[24] Using the homodesmotic reaction **9a**+neopentane $= 2 \times$ 2,3,3,4-tetramethylpentane and the standard enthalpies of formation for neopentane (-40.1 kcal mol^{-1})[25a] and 2,3,3,4-tetramethylpentane (-56.35 kcal mol^{-1}),[25b] the values of $\Delta H_f^0(g) = -72.4$ kcal mol^{-1} and strain energy (SE) $= 16.9$ kcal mol^{-1} can be estimated for **9a** using the strain-free model proposed by Schleyer et al.[26] The latter is considerably bigger than the strain energy of triisopropylmethane (7.7 kcal mol^{-1}) and dimethyldiisopropylmethane (8.7 kcal mol^{-1}).

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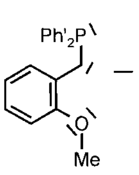
[27] For example, the barrier for the rotation of an isopropyl group in tetraisopropylethylene was found to be ~17 kcal mol^{-1}, whereas no freezing of the rotations in tetracyclopropylethylene was observed down to -150 °C: a) D. S. Bomse, T. H. Morton, *Tetrahedron Lett.* **1975**, 781–784; see also: b) M. Bruch, Y. M. Jun, A. E. Luedtke, M. Schneider, J. W. Timberlake, *J. Org. Chem.* **1986**, *51*, 2969–2973, and references therein. In an attempt to determine the rotational barrier in **9a, b** by low-temperature NMR measurements, the compound precipitated completely when a CD_2Cl_2/$CHCl_2F$ (1/1) solution was cooled to -130 °C (see also c) J. E. Anderson, K. H. Koon, J. E. Parkin, *Tetrahedron* **1985**, *41*, 561–567; d) J. E. Anderson, B. P. Bettels, *Tetrahedron* **1990**, *46*, 5353–5364).

Cyclopentadienyl-Free Calcium Alkyls with Heteroelement-Substituted Anionic Phosphane Ligands: Synthesis and Structure of a Trialkyl Calcate(II) and of an Organocalcium Heterocubane**

Volker Knapp and Gerhard Müller*

Characteristic for organocalcium chemistry is the predominant use of cyclopentadienyl[1] and related ligands.[2] Their bulk and electronic properties serve in an ideal way to solubilize the highly polar calcium organyls in organic solvents, to control their degree of association, and to kinetically stabilize otherwise highly reactive calcium species. In contrast, the number of cyclopentadienyl-free organocalcium complexes is very limited,[3] particularly noteworthy being $[Ca\{C(SiMe_3)_3\}_2]$.[4] Because of the extreme steric bulk and electron-donating properties of the tris(trimethylsilyl)methyl ligand, this compound is monomeric with a bent coordination geometry at the two-coordinate calcium center.[4]

By employing the moderately bulky, multidentate, oxygen-substituted anionic phosphanes **I** and **II**, we were able to synthesize and structurally characterize a sodium trialkyl calcate(II) (with the monoanionic ligand **I**) and a calcium organyl with a heterocubane structure (with the dianionic ligand **II**). Soft ligands (such as phosphanes) have been shown to be best suited for complex formation with the hard alkali and alkaline earth metals when they are anionic.[5]



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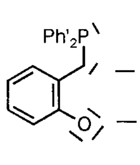
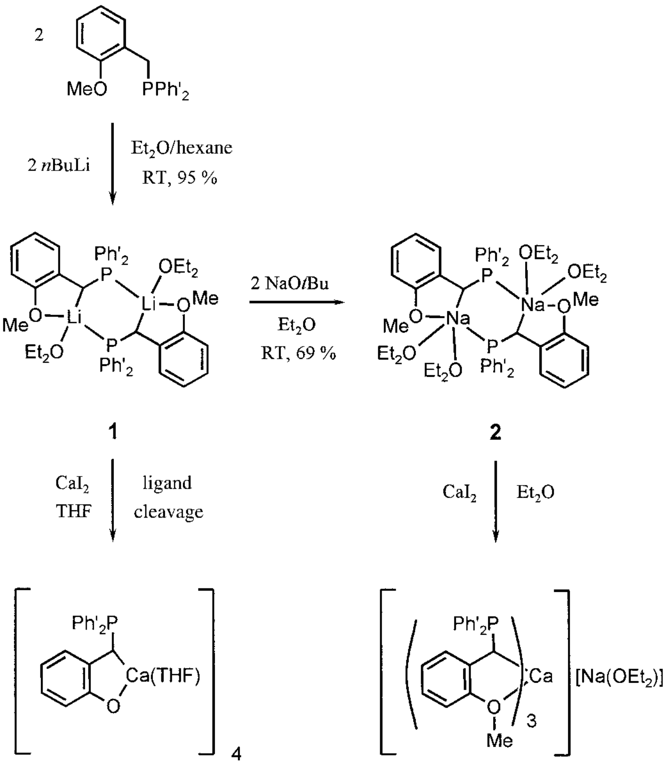


II

As starting materials for the novel calcium alkyls the lithium and sodium complexes of **I** were used. They are prepared in good yields by lithiation of 2-MeO-$C_6H_4CH_2PPh'_2$ (Ph' = *p*-tolyl) with *n*BuLi to give **1** (Scheme 1) which reacts by metathesis with NaO*t*Bu to give the sodium complex **2** (see Experimental Section). The constitution and structural details of **1** and **2** are based on crystal structure determinations.[6] The reaction of isolated **2** with CaI_2 (Scheme 1) is not the only way to prepare the trialkyl calcate(II) **3**, it may also be prepared in a one-pot synthesis starting from 2-$MeOC_6H_4CH_2PPh'_2$; the overall product yield is still 40%.



Scheme 1. Synthesis of complexes **1**–**4**. Ph' = *p*-tolyl.

Although the good solubility of **3** in aromatic solvents permits the recording of NMR spectra, (see Experimental Section), details of its composition and structure could only be obtained from a crystal structure determination.[7, 12] As Figure 1 shows, calcium is coordinated by the carbanionoid

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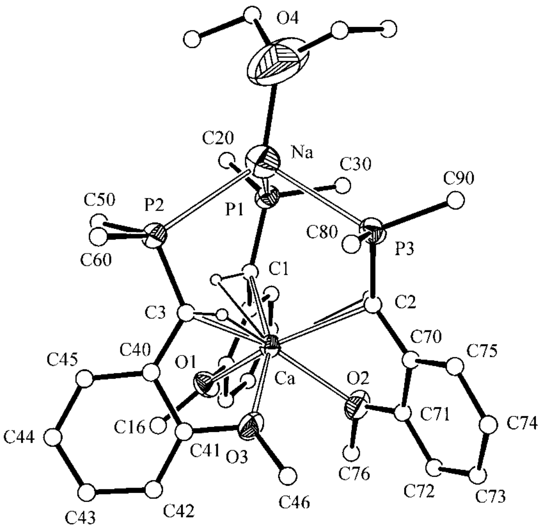

Figure 1. Molecular structure of **3** and numbering scheme (ORTEP-III; thermal ellipsoids at the 50 % level. C atoms with arbitrary radii. For clarity, only the C_{ipso} atoms of the *p*-tolyl substituents are shown and the H atoms are omitted except those at the carbanionoid C atoms. Of the disordered ether C atoms only one alternative is shown). Important distances [Å] and angles [°]: Ca-C1 2.573(4), Ca-C2 2.554(4), Ca-C3 2.532(4), Ca-H11 2.41(4), Ca-H21 2.40(3), Ca-H31 2.43(3), Ca-O1 2.438(3), Ca-O2 2.441(3), Ca-O3 2.423(3), Na-P1 2.851(2), Na-P2 2.934(2), Na-P3 2.871(2), Na-O4 2.150(7), P1-C1 1.761(4), C1-C10 1.457(5), C1-H11 0.90(4), P2-C2 1.764(4), C2-C40 1.455(5), C2-H21 0.85(3), P3-C3 1.774(4), C3-C70 1.458(5), C3-H31 1.04(3); C1-Ca-O1 66.4(1), C2-Ca-O2 66.7(1), C3-Ca-O3 66.2(1), C1-Ca-O2 159.7(1), C2-Ca-O3 152.1(1), C3-Ca-O1 153.5(1); O4-Na-P1 109.5(3), O4-Na-P2 128.1(3), O4-Na-P3 111.2(2), P1-Na-P2 102.5(1), P1-Na-P3 96.6(1), P2-Na-P3 104.2(1), Na-P1-C1 105.3(1), P1-C1-Ca 122.6(2), C10-C1-Ca 103.6(2), H11-C1-Ca 69(3), P2-C2-Ca 127.8(2), C40-C2-Ca 98.3(2), H21-C2-Ca 70(2), P3-C3-Ca 117.2(2), C70-C3-Ca 105.0(2), H31-C3-Ca 73(2).

carbon atoms and the ether oxygen atoms of three ligands **I**, resulting in the coordination number six and a coordination geometry almost exactly between octahedral and trigonal prismatic. Thereby the triangular faces of the coordination polyhedron are formed by three carbon atoms (C1, C2, C3) and three oxygen atoms (O1, O2, O3). They are not strictly parallel but tilted by 4.5° with respect to each other. The twist angle τ between the planes is 31.3°.[13] A noteworthy feature in the ligand coordination of **3** is that the calcium atom is not situated directly above the triangular planes of the coordinating carbon atoms C1 – C3 but rather tilted towards to the H atoms (H atoms refined). This results in short Ca–H distances of 2.41 Å (av). This bonding situation closely resembles agostic metal – hydrogen interactions as known from transition metal chemistry (Figure 1). We also attribute the noticeable pyramidalization of C1 – C3 (sum of the angles at C1, C2, C3 excluding Ca: 345.2, 347.0, and 349.0°, respectively) to this peculiar coordination mode. The Ca–O bonds in **3** (av 2.43 Å) are noticeably shorter than the Ca–C bonds (av 2.55 Å). Because of the metal coordination number of six and the special ligand coordination mode in **3**, not many reference compounds are at hand for comparison. In $[Ca\{C(SiMe_3)_3\}_2]$, containing a two-coordinate calcium center, the Ca–C bond distances are 2.459(9) Å,[4] while in the four-coordinate calcium complex $[Ca\{CH(SiMe_3)_2\}_2(1,4\text{-dioxane})_2]$ they are 2.483(5) Å.[3e] In the 2,3-dimethyl-1,4-diphenylbutadiene complex $[Ca(PhCH{=}CMe{-}CMe{=}CHPh)(thf)_4]$[3d] both the Ca–C bond distances (2.574(7), 2.588(7) Å; terminal butadiene C atoms) as well as the Ca–O bonds (2.397 – 2.445 Å) are very similar to those in **3**.

The phosphanyl groups in **3** are not coordinated to calcium but rather to the sodium counterion, resulting in a mixed-metal complex with a relatively short (nonbonding) Ca ··· Na distance of 4.11 Å. A distorted tetrahedral coordination geometry at the sodium atom is completed by one molecule of Et_2O. The Na–P distances are rather short (av. 2.885 Å) for $Na{-}PR_3$ bonds, although not many such interactions have been reported before.[5, 14, 15] We are not aware of any other example of a coordination environment at sodium comprising three phosphane and one ether donor. The calcate(II) **3** is the first structurally characterized trialkyl ate complex[16] of calcium.[17, 18]

Complex **4** was prepared during attempts to synthesize **3** from the lithium compound **1** in THF (Scheme 1). As is evident, the formation of the alkoxo phosphane ligand **II** results from an unexpected ligand cleavage reaction of **I** involving the loss of the methoxy methyl group. Consequently, the yields of **4** were low. As the starting complex **1** was pure (NMR spectroscopy), **II** must have been formed by ether cleavage during the prolonged reaction times of **1** with CaI_2 in THF. In contrast to the synthesis of **3**, in Et_2O under heterogeneous conditions, that of **4** is homogeneous in THF. Furthermore, the reaction and crystallization times for **4** were much longer than those for **3** (see Experimental Section). Therefore, it seems plausible that the ligand fragmentation occurs by nucleophilic attack of the iodide ion at the carbon atom of the calcium-coordinated methoxy group.[19]

In the solid state **4** is tetrameric with a cuboidal Ca_4O_4 core,[12, 20] the oxygen atoms belong to the μ_3-aryloxide groups (Figure 2). Although the structural motif of a cube with metal

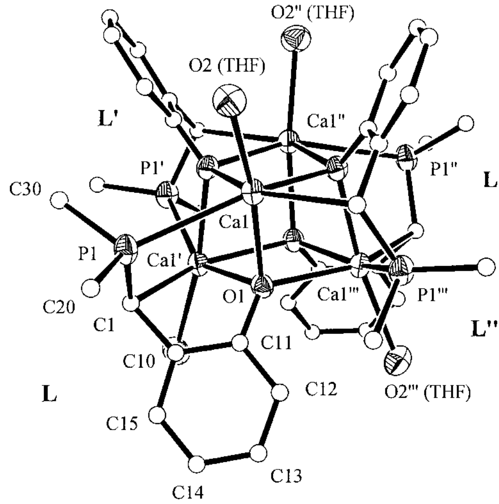

Figure 2. Molecular structure of **4** (ORTEP-III, thermal ellipsoids at the 50 % level. C atoms with arbitrary radii. For clarity, only the C_{ipso} atoms of the *p*-tolyl substituents and the O atoms of the THF molecules are shown. All H atoms are omitted). Selected distances [Å] and angles [°]: Ca-O1 2.346(4), Ca-O1′ 2.430(3), Ca-O1‴ 2.360(3), Ca-O2 2.387(4), Ca-C1‴ 2.591(5), Ca-P1 2.985(2), P1-C1 1.772(6), C1-C10 1.484(7), C1-H11 0.96(4); O1′-Ca-O1‴ 76.8(1), Ca′-O1-Ca‴ 103.2(1); Ca-P1-C1 99.7(2), P1-C1-C10 113.0(4), P1-C1-H11 114(2), C10-C1-H11 106(3), P1-C1-Ca′ 111.6(3), C10-C1-Ca′ 88.7(3), H11-C1-Ca′ 121(2). Symmetry : $L' = 1/4 - y, 1/4 + x, 1/4 - z$; $L'' = -x, 1/2 - y, z$; $L''' = -1/4 + y, 1/4 - x, 1/4 - z$.

and oxygen atoms at alternate corners has precedent in calcium chemistry,[21] to our knowledge it has not been observed in organocalcium compounds.

In **4** each individual calcium atom (compare Ca1 in Figure 1) is coordinated by the oxygen and the phosphanyl phosphorus atoms of one ligand (L), the oxygen and the carbanionoid carbon of a second ligand (L‴), and the oxygen atom of a third ligand (L′). The hexacoordination is completed by the oxygen atom of the coordinated THF molecule. The molecular structure has crystallographic $\bar{4}$ (S_4) symmetry. As compared to **3**, the Ca−O(ligand) bonds in **4** are slightly shorter while the Ca−C bonds are slightly longer. The Ca−P bond length of 2.986(3) Å in **4** can only be compared with those in the calcium diphosphanylmethanide complex [Ca{(PMe$_2$)$_2$C(SiMe$_3$)}$_2$(thf)$_3$] (av d(Ca−P) = 3.043 Å), which is the only other example of crystallographically characterized Ca−PR$_3$ bonds.[22, 23] The carbanionoid carbon C1 in **4** is pyramidalized as the sum of the angles excluding calcium of 333.0° shows. However, in contrast to **3**, in **4** no agostic-type interaction between calcium and the hydrogen atom at C1 is observed.

In summary, our results show that ligands of type **I** and **II** are particularly suitable for complex formation to calcium (and presumably to other hard and large metal centers). These ligands combine three donor sites consisting of two soft (P, C) and one hard (O) donor atom suitably located for chelate formation and thus producing a coordinatively saturated, shielded calcium center.

Experimental Section

Synthesis of **1**: A solution of *n*BuLi in hexane (2.5 M; 2.78 mL) was added dropwise to 2.32 g (6.93 mmol) of 2-MeOC$_6$H$_4$CH$_2$PPh$'_2$ dissolved in Et$_2$O (40 mL) whereupon the reaction mixture turned from yellow to dark orange. Stirring was continued for 3 h at room temperature. After evaporating the solvent under reduced pressure, the residue was washed twice with toluene (20 mL) and dried in vacuo; yield: 2.74 g (6.6 mmol, 95 %); m.p. 192 °C (sealed capillary, decomp); elemental analysis calcd for $C_{22}H_{22}LiOP \cdot C_4H_{10}O$ (%): C 75.7, H 7.3; found: C 74.2, H 7.0; ^{1}H NMR (400 MHz, [D$_8$]toluene/[D$_8$]THF (9/1), 25 °C, TMS): $\delta = 7.49$ (dd, ^3J(H-H) = 6.2 Hz, ^3J(H-P) = 6.2 Hz; *o*-H, *p*-tol), 6.89 (d, ^3J(H-H) = 7.7 Hz; *m*-H, *p*-tol), 7.25 (m, *o*-H, benzyl), 6.69 (t, ^3J(H-H) = 7.4 Hz; *m*-H, benzyl), 6.45 (d, ^3J(H-H) = 7.8 Hz; *m*-*H*CCOMe), 6.22 (t, ^3J(H-H) = 5.9 Hz; *p*-H, benzyl), 3.49 (s, OMe), 3.24 (q, CH$_2$, OEt$_2$), 2.55 (d, ^2J(H-P) = 5.5 Hz; PCH), 2.12 (s, Me, *p*-tol), 1.05 (t, Me, OEt$_2$); ^{13}C{^{1}H} NMR (101 MHz, [D$_8$]toluene/[D$_8$]THF (9/1), 25 °C, TMS): $\delta = 151.18$ (d, ^3J(C-P) = 7.3 Hz; *C*OMe), 145.45 (d, ^1J(C-P) = 9.6 Hz, *ipso*-C, *p*-tol), 144.89 (d, ^2J(C-P) = 20.3 Hz; *ipso*-C, benzyl), 134.81 (s, *p*-C, *p*-tol), 132.83 (d, ^2J(C-P) = 11.9 Hz; *o*-C, *p*-tol), 128.40 (d, ^3J(C-P) = 3.6 Hz; *m*-C, *p*-tol), 123.83 (s, *m*-C, benzyl), 120.05 (d, ^3J(C-P) = 17.8 Hz; *o*-C, benzyl), 110.63 (s, *p*-C, benzyl), 110.24 (s, *m*-*C*COMe), 55.54 (s, OMe), 36.52 (s, PCH), 21.08 (s, Me, *p*-tol); ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]toluene/[D$_8$]THF (9/1), 25 °C, ext. 85 % H$_3$PO$_4$): $\delta = -15.97$ (br. s); ^{7}Li{^{1}H} NMR (155 MHz, [D$_8$]toluene/[D$_8$]THF (9/1), 25 °C, ext. 1 M LiBr in [D$_8$]THF): $\delta = 0.07$ (s).

Synthesis of **2**: NaO*t*Bu (1.03 g, 9.35 mmol) was added to a solution of **1** (2.97 g, 7.21 mmol) in Et$_2$O (60 mL). The solution turned deep-red and after 30 min a yellow solid started to precipitate. Centrifugation and subsequent washing with Et$_2$O (2 x 10 mL) yielded **2** (2.51 g, 4.97 mmol, 69 %) as yellow powder. M.p. 202 °C (sealed capillary, decomp); elemental analysis calcd for $C_{22}H_{22}NaOP \cdot C_8H_{20}O_2$ (%): C 71.4, H 8.4; found: C 69.8, H 6.7; ^{1}H NMR (400 MHz, C$_6$D$_6$/[D$_8$]THF (9/1), 25 °C, TMS): $\delta = 7.72$ (dd, ^3J(H-H) = 6.6 Hz, ^3J(H-P) = 6.6 Hz; *o*-H, *p*-tol), 7.38 (m, *o*-H, benzyl), 6.97 (d, ^3J(H-H) = 7.6 Hz; *m*-H, *p*-tol), 6.74 (t, ^3J(H-H) = 7.1 Hz; *m*-H, benzyl), 6.54 (d, ^3J(H-H) = 7.7 Hz; *m*-*H*CCOMe), 6.19 (t, ^3J(H-H) = 7.2 Hz; *p*-H, benzyl), 3.56 (s, OMe), 3.25 (q, CH$_2$, OEt$_2$), 3.03 (d, ^2J(H-P) = 7.3 Hz; PCH), 2.15 (s, Me, *p*-tol), 1.08 (t, Me, OEt$_2$); ^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$/[D$_8$]THF (9/1), 25 °C, TMS): $\delta = 149.94$ (d, ^3J(C-P) = 10.0 Hz; *C*OMe), 144.46 (d, ^2J(C-P) = 17.68 Hz; *ipso*-C, benzyl), 144.19 (d, ^1J(C-P) = 11.5 Hz; *ipso*-C, *p*-tol), 135.13 (s, *p*-C, *p*-tol), 133.41 (d, ^2J(C-P) = 19.2 Hz; *o*-C, *p*-tol), 128.63 (d, ^3J(C-P) = 6.2 Hz; *m*-C, *p*-tol), 123.68 (s, *m*-C, benzyl), 117.14 (d, ^3J(C-P) = 23.1 Hz; *o*-C, benzyl), 110.70 (s, *m*-*C*COMe), 107.90 (s, *p*-C, benzyl), 56.14 (s, OMe), 37.22 (br. s, PCH), 21.13 (s, Me, *p*-tol); ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$/[D$_8$]THF (9/1), 25 °C, ext. 85 % H$_3$PO$_4$): $\delta = -18.87$ (br. s).

Synthesis of **3**: a solution of *n*BuLi in hexane (2.5 M; 2.5 mL) was added dropwise to 2-MeOC$_6$H$_4$CH$_2$PPh$'_2$ (2.12 g, 6.34 mmol) dissolved in Et$_2$O (30 mL). The reaction mixture was stirred for 3 h at room temperature then NaO*t*Bu (0.69 g, 6.34 mmol) was added. A yellow precipitate formed which was separated by centrifugation. It was washed twice with hexane and dried in vacuo. After it had been suspended in Et$_2$O (40 mL), anhydrous CaI$_2$ (0.72 g, 2.46 mmol) was added and the reaction mixture was stirred for 3 d. The precipitated NaI was separated by centrifugation and to the resulting clear red solution was carefully layered with hexane (3 mL). Yellow crystals suitable for X-ray analysis formed at 4 °C; yield: 2.88 g (40 %); m.p. 131 °C (sealed capillary); elemental analysis calcd for $C_{70}H_{76}CaNaO_4P_3$ (%): C 73.9, H 6.7; found: C 73.6, H 6.5; ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C, TMS): $\delta = 7.78/7.03$ (br. s, *o*-H, *p*-tol), 7.10/6.89 (br. s, *m*-H, *p*-tol), 6.94 (d, ^3J(H-H) = 7.0 Hz; *o*-H, benzyl), 6.60 (m, *m*-H, benzyl), 6.36 (t, ^3J(H-H) = 6.9 Hz; *p*-H, benzyl), 3.26 (q, CH$_2$, OEt$_2$), 2.40 (m, PCH), 2.23/2.13 (s, Me, *p*-tol), 1.08 (t, Me, OEt$_2$); ^{13}C {^{1}H} NMR (101 MHz, C$_6$D$_6$, 25 °C, TMS): $\delta = 152.29$ (s, *C*OMe), 139.61 (s, *ipso*-C, benzyl), 136.67 (s, *p*-C, *p*-tol), 135.28 (s, *ipso*-C, *p*-tol), 133.83 (s, *o*-C, *p*-tol), 131.79 (s, *m*-C, *p*-tol), 124.21 (s, *m*-C, benzyl), 115.45 (s, *p*-C, benzyl), 112.38 (s, *m*-*C*COMe), 57.68 (s, OMe), 34.6 (s, PCH), 21.21 (s, Me, *p*-tol); ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$, 25 °C, ext. 85 % H$_3$PO$_4$): $\delta = -22.34$ (br. s).

Synthesis of **4**: a solution of *n*BuLi in hexane (2.5 M; 1.4 mL) was added dropwise to a solution of 2-MeOC$_6$H$_4$CH$_2$PPh$'_2$ (1.16 g, 3.47 mmol) in THF (20 mL). The reaction mixture was stirred for 3 h at room temperature and CaI$_2$ (0.34 g, 1.17 mmol) was added. Stirring was continued for 2 d at room temperature. Yellow crystals suitable for X-ray analysis formed at 4 °C over a period of 4 weeks; yield: 0.06 g (0.035 mmol, 12 % based on CaI$_2$). The small amount of isolated substance allowed only the recording of the following preliminary NMR data: ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C, TMS): $\delta = 7.64$ (m, *o*-H, *p*-tol), 7.29 (t, ^3J(H-H) = 7.9 Hz; *m*-H, benzyl), 6.98 (m, *m*-H, *p*-tol), 6.86 (t, ^3J(H-H) = 6.6 Hz; *p*-H, benzyl), 6.76 (d, ^3J(H-H) = 7.6 Hz; *o*-H, benzyl), 6.45 (d, ^3J(H-H) = 8.1 Hz; *m*-HCCO$^-$, benzyl), 3.23 (s, PCH), 2.06/1.93 (s, Me, *p*-tol); ^{31}P {^{1}H} NMR (162 MHz, C$_6$D$_6$, 25 °C, ext. 85 % H$_3$PO$_4$): $\delta = 1.64$ (s).

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[6] V. Knapp, unpublished results. The sodium complex was characterized as its tmeda adduct (tmeda = *N,N,N′,N′*-tetramethylethylenediamine).

[7] Crystal structure data of **3** · 2 hexane: $C_{70}H_{76}CaNaO_4P_3 \cdot C_{12}H_{28}$, $M_r = 1309.71\ \mathrm{g\,mol^{-1}}$, monoclinic, space group $C2/c$ (No. 15), $a = 31.462(3)$, $b = 15.958(1)$, $c = 33.396(4)$ Å, $\beta = 117.395(5)°$, $V = 14887(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.169\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.203\ \mathrm{cm^{-1}}$, $F(000) = 5632$, $T =$

183(2) K. Enraf-Nonius CAD4, graphite monochromatized $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, ω scans, $\Delta\omega = 0.8°$, $((\sin\theta)/\lambda)_{max} = 0.592$ Å^{-1}, *hkl* range: +37, +18, −39 – +35. Of a total of 13282 measured reflexions, 13008 were unique ($R_{int} = 0.027$) and 7920 were "observed" with $I > 2\sigma(I)$. Refinement of 797 parameters was done on F^2 of all unique reflexions leading to $R(F)/wR(F^2) = 0.064/0.190$, $GoF = 1.06$, $w = 1/(\sigma^2(F_o^2) + (0.1086P)^2)$, $P = (\max(F_o^2,0) + 2F_c^2)/3$. $\Delta\rho_{fin}$ (max/min) = 0.62/−0.69 e Å^{-3}. In the refinement all non-H atoms were refined anisotropically, except the C atoms of the coordinated molecule Et_2O which were treated in a split atom model. H11, H21, H31 were refined freely with individual isotropic displacement parameters. While one of the interstitial hexane molecules could be refined satisfactorily, the second one was found to be severly disordered, thereby impeding any meaningful refinement. Therefore, it was excluded from structure factor calculations with the routine SQUEEZE[8] as included in PLATON.[9] Restraints were applied to the bonds between the disordered ether and hexane atoms. Programs used: SHELXS-97 (structure solution),[10] SHELXL-97 (structure refinement),[10] ORTEP-III (molecular drawings).[11]

[8] P. van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, 194–201.

[9] A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, The Netherlands, **2000**. See also: A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C34.

[10] G. M. Sheldrick, SHELXS-97, SHELXL-97, Programs for the Determination of Crystal Structures, Universität Göttingen, Germany, **1997**.

[11] C. K. Johnson, M. N. Burnett, ORTEP-III (version 1.0.2), Rep. ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN, **1996**; Windows version: Louis J. Farrugia, University of Glasgow, UK, **1999**.

[12] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-148258 (**3**) and CCDC-148259 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[13] For a regular octahedron $\tau = 60°$, for a trigonal prism $\tau = 0°$: K. R. Dymock, G. J. Palenik, *Inorg. Chem.* **1975**, *14*, 1220–1222.

[14] M. N. S. Hill, W. Clegg, K. Izod, P. O'Shaughnessy, *Organometallics* **2000**, *19*, 4531–4535; F. Paul, D. Carmichael, L. Ricard, F. Mathey, *Angew. Chem.* **1996**, *108*, 1204–1206; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1125–1127; M. D. Fryzuk, X. Gao, S. J. Rettig, *Can. J. Chem.* **1995**, *73*, 1175–1180; G. Lin, W.-T. Wong, *Polyhedron* **1994**, *13*, 3027–3030; P. B. Hitchcock, M. F. Lappert, I. A. MacKinnon, *J. Chem. Soc. Chem. Commun.* **1993**, 1015–1017; H. Schmidbaur, U. Deschler, B. Zimmer-Gasser, D. Neugebauer, U. Schubert, *Chem. Ber.* **1980**, *113*, 902–911.

[15] In the tmeda analogue of **2** a Na–P distance of 2.945(4) Å was found.[6]

[16] J. Cioslowski, P. Piskorz, M. Schimeczek, G. Boche, *J. Am. Chem. Soc.* **1998**, *120*, 2612–2615.

[17] Alkyl calcates(II) with a $[CaO_2C]^-$ and a $[CaC_3]^-$ core have been synthesized before.[3c]

[18] The only other structurally characterized calcate(II) is the π-complex $[Ca(cod)_2]^{2-}$ (cod = cyclooctadiene dianion): S. A. Kinsley, A. Streitwieser, Jr., A. Zalkin, *Organometallics* **1985**, *4*, 52–57.

[19] A similar ligand cleavage reaction of the phosphide ligand $[(2\text{-MeO})C_6H_4PR]^-$ ($R = CH(SiMe_3)_2$) has been observed upon reaction with CaI_2 and YbI_2, and was attributed to C–O bond activation by the metal centers and nucleophilic attack of the phosphido phosphorus atom at the methoxy carbon atom with formation of the methyl phosphane: K. Izod, W. Clegg, S. T. Liddle, *Organometallics* **2000**, *19*, 3540–3643; W. Clegg, K. Izod, S. T. Liddle, P. O'Shaughnessy, J. M. Sheffield, *Organometallics* **2000**, *19*, 2090–2096. It should be noted that the phosphane phosphorus atom in **I** is less nucleophilic than a phosphido group and that in the example above the ligand fragmentation might have been caused by the iodide ion leading to MeI which subsequently methylates the phosphido group.

[20] Crystal structure data of **4**: $C_{100}H_{108}Ca_4O_8P_4$, $M_r = 1722.06$, tetragonal, space group $I4_1/a$ (No. 88), $a = b = 25.091(9)$, $c = 14.050(9)$ Å, $V = 8845(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.293$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 3.74$ cm^{-1}, $F(000) = 3648$, $T = 183(2)$ K. Enraf-Nonius CAD4, graphite monochromatized $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, ω-scans, $\Delta\omega = 0.8°$, $((\sin\theta)/\lambda)_{max} = 0.50$ Å^{-1}, *hkl* range: ±25, ±25, +14. Of a total of 10451 measured reflexions, 2369 were unique ($R_{int} = 0.122$) and 1380 were "observed" with $I > 2\sigma(I)$. Refinement of 302 parameters on F^2 of all unique reflexions leading to $R(F)/wR(F^2) = 0.046/0.104$, $GoF = 1.01$, $w = 1/(\sigma^2(F_o^2) + (0.0456P)^2 + (10.2187P))$, $P = (\max(F_o^2,0) + 2F_c^2)/3$. $\Delta\rho_{fin}$ (max/min) = 0.22/−0.26 e Å^{-3}. In the refinement all non-H atoms were refined anisotropically. Some of the H atoms including that at C1 were refined freely with individual isotropic displacement parameters.

[21] K. M. Fromm, *Chem. Commun.* **1999**, 1659–1660; V. C. Arunasalam, I. Baxter, S. R. Drake, M. B. Hursthouse, K. M. A. Malik, D. J. Otway, *Inorg. Chem.* **1995**, *34*, 5295–5306; A. I. Yanovsky, N. Y. Turova, E. P. Turevskaya, V. G. Kessler, Y. T. Struchkov, *Zh. Neorg. Khim.* **1993**, *38*, 779–783; N. Y. Turova, E. P. Turevskaya, V. G. Kessler, A. I. Yanovsky, Y. T. Struchkov, *J. Chem. Soc. Chem. Commun.* **1993**, 21–23.

[22] H. H. Karsch, M. Reisky, *Eur. J. Inorg. Chem.* **1998**, 905–911.

[23] Also in calcium phosphides the Ca–P bond lengths are comparable to those in **4**: M. Westerhausen, *Coord. Chem. Rev.* **1998**, *176*, 157–210, and refs therein; M. Westerhausen, M. H. Digeser, W. Schwarz, *Inorg. Chem.* **1997**, *36*, 521–527.

The Unusual Photochemistry of Dendrimers with an Anthracene Core**

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Monodisperse dendrimers represent a link between organic compounds with low molecular masses and polymers, and are distinguished by a number of special properties.[1] The objective of the present work was to study the photochemistry and the photophysics of anthracene when used as a core of a dendritic structure. Thus, dendrons of the Fréchet type[2] were attached in the 9 and 10 positions of anthracene. The nucleophilic substitution of the halogen atoms in 9,10-bis(chloromethyl)- or 9,10-bis(bromomethyl)anthracene (**2**) with 3,5-dialkoxy-substituted benzyl alcohols **1a–c** in an alkaline medium under phase-transfer conditions provided yields between 66 and 30% (Scheme 1). An increase in the branching makes the reaction less effective.[3] For comparitive purposes the methoxy compound **3d** was prepared by an analogous procedure.

The ^1H and ^{13}C NMR data of the dendrimers **3a–c** are summarized in Table 1; they differ little from the model compound **3d**, apart from the presence of methoxy groups in

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