

Syntheses and Structure of the Solvent-Separated Calcium Cuprate $[(\text{thf})_3\text{Ca}(\mu\text{-Ph})_3\text{Ca}(\text{thf})_3]^+[\text{Ph-Cu-Ph}]^-$

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Summary: The transmetalation of phenylcopper yields the solvent-separated cuprate $[(\text{thf})_3\text{Ca}(\mu\text{-Ph})_3\text{Ca}(\text{thf})_3]^+[\text{Ph-Cu-Ph}]^-$. This derivative extends the known classes of organic calcium compounds by an organometallic complex cation, in addition to the already well-known neutral diarylcalcium and trialkylcalcium anions.

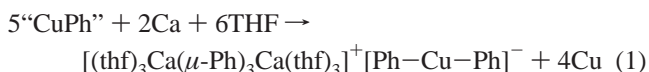
Organic homoleptic cuprates of the type $\text{M}[\text{CuR}_2]$ with $\text{M} = \text{Li}, \text{MgX}$ are a very common class of organocopper reagents, often called Gilman cuprates.¹ These reagents can be prepared via the metathesis reactions of copper(I) halides with arylmagnesium and alkylmagnesium halides or organolithium compounds.² Sometimes a catalytic amount of copper(I) iodide is sufficient in order to form the Gilman cuprates as an intermediate. The addition of small or stoichiometric amounts of copper salts to the reaction solutions can alter the regiochemistry, as was observed in the conjugate addition reactions of α,β -unsaturated esters and ketones.

Despite manifold investigations regarding various applications,^{2,3} solution structures,^{4,5} mechanistic studies,⁶ and the generality and variety of the synthetic procedures of the Gilman cuprates,⁷ information on the organocuprates of the heavier alkaline earth metals is very limited. To our knowledge only one example of such a derivative has been characterized structurally. The reaction of ethynylsodium with CuI in liquid ammonia gave the highly soluble $\text{Na}_2[\text{Cu}(\text{C}\equiv\text{CH})_3]$, which was transferred into the sparingly soluble calcium derivative via a metathesis reaction with calcium nitrate.⁸ This compound crystallized as the solvent-separated ion pair $[\text{Ca}(\text{NH}_3)_6]^{2+}[\text{Cu}(\text{C}\equiv\text{CH})_3]^{2-}$ with Cu-C bond lengths of 2.031(7) Å and a nearly trigonal-planar environment of the copper atom ($\text{C-Cu-C} = 119.89(4)^\circ$).

Difficulties in obtaining diphenylcalcium prompted us to consider transmetalation reactions. Reactions of the alkaline-earth metals with bis[(trimethylsilyl)methyl]zinc led to transmetalation reactions; however, only the corresponding $\text{M}[\text{Zn}(\text{CH}_2\text{SiMe}_3)_2]$ species of calcium,⁹ strontium, and barium¹⁰ were

obtained. Therefore, aryl compounds of copper, which is nobler than zinc, were used in this reaction.

The reaction of calcium metal, activated via dissolution in liquid ammonia and drying under vacuum in the absence of ammonia, with 2 equiv of phenylcopper in THF led to a copper colloid and the formation of the sparingly soluble ionic compound $[(\text{thf})_3\text{Ca}(\mu\text{-Ph})_3\text{Ca}(\text{thf})_3]^+[\text{Ph-Cu-Ph}]^-$ (**1**) in moderate yield according to the idealized equation (1).^{11,12} The



insolubility of this aryl-rich cuprate in common organic solvents prevented a further transmetalation and, hence, the formation of very soluble diarylcalcium, which was accessible via the Schlenk equilibrium from the direct synthesis of calcium with iodoarenes.^{13–15}

The lithium cuprates show very rich aggregation chemistry in solution⁵ and initiated numerous structural investigations.

(11) Synthesis: CuBr (5.0 g, 34.8 mmol) was suspended in 80 mL of THF at 0 °C. A solution of 38.5 mL of a 0.91 M solution of phenylmagnesium bromide (34.58 mmol) in THF was dropped into the solution at 0 °C within 1 h, similar to a literature procedure.¹² At this point the reaction mixture was stirred for 2 h at room temperature. The pale yellow precipitate was separated with a Schlenk frit. (*Caution!* Dry phenylcopper is explosive!) The precipitate was thoroughly washed with three 50 mL portions of THF, leaving 25 mmol of CuPh , which was suspended in 70 mL of THF. This suspension was cooled to -78 °C and added to a flask at -78 °C containing 0.5 g of calcium powder (12.47 mmol) and approximately 1000 glass balls with a diameter of 5 mm. The flask was shaken continuously while it became gradually warmer. The color of the suspension changed to dark red-brown. The gray calcium powder disappeared, and fine colorless crystals precipitated. The reaction mixture was shaken for an additional 1 h at room temperature and finally stored overnight at -20 °C. The colorless microcrystalline precipitate was collected on a Schlenk frit, washed with THF, and dried in vacuo. From the filtrate several single crystals of pure product **1** crystallized at -40 °C. Yield: 4.6 g (76% based on employed Ca) of fine crystals of crude $[\text{Ca}_2(\mu\text{-Ph})_3(\text{thf})_6][\text{CuPh}_2]$. Purification difficulties arose from the insolubility of excess Ca, precipitated Cu, and sparingly soluble CuPh and **1** as well as from the necessity to maintain a THF-saturated atmosphere in order to prevent aging of the crystals. Therefore, only a rather poor elemental analysis was obtained. (Anal. Found for $\text{C}_{54}\text{H}_{73}\text{Ca}_2\text{CuO}_6$ ($M_r = 961.8$): Ca, 8.84; Cu, 7.86. Calcd: Ca, 8.33; Cu, 6.61.) After removal of all solid materials, the dark mother liquor was treated overnight with a few grams of mercury in order to remove colloidal copper. The dark color of the solution disappeared, and the amalgam was removed. The volume of the solution was reduced to one-fourth of its original volume and stored at -40 °C. Approximately 0.1 g of colorless crystals of $[\{(\text{thf})_2\text{Ca}(\text{Ph})\text{Br}\}_3\text{MgO}]$ (**2**) precipitated within a few days, due to residual MgBr_2 from the preparation of CuPh .

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Tetranuclear contact ion pairs in $\text{Li}_2\text{Cu}_2\text{R}_4^{16}$ and solvent-separated ions with oligonuclear cuprate anions are well-known. In pentanuclear cuprates such as $[\text{Cu}_5\text{Ph}_6]^-$ the copper atoms formed a trigonal bipyramid with Cu–C bond lengths of 1.99(2) and 2.19(2) Å to the equatorial and axial copper atoms, respectively.¹⁷ One¹⁸ or both¹⁹ of the axial copper atoms can be substituted by electropositive lithium or magnesium atoms. A higher content of electropositive metals led to more open structures of the higher order cuprates.²⁰ Often not all halogen atoms are substituted by aryl groups, and heteroleptic cuprates such as $[\text{Cu}_5(\text{C}_6\text{H}_4\text{CH}=\text{CH}_2)_2\text{Br}_4]^-$ crystallized.²¹ The cyanide, which can be regarded as a pseudohalide, bridges the cations and anions, thus leading to chain structures.²² The diphenylcuprate anion can be part of the solvent-separated $[\text{Li}(12\text{-crown-4})_2][\text{Ph-Cu-Ph}]$ (average Cu–C = 1.925(10) Å)²³ or contact ion pairs such as $[\text{Li}_2\text{Cu}(\text{aryl})_2\text{Br}]$ (average Cu–C = 1.941(4) Å; aryl = $\text{C}_6\text{H}_4\text{-2-CH}_2\text{N(R)CH}_2\text{CH}_2\text{NR}_2$ with R = Me, Et).²⁴

In the chemistry of solvent-separated organocuprates cited above, the aryl groups were bound to the copper atoms and the electropositive cations (lithium and magnesium) were coordinated by ether molecules or halide anions, thus forming, for example, $[\text{Li}(\text{thf})_4]^+$,¹⁷ $[\text{Li}_4\text{Cl}_2(\text{OEt}_2)_{10}]^{2+}$,¹⁹ $[\text{Mg}(\text{thf})_6]^{2+}$, and $[\text{Mg}(\text{thf})_5\text{Cl}]^+$.²¹

The molecular structure of **1** consists of solvent-separated ions and is shown in Figure 1.²⁵ The dinuclear cation contains the hexacoordinate calcium atoms in distorted-octahedral environments with bridging phenyl groups and terminally bound THF molecules which leads to a facial arrangement of the substituents. Due to the bridging position of the phenyl groups, the Ca–C bond lengths vary between 2.605(3) and 2.625(2) Å and are slightly larger than those observed for arylcalcium iodides. The C–Ca–C angles have values in the rather narrow

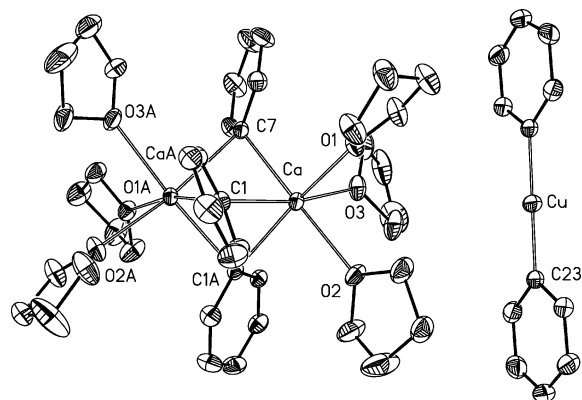


Figure 1. Molecular structure of $[(\text{thf})_3\text{Ca}(\mu\text{-Ph})_3\text{Ca}(\text{thf})_3]^+[\text{Ph-Cu-Ph}]^-$ (**1**). The ellipsoids represent a probability of 40%; H atoms are omitted for clarity reasons. Selected bond lengths (Å) and angles (deg): Ca–O1 = 2.404(2), Ca–O2 = 2.414(2), Ca–O3 = 2.418(2), Ca–C1 = 2.625(2), Ca–C1A = 2.613(2), Ca–C7 = 2.605(3), Cu–C23 = 1.910(3), Ca \cdots CaA = 3.1799(9); Ca–C1–CaA = 74.76(7), Ca–C7–CaA = 75.2(1), C23–Cu–C23A = 180.0(2), C2–C1–C6 = 113.4(2), C8–C7–C8A = 112.5(3), C24–C23–C28 = 114.1(3).

range 84.80(9)–87.98(7)°, and the Ca–C–Ca bonds can be described as three-center–two-electron bonds. Neglect of the THF ligands leads to a pyramidal arrangement of the hydrocarbyl ligands at calcium, which was also observed for the tris[bis(trimethylsilyl)methyl]calcium anion with a trigonal-pyramidal environment of the three-coordinate calcium atom, similar to the case for the isotypic Yb derivative.²⁶ In this anion, the Ca–C distances display values between 2.474(4) and 2.556(4) Å and C–Ca–C angles between 107.9(1) and 116.1(1)°. With this anion in mind, the cation of **1** can also be regarded as a pyramidal triphenylcalcium coordinating to another calcium atom, leading to a Ca \cdots Ca distance of 3.1799(9) Å; the vacant coordination sites are occupied by THF molecules. Comparable structures are unknown for the magnesium derivatives. In $[\text{Ph}_2\text{Mg}(\mu\text{-Ph})_2\text{MgPh}_2]^{2-}$ the magnesium atoms display distorted-tetrahedral coordination spheres.²⁷ In oligomeric arylmagnesium compounds, the molecular structures can also be derived according to VSEPR rules.^{28,29}

The diphenylcuprate anion is strictly linear, due to crystallographic inversion symmetry. The Cu–C distances with values of 1.910(3) Å are slightly shorter than those observed for solvent-separated $[\text{Li}(12\text{-crown-4})_2][\text{Ph-Cu-Ph}]$.²³

The magnesium halide from the metathesis reaction of CuBr with PhMgBr has to be washed out thoroughly in order to avoid side reactions. When MgBr_2 was present during the transmetalation reaction, not only did the sparingly soluble $[(\text{thf})_3\text{Ca}(\mu\text{-Ph})_3\text{Ca}(\text{thf})_3][\text{Ph-Cu-Ph}]$ precipitate but also the black solution still contained phenyl groups. After workup procedures,¹¹ $\{[(\text{thf})_2\text{Ca}(\text{Ph})\text{Br}]_3 \cdot \text{MgO}\}$ (**2**) with an oxygen-centered MgCa_3 tetrahedron precipitated at low temperatures in the shape of colorless crystals. The oxygen stems from ether cleavage, as described earlier.^{13,15} Heterobimetallic Mg–Ca organometallic compounds are rare, and examples include $\text{R}_2\text{N-Ca}(\mu\text{-NR}_2)_2\text{-Mg-NR}_2$ with R = SiMe_3 .³⁰ The molecular structure of **2** is

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(25) X-ray structure determination of **1**: intensity data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo K α radiation. Data were corrected for Lorentz–polarization and for absorption effects. Crystallographic data as well as structure solution and refinement details for **1**: $\text{C}_{54}\text{H}_{73}\text{Ca}_2\text{CuO}_6$, $M_r = 961.82$, colorless prism, size $0.04 \times 0.04 \times 0.03 \text{ mm}^3$, monoclinic, space group $C2/c$, $a = 22.5330(7) \text{ \AA}$, $b = 11.2561(4) \text{ \AA}$, $c = 20.6374(6) \text{ \AA}$, $\beta = 91.917(2)^\circ$, $V = 5231.4(3) \text{ \AA}^3$, $T = -90^\circ\text{C}$, $Z = 4$, $\rho_{\text{calcd}} = 1.221 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 6.59 \text{ cm}^{-1}$, multiscan, minimum/maximum transmission 0.8898/0.9198, $F(000) = 2056$, 18 399 reflections in h (–29 to +29), k (–14 to +12), l (–26 to +26), measured in the range $2.72^\circ \leq \theta \leq 27.51^\circ$, completeness $\theta_{\text{max}} = 99.5\%$, 6000 independent reflections, $R_{\text{int}} = 0.0545$, 3943 reflections with $F_o > 4\sigma(F_o)$, 287 parameters, 0 restraints, $R1(\text{obsd}) = 0.0488$, $wR2(\text{obsd}) = 0.1136$, $R1(\text{all}) = 0.090$, $wR2(\text{all}) = 0.1316$, $\text{GOF} = 1.010$, largest difference peak/hole $0.547/–0.429 \text{ e \AA}^{-3}$.

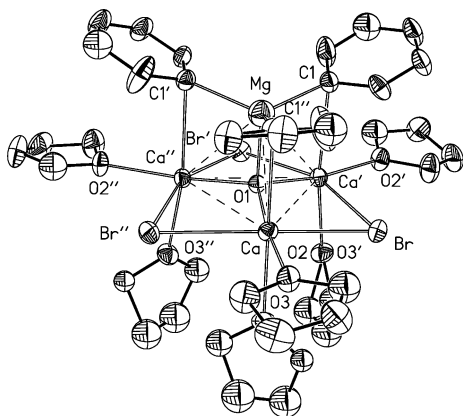


Figure 2. Molecular structure of $[(\text{thf})_2\text{Ca}(\text{Ph})\text{Br}]_3 \cdot \text{MgO}$ (**2**). The ellipsoids represent a probability of 40%; H atoms are neglected for clarity reasons. Symmetry-related atoms are marked with one ($-x + y - 2, -x - 1, z$) or two primes ($-y - 1, x - y + 1, z$). Selected bond lengths (Å) and angles (deg): Mg–C1 = 2.238(5), Mg–O1 = 1.995(5), Ca–C1' = 2.779(5), Ca–O1 = 2.169(1), Ca–O2 = 2.397(3), Ca–O3 = 2.420(4), Ca–Br = 2.968(1); C1–Mg–C1' = 115.9(1), Mg–C1–Ca'' = 77.2(2), Mg–O1–Ca = 98.5(1), Ca–O1–Ca' = 117.85(6), Ca–Br–Ca'' = 77.07(3), Br–Ca–Br' = 160.40(4), C2–C1–C6 = 113.3(5).

shown in Figure 2.³¹ The phenyl groups bridge the heterometallic Mg–Ca edges (Mg–C1 = 2.238(5) Å, Ca–C1 = 2.779(5) Å), whereas the bromine atoms bridge the homometallic Ca–Ca edges (Ca–Br = 2.968(1) Å and Ca–Br' = 2.995(1) Å). Due to strong electrostatic attractions, short Mg–O1 (1.995(5) Å) and Ca–O1 (2.169(1) Å) bonds were observed, whereas the Ca–O2 bond lengths to the THF molecules lie in a characteristic region (Ca–O2 = 2.397(3) Å and Ca–O3 = 2.420(4) Å). This strong electrostatic attraction leads to rather small Mg···Ca and Ca···Ca contacts of 3.156(2) and 3.715(1) Å, respectively.

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With $[(\text{thf})_3\text{Ca}(\mu\text{-Ph})_3\text{Ca}(\text{thf})_3][\text{Ph-Cu-Ph}]$ the range of organocalcium compounds has been extended: examples of anionic $[\text{Ca}\{\text{CH}(\text{SiMe}_3)_2\}_3]^-$,²⁶ neutral $[(\text{thf})_3\text{Ca}(\text{Mes})_2]$,¹³ and cationic $[(\text{thf})_3\text{Ca}(\mu\text{-Ph})_3\text{Ca}(\text{thf})_3]^+$ species have been structurally characterized. The field of heavy Grignard reagents is gaining generality, a requirement for the implementation of these highly reactive compounds in synthetic organic and organometallic chemistry.

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Supporting Information Available: CIF files giving data collection and refinement procedures as well as positional coordinates of all atoms. This material is available free of charge via the Internet at <http://pubs.acs.org>. In addition, the data deposited at the Cambridge Crystallographic Data Centre under CCDC-637913 (**1**) and CCDC-642882 (**2**) contain the supplementary crystallographic data, excluding structure factors; these data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax (+44) 1223-336-033; deposit@ccdc.cam.ac.uk).

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(31) X-ray structure determination of **2**: intensity data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo K α radiation. Data were corrected for Lorentz–polarization and for absorption effects. Crystallographic data as well as structure solution and refinement details for **2**: $\text{C}_{42}\text{H}_{63}\text{Br}_3\text{Ca}_3\text{MgO}_7$, $M_r = 1064.20$, colorless prism, size $0.05 \times 0.05 \times 0.04$ mm³, rhombohedral, space group $R3c$, $a = 19.5010(4)$ Å, $b = 19.5010(4)$ Å, $c = 22.1204(5)$ Å, $V = 7285.1(3)$ Å³, $T = -90$ °C, $Z = 6$, $\rho_{\text{calcd}} = 1.455$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 28.65$ cm⁻¹, multiscan, minimum/maximum transmission 0.6221/0.6846, $F(000) = 3288$, 16 070 reflections in h (–23 to +25), k (–23 to +25), l (–24 to +28), measured in the range $4.18^\circ \leq \theta \leq 27.46^\circ$, completeness $\theta_{\text{max}} = 99.5\%$, 3578 independent reflections, $R_{\text{int}} = 0.0518$, 3036 reflections with $F_o > 4\sigma(F_o)$, 156 parameters, 1 restraint, $R1(\text{obsd}) = 0.0433$, $wR2(\text{obsd}) = 0.1049$, $R1(\text{all}) = 0.0579$, $wR2(\text{all}) = 0.1128$, GOF = 1.032, Flack parameter 0.28–(1), largest difference peak/hole 0.727/–0.450 e Å⁻³.