Diarylcalcium

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An Efficient General Synthesis of Halide-Free Diarylcalcium**

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Contradictory reports on the synthesis and stability of arylcalcium compounds can be found in the literature, which reflects the difficulties that has hampered the broad acceptance of these heavy Grignard reagents. First reports date back to 1905, when Beckmann first published the synthesis of phenylcalcium halides.[1] Doubts concerning these results were raised by Gilman and Schulze, who also noticed that the obtained yields were usually far from satisfactory.[2] Whereas some research groups heat the reaction solutions to complete the turnover,[3] other groups recommend performing the direct synthesis at low temperatures and using the formed reagents immediately.[4] The main reasons for contradictory reports on the preparative procedures and on the stability of arylcalcium derivatives in ether solutions are rooted in the large discrepancy between the rather unreactive metal itself and the high reactivity of the organocalcium derivative, the necessity to activate the metal prior to use, and, last but not least, the tendency for the ether solvent to be cleaved during the direct synthesis of arylcalcium halides. Re-investigation of the synthesis of arylcalcium compounds led to the isolation of oxygen-centered arylcalcium cages,[5–7] calcium vinylate derivatives,[8] and after prolonged heating of phenylcalcium iodide in THF even to aryl-free $[(CaO)_4\{(thf)_3Ca(\mu\text{-}I)_2\}_4]$.[8] For these reasons, the direct synthesis of arylcalcium iodides from activated calcium and aryliodides has to be performed at low temperatures.[9] A solvent-dependent equilibrium leads to the formation of calcium diiodide and diarylcalcium.[10] A separation was, however, only successful (in a rather low yield) for $[(thf)_3CaMes_2]$ (Mes = 2,4,6-trimethylphenyl), but this derivative is extremely reactive because of the rather low coordination number of the calcium and its tendency to form more stable benzyl compounds.[11] Metathesis reactions of $[(thf)_4Ca(aryl)I]$ with potassium compounds allow exchange of the halide by phosphanides and amides.[7]

An efficient high-yielding synthesis of halide-free diarylcalcium is necessary to expedite the development of organocalcium chemistry. In principle, two routes seem to be appropriate. Transmetalation of readily accessible diarylmercury allows the preparation of diarylcalcium.[12] However, the reactions of calcium with other arylmetal compounds often yield metalates such as $[(thf)_3Ca(\mu\text{-}Ph)_3Ca(thf)_3]^+$ $[Ph\text{-}Cu\text{-}Ph]^-$.[13] A quantitative shift of the Schlenk equilibrium toward diarylcalcium and calcium diiodide offers another preparative method. However, the 1,4-dioxane precipitation method,[14] which was applied successfully in organomagnesium reactions, failed for the heavier congeners.

Halide-free diphenylmanganese reacts readily with activated calcium powder to give an aryl-rich heterobimetallic ion pair $[(thf)_3Ca(\mu\text{-}Ph)_3Ca(thf)_3]^+$ $[(thf)_2PhCa(\mu\text{-}Ph)_3MnPh]^-$ (**1**) according to Equation (1). A complete substitution of manganese by calcium was impossible by this procedure. The complex cation of **1** is isostructural to the cation of the aforementioned cuprate.[13] The anion has a remarkable structure since it contains a calcium as well as a manganese atom, which are bridged by three phenyl groups. Both metal atoms also bind to another terminal phenyl substituent. The coordination spheres of the calcium atoms are saturated by THF molecules. In heterobimetallic compounds, the cation contains the more electropositive metal whereas the anion contains the less electropositive ones. Here we report one of the very rare examples of a heterodimetallic manganate anion that contains the transition metal as well as the electropositive calcium.

$$4\ \{MnPh_2\} + 3\ Ca^* \xrightarrow[-\ 3\ Mn]{THF} \underset{\mathbf{1}}{[(thf)_3Ca(\mu\text{-}Ph)_3Ca(thf)_3]^+\ [(thf)_2PhCa(\mu\text{-}Ph)_3MnPh]^-} \quad (1)$$

The molecular structure and numbering scheme of the complex anion of **1** are shown in Figure 1. The bridging phenyl groups of the anion show an average Ca–C bond length of 282.3 pm, whereas the average Ca–C bond length of

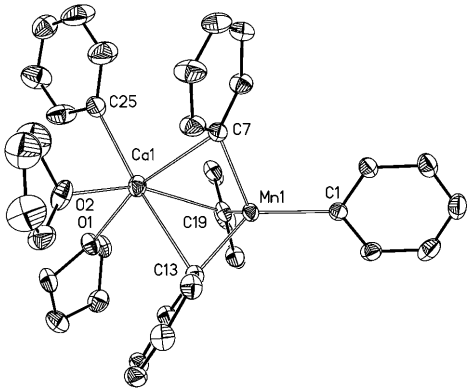

Figure 1. Structure of the anion $[(thf)_2PhCa(\mu\text{-}Ph)_3MnPh]^-$ of **1**. The counter cation is already known and, therefore, omitted for clarity. The ellipsoids represent a probability of 40%, hydrogen atoms are not shown. Selected bond lengths [pm]: Mn1–C1 213.8(4), Mn1–C7 223.3(4), Mn1–C13 221.4(4), Mn1–C19 222.9(4), Ca1–C7 275.7(4), Ca1–C13 298.7(4), Ca1–C19 272.6(4), Ca1–C25 248.6(5), Ca1–O1 240.2(3), Ca1–O2 235.9(3).

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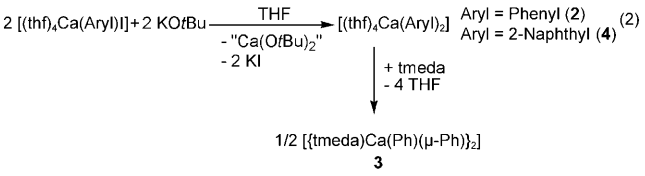
the cation is much smaller (260.6 pm). The long Ca–(μ-C) bonds of the anion allow for a short bond between Ca1 and the terminally bound phenyl group (Ca1–C25 248.6(5) pm, 13.6% smaller than the Ca–(μ-C) bonds). The terminal Mn1–C1 bond length is 4.1% shorter than the Mn–(μ-C) bonds. As expected, the Mn^{II} atom lies in a distorted tetrahedral environment and exhibits a high-spin state.

Another pathway was developed for easy access to halide-free diarylcalcium compounds. Commercially available KO*t*Bu was added to [(thf)$_4$Ca(aryl)I] (aryl = phenyl, naphthyl in an equimolar ratio, taking advantage of the insolubility of KI in organic solvents. Intermediate heteroleptic [(thf)$_4$Ca(aryl)O*t*Bu] dismutates immediately to yield insoluble Ca(O*t*Bu)$_2$ and highly soluble diarylcalcium. After removal of the precipitates, solely diarylcalcium is observed and can be crystallized in good yields from concentrated mother liquors. The extremely high solubility of [(thf)$_4$CaPh$_2$] (**2**) in THF makes it difficult to isolate the compound in higher yields. Recrystallization in 1,2-bis(dimethylamino)ethane (tmeda) gave dinuclear [{(tmeda)Ca(Ph)(μ-Ph)}$_2$] (**3**). The precipitation of Ca(O*t*Bu)$_2$ offers general access to diarylcalcium derivatives in THF. As a representative example, [(thf)$_4$Ca(Naph)$_2$] (**4**; Naph = naphthyl) was also prepared according to this protocol [Eq. (2)].



The metal center in **4** lies in a slightly distorted octahedral environment, with the naphthyl anions in a *trans* arrangement (Figure 2). The average Ca–C bond length of 262.9 pm is slightly longer than those of the heavy Grignard compounds [(thf)$_4$Ca(aryl)X] with hexacoordinate calcium atoms (for example, [(thf)$_4$Ca(Naph)I],[10] Ca–C 255.2 pm). This elongation stems from a reduced charge on the calcium center as a result of the higher covalency of the Ca–C bonds compared with calcium–halide interactions.

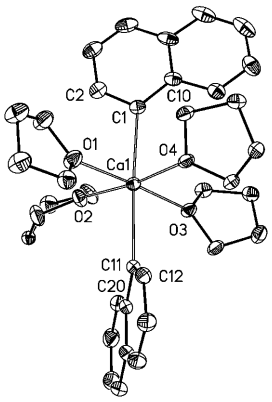


Figure 2. Molecular structure of [(thf)$_4$Ca(Naph)$_2$] (**4**). The ellipsoids represent a probability of 40%. Hydrogen atoms are omitted for clarity. Selected bond lengths [pm]: Ca1-C1 261.8(4), Ca1-C11 263.9(3), Ca1-O1 241.6(3), Ca1-O2 239.8(2), Ca1-O3 240.4(2), Ca1-O4 239.0(2). Angles [°]: C1-Ca1-C11 176.8(1), Ca1-C1-C2 115.2(3), Ca1-C1-C10 131.7(2), Ca1-C11-C12 119.1(3), Ca1-C11-C20 126.6(3).

The formation of dimeric [{(tmeda)Ca(Ph)(μ-Ph)}$_2$] (**3**) is remarkable because the addition of tmeda leads to a complete loss of thf ligands, with the dimerization occuring through bridging phenyl groups (Figure 3). A coordination number of

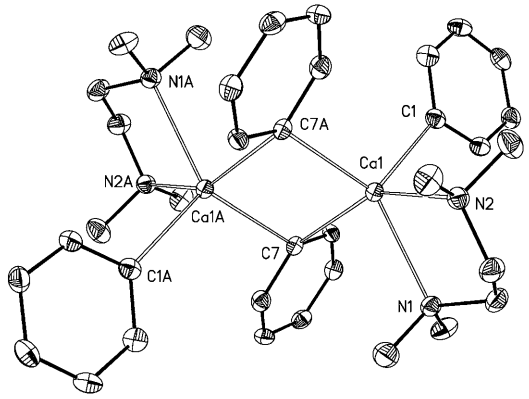


Figure 3. Molecular structure of dinuclear [(tmeda)Ca(Ph)(μ-Ph)]$_2$ (**3**). Symmetry-related atoms (−*x*, −*y*, −*z*+1) are marked with the letter "A". The ellipsoids represent a probability of 40%, hydrogen atoms are omitted for clarity. Selected distances [pm]: Ca1-C1 250.8(3), Ca1-C7 261.8(2), Ca1-C7A 257.1(2), Ca1-N1 257.1(2), Ca1-N2 261.0(2).

five results in short Ca–C bonds of 250.8 and 259.5 pm for terminally bound and bridging phenyl groups, respectively. A rather narrow C-C-C angle is observed in all calcium-bound phenyl groups at the *ipso*-carbon atoms (C2-C1-C6 112.2°, C8-C7-C13 113.0°). This fact can be explained by repulsive interactions between the lone pair of electrons on the *ipso*-carbon atoms and the neighboring C–C bonds, and is a typical feature of phenyl groups bound to electropositive metals.[15]

The easy and straightforward synthesis of diarylcalcium derivatives allows the application of organocalcium compounds in various fields of chemistry, comparable to the widely used lithium and Grignard reagents. The diarylcalcium compounds can be handled for a limited time at room temperature in THF solution (an exception is the *ortho*-methyl-substituted derivatives, which have a tendency to form very stable benzylcalcium moieties). Diarylcalcium compounds are highly soluble in common organic solvents; the tmeda complex **3** is even soluble in benzene, which allows handling and manipulation under ether-free conditions, thus avoiding any kind of ether degradation. In benzene solution, only one set of signals is observed for the phenyl group as a consequence of an exchange process that is fast on the NMR time scale. The reactivity pattern of organocalcium compounds should be different from organolithium and -magnesium compounds because of the participation of available d orbitals.[9] Thus organocalcium derivatives enrich the spectrum of organometallic reagents available, for example, for organometallic synthesis, catalysis, and macromolecular chemistry.

Experimental Section

The manipulation and handling of all compounds were performed in an argon atmosphere. Solvents were dried thoroughly and distilled under argon. Phenylcalcium iodide,[16] naphthylcalcium iodide,[10] and diphenylmanganese[17] were prepared according to literature procedures. The necessity to maintain a THF-saturated atmosphere to prevent aging of the crystals and their extreme sensitivity towards moisture and air, especially their highly pyrophoric nature, made the analytical characterization difficult.

Synthesis of **1**: A solution of $[\{MnPh_2\}_\infty]$ (2.85 g, 13.63 mmol) in THF (30 mL) was cooled to −60 °C and added to a suspension of activated calcium (0.82 g, 20.46 mmol) in THF (20 mL) at −78 °C. The mixture was shaken at −60 °C for 4 h and then for an additional 2 h at RT. The excess of calcium powder and precipitated manganese was removed at −40 °C with a Schlenk frit covered with diatomaceous earth. The resulting dark-brown mother liquor was treated overnight with mercury (6.00 g) to remove colloidal manganese. Storage at −40 °C for 2 weeks led to crystallization of pale-yellow single crystals of pure **1**. Separation, washing with THF (5 mL, cooled to −78 °C), and gentle drying under vacuum yielded 1.32 g (0.96 mmol, 28 %) of pyrophoric **1**. Another crop of **1** (1.9 g, 41 %) contaminated with traces of colloidal manganese was obtained after concentration of the mother liquor to half of its original volume. M.p. > 240 °C. Elemental analysis calcd for $C_{80}H_{104}Ca_3MnO_8$ (1368.85 g mol^{-1}): Ca 8.78, Mn 4.01; found: Ca 8.47, Mn 3.82. EPR (THF solution, RT): $g = 1.998$, sextet hyperfine coupling, $A(^{55}Mn) = 88(\pm 7)$G. Susceptibility measurements (Gouy magnetic balance, 294 K): $\chi_v = 6.802 \times 10^{-6}$, $\chi_g = 1.068 \times 10^{-5}$ cm^3 g^{-1}, $\chi_m = 1.462 \times 10^{-2}$ cm^3 mol^{-1}, $\mu_{eff} = 5.75$ BM ($Mn^{2+}(d^5)$, high spin: $\mu_{theor} = 5.65$–6.10 BM). IR (Nujol, KBr): $\tilde{\nu}$ = 2927 (vs, br), 2725 (s), 2346 (w), 1735 (w), 1719 (w), 1702 (w), 1686 (w), 1648 (w), 1637 (w), 1578 (w), 1561 (m), 1457 (vs), 1377 (vs), 1306 (m), 1169 (m), 1074 (m), 1033 (m), 973 (m), 917 (m), 889 (m), 722 (s), 674 (m), 611 cm^{-1} (m).

Synthesis of **2**: Solid KO*t*Bu (0.34 g, 3.03 mmol) was added at RT to a solution of $[(thf)_4Ca(Ph)I]$ (1.62 g, 3.04 mmol) in THF (10 mL). After 30 min all solids were removed by filtration. Storage of the yellow-orange mother liquor at −40 °C for 1 week led to precipitation of 0.37 g of colorless **2** (0.77 mmol, 50 %). ^{1}H NMR (200.1 MHz, [D$_8$]THF, 300 K): $\delta = 6.7$–7.1 (m, 6H, *m*-CH and *p*-CH), 8.00 ppm (m, 4H, *o*-CH). ^{13}C{^{1}H}-NMR (50.3 MHz, [D$_8$]THF, 300 K): $\delta = 123.7$ (br s, 2C, *p*-C (Ph)), 125.6 (s, 4C, *m*-C (Ph)), 142.7 (br s, 4C, *o*-C (Ph)), 190.0 ppm (br s, 2C, *i*-C (Ph)).

Recrystallization of **2** from tmeda gave **3** quantitatively. ^{1}H NMR (200.1 MHz, [D$_6$]benzene, 300 K): $\delta = 1.42$ (s, 8H, CH_2 (tmeda)), 1.49 (s, 24H, CH_3 (tmeda), 7.35 (m, 4H, *p*-CH (Ph)), 7.49 (m, 8H, *m*-CH (Ph)), 8.56 ppm (m, 8H, *o*-CH (Ph)). ^{13}C{^{1}H} NMR (50.3 MHz, [D$_6$]benzene, 300 K): $\delta = 44.9$ (br s, 8C, CH_3 (tmeda)), 56.2 (br s, 4C, CH_2 (tmeda)), 125.7 (s, 4C, *p*-C (Ph)), 126.9 (s, 8C, *m*-C (Ph)), 141.9 (s, 8C, *o*-C (Ph)), 186.0 ppm (br s, 4C, *i*-C (Ph)).

Synthesis of **4**: Solid KO*t*Bu (0.13 g; 1.16 mmol) was added at RT to a solution of $[(thf)_4Ca(Naph)I]$ (0.67 g, 1.15 mmol) in THF (12 mL). The resulting suspension was stirred for 30 min, and then all solids were removed. Storage of the yellow mother liquor at −40 °C for 2 days led to precipitation of 0.23 g of yellow crystals of **4** (0.35 mmol, 61 %), which were dried under vacuum. ^{1}H NMR (200.1 MHz, [D$_8$]THF, 300 K): $\delta = 7.0$–7.2 (m, 6H), 7.30 (m, 2H), 7.5–7.6 (m, 2H), 7.95–8.1 ppm (m, 4H). ^{13}C{^{1}H} NMR (50.3 MHz, [D$_8$]THF, 300 K): $\delta = 122.0$ (C6), 122.6 (C4), 123.0 (C7), 124.4 (C3), 128.8 (C5), 134.1 (C10), 137.7 (C8), 138.4 (C2), 146.9 (C9), 198.9 ppm (C1).

Crystal-structure determinations: The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K$_\alpha$ radiation. Data were corrected for Lorentz and polarization effects, but not for absorption effects.[18,19]

The structures were solved by direct methods (SHELXS[20]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[21]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen, non-disordered atoms were refined anisotropically.[21] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal data for **1**:[22] $[C_{42}H_{63}Ca_2O_6]^+ [C_{38}H_{41}CaMnO_2]^- \cdot 0.5\,C_4H_8O$, $M_r = 1404.86$ g mol^{-1}, colorless prism, dimensions $0.05 \times 0.05 \times 0.05$ mm^3, monoclinic, space group $P2_1$, $a = 10.8741(2)$, $b = 25.0901(4)$, $c = 14.7612(3)$ Å, $\beta = 96.570(1)°$, $V = 4000.88(13)$ Å^3, $T = -90$ °C, $Z = 2$, $\rho_{calcd} = 1.166$ g cm^{-3}, μ(Mo-K$_\alpha$) = 4.09 cm^{-1}, $F(000) = 1505$, 24994 reflections in $h(-14/12)$, $k(-32/32)$, $l(-19/17)$, measured in the range $2.74° \le \Theta \le 27.51°$, completeness $\Theta_{max} = 95.7$ %, 16829 independent reflections, 13406 reflections with $F_o > 4\sigma(F_o)$, 840 parameters, 1 restraint, $R1_{obs} = 0.0541$, $wR2_{obs} = 0.1375$, $R1_{all} = 0.0754$, $wR2_{all} = 0.1511$, GOF = 1.027, Flack parameter −0.038(17), max/min residual electron density 0.935/−0.426 e Å^{-3}.

Crystal data for **3**:[22] $C_{36}H_{52}Ca_2N_4$, $M_r = 620.98$ g mol^{-1}, colorless prism, dimensions $0.04 \times 0.04 \times 0.04$ mm^3, triclinic, space group $P\bar{1}$, $a = 8.8682(6)$, $b = 10.2935(8)$, $c = 11.0075(8)$ Å, $\alpha = 111.732(3)$, $\beta = 98.610(4)$, $\gamma = 103.394(4)°$, $V = 876.64(11)$ Å^3, $T = -90$ °C, $Z = 1$, $\rho_{calcd} = 1.176$ g cm^{-3}, μ(Mo-K$_\alpha$) = 3.54 cm^{-1}, $F(000) = 336$, 5698 reflections in $h(-10/11)$, $k(-13/12)$, $l(-14/14)$, measured in the range $2.75° \le \Theta \le 27.46°$, completeness $\Theta_{max} = 95.8$ %, 3849 independent reflections, $R_{int} = 0.0396$, 2402 reflections with $F_o > 4\sigma(F_o)$, 194 parameters, 0 restraints, $R1_{obs} = 0.0501$, $wR2_{obs} = 0.0905$, $R1_{all} = 0.1084$, $wR2_{all} = 0.1084$, GOF = 0.952, max/min residual electron density 0.300/−0.259 e Å^{-3}.

Crystal data for **4**:[22] $C_{36}H_{46}CaO_4 \cdot C_4H_8O$, $M_r = 654.91$ g mol^{-1}, colourless prism, dimensions $0.05 \times 0.05 \times 0.04$ mm^3, triclinic, space group $P\bar{1}$, $a = 11.7644(4)$, $b = 12.9408(5)$, $c = 14.8181(6)$ Å, $\alpha = 103.495(2)$, $\beta = 103.493(2)$, $\gamma = 115.009(2)°$, $V = 1841.49(12)$ Å^3, $T = -90$ °C, $Z = 2$, $\rho_{calcd} = 1.181$ g cm^{-3}, μ(Mo-K$_\alpha$) = 2.11 cm^{-1}, $F(000) = 708$, 8322 reflections in $h(-15/15)$, $k(-16/16)$, $l(-19/19)$, measured in the range $2.45° \le \Theta \le 27.47°$, completeness $\Theta_{max} = 98.5$ %, 8322 independent reflections, $R_{int} = 0.0496$, 5435 reflections with $F_o > 4\sigma(F_o)$, 414 parameters, 0 restraints, $R1_{obs} = 0.0824$, $wR2_{obs} = 0.2209$, $R1_{all} = 0.1284$, $wR2_{all} = 0.2514$, GOF = 1.039, max/min residual electron density 0.704/−0.401 e Å^{-3}.

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[22] CCDC 728236 (**1**), 728238 (**3**), and 728237 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

