Calcium Compounds

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A Well-Defined Hydrocarbon-Soluble Calcium Monofluoride, [{LCaF(thf)}$_2$]: The Application of Soluble Calcium Derivatives for Surface Coating**

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Dedicated to Professor Paul Hagenmuller

CaF_2 is the most important fluoride of the alkaline-earth metals since its mineral fluorspar is the only large-scale source of hydrogen fluoride. Moreover, CaF_2 is a high-melting solid (1418 °C), whose low solubility in water allows quantitative precipitation in analytical chemistry.[1] Although CaF_2 has broad applications in chemistry, to date it is not available to organometallic chemistry because of its poor solubility in common organic solvents.[2] To address this issue our group reported the first soluble CaF_2 complex $[(Cp^*TiF_2)_6CaF_2(thf)_2]$ ($Cp^* = C_5Me_5$).[3] This complex was prepared by adding a solution of $[Cp^*TiF_3]$ to a suspension of calcium metal in the presence of mercury at 0 °C. Also the reaction of CaF_2 (prepared in situ) with either $[Cp^*TiF_3]$ or $[(C_5Me_4Et)TiF_3]$ results in the formation of either $[\{Cp^*TiF_3\}_4CaF_2]$ or $[\{(C_5Me_4Et)TiF_3\}_4CaF_2]$. In all these examples, CaF_2 is trapped in a soluble organometallic matrix.[4] Nevertheless, it did not allow us to explore the chemistry of the Ca–F bond. Therefore, we became interested in synthesizing a well-defined hydrocarbon-soluble molecular compound of composition LCaF ($L = 2,6\text{-}i\mathrm{Pr}_2C_6H_3NC(CH_3)CHC(CH_3)NC_6H_3\text{-}2,6\text{-}i\mathrm{Pr}_2 = CH\{(CMe)(2,6\text{-}i\mathrm{Pr}_2C_6H_3N)\}_2$). This target has never been accomplished, but there are some ill-defined substituted calcium monofluoride species. For example, arylcalcium fluoride (ArCaF) is formed as a reactive brown solid by vaporization and co-condensation of calcium metal with excess ArF at 77 K.[5] The deposition of calcium vapor with argon at 9 K generates calcium atoms and calcium clusters which react with MeF to form species of composition $MeCa_xF$ ($x = 1, 2$). None of these compounds has been structurally characterized.[6] Also, the synthesis of a well-defined LCaF complex gains importance in view of its expected use as soluble precursor for the preparation of CaF_2 coatings, which would eradicate the high resources- and energy-consuming methods conventionally used for making such coatings.[7] These CaF_2 coatings are used as window materials for both infrared and ultraviolet wavelengths and exhibit extremely weak birefringence. Therefore, when applied on the surface of substrates, such as glass or metal, they impart a change in its optical properties. Moreover, thin layers of CaF_2 have been used recently as fluoride-ion conductors.[8]

Herein, we report the first example of a well-defined soluble calcium monofluoride, [{LCaF(thf)}$_2$] (**2**; $L = CH\{(CMe)(2,6\text{-}i\mathrm{Pr}_2C_6H_3N)\}_2$). This compound is obtained from the reaction of $[LCaN(SiMe_3)_2(thf)]$ (**1**)[9] with Me_3SnF[10] (Scheme 1).

Compound **2** is a white solid that is soluble in benzene, toluene, *n*-hexane, and THF. It was thoroughly characterized by ^1H, ^{13}C, ^{19}F NMR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis. The ^1H NMR spectrum of compound **2** shows a singlet at $\delta = 4.72$ ppm for the γ-C*H* protons and one septet ($\delta = 3.14$ ppm) corresponding to the C*H* protons of the *i*Pr moieties. Also, the complete disappearance of the peak arising from $SiMe_3$ ($\delta = 0.20$ ppm) in **1** clearly indicates the formation of compound **2**. The ^{19}F NMR spectrum of **2** shows a singlet at $\delta = -78$ ppm. No molecular ion peak of **2** was detected in the EI mass spectrum and only small fragment ions were found.

The molecular structure of **2** has been determined by single crystal X-ray diffraction analysis (Figure 1) which demonstrates that the complex exists as a fluorine bridged dimer in the solid state. Single crystals of **2**[11] suitable for X-ray structural analysis were obtained by slowly cooling a hot toluene/THF (10:1) solution of **2** to 0 °C. Compound **2** crystallizes in the triclinic space group $P\bar{1}$, with one half dimer in the asymmetric unit. Each calcium atom is pentacoordinate and the coordination geometry around the metal center is distorted trigonalbipyramidal with the oxygen atom of the THF molecule and one of the fluorine atoms occupying the axial positions. The equatorial sites are occupied by both the nitrogen atoms of the ligand L and the other fluorine atom. The dimeric nature of **2** results in the formation of three rings namely the central Ca_2F_2 four-membered ring and two

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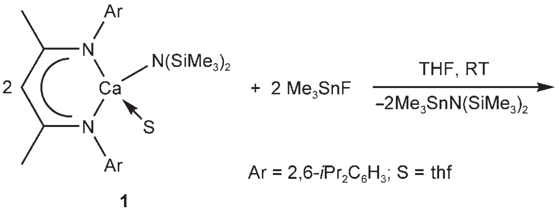
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.



Scheme 1. Synthesis of a calcium monofluoride.

$$[\{\mathrm{LCaF\cdot thf}\}_2] + 2\,\mathrm{HF\cdot Py} \longrightarrow 2\,\mathrm{CaF_2} + 2\,\mathrm{LH} + 2\,\mathrm{Py} + 2\,\mathrm{THF} \qquad (1)$$
2

$$[\mathrm{LCaN(SiMe_3)_2\cdot thf}] + 2\,\mathrm{HF\cdot Py} \longrightarrow \mathrm{CaF_2} + \mathrm{LH} + \mathrm{NH(SiMe_3)_2} + 2\,\mathrm{Py} \qquad (2)$$
1

$$[\mathrm{Ca\{N(SiMe_3)_2\}_2}]\cdot 2\,\mathrm{THF} + 2\,\mathrm{HF\cdot Py} \longrightarrow \mathrm{CaF_2} + 2\,\mathrm{NH(SiMe_3)_2} + 2\,\mathrm{Py} + 2\,\mathrm{THF} \qquad (3)$$
3

$$\mathrm{LCaL} + 2\,\mathrm{HF\cdot Py} \longrightarrow \mathrm{CaF_2} + 2\,\mathrm{LH} + 2\,\mathrm{Py} \qquad (4)$$
4

$$[\{\mathrm{LCaOH\cdot thf}\}_2] + 4\,\mathrm{HF\cdot Py} \longrightarrow 2\,\mathrm{CaF_2} + 2\,\mathrm{LH} + 2\,\mathrm{H_2O} + 4\,\mathrm{Py} + 2\,\mathrm{THF} \qquad (5)$$
5

Scheme 2. Reactions of HF·Py (Py = pyridine) with the soluble calcium compounds **1**–**5**.

adjacent C_3N_2Ca six-membered rings. The four-membered ring is perfectly planar, but the six-membered rings are puckered with a mean plane deviation of 0.191 Å (the deviation [Å] of the individual atoms from the mean plane defined by themselves are Ca1 0.033, N1 −0.305, C2 0.080, C3 0.346, C4 0.077, and N2 −0.305). Also the dihedral angle of 86.88° between the Ca_2F_2 four-membered ring and the C_3N_2Ca six-membered rings unequivocally indicates that the four- and six- membered rings are almost perpendicular to each other. The average Ca−F bond length of 2.180 Å is slightly shorter than the Ca−OH distance of 2.231 Å in [{(LCaOH(thf)}$_2$]·toluene **5**[12] and considerably longer than the Mg−F distance of 1.9507(17) Å in the magnesium analogue of **2**.[13] The average Ca−N and Ca−O(thf) bond lengths of 2.379 Å and 2.433 Å respectively, are longer than those of the magnesium analogue (ca. 2.147(2) Å and 2.078(2) Å respectively). Finally the average Ca−F bond length of 2.180 Å is shorter than the Ca−F bond length (2.366 Å) found in CaF_2.[14]

To test the feasibility of obtaining CaF_2 coatings in situ from **2**, we investigated the reaction of **2** on a pure unpolished silicon surface (see Experimental Section) with a toluene solution of HF·pyridine [Eq. (1) in Scheme 2]. A SEM micrograph of an unpolished pure silicon substrate before and after dip-coating with **2** is shown in Figure 2. The SEM micrograph after the dip-coating clearly reveals the formation of CaF_2 coatings. Furthermore, the energy-dispersive X-ray (EDX) spectroscopic analysis (Figure 3) confirms the existence of CaF_2 on the surface of the substrate by showing distinct lines for both calcium and fluorine.[15] In view of this interesting result, we investigated the utility of other hydrocarbon-soluble calcium precursors such as **1**, **3**, **4**, and **5** for obtaining CaF_2 coatings [Eqs. (2)–(5) in Scheme 2]. The SEM and EDX analyses reveal (see the Supporting Information) that precursors **1**, **3**, **4**, and **5** are also amenable for the preparation of CaF_2 coatings. From these studies it appears that further soluble calcium precursors may lead to the formation of CaF_2 coatings when treated with suitable fluoride source.

In summary, compound **2** is the first example for a calcium monofluoride that shows exceptional solubility in organic

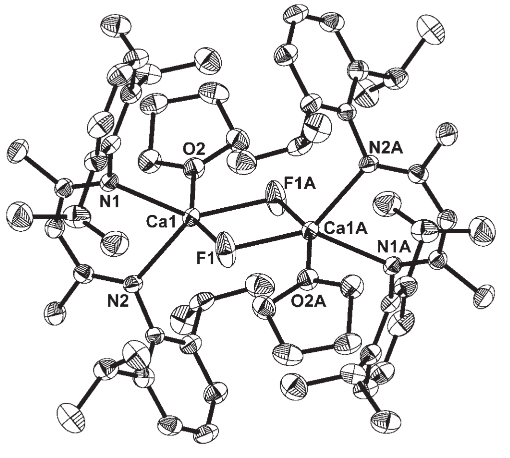


Figure 1. Molecular structure of compound **2**; thermal ellipsoids are set at 50% probability and all the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Ca1–F1 2.170(2), Ca1–F1A 2.189(2), Ca1–O2 2.433(2), Ca1–N1 2.379(2), Ca1⋯Ca1A 3.463(1); Ca1-F1-Ca1A 105.21(7), F1-Ca1-F1A 74.79(7), F1-Ca1-N1 102.45(7), F1-Ca1-O2 154.27(6).

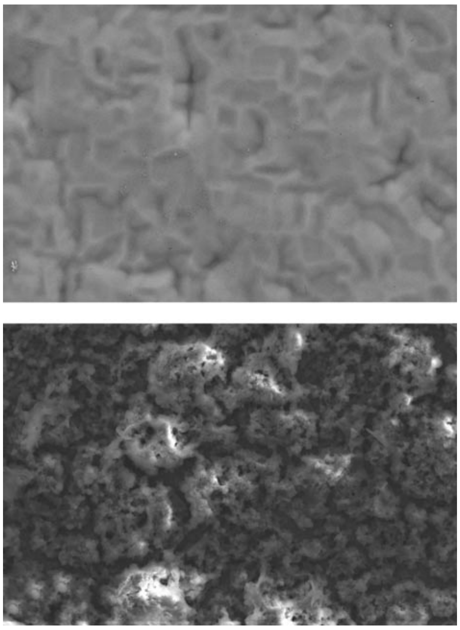


Figure 2. SEM micrograph for a pure silicon substrate before (top) and after (bottom) dip-coating with **2**.

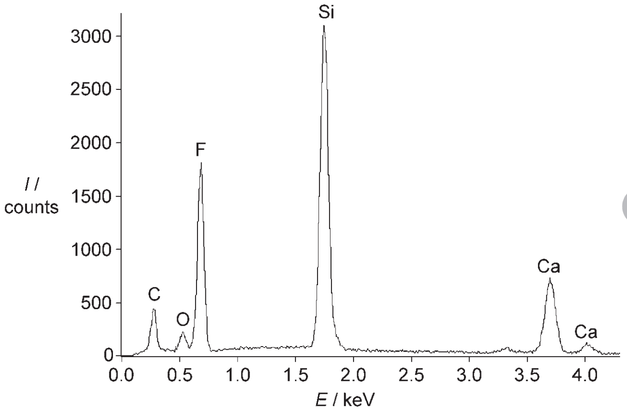


Figure 3. An EDX spectrum of a CaF_2 coating obtained from **2**.

solvents. We are currently exploring the reactivity of this interesting complex. Furthermore, the dip-coating experiments reveal the feasibility of CaF_2 coating on a given substrate. We have extended these dip-coating studies to other soluble calcium precursors such as **1**, **3**, **4**, and **5** for the preparation of thin layers of CaF_2. Based on these results, a broad application of CaF_2 coatings can be expected.

Experimental Section

All manipulations were performed in a dry and oxygen-free atmosphere (N_2 or Ar) by using Schlenk-line and glove-box techniques. Hydrogen fluoride pyridine (hydrogen fluoride ca. 70%, pyridine ca. 30%) was purchased from Aldrich and used as such. Compounds **1**,[9] Me_3SnF,[10] **3**,[16] **4**,[9,17] and **5**[12] were prepared according to literature methods. The instrumental methods employed have been described elsewhere.[18] The surface investigations and the EDX measurements were accomplished with a Leo Supra 35 scanning electron microscope equipped with a Noran EDX-system. The microscope was operated at an accelerating voltage of 10 kV.

2: A clear solution of $[LCaN(SiMe_3)_2(thf)]$ (**1**) (1.38 g, 2.00 mmol) in THF (30 mL) was added to a suspension of Me_3SnF (0.368 g, 2.00 mmol) in THF (10 mL). The mixture was stirred at room temperature for 16 h, dissolution of Me_3SnF indicated completion of the fluorination. All the volatiles were removed in vacuo and the residue extracted with hexane (60 mL). The solution, upon concentration in vacuo, afforded compound **2** as a white solid. An analytically pure sample of **2** was obtained by crystallizing it from hot toluene and THF. Yield (0.65 g, 60%). m.p. 277–280°C. ^{1}H NMR (500 MHz, C_6D_6,): $\delta = 7.09$ (s, 12H, *m*-, *p*-Ar-*H*), 4.72 (s, 2H, γ-C*H*), 3.54 (m, 8H,O-CH_2-CH_2), 3.14 (sept, 8H, C*H*$(CH_3)_2$), 1.64 (s, 12H, CH_3), 1.42 (m, 8H, O-CH_2-CH_2), 1.24–1.22 (d, 24H, CH(CH_3)$_2$), 1.02–1.01 ppm (d, 24H, CH(CH_3)$_2$). ^{13}C{1H} NMR (125.77 MHz, C_6D_6): $\delta = 165.1$, 147.2, 141.8, 123.8, 123.4, 93.4, 69.0, 27.9, 25.4, 25.3, 24.5 ppm; ^{19}F NMR (188.77 MHz, C_6D_6): $\delta = -78$ ppm. MS (70 eV): *m*/*z* (%): 202 (100) $[DippNCCH_3]^+$ (Dipp = 2,6-*i*$Pr_2C_6H_3$). Elemental analysis (%) calcd. for $C_{66}H_{98}Ca_2F_2N_4O_2$ (1093.68): C 72.26, H 8.94, N 5.11; found: C 72.45, H 8.84, N 4.65.

Dip-coating experiments: The pure unpolished silicon substrate was dipped in the toluene (20 mL) solution of **2** (1.00 g, 0.84 mmol) and dried. The substrate was then dipped in a moderate excess of the fluorinating agent HF·pyridine (0.063 g, 2.18 mmol) in toluene (20 mL). These two processes were carried out alternatively 10–12 times. Finally, the silicon substrate was washed with toluene to remove all the soluble side products. After drying at room temperature for 30 min a white solid remained on the substrate. This was subjected to the SEM and EDX analyses. The same procedure was applied for the CaF_2 coatings using precursors **1**, **3**, **4**, and **5**.

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[11] Crystal data for compound **2**: $C_{66}H_{98}Ca_2F_2N_4O_2$·toluene, $M_r = 1189.78$, triclinic, space group $P\bar{1}$, $a = 12.454(10)$, $b = 13.124(10)$, $c = 13.308(11)$ Å, $V = 1726.4(2)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.144$ Mg m^{-3}, $F(000) = 646$, $T = 133(2)$ K, $\mu(Mo_{K\alpha}) = 0.216$ mm^{-1}. The data were collected on a STOE IPDS II instrument. Of the 25302 measured reflections, 5909 were independent ($R_{int} = 0.1045$). The final refinement converged to $R1 = 0.0516$ for $I > 2\sigma(I)$, $wR2 = 0.0825$ for all data. The final difference Fourier synthesis gave a min/max residual electron density of $-0.344/+0.542$ e Å^{-3}. The structure was solved by direct methods with SHELXS-97[19] and refined on F^2 with SHELXL-97[20]. CCDC-616484 (**2**) contains 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.

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