6.7 (t, 2 H), 3.4 (s, 12H THF), 1.9 (s, 12 H, THF), 1.4 (s, 36 H, CH_3) ppm. ^{13}C NMR (500 MHz, C_6H_6) 164.4 (C_{ipso}), 137.4 C_{ortho}), 125.0 (C_{meta}), 112.8 (C_{para}), 69.1 (THF), 35.4 $(CCH_3)_3$, 31.4 (CH_3), 25.1 (THF) ppm. IR (Nujol mull; major vibrations): $\tilde{\nu}$ = 2887 (m), 1416 (m) 1382 (s), 1228 (m), 1037 (s), 898 (m), 809 (m), 519 (m) cm^{-1}.

Synthesis of [Ca(2,6-*t*Bu$_2$-4-MeC$_6$H$_2$O)$_2$(THF)$_3$] (3b): This reaction yielded 0.55 g (98% yield) of **3b** as an off-white solid. ^1H and ^{13}C NMR spectroscopic data (500 MHz C_6H_6) agree with literature values.[12]

Synthesis of [Ca(2,4,6-*t*Bu$_3$C$_6$H$_2$O)$_2$]·3THF (3c): This reaction yielded 0.59 g (97%) of **3c** as an off-white solid. ^1H and ^{13}C NMR (500 MHz C_6H_6) agree with literature values.[32] X-ray quality crystals were grown from a concentrated THF solution at +5 °C over a period of one week.

Synthesis of [Ca{OC(C$_6$H$_5$)$_3$}$_2$(THF)$_3$] (4): This reaction yielded 0.77 g (95%) of **4** as a pale white solid. A colourless single crystal of **4** for X-ray diffraction studies was grown from a concentrated THF solution at +5 °C over 10 d. ^1H NMR (500 MHz, C_6H_6) δ = 7.30 (d, 12 H, CH C_6H_5), 7.10−7.01 (m, 18 H, C_6H_5), 3.41 (m, 16 H, THF), 1.36 (m, 16 H, THF) ppm. IR (Nujol mull; major bands): $\tilde{\nu}$ = 3056 (s), 2919 (m), 1490 (m), 1444 (m), 1230 (s), 1031 (vs), 1015 (s), 823 (m), 776 (m), 754 (m), 727 (m), 700 (s), 671 (m), 617 (m), 512 (m) cm^{-1}.

X-ray Crystallographic Study of 3c and 4: The data for **3c** and **4** were collected at 173(2) K from shock-cooled crystals with a BRUKER SMART-APEX diffractometer (graphite-monochromated Mo-K_α radiation, λ = 71.073 pm), equipped with a low-temperature device.[32] The crystal data are summarized in Table 4. The structure was solved by direct methods (SHELXS-NT97)[33] and refined by full-matrix, least-squares methods against F^2 (SHELXL-NT97).[34] R values defined as $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$, $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$, $P = 1/3[\max(F_o^2,0) + 2F_c^2]$. SADABS 2.0 was employed as a program for empirical absorption correction.[35] In addition to the calcium complex **3c**, the unit cell also contained 2.5 noncoordinating THF molecules. The THF molecule (O7−C57) is disordered and was refined to split occupancies of 0.68/0.32. The disordered *tert*-butyl moiety (C12−C14) was refined to a split occupancy of 0.65/0.35. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were geometrically idealised and refined with a riding model. In addition to the calcium complex **4**, the unit cell also contains one noncoordinating THF molecule. The coordinated THF molecule (O3−C27) was disordered and could be refined to split occupancies of 0.73/0.27. Bond length and similarity restraints were used in the refinement of the disorder. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were geometrically idealised and refined with a riding model. CCDC-190905 (**3c**) and -190906 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Theoretical Methods: For determination of the structures, spectroscopic data, and reaction enthalpies of intermediates in the reaction mechanisms, the application of theoretical methods has proven advantageous. For this purpose the program package GAUSSIAN98[36] implemented on a DEC Alpha workstation (500 MHz CPU/256 MB RAM) or an Origin 200 eight-processor cluster (SGI, 180 MHz CPU/2 GB RAM) was used. Ab initio calculations were performed at the DFT level of theory (B3LYP) with the 6-31G** basis set for C, H, and N. The chosen general basis set for calcium was AKR4, which was used by us in another study on organocalcium complexes.[6] Harmonic vibrational frequencies, calculated at the same level, characterised stationary points and gave the zero-point energies. The difference in the sum of the electronic and the zero-point energies were interpreted as reaction enthalpies at 0 K.

Table 4. Crystallographic data for [Ca{2,4,6-*t*Bu$_3$C$_6$H$_2$O}$_2$(THF)$_3$] (**3c**) and [Ca(OPh$_3$)$_2$(THF)$_4$] (**4**) at T = 173 K

	3c	**4**
Empirical formula	$C_{48}H_{82}CaO_5$+2.5C_4H_8O	$C_{58}H_{70}CaO_7$
Formula mass	959.48	919.22
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	*Pccn*
a [Å]	9.942(2)	14.564(8)
b [Å]	35.933(8)	16.580(9)
c [Å]	16.138(3)	21.182(13)
β [°]	94.206(4)	90
V [Å^3]	5750(2)	5115(5)
Z	4	4
Calcd. density [Mg/m^3]	1.108	1.194
Absorption coeff. [mm^{-1}]	0.158	0.174
F(000)	2120	1976
Crystal size [mm]	0.3 × 0.3 × 0.2	0.6 × 0.5 × 0.3
θ range [°]	1.39−22.46	1.86−25.03
Reflections collected	62291	48730
Independent reflections	11975 [R(int) = 0.0612]	5776 [R(int) = 0.0274]
Completeness at $\theta_{max.}$ [%]	99.9	100.0
Data/restraints/param.	7481/636/761	4528/110/367
Goodness-of-fit on F^2	1.192	1.156
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0890, $wR2$ = 0.1979	$R1$ = 0.0550, $wR2$ = 0.1313
R indices (all data)	$R1$ = 0.0949, $wR2$ = 0.2015	$R1$ = 0.0575, $wR2$ = 0.1331
Largest diff. peak/hole [e·A^{-3}]	0.601/−0.417	0.336/−0.266

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