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Mechanistic Elucidation of the Formation of the Inverse Ca(I) Sandwich Complex [(thf)$_3$Ca(μ-C$_6$H$_3$-1,3,5-Ph$_3$)Ca(thf)$_3$] and Stability of Aryl-Substituted Phenylcalcium Complexes

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Abstract: The formation of the stable inverse Ca(I) sandwich complex [(thf)$_3$Ca(μ-C$_6$H$_3$-1,3,5-Ph$_3$)Ca(thf)$_3$] (**1**) has been investigated mechanistically by the reaction of bromo-2,4,6-triphenylbenzene with calcium in varying stoichiometric ratios. The key intermediate consists of a solvent-separated ion pair consisting of a dinuclear calcium cation with a bridging doubly deprotonated triphenylbenzene and a triphenylbenzene radical counteranion [(thf)$_3$Ca(μ-C$_6$H$_2$−C$_6$H$_4$Ph$_2$)(μ-O−CH=CH$_2$)Ca(thf)$_3$][C$_6$H$_3$Ph$_3$] (**4**). A precondition of the formation of **1** is the lability of the heavy Grignard reagent [{2,4,6-Ph$_3$C$_6$H$_2$}Ca(thf)$_3$Br] (**2**), which has been studied along with the role of ether degradation reactions. The strong reducing reagent **1** is stable in THF solution, and ether cleavage does not occur. However, toluene is metalated in good yields, and the dibenzylcalcium complex [(tmta)$_2$Ca(CH$_2$C$_6$H$_5$)$_2$] (**5**) is generated after addition of 1,3,5-trimethyl-1,3,5-triazinane (tmta). The substitution pattern of arylcalcium halides was modified, and it was found that phenyl substituents at the para position induce lability, leading to an enhanced tendency to cleave ethers. Kinetic stabilization of the Ca−C$_{ipso}$ bond can be achieved by ortho substitution using *m*-terphenyl-based ligands. Direct reaction of iodo-2,6-di(4-tolyl)benzene (**6**) with activated calcium in THF at low temperatures yielded the first example of a stable *m*-terphenylcalcium halide, namely, [{2,6-(4-tol)$_2$C$_6$H$_3$}Ca(thf)$_3$I] (**8**). The latter reacts via insertion of carbon dioxide to form the dimeric benzoate [{2,6-(4-tol)$_2$C$_6$H$_3$CO$_2$}Ca(thf)$_3$I]$_2$ (**9**).

Introduction

Compounds with subvalent electropositive metals have attracted much attention because, despite the fact that sophisticated preparative skills often meet exceptional bonding situations associated with high thermal stability in the solid state and in solution, these compounds possess reducing properties toward a wide range of substrates.[1] Several approaches have proven to be effective in stabilizing subvalent compounds of s-block metals. The suboxides of rubidium and cesium, Rb_9O_2 and $Cs_{11}O_3$, contain two or three oxygen-centered metal octahedrons interconnected via common faces. The bonding situations can best be formulated as $[(Rb_9O_2)^{5+}\cdot 5e^-]$ and $[(Cs_{11}O_3)^{5+}\cdot 5e^-]$, respectively; additional metal atoms can offer a metal matrix for the "free" electrons, leading to more metal-rich compounds such as Rb_6O and Cs_4O or Cs_7O.[2] A similar concept has been used to discuss the structures and bonding situations in solids such as M_2N (M = Ca, Sr, Ba)[3] and ternary compounds such as $LiBa_2N$ and $LiBa_3N$.[4] Another possibility is the formation of discrete homodinuclear metal−metal bonds leading to M_2^{2+} units, which is well-known for Hg_2^{2+} and has recently been published for the lighter homologous $[(L)_3Zn-Zn(L)_3]^{2+}$ (L = 4-dimethylaminopyridine).[5] There are also several examples of molecular RMg−MgR derivatives having bulky R groups for kinetic protection of the reactive Mg−Mg bonds, thereby suppressing dismutation reactions.[6] These dimeric magnesium(I) complexes are surprisingly stable and offer a rich coordination and redox chemistry, acting as selective double one-electron reductants.[7] In contrast, the subvalent magnesium(I) chloride or hydride species XMg−MgX (X = Cl, H) have been

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characterized spectroscopically after trapping in an argon or nitrogen matrix.[8] Calculations have shown that Ca−Ca bonds should also be feasible,[9] although the Ca−Ca bond energy is on the same order of magnitude as the atomization energy of calcium metal. Therefore, the atomization energy has to be invested in order to be able to prepare subvalent organometallic compounds. This can be achieved by employing the cocondensation of metal vapor with substrate. Because of the isoelectronic relationships Sc^{3+}/Ca^{2+}, Sc^{2+}/Ca^{+}, and Sc^{+}/Ca^{0}, subvalent scandium species are interesting in this context. Cocondensation of scandium with 1,3,5-tri-*tert*-butylbenzene yields Sc(0) and Sc(II) compounds,[10] whereas cocondensation of Sc vapor with 2-*tert*-butyl-1-phosphaethyne leads to the formation of Sc(I) and Sc(II) complexes.[10,11] Scandium(I) bromide can be stabilized with an organomagnesium matrix.[12] Reduction of a cyclopentadienylscandium compound with potassium offers suitable access to subvalent scandium derivatives as well.[11] The stability of this kind of complexes, the lighter magnesium(I) congener and the valence isoelectronic d-block metal scandium, suggest that organic Ca(I) species should also be feasible.

The recently reported synthesis of the inverse Ca(I) sandwich complex $[(thf)_3Ca(\mu\text{-}C_6H_3\text{-}1,3,5\text{-}Ph_3)Ca(thf)_3]$ (**1**) shows an alternative for stabilization of Ae(I) derivatives.[13] To date, however, this compound is the only example of a stable subvalent organometallic compound of a heavier alkaline earth (Ae) metal. Surprisingly, the straightforward reduction of an arene with calcium metal does not lead to this inverse sandwich complex, but the presence of at least catalytic amounts of bromoarenes proved to be essential. In order to understand the formation of **1**, the mechanism must be elucidated. Therefore, we studied the reduction of bromo-2,4,6-triphenylbenzene (tpbBr) with calcium powder using various stoichiometric ratios in order to detect intermediates. In addition, the aryl substitution pattern strongly influences the stability of diverse phenyl-substituted arylcalcium complexes.

Results and Discussion

During the reaction of tpbBr with an excess of activated calcium in THF at low temperatures, deeply colored solutions were obtained and the title inverse sandwich complex $[(thf)_3Ca(\mu\text{-}C_6H_3\text{-}1,3,5\text{-}Ph_3)Ca(thf)_3]$ (**1**) was isolated.[13] The molecular structure showed that the calcium atoms lie on a C_3 axis on opposite sides of a strictly planar arene dianion. In contrast, the neutral 1,3,5-triphenylbenzene (tpb) ligand shows a propeller-like arrangement with a twist angle of 38° for the phenyl substituents.[14] The bonding situation was clarified with quantum-chemical calculations, which showed that metal orbitals with d symmetry[15] stabilize this inverse sandwich complex. However, the reaction mechanism still remained unknown.

The haloarene tpbBr is very reactive toward insertion reactions of metals because of the high electron density in the central arene unit, as a consequence of the symmetric induction by the electron-donating phenyl substituents. The reaction of activated calcium with tpbBr and also the direct reaction of calcium powder with 1,3,5-triphenylbenzene in the presence of a catalytic amount (10 mol %) of tpbBr both give calcium(I) complex **1** in good yields of more than 80%. During either reaction pathway, ether cleavage reactions occur and play a prominent role. In order to study the mechanism of the formation of **1**, we reduced tpbBr with calcium powder in a strictly equimolar ratio in THF, which yielded the postulated species $[\{2,4,6\text{-}Ph_3C_6H_2\}Ca(thf)_3Br]$ (**2**). During the reaction time of 30 min at −60 °C, all of the metal powder dissolved, generating a slightly yellowish solution of **2**. This heavy Grignard solution proved to be rather reactive and cleaved THF via α-deprotonation, yielding 1,3,5-triphenylbenzene nearly quantitatively over 2 h. For this reason, several attempts to isolate **2** failed. This behavior is in agreement with earlier reports on arylcalcium halides.[16] Ether degradation reactions are common in the organometallic chemistry of strongly electropositive s-block metals, involving in the case of THF α-metalation and subsequent cycloreversion combined with liberation of ethenolate and ethene.[17] Addition of iodine to a solution of **2** at low temperatures gave $2,4,6\text{-}Ph_3C_6H_2I$ (tpbI, **3**), clearly supporting the conversion of the initial bromoarene to the heavy Grignard-type species (Scheme 1). This lack of stability contrasts with that of the well-known 2,4,6-triarylphenyllithium $[(Et_2O)_2Li(C_6H_2\text{-}2,4,6\text{-}Ph_3)]$[18] and -magnesium $[(thf)_2Mg(Br)C_6H_2\text{-}2,4,6\text{-}Ph_3]$[13] derivatives, which have been isolated and structurally characterized. Neither excess metal nor storage in THF at ambient temperature decreased the stability of these lithium and magnesium derivatives.

Addition of a slight excess of calcium to an intermediately generated solution of **2** immediately produced a deep-blue solution, which indicated the formation of paramagnetic 1,3,5-triphenylbenzene radical anions. These anions are formed as one of the products of α-deprotonation of THF and subsequent reduction with surplus calcium metal. Reactions in $[D_8]$THF generated monodeuterated $[D_1]$1,3,5-triphenylbenzene, which also supports the importance of ether solvents acting as Brønsted acids. A similar reaction (with in situ formation of **2**, prepared via the reaction of tpbBr with 1.5 equiv of activated calcium) and subsequent storage of the dark-blue reaction solution at low temperatures led to crystallization of the black, opalescent, and

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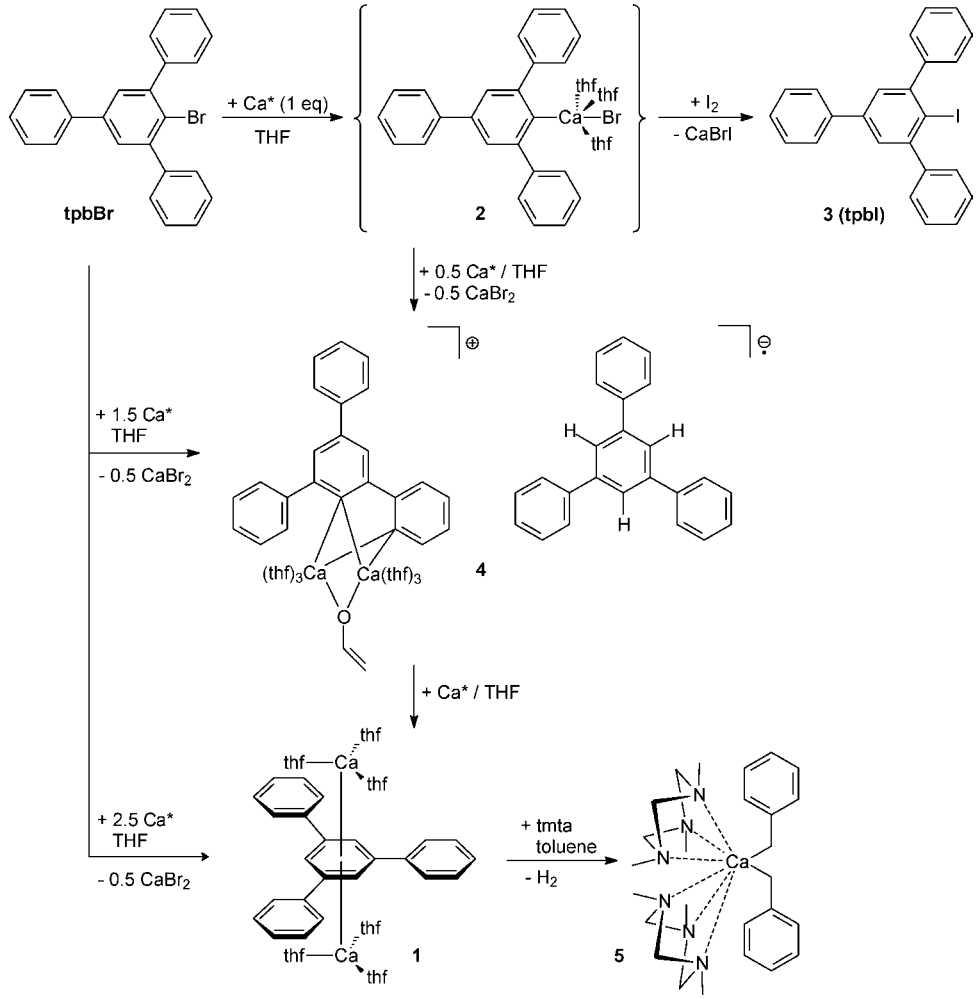
Scheme 1. Reaction of Bromo-2,4,6-triphenylbenzene (tpbBr) with Activated Calcium Powder and Its Dependence on the Stoichiometric Ratio



highly pyrophoric compound $[(thf)_3Ca(\mu\text{-}C_6H_2{-}C_6H_4Ph_2)(\mu\text{-}O{-}CH{=}CH_2)Ca(thf)_3][C_6H_3Ph_3]$ (**4**), as shown in Scheme 1. The solvent-separated ion pair consists of a 1,3,5-triphenylbenzene radical monoanion and a dinuclear cation. The latter contains a bridging vinylate anion that stems from THF degradation, representing an essential step in the stoichiometric ratio as the hydrogen source for the formation of calcium(I) complex **1**. The importance of the ether cleavage step was verified by the necessity of at least 10 mol % tpbBr, as the direct synthesis of **1** using activated calcium and 1,3,5-triphenylbenzene failed in each case. The bromoarene does not simply function as activating reagent (comparable to the addition of iodine to magnesium chips as a classical Grignard activation procedure) because the addition of 10 mol % iodine to a mixture of 1,3,5-triphenylbenzene and excess calcium in THF exclusively led to the formation of the corresponding amount of the calcium diiodide complex $[(thf)_4CaI_2]$. However, the presence of iodine does not initiate the formation of **1**.

The EPR spectrum of **4** in THF solution, pictured in Figure 1,[19] is well-resolved and suggests the presence of only one paramagnetic species, in accordance with the studies of De Boer and co-workers,[20] indicating the free radical monoanion of 1,3,5-triphenylbenzene. The high symmetry of the EPR resonance in combination with the g value of the free electron ($g = 2.0023$) excludes a metal-centered radical. Additional susceptibility measurements gave a magnetic moment (μ_{eff}) of $1.62\mu_B$, supporting the presence of only "one" unpaired electron and hence underlining the radical monoanion character of **4**. These

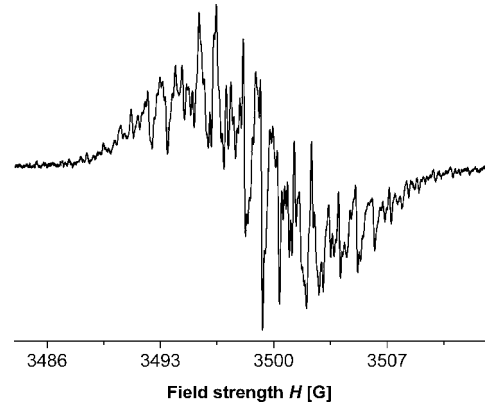


Figure 1. X-band EPR spectrum of a solution of $[(thf)_3Ca(\mu\text{-}C_6H_2{-}C_6H_4Ph_2)(\mu\text{-}O{-}CH{=}CH_2)Ca(thf)_3]^+[C_6H_3Ph_3]^-$ (**4**) in THF recorded at 298 K ($g = 2.0023$).

(19) For several EPR studies (experimental and via simulation) of 1,3,5-triphenylbenzene monoanions with varioous metal countercations, see: Krieck, S.; Görls, H.; Westerhausen, M. *J. Am. Chem. Soc.*, submitted.

findings are consistent with studies of alkali-metal monoadducts of 1,3,5-triphenylbenzene by Lühder.[21]

After definite quenching of a solution of crystalline **4** in THF with [D_4]methanol, the vinylate moieties were detected via NMR spectroscopy. Treatment of a THF solution with bromine led to formation of 2-(2′-bromophenyl)-4,6-diphenylbromobenzene,[22] whereas tpbBr was not detected.

The directed ortho metalation of a phenyl group in the ortho position leads to a moiety of the type 1,1′-biphenyl-2,2′-diyldicalcium having two additional phenyl groups at the 3- and 5-positions. The formation of **4** shows that not only THF molecules (which finally yielded the vinylate anions) but also the triphenylphenyl system served as proton sources in this reaction sequence. A similar 1,1′-biphenyl-2,2′-diyldilithium moiety is well-known and a valuable synthon in numerous ligand transfer reactions.[23]

Because of the detected paramagnetism of **4** (particularly of the 1,3,5-triphenylbenzene monoanion, confirming at the same time the presence of a delocalized radical anion instead of a localized carbanion), NMR techniques were not a suitable tool for fully characterizing this complex. Therefore, we grew single crystals suitable for determination of the X-ray crystal structure after numerous recrystallization steps. The molecular structures and numbering schemes for the cation and anion in **4** are presented in Figure 2a,b, respectively. The calcium atoms, which have a Ca···Ca′ distance of 323.24(10) pm, are in distorted octahedral environments and show an average Ca−C bond length of 260.1 pm. Because of the stronger electrostatic attraction, the Ca−O bonds to the bridging vinylate anion [Ca′−O−Ca, 50.06(8)°] are shorter (av. Ca−O, 231.3 pm) than those to the THF ligands (av. Ca−O, 237.0 pm) but adopt characteristic values.[17a,24] The C−C bond length [123.2(10) pm] in the O−CH═CH_2 moiety verifies the constitution as an ethenolate unit.

The 1,1′-biphenyl-2,2′-diyl unit shows only a slight torsion around the C2−C7 bond. A much stronger deviation from planarity is realized by the phenyl groups; however, all of the interaryl bonds represent characteristic single-bond character.

The radical anion shows a remarkable structure. The phenyl group at C28 is slightly tilted (17°) with respect to the remaining planar 1,3-diphenylbenzene (*m*-terphenyl) unit. This feature strongly influences the bond lengths of the inner carbon ring. The carbon atom C31 on the opposite side of the twisted phenyl ring shows remarkably large C31−C bond lengths of 149.8 and 150.2 pm, whereas the other C−C distances have values characteristic for aromatic systems. In contrast, systems with localized 1,3,5-triphenylphenyl carbanions possess a propeller-like arrangement of the phenyl substituents, as realized in, for example, [(thf)$_2$Mg(Br)$C_6H_2Ph_3$],[13] [$(Et_2O)_2$Li($C_6H_2Ph_3$)],[18] and [Bi($C_6H_2Ph_3$)$_3$].[25]

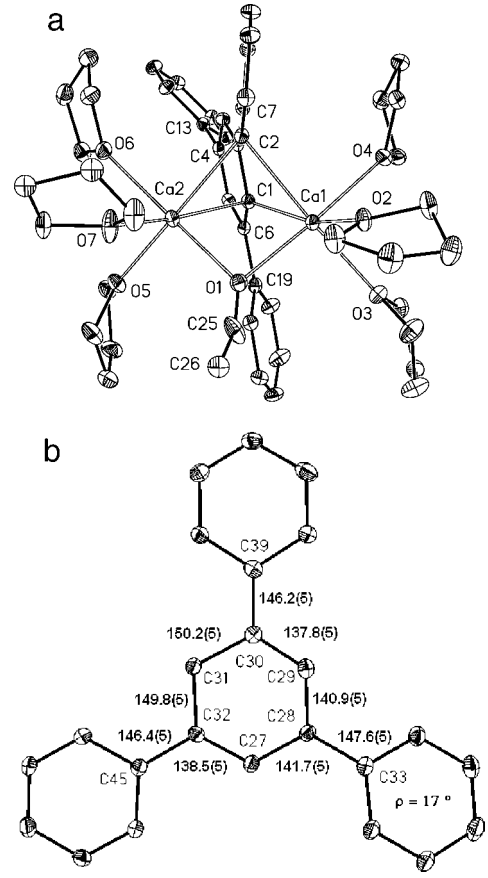


Figure 2. (a) Molecular structure and numbering scheme for the cation of **4**, [(thf)$_3$Ca(μ-C_6H_2−$C_6H_4Ph_2$)(μ-O−CH═CH_2)Ca(thf)$_3$]$^+$. H atoms have been omitted for clarity; ellipsoids represent a probability of 40%. Selected bond lengths (pm) and angles (deg): Ca1−C1, 259.9(3); Ca2−C1, 267.3(3); Ca1−C8, 259.8(3); Ca2−C8, 253.3(4); Ca1−O1, 231.9(3); Ca2−O1, 230.7(3); O1−C25, 118.2(5); C25−C26, 123.2(10); Ca1−O2, 236.6(3); Ca1−O3, 238.4(3); Ca1−O4, 238.1(3); Ca···CaA, 323.24(10); Ca1−C1−Ca2, 53.32(8); Ca1−C8−Ca2, 50.06(8); Ca1−O1−Ca2, 45.53(7); O3−Ca1−C8, 173.77(10); O1−Ca1−O4, 174.85(10). (b) Molecular structure and numbering scheme of the 1,3,5-triphenylbenzene radical anion [$C_6H_3Ph_3$]$^-$ in **4**. H atoms have been omitted for clarity; ellipsoids represent a probability of 40%. Selected bond lengths (pm) and the torsion angle of the phenyl group, ρ (deg), are given.

Addition of another equivalent of calcium powder to a THF solution of twice-recrystallized **4** led to the initial formation of [{(thf)$_3$Ca}$_2$(μ-C_6H_3-1,3,5-Ph_3)] (**1**), which was verified by repeated determination of the crystallographic cell parameters using X-ray diffractometry. The detailed mechanism for the formation of **1** from **4** remains unclear at present. The sum of possible reaction sequences (starting from tpbBr, **2**, or **4**) to the final formation of the homodinuclear inverse sandwich complex **1** consists of subsequent steps of deprototation and protonation reactions (both via ether degradation) as well as several reduction and probably also synproportionation processes.

In the persistent organic π-diradical **1**, the dianionic charge of the 1,3,5-triphenylbenzene system is stabilized by effective delocalization, resulting in a reduced nucleophilicity of the complex. Therefore, ethereal solutions of **1** are stable at ambient temperature over a long period of time and no tendency toward

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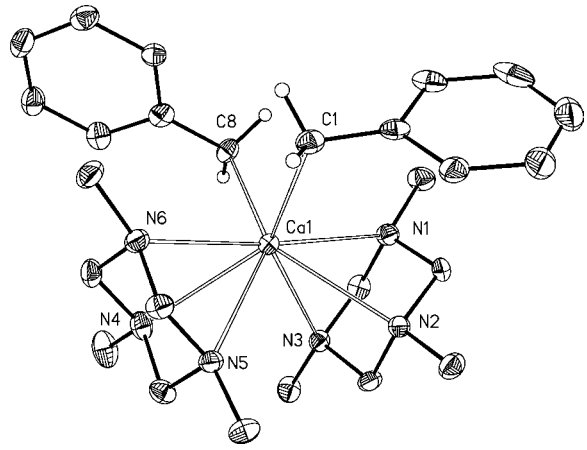

Figure 3. Molecular structure and numbering scheme for $[(tmta)_2Ca(CH_2C_6H_5)_2]$ (**5**). H atoms have been omitted for clarity; ellipsoids represent a probability of 40%. Selected bond lengths (pm) and angles (deg): Ca1−C1, 261.5(3); Ca1−C8, 263.0(3); Ca1−N1, 268.5(3); Ca1−N2, 270.3(2); Ca1−N3, 268.0(2); Ca1−N4, 270.8(2); Ca1−N5, 270.8(2); Ca1−N6, 264.1(2); C1−Ca1−C8, 98.07(10); C2−C1−Ca1, 111.03(19); C9−C8−Ca1, 113.0(2).

ether cleavage reactions is observed, in accordance with observations for systems containing homodinuclear Mg(I)−Mg(I) bonds, which are even stable as various Lewis base adducts.[7c,26] Furthermore, solutions of **1** are also stable under reflux conditions and show no tendency to undergo redox dismutation of Ca(I) to derivatives of Ca(II) and Ca(0), contrary to the behavior of the thermolabile anthracene complexes $[(thf)_nAe^{II}(anthracene)]$ (Ae = Mg, Ca, Sr, Ba), which can therefore be used for metal activation purposes according to Bogdanović and co-workers.[27] Alkali metal (A) adducts of 1,3,5-triphenylbenzene also show an equilibrium between $A_2(tpb)$ on the one hand and A(tpb) + A on the other.[21]

In general, the stability of a compound is associated with its reactivity, and often these trends are adverse. Despite the resonance stabilization of the 1,3,5-triphenylbenzene dianion, complex **1** functions as a strong reducing agent because of the unusual +1 oxidation state of the calcium atoms. Addition of iodine to a solution of **1** quantitatively yielded $[(thf)_4CaI_2]$ and 1,3,5-triphenylbenzene, transferring four reduction equivalents in all. A solvent change from ether to toluene led within 5 days to the formation of dibenzylcalcium, which crystallized as the colorless adduct $[(tmta)_2Ca(CH_2C_6H_5)_2]$ (**5**) after addition of 1,3,5-trimethyl-1,3,5-triazinane (tmta). The molecular structure and numbering scheme for the dibenzylcalcium complex **5** are displayed in Figure 3. Benzylcalcium compounds are well-known and have been prepared via salt metathesis of benzylpotassium with CaI_2.[28]

The calcium atom in **5** adopts the large coordination number of eight. This fact induces steric strain, which leads to a rather large average Ca−C bond length of 262.3 pm. The Ca−N distances to the tmta ligands show an average value of 268.1 pm, which is slightly larger than that observed for $[(tmta)_2Ca\{P(SiMe_3)_2\}_2]$ (av. Ca−N, 264.7 pm)[29] and indicative of the enhanced steric strain. As a result of the bulkiness of the tmta ligands, a rather small C1−Ca1−C8 angle of 98.1° was observed. However, the tetrahydrofuran complex $[(thf)_4Ca(CH_2C_6H_5)_2]$ shows a cis arrangement of the benzyl anions with an average bond angle of 94.1°, whereas the 4-*tert*-butylbenzyl derivative crystallizes as the trans isomer of $[(thf)_4Ca(CH_2C_6H_4\text{-}4\text{-}tBu)_2]$.[28]

The formation of **5** is accompanied by a color change of the solution from an initial deep-blue to a final dark-violet. EPR spectroscopic investigations in a sealed tube showed a nearly constant concentration of 1,3,5-triphenylbenzene anions. These findings suggest that the reduction equivalents originate preferentially from the oxidation of Ca(I) to Ca(II). In **1**, the two calcium(I) atoms are located on opposite sides of the bridging arene system, and their d orbitals interact with each other via an arene-centered orbital, leading to the intrinsic stability of the subvalent homodinuclear organocalcium complex **1**. A change in the oxidation state of one of the calcium centers consequently disturbs this bonding situation, and a constitutional change follows, preserving the radical character on 1,3,5-triphenylbenzene as a mono- or dianionic species.[30] Unfortunately, all attempts to isolate the corresponding species containing $\{(thf)_xCa^{II}(C_6H_3\text{-}1,3,5\text{-}Ph_3)\}$ failed. Nevertheless, the metal atoms in β-diketiminate complexes of Mg^I with Mg^I-Mg^I bonds can be oxidized with preservation of the magnesium β-diketiminate unit.[1] Carmona and co-workers[31] recently published reactions of the decamethyldizincocene species [Cp*Zn−ZnCp*] (Cp* = C_5Me_5) with unusual preservation of the metal−metal bond. The magnesium and zinc species possess sterically shielded diamagnetic divalent homodinuclear metal centers and therefore show binding situations that are fundamentally different from that in the intrinsically stable paramagnetic calcium(I) inverse sandwich complex without a discrete metal−metal bond.[1]

Extensive studies of the reaction of 1,3,5-triphenylbenzene with calcium in liquid ammonia as the solvent at low temperatures indicated the formation of polymeric structures. In both pure ammonia and solvent mixtures of ammonia and donor solvents [pyridine, THF, 1,2-dimethoxyethane (DME)], the reaction of 1,3,5-triphenylbenzene and calcium in a 1:1 molar ratio yielded a violet solid that was completely insoluble in common organic solvents. Even extraction with strong chelating bases (DME, tmeda, tmta) failed. Identification via classical digestion methods and subsequent determination of the metal content suggested a constitution formula without additional coordinating ligands as $[Ca(C_6H_3\text{-}1,3,5\text{-}Ph_3)]_\infty$. Similar solubility properties are well-known for polymeric calciocene $[Cp_2Ca]_\infty$ (Cp = C_5H_5),[32] whereas the bisdonor adducts $[(thf)_2CaCp_2]$ dissolve easily in donor solvents.[33]

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(27) (a) Bönnemann, H.; Bogdanović, B.; Brinmann, R.; Egeler, N.; Benn, R.; Topalovic, I.; Seevogel, K. *Main Group Met. Chem.* **1990**, *13*, 341–362. (b) Bogdanović, B.; Janke, N.; Kinzelmann, H.-G.; Westeppe, U. *Chem. Ber.* **1988**, *121*, 33–37. (c) Bogdanović, B.; Liao, S.-T.; Mynott, R.; Schlichte, K.; Westeppe, U. *Chem. Ber.* **1984**, *117*, 1378–1392.
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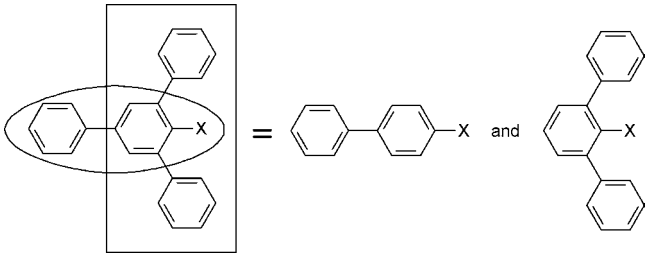
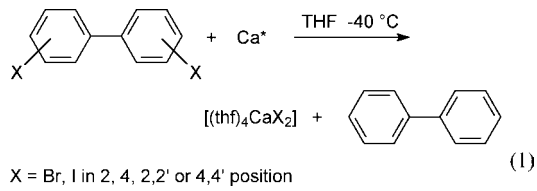
(32) (a) Ziegler, K.; Froitzheim-Kühlhorn, H.; Hafner, H. *Chem. Ber.* **1956**, *89*, 434–443. (b) Zerger, R.; Stucky, G. D. *J. Organomet. Chem.* **1974**, *80*, 7–17.
(33) Fischer, E. O.; Stölzle, G. *Chem. Ber.* **1961**, *94*, 2187–2193.

Scheme 2. Representation of the Biphenyl (Round Line) and *m*-Terphenyl (Rectangular Line) Subunits of Halogeno-2,4,6-triphenylbenzene



A central issue in the reaction cascade that generates **1** is the enormous instability of the heavy Grignard reagent [{2,4,6-$Ph_3C_6H_2$}Ca(thf)$_3$Br] (**2**) during generation in solution. Therefore, further studies were performed to address the influence of the aryl substitution pattern of phenylcalcium halides. Our earlier studies of a broad portfolio of heavy Grignard reagents showed that arylcalcium halides tolerate a variety of para substituents, such as halogen, methoxy, amino, and alkyl groups.[34,16] To date, only arylcalcium halides without substituents that enable extended increasing delocalization have been isolated, with 1-naphthylcalcium halides being an exception.[17d] These findings are contradictory to the additional stabilization effects based on the reduced nucleophilicity combined with enhanced delocalization and charge-stabilization effects. According to Scheme 2, the halogeno-2,4,6-triphenylbenzene system can be regarded in two ways: (i) a *p*-phenyl-substituted system representing a biphenyl subunit and (ii) a 2,6-diphenylphenyl system representing a *m*-terphenyl subunit.

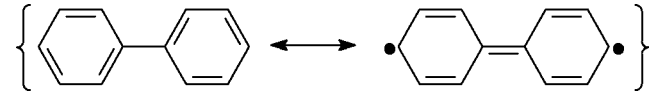
In all cases, reactions of 2- and 4-halogenobiphenyl as well as 2,2′- and 4,4′-dihalogenobiphenyl (halogen = Br, I) in THF at low temperatures with stoichiometric amounts of activated calcium powder led to the formation of the calcium dihalide complex [(thf)$_4$CaX$_2$] and biphenyl in nearly quantitative yields (eq 1). However, in neither case was a stable corresponding heavy Grignard reagent observed.



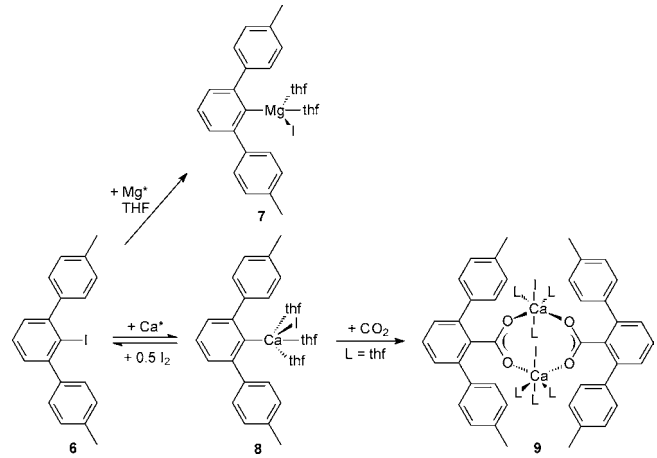
Phenyl substituents at the 4-position drastically enhance the tendency for ether degradation reactions, yielding biphenyl after α-deprotonation of the ether solvent. Perhaps the intrinsic instability of the Ca−C$_{ipso}$ σ bond in biphenyl derivatives can be attributed to the formation of chinoid instead of benzenoid structures (Scheme 3), which would destabilize the arylcalcium halides. Reactions of an excess of calcium metal (more than 2 equiv) with different substituted (di)halogenobiphenyl derivatives gave deep-green solutions. EPR measurements confirmed the formation of biphenyl dianions in accordance with Rieke's method of metal activation[35] as well as with studies of alkali-metal−biphenyl adducts.[36]

(34) (a) Westerhausen, M. *Z. Anorg. Allg. Chem.* **2009**, *635*, 13–32. (b) Westerhausen, M. *Coord. Chem. Rev.* **2008**, *252*, 1516–1531. (c) Westerhausen, M.; Gärtner, M.; Fischer, R.; Langer, J. *Angew. Chem.* **2007**, *119*, 1994−2001; *Angew. Chem., Int. Ed.* **2008**, *46*, 1950−1956.

Scheme 3. Resonance between the Benzenoid and Chinoid Forms of Biphenyl



Scheme 4. Synthesis and Reactivity of the Classical Grignard Reagent **7** and Heavy Grignard Reagent **8**



To this point, bulky groups were employed in order to kinetically protect the Ca−C bonds using the *m*-terphenyl ligand for stabilization reasons. The reaction of iodo-2,6-di(4-tolyl)-benzene (**6**) with activated magnesium (Rieke magnesium) in THF gave the classical Grignard reagent [{2,6-(4-tol)$_2$C$_6$H$_3$}-Mg(thf)$_2$I] (**7**) in high yield (Scheme 4). The structural motif of **7** is displayed in Figure 4 and shows the expected tetrahedral coordination sphere of the magnesium center. Treatment of **6** with an excess of magnesium metal under reflux conditions also exclusively generated the Grignard compound.

The direct reaction of activated calcium with **6** in THF at 20 °C led to complete dissolution of the metal. However, fast decomposition of intermediate arylcalcium derivatives was observed. Strict maintenance of the reaction conditions at −60 °C and use of an exact 1:1 stoichiometric ratio of iodoarene to metal led to the formation of pale-violet [{2,6-(4-tol)$_2$C$_6$H$_3$}Ca(thf)$_3$I] (**8**) (Scheme 4), contrary to earlier

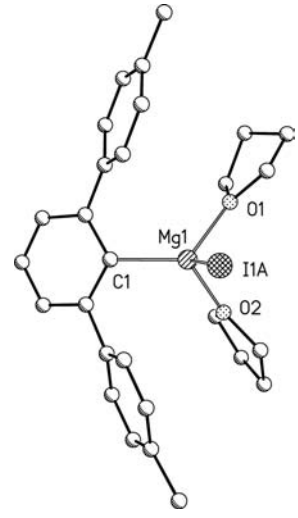


Figure 4. Representation of the structural motif of [{2,6-(4-tol)$_2$C$_6$H$_3$}-Mg(thf)$_2$I] (**7**).

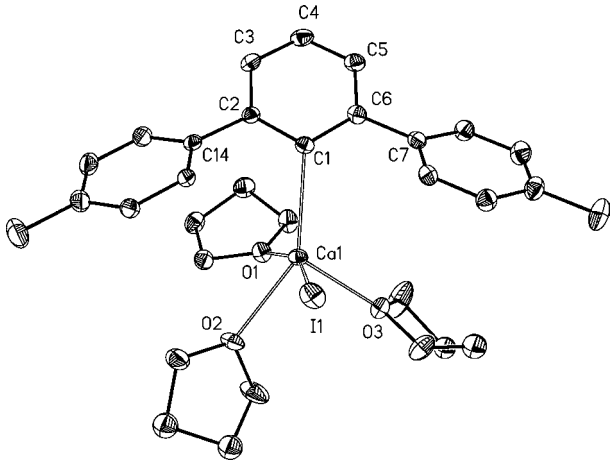


Figure 5. Molecular structure and numbering scheme for [{2,6-(4-tol)$_2$C$_6$H$_3$}Ca(thf)$_3$I] (**8**). Ellipsoids represent a probability of 40%; H atoms have been omitted for clarity. Selected bond lengths (pm) and angles (deg): Ca1−I1, 307.54(7); Ca1−C1, 251.7(4); Ca1−O1, 238.4(4); Ca1−O2, 239.0(3); Ca1−O3, 234.4(3); C1−Ca1−I1, 108.20(9); C1−Ca1−O1, 84.8(1); C1−Ca1−O2, 144.7(1); C1−Ca1−O3, 115.1(1); I1−Ca1−O1, 160.6(1); I1−Ca1−O2, 85.54(7); I1−Ca1−O3, 97.50(8); O1−Ca1−O2, 75.9(1); O1−Ca1−O3, 89.5(1); O2−Ca1−O3, 94.1(1); Ca1−C1−C2, 116.9(3); Ca1−C1−C6, 124.6(3); C2−C1−C6, 114.7(3).

findings.[16,34] An ethereal solution of **8** showed ∼20% decomposition during storage for 24 h at −40 °C, and in the solid state, storage at −20 °C for several days without noticeable decomposition was possible.

The reactions of excess activated calcium with **6** and **8** in ethereal solutions led to formation of deep-red-violet solutions. However, because of the thermolability of these solutions, several attempts to isolate the species failed, and spontaneous decolorization of the solutions combined with metal precipitation was observed, comparable to the findings of Bogdanović and co-workers.[27]

The molecular structure and numbering scheme for the first structurally characterized *m*-terphenyl-based Grignard-type complex, [{2,6-(4-tol)$_2$C$_6$H$_3$}Ca(thf)$_3$I] (**8**), are shown in Figure 5. In comparison to [{2,6(4-tol)$_2$C$_6$H$_3$}Mg(thf)$_2$I] (**7**), a rather similar molecular structure is found for **8**, with a pentacoordinate calcium atom. In the distorted trigonal bipyramidal coordination sphere, the bulky aryl fragment is positioned in the equatorial plane and the atoms O1 and I1 occupy the axial positions [Ca1−O1, 238.4(4) pm; Ca1−I1, 307.54(7) pm; O1−Ca1−I1, 160.6(1)°], in accordance with the VSEPR model. The bond lengths of Ca1−C1 [251.7(4) pm] and Ca1−I1 are rather short because of the low coordination number of calcium but lie in the characteristic region for arylcalcium derivatives.[34,16] In the equatorial plane, the C1−Ca1−O2 angle is very wide as a result of an additional agostic interaction between Ca1 and C15 of the tolyl group [Ca1−C15, 313.0(4) pm]. The ipso C (Ca−C$_{ipso}$) shows a ^{13}C NMR shift of 196.4 ppm, which is a typical low-field-shifted resonance for arylcalcium halides.[16,17d]

The reaction of **8** with iodine regenerated the starting material iodo-2,6-di(4-tolyl)benzene (**6**), showing that ether degradation reactions were minor side reactions in this case. Substitution of the iodide in **8** via a metathesis reaction with potassium triethylborohydride led to the formation of [{2,6-(4-tol)$_2$C$_6$H$_3$}Ca(μ-H)BEt$_3$] as a contact ion pair.[37] However, when the heterocumulene carbon dioxide was supplied, the corresponding *p*-ditolylbenzoate dimer [{2,6-(4-tol)$_2$C$_6$H$_3$CO$_2$}Ca(thf)$_3$I]$_2$ (**9**) was isolated (Scheme 4), representing the well-known reactivity observed for classical Grignard reagents.

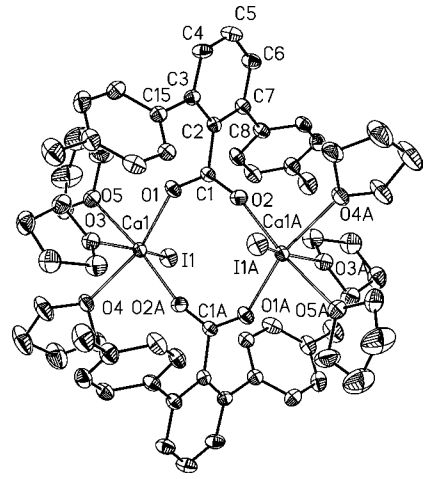


Figure 6. Molecular structure and numbering scheme for [{2,6-(4-tol)$_2$C$_6$H$_3$CO$_2$}Ca(thf)$_3$I]$_2$ (**9**). Symmetry-related atoms (−x + 1, −y, −z) are marked with an "A". Ellipsoids represent a probability of 40%; H atoms have been omitted for clarity. Selected bond lengths (pm): Ca1−I1, 312.84(9); Ca1−O1, 228.2(3); Ca1−O2A, 226.1(4); Ca1−O3, 236.0(3); Ca1−O4, 241.1(3); Ca1−O5, 242.5(4); C1−O1, 125.4(5); C1−O2, 124.4(5); C1−C2, 151.6(6).

The molecular structure and numbering scheme for **9** are shown in Figure 6. In this complex, which has a hexacoordinate calcium center, the THF molecules show a facial arrangement. The benzoate anions in **9** show a μ,η^1,η^1-O,O′ coordination mode with an average Ca−O distance of 227.2 pm, leading to an eight-membered (Ca−O−C−O)$_2$ dimetallacycle with an orthogonal orientation of the *m*-terphenyl units. The inner eight-membered (Ca−O−C−O)$_2$ ring shows charge delocalization within the carboxylate units. The Ca−O$_{thf}$ distances are significantly larger than those to the carboxylate oxygens because in the latter an additional electrostatic attraction strengthens the interactions. The carboxylate moiety and the aryl fragment show no π interaction [C1−C2, 151.6(6) pm]. Because of the larger coordination number, the Ca1−I1 bond length of 312.84(9) pm is larger than that in **8**.

Conclusion

These investigations have clearly demonstrated the complexity of redox reactions of halogenoarenes with activated calcium. Whereas lithium and magnesium quantitatively insert into the carbon−halogen bond, a similar arylcalcium halide is strongly destabilized when *p*-aryl substituents are bound. In this case, the strongly enhanced reactivity leads to fast ether degradation reactions. In the presence of additional calcium powder, the ether degradation is accompanied by a directed ortho metalation (DOM) reaction of the triphenylphenyl group, leading to the formation of a 3,5-diphenyl-1,1′-biphenyl-2,2′-diyl group (attached as a bridging ligand between two calcium atoms) and a 1,3,5-triphenylbenzene radical anion, which crystallize as [(thf)$_3$-Ca(μ-C$_6$H$_2$−C$_6$H$_4$Ph$_2$)(μ-O−CH═CH$_2$)Ca(thf)$_3$][C$_6$H$_3$Ph$_3$] (**4**). This complex can be isolated, redissolved in THF, and reduced with another equivalent of activated calcium, yielding the inverse calcium(I) sandwich complex [{(thf)$_3$Ca}$_2$(μ-C$_6$H$_3$-1,3,5-Ph$_3$)] (**1**). Solvent THF molecules as well as the 2,4,6-triphenylphenyl anion (yielding the 1,1′-biphenyl-2,2′-diyl anion) act as proton

(35) Wu, T.-C.; Xiong, H.; Rieke, R. D. *J. Org. Chem.* **1990**, *55*, 5045–5051.

sources, which are mandatory for the conversion of the triarylphenyl groups into 1,3,5-triphenylbenzene molecules. A direct synthesis of **1** from calcium and 1,3,5-triphenylbenzene was not successful, and at least catalytic amounts of the corresponding bromoarene are needed to initiate the reaction. This behavior contrasts with the reaction pattern for lithium and magnesium compounds (which yield stable aryllithium and arylmagnesium halides, respectively) and therefore allows the synthesis of an organocalcium(I) complex. To the best of our knowledge, no isolated and structurally characterized derivatives of mono- or dimetalated 1,1′biphenyl-4,4′-diyl systems with lighter s-block metals are known. A similar inverse sandwich complex of magnesium(I) is unknown at present. The inverse sandwich complex **1** is a strong reducing agent that is able to metalate toluene with generation of the dibenzylcalcium complex $[(tmta)_2Ca(CH_2C_6H_5)_2]$ (**5**). In contrast to *p*-phenyl-substituted arylcalcium halides, 2,6-diaryl-substituted congeners are stable, both in solution and in the solid state. The synthesis of the first *m*-terphenylcalcium compound, $[\{2,6\text{-}(4\text{-tol})_2C_6H_3\}Ca(thf)_3I]$ (**8**), and its derivatization as the corresponding benzoate dimer, $[\{2,6\text{-}(4\text{-tol})_2C_6H_3CO_2\}Ca(thf)_3I]_2$ (**9**), succeeded.

This study has demonstrated once again the limitations and importance of the solvent used in organocalcium chemistry: ether solvents often are easily cleaved under decomposition of the organometallic derivative, and aromatic hydrocarbons can be deprotonated, whereas aliphatic hydrocarbons are poor solvents for saltlike organoalkaline-earth metal compounds with strongly heteropolar metal−carbon bonds.

Experimental Section

Manipulation and handling of all compounds were performed under strictly anaerobic conditions using standard Schlenk techniques in an argon atmosphere. Solvents were dried thoroughly and distilled under argon. 1,3,5-Triphenylbenzene was purchased from Aldrich, and tpbBr was prepared from 1,3,5-triphenylbenzene and bromine in tetrachloromethane.[38,39] Calcium granules as purchased from Aldrich were used for the activation process[40] without further purification. Rieke magnesium was prepared according to a literature procedure,[41] washed several times with hot acetone, and dried in vacuum at 80 °C. The necessity to maintain a THF-saturated atmosphere in order to prevent aging of the crystals and the extreme sensitivity toward moisture and air, especially the highly pyrophoric nature of some compounds, made the analytical characterization challenging.

For the NMR assignments, atoms in the central ring are unprimed, atoms in the *o*-phenyl groups are primed, and atoms in the *p*-phenyl group are doubly primed.

Synthesis of 2,4,6-$Ph_3C_6H_2$I (3) via [{2,4,6-$Ph_3C_6H_2$}Ca(thf)$_3$Br] (2). A solution of tpbBr (1.00 g, 2.60 mmol) in THF (10 mL) was cooled to −40 °C and added to a suspension of activated calcium powder (0.104 g, 2.60 mmol) in THF (20 mL) at −78 °C. The mixture was shaken at −60 °C for 30 min, yielding a clear yellowish solution. Thereafter, the solution of **2** was quenched with iodine (1.00 g, 3.94 mmol) in THF (20 mL) at −20 °C. The mixture was stirred for 12 h at room temperature and then extracted with chloroform; the organic layer was separated, washed with $Na_2S_2O_3$ and several times with brine, and dried over Na_2SO_4. Next, the solvent was evaporated, and the resulting yellowish oil was treated with ethanol (150 mL) under reflux conditions. After filtration, storage at −20 °C afforded colorless needles of **3** (1.03 g, 2.38 mmol, 92%).

Physical Data for 3. Mp: 128 °C (EtOH). Anal. Calcd for $C_{24}H_{17}I$ (432.3 g mol^{-1}): C, 66.68; H, 3.96; I, 29.36. Found: C, 66.45; H, 3.72; I, 29.21. ^{1}H NMR (400.25 MHz, 25 °C, $CDCl_3$): δ 7.32 (1H, t, $^3J_{H-H}$ = 8.0 Hz, *p*″-C*H*), 7.38 (2H, t, $^3J_{H-H}$ = 7.4 Hz, *p*′-C*H*), 7.50 (2H, t, $^3J_{H-H}$ = 7.6 Hz, *m*″-C*H*), 7.54 (4H, t, $^3J_{H-H}$ = 7.6 Hz, *m*′-C*H*), 7.58 (2H, s, *m*-C*H*), 7.60 (4H, d, $^3J_{H-H}$ = 7.2 Hz, *o*′-C*H*), 7.70 (2H, d, $^3J_{H-H}$ = 7.2 Hz, *o*″-C*H*). ^{13}C{^{1}H} NMR (100.65 MHz, 25 °C, $CDCl_3$): δ 96.3 (1C, C_{ipso}), 126.1 (2C, *o*″-*C*H), 126.4 (2C, *m*-*C*H), 127.1 (2C, *p*′-*C*H), 127.5 (1C, *p*″-*C*H), 128.0 (4C, *m*′-*C*H), 128.9 (2C, *m*″-*C*H), 129.9 (4C, *o*′-*C*H), 139.0 (1C, C''_{ipso}), 140.1 (1C, *p*-*C*), 141.5 (2C, C'_{ipso}), 146.9 (2C, *o*-*C*H). ESI-MS (*m*/*z* [%]): 432 [78] (M), 306 [100] (M − I).

Synthesis of [(thf)$_3$Ca(μ-C_6H_2−$C_6H_4Ph_2$}(μ-O−CH=CH_2)-Ca(thf)$_3$][$C_6H_3Ph_3$] (4). Calcium (0.16 g, 3.99 mmol) was activated and dried according to standard procedures and suspended in 25 mL of THF. A solution of tpbBr (1.00 g, 2.59 mmol) in 10 mL of THF was added at −78 °C. Thereafter, the mixture was shaken for 4 h at −60 °C. Filtration and storage of the deep-blue-violet mother liquor led to crystallization of a black, opalescent, and pyrophoric solid. Several steps of recrystallization allowed the isolation of black, opalescent, highly pyrophoric crystals of **4** (1.07 g, 0.91 mmol, 70%).

Physical Data for 4. Decomp.: 37 °C. Anal. Calcd for $C_{75}H_{88}Ca_2O_7$ (1181.65 g mol^{-1}): Ca, 6.78. Found: Ca, 6.51. Susceptibility measurements (Gouy magnetic balance, 294 K): $\chi_v = 1.381 \times 10^{-6}$, $\chi_g = 2.527 \times 10^{-5}$ cm^3 g^{-1}, $\chi_m = 1.379 \times 10^{-3}$ cm^3 mol^{-1}, $\mu_{eff} = 1.62\mu_B$. EPR measurements (thf, r.t.): g = 2.0024, hyperfine structure pattern corresponding to a 1,3,5-triphenylbenzene radical.

Characterization of the Vinylate Species (after Addition of 3 Equiv of [D$_4$]Methanol). ^{1}H NMR (400.25 MHz, 25 °C, [D$_8$]THF): δ 4.09 (2H, m, O−CH=C*H*$_2$), 6.32 (1H, m, O−C*H*=CH$_2$). ^{13}C{^{1}H} NMR (100.65 MHz, 25 °C, [D$_8$]THF): δ 69.7 (1C, O−CH=*C*H$_2$), 80.1 (1C, O−*C*H=CH$_2$).

Synthesis of [(tmta)$_2$Ca(CH$_2$C$_6$H$_5$)$_2$] (5). All volatiles of a solution of [(thf)$_3$Ca(μ-Ph$_3$C$_6$H$_3$)Ca(thf)$_3$] (10 mL, 2.41 mmol, 0.241 M) in THF were removed in vacuo at 4 °C. The black residue was then dried (1 h) and extracted with toluene (8 mL). The extract was filtered off and stirred at room temperature (r.t.) for 24 h, during which time the color of the solution changed from dark-blue to dark-violet. Addition of tmta (1 mL) and subsequent filtration led to the formation of **5** (0.95 g, 1.98 mmol, 82%) as colorless prisms at r.t. within 5 days.

Physical Data for 5. Decomp.: 58 °C. Anal. Calcd for $C_{26}H_{44}CaN_6$ (480.75 g mol^{-1}): C, 64.96; H, 9.23; N, 17.47; Ca, 8.34. Found: C, 65.09; H, 9.41; N, 17.13; Ca, 8.50. ^{1}H NMR (400.25 MHz, 25 °C, [D$_6$]benzene): δ 1.35 (4H, s, C*H*$_2$−Ph), 2.06 (18H, s, C*H*$_3$, tmta), 3.00 (12H, s(br), C*H*$_2$, tmta), 6.92−7,23 (10H, m, Ph). ^{13}C{^{1}H} NMR (100.65 MHz, 25 °C, [D$_6$]benzene): δ 30.2 (2C, *C*H$_2$−Ph), 40.4 (6C, *C*H$_3$, tmta), 77.7 (6C, *C*H$_2$, tmta), 106.2 (2C, *p*-*C*), 120.2 (4C, *o*,*o*′-*C*H), 128.3 (4C, *m*,*m*′-*C*H), 157.8 (2C, C_{ipso}). IR (nujol, KBr) ν (cm^{-1}): 2853 (vs), 2280 (s), 1888 (m), 1455 (s), 1377 (s), 1259 (m), 1234 (s), 1157 (s), 1115 (vs), 1048 (m), 1026 (m), 1003 (s), 914 (s), 860 (s), 811 (m), 727 (s), 693 (m).

Synthesis of 2,6-(4-tol)$_2$C$_6$H$_3$I (6). The synthesis of **6** was performed according to slightly modified literature procedures.[42−44]

Physical Data for 6. Mp: 140 °C (EtOH). Anal. Calcd for $C_{20}H_{17}I$ (384.26 g mol^{-1}): C, 62.51; H, 4.46; I, 33.03. Found: C, 62.40; H, 4.28; I, 32.80. ^{1}H NMR (400.25 MHz, 25 °C, $CDCl_3$): δ 2.45 (6H, s, C*H*$_3$), 7.22−7.43 (11H, m, aryl). ^{13}C{^{1}H} NMR (100.65 MHz, 25 °C, $CDCl_3$): δ 21.3 (2C, *C*H$_3$), 104.2 (1C, C_{ipso}), 127.5 (2C, *m*-*C*H), 128.5 (5C, *o*′,*p*-*C*H), 129.3 (4C, *m*′-*C*H), 137.2 (2C,

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Table 1. Crystal Data and Refinement Details for the X-ray Structure Determinations of Compounds **4**, **5**, **7**, **8**, and **9**

	4	**5**	**7**	**8**	**9**
formula	$[C_{50}H_{67}Ca_2O_7][C_{24}H_{18}]\cdot 3.5C_4H_8O$	$C_{26}H_{38}CaN_6$	$C_{28}H_{33}IMgO_2$	$C_{32}H_{41}CaIO_3$	$C_{66}H_{82}Ca_2I_2O_{10}\cdot 2C_4H_8O$
fw (g mol^{-1})	1418.94	474.70	552.75	640.63	1513.48
T (°C)	−140(2)	−140(2)	−90(2)	−90(2)	−90(2)
crystal system	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$Pca2_1$	$P\bar{1}$	Cc	$P2_1/c$
a (Å)	24.6771(5)	16.2058(3)	7.9095(3)	10.3305(2)	13.6756(6)
b (Å)	14.9476(4)	8.3923(2)	8.8456(3)	39.9525(9)	18.0856(4)
c (Å)	22.7395(5)	20.4013(7)	37.1188(15)	8.7003(3)	16.8440(6)
α (deg)	90.00	90.00	91.238(2)	90	90
β (deg)	92.546(1)	90.00	91.204(2)	121.825(2)	93.290(2)
γ (deg)	90.00	90.00	90.096(2)	90	90
V (Å^3)	8379.5(3)	2774.66(13)	2595.80(17)	3051.03(14)	4159.2(3)
Z	4	4	4	4	2
ρ (g cm^{-3})	1.125	1.136	1.414	1.395	1.209
μ (mm^{-1})	1.91	2.49	12.79	12.47	9.3
measured data	57700	18124	12092	10805	29291
data with $I > 2\sigma(I)$	10570	4804	7031	5257	5600
unique data/R_{int}	19010/0.0895	5985/0.0482	10098/0.0349	6359/0.0326	9507/0.0687
wR_2 (all data, on F^2)[a]	0.2772	0.1346	0.3744	0.0771	0.1957
R_1 [$I > 2\sigma(I)$][a]	0.0847	0.0491	0.1218	0.0354	0.0611
S[b]	1.037	1.043	1.059	0.994	1.025
resid. density (e Å^{-3})	1.428/−0.395	0.434/−0.290	1.624/−1.850	0.484/−0.590	0.882/−0.582
absorption method	none	none	none	none	none
CCDC no.	771312	771313	motif	745124	745125

[a] Definitions of the R indices: $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, in which $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [2F_c^2 + \max(F_o^2)]/3$. [b] $S = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

*p′-C*H), 142.9 (2C, C'_{ipso}), 148.0 (2C, *o-C*). ESI-MS (*m*/*z* [%]): 384 [65] (M), 258 [32] (Tol_2Ph), 169 [100] ($C_{13}H_{13}$), 258 [32] (Tol_2Ph).

Synthesis of [{2,6-(4-tol)$_2$C$_6$H$_3$}Mg(thf)$_2$I] (7). A solution of **6** (1.25 g, 3.25 mmol) in THF (15 mL) was added dropwise to a suspension of Rieke magnesium (0.97 g, 4.00 mmol) in THF (20 mL). The mixture was heated for 2 h under reflux and then filtered, after which storage of the mother liquor at +4 °C led to crystallization of colorless needles. Separation, washing with *n*-pentane (10 mL, cooled to −40 °C), and gentle drying in vacuum gave 1.51 g of **7** (2.73 mmol, 84%).

Physical Data for 7. Mp: 108 °C. Anal. Calcd for $C_{28}H_{33}MgIO_2$ (552.78 g mol^{-1}): C, 60.84; H, 6.02; Mg, 4.40; I, 22.96. Found: C, 61.20; H, 6.43; Mg, 4.21; I, 22.51. ^{1}H NMR (400.25 MHz, 25 °C, [D8]THF): δ 1.77 (8H, m, CH_2, thf), 2.36 (6H, s, CH_3), 3.62 (8H, m, CH_2O, thf), 7.22 (4H, d, $^3J_{H-H}$ = 8.00 Hz, *m′-C*H), 7.44 (1H, t, $^3J_{H-H}$ = 8.1 Hz, *p-C*H), 7.53 (2H, dd, $^3J_{H-H}$ = 7.6 Hz, *m-C*H), 7.72 (4H, d, $^3J_{H-H}$ = 8.00 Hz, *o′-C*H). ^{13}C{^{1}H} NMR (100.65 MHz, 25 °C, [D8]THF): δ 20.9 (2C, *C*H$_3$), 26.2 (4C, *C*H$_2$, thf), 67.7 (4C, *C*H$_2$O, thf), 126.0 (2C, *m-C*H), 127.5 (4C, *o′-C*H), 129.7 (1C, *p-C*H), 130.0 (4C, *m′-C*H), 137.6 (2C, *o-C*), 139.1 (2C, *p′-C*), 142.4 (2C, C'_{ipso}), 164.7 (1C, C_{ipso}). ESI-MS (*m*/*z* [%]): 169 [100] ($C_{13}H_{13}$), 258 [32] (Tol_2Ph). IR (Nujol, KBr) ν (cm^{-1}): 2862 (vs(br)), 2372 (m), 1915 (m), 1856 (w), 1795 (w), 1648 (w), 1604 (w), 1561 (w), 1537 (m), 1509 (s), 1548 (vs), 1631 (s), 1378 (s), 1347 (s), 1298 (m), 1251 (m), 1230 (m), 1211 (w), 1181 (s), 1111 (m), 1095 (m), 1074 (m), 1026 (vs), 950 (m), 917 (m), 882 (s), 832 (s), 786 (vs), 752 (w), 720 (m), 693 (m).

Synthesis of [{2,6-(4-tol)$_2$C$_6$H$_3$}Ca(thf)$_3$I] (8). A solution of **6** (1.50 g, 3.90 mmol) in THF (10 mL) was added to a suspension of activated calcium (0.156 g, 3.90 mmol) in THF (25 mL) at −60 °C. The mixture was shaken for 6 h at −60 °C and then filtered at −40 °C. The resulting orange solution was stored at −40 °C, which led to the crystallization of pale-violet platelets. Separation, washing with Et$_2$O (8 mL, cooled to −78 °C), and gentle drying in vacuum gave 1.89 g of **8** (2.95 mmol, 76% based on employed aryliodide).

Physical Data for 8. Mp: 213 °C. Anal. Calcd for $C_{32}H_{41}CaIO_3$ (640.65 g mol^{-1}): Ca, 6.21; I, 19.81. Found: Ca, 6.12; I, 19.69. ^{1}H NMR (400.25 MHz, 25 °C, [D$_8$]THF): δ 1.64 (12H, m, CH_2, thf), 2.32 (6H, s, CH_3), 3.55 (12H, m, CH_2O, thf), 7.20 (4H, d, $^3J_{H-H}$ = 8.00 Hz, *m′-C*H), 7.40 (1H, t, $^3J_{H-H}$ = 6.8 Hz, *p-C*H), 7.49 (2H, dd, $^3J_{H-H}$ = 6.8 Hz, *m-C*H), 7.53 (4H, d, *o′-C*H). ^{13}C{^{1}H} NMR (100.65 MHz, 25 °C, [D$_8$]THF): δ 21.0 (2C, *C*H$_3$), 26.3 (6C, *C*H$_2$, thf), 68.1 (6C, *C*H$_2$O, thf), 126.1 (2C, *m-C*H), 127.6 (4C, *o′-C*H), 129.7 (1C, *p-C*H), 130.1 (4C, *m′-C*H), 137.6 (2C, *o-C*), 139.2 (2C, *p′-C*), 142.4 (2C, C'_{ipso}), 196.4 (1C, C_{ipso}). IR (Nujol, KBr) ν (cm^{-1}): 2894 (vs), 2246 (m), 1913 (w), 1803 (w), 1735 (w), 1719 (w), 1648 (w), 1603 (m), 1566 (w), 1517 (m), 1457 (vs), 1377 (vs), 1307 (m), 1248 (m), 1172 (m), 1111 (m), 1074 (s), 1029 (s), 915 (m), 888 (m), 822 (s), 786 (vs), 754 (m), 721 (m), 696 (m), 669 (m).

Synthesis of [{2,6-(4-tol)$_2$C$_6$H$_3$CO$_2$}Ca(thf)$_3$I]$_2$ (9). A solution of **8** (50 mL, 4.54 mmol) in THF was prepared at −60 °C in an argon atmosphere. The argon atmosphere was exchanged for an atmosphere of carbon dioxide. The pale-yellow solution was stored at −78 °C, which led to the crystallization of colorless cubes within 4 days. Separation, washing with Et$_2$O (5 mL, cooled to −78 °C), and gentle drying in vacuum yielded 2.12 g of **9** (1.55 mmol, 68%).

Physical Data for 9. Decomp.: 48 °C. Anal. Calcd for $C_{66}H_{82}Ca_2I_2O_{10}$ (1369.32 g mol^{-1}): C, 57.89; H, 6.04; Ca, 5.85; I, 18.54. Found: C, 57.13; H, 5.84; Ca, 5.92; I, 18.16. ^{1}H NMR (400.25 MHz, 25 °C, [D$_8$]THF): δ 1.68 (24H, m, CH_2, thf), 2.34 (12H, s, CH_3), 3.58 (24H, m, CH_2O, thf), 7.12 (12H, m, *m′,m-C*H), 7.23 (2H, t, $^3J_{H-H}$ = 7.6 Hz, *p-C*H), 7.47 (8H, d, $^3J_{H-H}$ = 8.0 Hz, *o′-C*H). ^{13}C{^{1}H} NMR (100.65 MHz, 25 °C, [D$_8$]THF): δ 21.1 (4C, *C*H$_3$), 26.2 (12C, *C*H$_2$, thf), 68.1 (12C, *C*H$_2$O, thf), 126.6 (2C, *p-C*H), 129.1 (8C, *m′-C*H), 129.3 (4C, *m-C*H), 130.0 (8C, *o′-C*H), 135.7 (2C, C_{ipso}), 136.3 (4C, C'_{ipso}), 139.0 (4C, *o-C*), 140.9 (4C, *p′-C*), 160.1 (2C, *C*OO). ESI-MS (*m*/*z* [%]): 169 [100] ($C_{13}H_{13}$), 258 [25] (tol_2Ph), 341 [72] ($tol_2PhCOOCa$). IR (Nujol, KBr) ν (cm^{-1}): 2928 (vs), 2727 (m), 2371 (m), 1944 (w), 1846 (w), 1831 (w), 1794 (w), 1735 (w), 1647 (w), 1610 (s), 1560 (s), 1508 (m), 1457 (vs), 1377 (vs), 1305 (m), 1212 (m), 1170 (m), 1120 (m), 1072 (m), 1035 (s), 973 (m), 888 (m), 842 (m), 805 (m), 768 (m), 721 (s), 680 (s).

Crystal Structure Determination. The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromatized Mo Kα radiation. The data were corrected for Lorentz and polarization effects but not for absorption effects.[45,46]

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The structures were solved by direct methods (SHELXS[47]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[47]). All of the hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-disordered non-hydrogen atoms were refined anisotropically.[47] After repeated recrystallization, the crystals of **7** were extremely thin and of low quality, resulting in a substandard data set; however, the structure was sufficient to show connectivity and geometry despite the high final *R* value. Here we are publishing only the conformation of the molecule and the crystallographic data. Deposition of the data in the Cambridge Crystallographic Data Centre is not intended because of this. Crystallographic data as well as structure solution and refinement details are summarized in Table 1. XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-771312 (**4**), CCDC-771313 (**5**), CCDC-745124 (**8**), and CCDC-745125 (**9**). Copies of the data can be obtained free of charge upon application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (E-mail: deposit@ccdc.cam.ac.uk).

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