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Published on Web 10/27/2006

A Well-Defined Hydrocarbon-Soluble Calcium Hydroxide: Synthesis, Structure, and Reactivity

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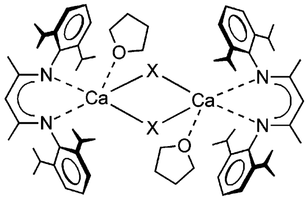
Abstract: Controlled hydrolysis of a (β-diketiminate)calcium-amide gave a heteroleptic (β-diketiminate)-calcium-hydroxide complex that is remarkably stable against ligand exchange and formation of $Ca(OH)_2$. The structure of this dimeric complex shows OH^- units that symmetrically bridge the Ca^{2+} ions. This hydrocarbon-soluble calcium hydroxide reacted rapidly with CO_2 to produce a gel from which amorphous $CaCO_3$ slowly separated. This reaction behavior allows for sol−gel coating with $CaCO_3$ from an organic solvent. Reaction with benzophenone did not lead to nucleophilic attack of OH^- to the carbonyl but gave a red benzophenone adduct instead.

Introduction

In contrast to the rich organometallic chemistry of Mg, syntheses and isolation of complexes of the heavier alkaline-earth metals Ca, Sr, and Ba have always been plagued by their high reactivity and fast ligand exchange.[1] Over the past decade, however, rapid development of the organometallic chemistry of the elements in this group of the periodic table has been observed: its early cyclopentadienyl chemistry[2] has evolved to synthetic routes for alkyl,[3] allyl,[4] benzyl,[5] and aryl[6] complexes. Recently, also a preparative procedure for a heteroleptic well-soluble calcium hydride $[(\text{DIPP-nacnac})Ca(H){\cdot}THF]_2$ (**1**) was introduced.[7]

Its unusual stability against ligand exchange and formation of insoluble CaH_2 is presumably due to the rather bulky and strongly chelating β-diketiminate ligands that form a cage around the central $(CaH)_2$-core. The unique property of the DIPP-nacnac ligand system (DIPP-nacnac = $CH\{(CMe)(2,6\text{-}{}^iPr_2C_6H_3N)\}_2$) to stabilize unusual coordination environments has also been successfully applied in the syntheses of various well-defined hydroxide complexes of the late main-group metals Al,[8,9] Ga,[10,11] and Ge.[12] The latter metal hydroxides could be obtained by selective hydrolysis of tailor-made precursors. Recently, the structure of $[(\text{DIPP-nacnac})Mg(OH){\cdot}THF]_2{\cdot}4THF$, obtained by accidental hydrolysis of an allyl precursor, has been reported.[13] These precedents suggest that the DIPP-nacnac ligand might also be successful in the synthesis of the kinetically much more labile calcium analogue $[(\text{DIPP-nacnac})Ca(OH){\cdot}THF]_2$ (**2**).



1 X = H
2 X = OH

To our knowledge, the Ca−OH functionality has only been observed in larger mixed metal (Li/Ca) clusters.[14] Access to a homometallic well-defined calcium hydroxide complex, which is soluble in organic solvents, would enable studies on the reactivity of this functionality on a molecular level. It could also be of interest in sol−gel coating,[15] polymerization cataly-

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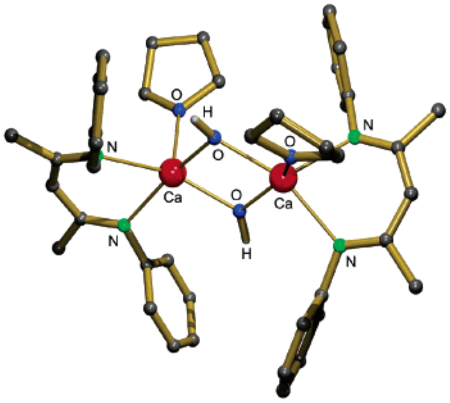

Figure 1. Crystal structure of **2** (crystals obtained from hexane). The ^{i}Pr groups and hydrogen atoms, except that of the hydroxide group, have been omitted for clarity.

sis,[16] or as a potential precursor in the syntheses of well-defined heterobimetallic catalysts.[8]

Results and Discussion

First attempts to prepare complex **2** by diffusion of water vapor into a hexane solution of (DIPP-nacnac)CaN(SiMe$_3$)$_2$·THF[16] gave hydrolysis of the amide as well as the β-diketiminate ligand and resulted in a fine precipitate of CaO. Slow diffusion of water through a hexane layer, however, gave after 2−4 days reproducible formation of large colorless crystals of **2** in reasonable yield (44%). Alternatively, **2** can also be obtained by reaction of (DIPP-nacnac)CaN(SiMe$_3$)$_2$·THF with a stoichiometric amount of water in THF at −40 °C. The raw product (89%) can be further purified by crystallization from toluene, which gives the complex as the toluene solvate: **2**·toluene.

Crystals of the calcium hydroxide complex **2** obtained from hexane are isomorphous to the calcium hydride **1**.[17] The asymmetric unit consists of the dimeric unit, [(DIPP-nacnac)-CaOH·THF]$_2$, with no obvious symmetry (Figure 1). The hydroxide moieties bridge symmetrically between the Ca^{2+} ions, and the Ca$_2$O$_2$-ring is nearly planar. The average Ca−OH bond distance of 2.220(2) Å is only slightly longer than the Ca−H distance of 2.15(3) Å in **1** and considerably longer than the Mg−OH distance (1.988(2) Å) in the Mg-analogue.[13] The average Ca−N and Ca−O(THF) bond distances of 2.418(2) and 2.410(2) Å are slightly longer yet comparable to bond distances in **1**: 2.386(1) and 2.373(1) Å, respectively. Replacement of H$^-$ for OH$^-$ apparently results in a slight expansion of the ligand cage around the Ca^{2+} ions. Although the coordination geometries around the crystallographically inequivalent Ca centers are different, both are essentially of the distorted square-pyramidal type (Figure 2a). For Ca1, the square base is formed by the hydroxide oxygen atoms (O1 and O2), the oxygen atom of the coordinated THF (O3), and one nitrogen atom of the chelating DIPP-nacnac ligand (N2), whereas for Ca2 the base is formed by the hydroxide oxygen atoms (O1 and O2) and two nitrogen atoms of the chelating DIPP-nacnac ligand (N3 and N4).

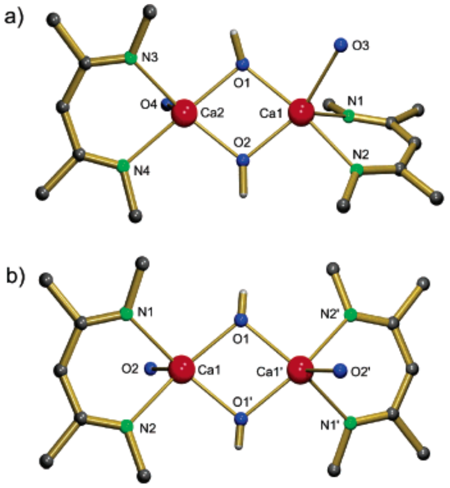

Figure 2. Coordination geometries for the Ca^{2+} ions in the two different structures of **2** (partial structures shown for clarity). (a) [(DIPP-nacnac)-Ca(OH)·THF]$_2$; selected bond distances (Å) and angles (deg): Ca1−O1 2.224(2), Ca1−O2 2.218(2), Ca1−N1 2.414(1), Ca1−N2 2.414(2), Ca1−O3 2.449(1), Ca2−O1 2.209(2), Ca2−O2 2.228(2), Ca2−N3 2.426(1), Ca2−N4 2.418(1), Ca2−O4 2.372(1), Ca1···Ca2 3.505(1); O1−Ca1−O2 75.67(6), O1−Ca1−O3 83.75(6), O2−Ca1−N2 96.77(5), O3−Ca1−N2 92.80(5), N1−Ca1−O3 96.12(5), O1−Ca2−O2 75.77(6), O2−Ca2−N4, 102.74(5), N3−Ca2−N4 78.07(5), N3−Ca2−O1 95.69(6), O1−Ca2−O4 98.38(7). (b) [(DIPP-nacnac)Ca(OH)·THF]$_2$·(toluene); selected bond distances (Å) and angles (deg): Ca1−O1 2.221(3), Ca1−O1′ 2.231(3), Ca1−N1 2.422(3), Ca1−O2 2.414(2), Ca1···Ca1′ 3.495(1); O1−Ca1−O1′ 76.5(1), N1−Ca−N2 78.70(8), O1−Ca1−N1 96.03(9), O2−Ca1−N1 97.04(8), Ca1−O1−Ca1′ 103.5(1), O1−Ca1−O2 111.2(1).

The crystal structure of the toluene solvate (**2**·toluene) is slightly different from that of **2**. The unit cell consists of a centrosymmetric calcium hydroxide dimer in which the hydroxide moieties bridge symmetrically between the Ca^{2+} ions, and the Ca$_2$O$_2$-ring is perfectly planar due to the center of symmetry (Figure 2b). All bond distances in the Ca coordination geometries of the two different crystal structures are equal within standard deviations. The coordination geometry around the Ca center is a distorted square-pyramid with hydroxide oxygen atoms (O1 and O1′) and two nitrogen atoms of the DIPP-nacnac ligand (N1 and N2) at the base. The only difference between the two crystal structures is in the orientation of the DIPP-nacnac ligands relative to each other. This suggests that the ligand framework around the Ca$_2$(OH)$_2$ core is quite flexible with respect to rotation around Ca, which results in exchange of apical and basal positions in the square-pyramidal coordination geometry.

The calcium hydroxide complex **2** dissolves well in benzene and is remarkably stable toward ligand exchange. Refluxing a benzene solution of **2** for 24 h only resulted in minor decomposition (<10%) into (DIPP-nacnac)$_2$Ca and insoluble Ca(OH)$_2$. The ^{1}H NMR resonance for the hydroxide (−0.78 ppm) is at considerable higher field than those for comparable late main group metal hydroxides or than that for Cp*$_2$ZrMe(OH)[18] (Table 1). This reflects a substantial negative charge on the OH group and is in line with the highly ionic nature of the Ca−OH bond. Stepwise addition of THF and even dissolution in pure THF does not lead to large changes in the ^{1}H NMR spectrum, which suggests that dimeric aggregation of **2** is maintained under polar conditions. The IR spectrum of **2**

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(17) The cell parameters show a good resemblance. **1**: $a = 47.980(2)$ Å, $b = 12.5912(4)$ Å, $c = 22.2426(8)$ Å, $\beta = 103.069(2)°$, $V = 13089.2(8)$ Å^3. **2**: $a = 48.190(5)$ Å, $b = 12.595(1)$ Å, $c = 22.291(2)$ Å, $\beta = 102.850(6)°$, $V = 13191(2)$ Å^3.

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Table 1. ^{1}H NMR Chemical Shifts for the OH Functionality in Various Metal Hydroxide Complexes[a]

compound	chemical shift δ (ppm)
$Cp_2^*ZrMe(OH)$[18]	4.20
(DIPP-nacnac)Ge(OH)[12]	1.54
(DIPP-nacnac)AlMe(OH)[8]	0.53
(DIPP-nacnac)$Al(OH)_2$[9]	0.22
(DIPP-nacnac)GaMe(OH)[10]	0.08
(DIPP-nacnac)$Ga(OH)_2$[11]	−0.27
[(DIPP-nacnac)Ca(OH)]$_2$	−0.78

[a] DIPP-nacnac = CH{(CMe)(2,6-^{i}$Pr_2C_6H_3N$)}$_2$.

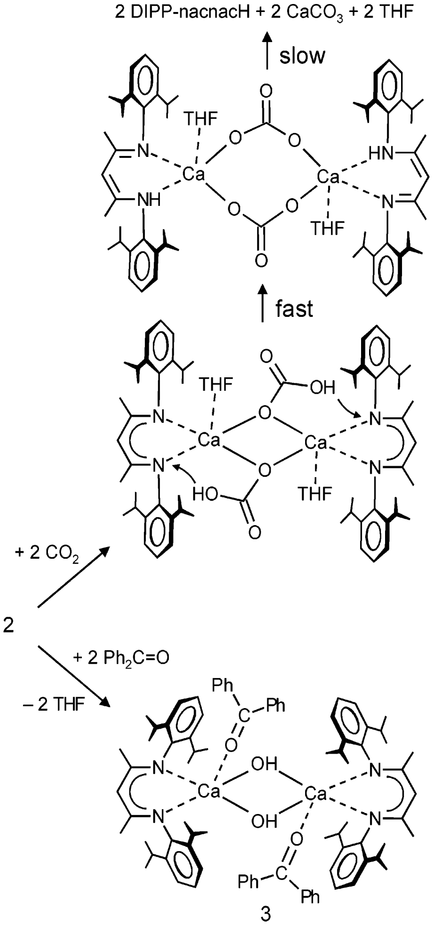
displays a sharp absorption at 3697 cm^{-1}, which is attributed to the hydroxide stretching frequency. A much smaller absorption at 3646 cm^{-1} compares well with that for $Ca(OH)_2$ and is likely the result of partial hydrolysis.

The good solubility of the calcium hydroxide complex **2** in hydrocarbon solvents allows further reactivity studies in nonpolar organic medium. Herein, we report initial results concerning the reactivity of **2**.

Recently reported syntheses of cluster compounds containing a formal CaO unit[6b,c] raised the question of whether further deprotonation of the OH functionality in **2** is feasible. Heating a benzene solution of calcium hydroxide **2** and calcium hydride **1** at 85 °C overnight did not react to give (DIPP-nacnac)Ca−O−Ca(DIPP-nacnac) and H_2. The ^{1}H NMR spectrum of the reaction mixture only showed signals for the starting materials **1** and **2**. Not even exchange of hydride and hydroxide anions, which would result in a mixed hydride/hydroxide dimer, was observed. This underscores the striking stability of the dimeric unit even at higher temperatures.

Of fundamental interest is the comparison of the reactivity of the present well-defined calcium hydroxide complex with that of carbonic anhydrase or those of several mimetic zinc hydroxide complexes.[19] The enzyme carbonic anhydrase "-$(His)_3ZnOH$" reacts with CO_2 to $(His)_3Zn(HCO_3)$; this is a reversible reaction of significant importance in living organisms.[19] A similar reaction also occurs with $Ca(OH)_2$, which acts as CO_2 scavenger.[20] Reaction of **2** dissolved in benzene with 1 bar of dry CO_2 resulted in immediate disappearance of the OH resonance in the ^{1}H NMR spectrum. The concomitant appearance of a low-field singlet (+12.47) ppm and the chemical shifts of the remaining signals are conclusive for the formation of DIPP-nacnacH. The resulting clear yellow solution thickened over the period of 1 h to a transparent gel. After another few hours, a white precipitate separated, which was analyzed as amorphous calcium carbonate. These observations can be explained by the reaction sequence in Scheme 1. Nucleophilic attack of the hydroxide at CO_2 gives a $Ca(HCO_3)$-functionality. Protonation of the DIPP-nacnac ligand by the relatively acidic HCO_3^- ion (pK_a = 10.3)[21] yields a molecular calcium carbonate. The weak bonding between the neutral DIPP-nacnacH ligand and Ca^{2+} results in dissociation and growth of larger calcium carbonate units, which eventually separate as $(CaCO_3)_\infty$. In contrast to the reaction of a zinc hydroxide with CO_2, the current complex reacts irreversibly with this substrate (removal of all solvents and CO_2 in the initial stages did not give reverse reaction to **2**). This is due to fast irreversible protonation of the basic DIPP-nacnac ligand.

Scheme 1



Precipitation of $CaCO_3$ from a benzene solution could have potential application in dip coating technology. Initial experiments showed that objects can be coated with amorphous $CaCO_3$ by dipping these in a solution of **2**, which has been treated with CO_2 (Figure 3).

The reactivity of **2** with other carbonyl functionalities was further explored by its reaction with benzophenone. This might result in formation of $Ph_2CO_2^{2-}Ca^{2+}$, that is, the salt of the unstable *gem*-diol $Ph_2C(OH)_2$. Reaction of a colorless benzene solution of **2** with 2 equiv of benzophenone immediately changed the solution to red, and rapidly well-shaped orange-red crystals formed. The crystal structure determination (Figure 4) revealed a centrosymmetric calcium hydroxide dimer with two coordinated benzophenone molecules (**3**, Scheme 1). Like in **2**, the coordination geometry for the Ca^{2+} ion is square-pyramidal with the benzophenone ligand at the apex. Exchange of THF with benzophenone results in slight elongation of the Ca−O and Ca−N bonds (av values in **3**: 2.2329(7) and 2.4436(7) Å, respectively). Although salts of *gem*-diols have been trapped as ligands in metal complexes,[22] the expected dianion $Ph_2CO_2^{2-}$ is not formed (not even at higher temperatures). The contact between the hydroxide oxygen and the carbonyl carbon is rather long (5.017(2) Å).

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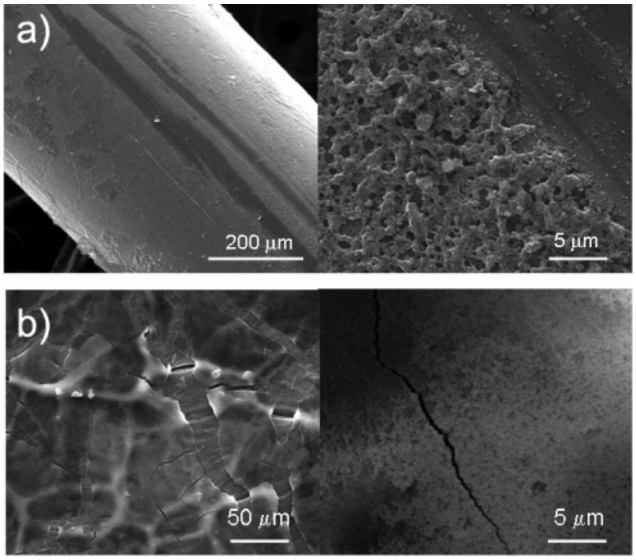

Figure 3. Scanning electron microscope images of calcium carbonate films. (a) Dip coating of a metal wire. The magnification of the central part (right) shows a porous amorphous $CaCO_3$ layer on partially uncovered metal. (b) Dip coating of carbon foil.

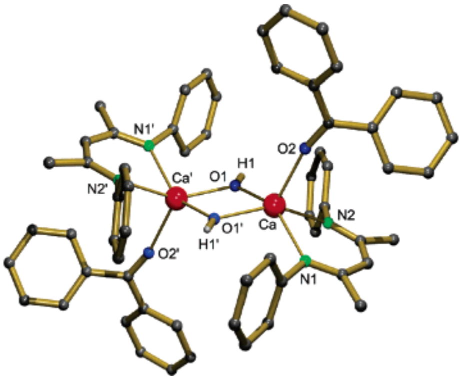

Figure 4. Crystal structure of **3**. The ^{i}Pr groups and hydrogen atoms, except that of the hydroxide group, have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ca−O1 2.2273(7), Ca−O1′ 2.2384(7), Ca−N1 2.4438(7), Ca−N2 2.4433(7), Ca−O2 2.4172(9), Ca···Ca′ 3.5241(7); O1−Ca−O1′ 75.79(2), N1−Ca−N2 78.54(2), O1−Ca−N2 97.28(2), O1′−Ca−N1 93.59(2), N1−Ca−O2 96.16(2), N2−Ca−O2 97.34(2), Ca−O1−Ca′ 104.21(3).

Orange-red crystals of **3** do not dissolve in aromatic solvents but dissolve in THF to yield a colorless solution of **2** and benzophenone. The origin of the red color upon benzophenone coordination is not clear but is likely related to charge transfer from the hydroxide or β-diketiminate ligand to benzophenone.[23] However, extensive ketyl character, like in the intensively blue calcium ketyl complex $Ca^{2+}(Ph_2CO^{\bullet-})_2$,[24] is excluded. The C−O bond length of 1.234(1) Å in the coordinated benzophenone ligand compares well with that in free benzophenone (1.23(1) Å)[25] but not with that in the ketyl (1.31(1) Å).[24] Also, the C=O stretching frequency in **3** (1667 cm^{-1}) is comparable to that in free benzophenone (1656 cm^{-1}).

Conclusions

The preparation of the first hydrocarbon-soluble homometallic calcium hydroxide complex was accomplished by stabilizing the Ca−OH functionality by the DIPP-nacnac ligand system. This dimeric calcium hydroxide complex displays an unusual stability toward ligand exchange: that is, only slight decomposition into $Ca(OH)_2$ is observed after prolonged heating in solution. Likewise, no ligand exchange and reaction with the analogue dimeric calcium hydride was observed. The calcium hydroxide complex **2** does not react with benzophenone but forms a coordination complex with this reagent instead. Reaction with CO_2, however, is fast and leads via a proposed HCO_3^- intermediate to the irreversible formation of $CaCO_3$. The precipitation of $CaCO_3$ from an organic solvent under mild reaction conditions (1 bar, room temperature) is shown to be useful in sol−gel coating and might have other interesting applications.

Experimental Section

All manipulations were performed under a dry and oxygen-free atmosphere (N_2 or Ar) by using Schlenk line and glovebox techniques. The reactants (DIPP-nacnac)Ca(N(SiMe$_3$)$_2$)·THF[16] and (DIPP-nacnac)-CaH·THF (**1**)[7] were prepared according to the literature.

Synthesis of 2. Method A: (DIPP-nacnac)CaN(SiMe$_3$)$_2$·THF (1.00 g, 1.45 mmol) was dissolved in 10 mL of hexane. Connection of a reaction vessel with degassed water layered with hexane gave slow diffusion of water vapor into the calcium amide solution and resulted after 2−4 days in crystallization of the product as large colorless crystals. This procedure could be reproduced many times. Yield: 350 mg, 0.64 mmol, 44%. Method B: Degassed water (40 μL, 2.22 mmol) was added to a solution of (DIPP-nacnac)CaN(SiMe$_3$)$_2$·THF (1.50 g, 2.18 mmol) in THF at −40 °C, and then allowed to warm to room temperature. After having been stirred at room temperature for 30 min, the slurry was dried in vacuo. The resulting solid of **2** was washed with hexane (8 mL) and finally dried in vacuo. Yield: 1.06 g, 1.94 mmol, 89%. The product can be recrystallized by cooling a saturated hot toluene solution to 0 °C. Analyses: mp 277−280 °C. Anal. Calcd for $C_{66}H_{100}Ca_2N_4O_4$ (M = 1093.68): C, 72.48; H, 9.22; N, 5.12. Found: C, 72.82; H, 8.87; N, 4.90. MS (70 eV) m/z (%): 202 (100) $[DippNCCH_3]^+$. ^{1}H NMR (300 MHz, C_6D_6): δ −0.78 (s, 2H, Ca−OH), 1.05 (d, J = 6.9 Hz, 24H, CH(CH$_3$)$_2$), 1.22 (d, J = 6.8 Hz, 24H, CH(CH$_3$)$_2$), 1.41 (m, 8H, THF), 1.69 (s, 12H, CH$_3$), 3.15 (sept, J = 6.9 Hz, 8H, CH(CH$_3$)$_2$), 3.48 (m, 8H, THF), 4.74 (s, 2H, CH-backbone), 7.06 (s, 12H, Ar−H). ^{1}H NMR (300 MHz, THF-d_8): δ −1.09 (s, 2H, Ca−OH), 0.87 (d, J = 6.9 Hz, 24H, CH(CH$_3$)$_2$), 1.01 (d, J = 6.8 Hz, 24H, CH(CH$_3$)$_2$), 1.44 (s, 12H, CH$_3$), 1.73 (m, 8H, THF), 2.96 (sept, J = 6.9 Hz, 8H, CH(CH$_3$)$_2$), 3.58 (m, 8H, THF), 4.44 (s, 2H, CH-backbone), 6.87 (s, 12H, Ar−H). ^{13}C NMR (75 MHz, C_6D_6): δ 24.2, 24.3, 25.0, 25.3, 27.8, 68.4, 93.0, 123.2, 123.4, 141.3, 147.6, 164.4. IR (Nujol): $\tilde{\nu}$ = 3697, 3646, 1623, 1548, 1511, 1461, 1406, 1378, 1313, 1225, 1168, 1098, 1037, 1018, 924, 881, 784, 757 cm^{-1}.

Synthesis of 3. Benzophenone (12.6 mg, 69.2 μmol) was added to a solution of **2** (37.8 mg, 34.6 μmol) in 0.5 mL of benzene. The solution immediately turned red, and incipient crystallization of orange-red blocks was observed. Yield: 21.0 mg, 16.0 μmol, 46%. IR (Nujol): $\tilde{\nu}$ = 3697, 3647, 1667, 1623, 1552, 1463, 1377, 1317, 1276, 1175, 1100, 1027, 939, 920, 785, 758 cm^{-1}. Anal. Calcd for $C_{66}H_{100}Ca_2N_4O_4$ (M = 1313.94): C, 76.79; H, 7.98; N, 4.26. Found: C, 76.92; H, 7.82; N, 3.98.

Crystal Structure Determination. Structures have been solved by direct methods (SHELXS-97)[26] and were refined with SHELXL-97.[27] All geometry calculations and graphics have been performed with

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PLATON.[28] Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 611564, 614005, and 614006. 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).

Crystal Data for 2 (Crystals Obtained from Hexane). $C_{66}H_{100}Ca_2N_4O_4$, $M_r = 1093.66$, monoclinic, space group $C2/c$, $a = 48.190(5)$ Å, $b = 12.5951(13)$ Å, $c = 22.291(2)$ Å, $\beta = 102.850(6)°$, $V = 13191(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.101$ Mg m^{-3}, $F(000) = 4768$, μ(Mo K$_\alpha$) = 0.219 mm^{-1}. The data were collected on a Siemens SMART CCD diffractometer at −90 °C. Of the 135 534 measured reflections, 18 675 were independent ($R_{int} = 0.056$) and 12 469 observed ($I > 2\sigma(I)$). The final refinement converged to $R1 = 0.052$ for $I > 2\sigma(I)$, $wR2 = 0.152$ for all data. The final difference Fourier synthesis gave a min/max residual electron density of −0.47/+0.60 e Å^{-3}. The hydroxide hydrogen atoms have been located in the Fourier-difference map and have been refined isotropically.

Crystal Data for 2 (Crystals Obtained from Toluene). $C_{66}H_{100}Ca_2N_4O_4 + C_7H_8$ (toluene), $M_r = 1185.79$, triclinic, space group $P\bar{1}$, $a = 12.666(9)$ Å, $b = 12.708(9)$ Å, $c = 13.298(10)$ Å, $\alpha = 98.42(6)°$, $\beta = 113.73(5)°$, $\gamma = 110.98(6)°$, $V = 1720.6(2)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.144$ Mg m^{-3}, $F(000) = 646$, μ(Mo K$_\alpha$) = 0.215 mm^{-1}. The data were collected on a STOE IPDS II instrument at −140 °C. Of the 23 691 measured reflections, 5409 were independent ($R_{int} = 0.112$) and 3120 observed ($I > 2\sigma(I)$). The final refinement converged to $R1 = 0.0560$ for $I > 2\sigma(I)$, $wR2 = 0.0890$ for all data. The final difference Fourier synthesis gave a min/max residual electron density of −0.30/+0.53 e Å^{-3}. The hydroxide hydrogen atoms have been located in the Fourier-difference map and have been refined isotropically.

Crystal Data for 3. $C_{84}H_{104}Ca_2N_4O_4 + C_6H_6$ (benzene), $M_r = 1391.98$, triclinic, space group $P\bar{1}$, $a = 12.7720(3)$ Å, $b = 13.1364(3)$ Å, $c = 14.9127(4)$ Å, $\alpha = 94.776(1)°$, $\beta = 111.066(1)°$, $\gamma = 116.428(1)°$, $V = 2000.27(9)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.156$ Mg m^{-3}, $F(000) = 750$, μ(Mo Kα) = 0.195 mm^{-1}. The data were collected on a Siemens SMART CCD diffractometer at −90 °C. Of the 120 357 measured reflections, 19 058 were independent ($R_{int} = 0.029$) and 15 378 observed ($I > 2\sigma(I)$). The final refinement converged to $R1 = 0.041$ for $I > 2\sigma(I)$, $wR2 = 0.118$ for all data. The final difference Fourier synthesis gave a min/max residual electron density of −0.22/+0.51 e Å^{-3}. The hydroxide hydrogen atoms have been located in the Fourier-difference map and have been refined isotropically.

Sol−Gel Coating and Scanning Electron Microscopy. A colorless solution of **2** (0.18 M) was charged with carbon dioxide over a period of 10 min. Objects were cleaned by flushing with ethanol and air-dried. Subsequently, they were dipped 2−3 times in the solution of **2** saturated with CO_2 and, after having been air-dried, washed with hexane to remove organic residue. The samples were attached to graphite foil by graphite glue and covered with gold by sputtering. The morphologies of the deposited $CaCO_3$ films were examined by scanning electron microscopy (SEM; ESEM Quanta 400), and the chemical composition was investigated by XRD measurements.

Acknowledgment. S.N., A.H., J.M., and H.W.R. greatly acknowledge support from the Göttinger Akademie der Wissenschaften. Prof. R. Boese and D. Bläser (Universität Duisburg-Essen) are thanked for collection of part of the X-ray diffraction data. Mr. S. Boukercha (Universität Duisburg-Essen) is acknowledged for recording the SEM pictures and XRD spectra.

Supporting Information Available: Crystal data (CIF) for **2** and **3**; more SEM pictures as well as an XRD spectrum for the $CaCO_3$ precipitate. This material is available free of charge via the Internet at http://pubs.acs.org.

JA065631T

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[28] Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2000.