

$\{[\mu\text{-Cy}_8\text{Si}_8\text{O}_{13}]_2\text{Ca}(\text{DME})\text{Ca}(\text{THF})_2\}$ – The First Metallasilsesquioxane Derivative of a Heavier Alkaline Earth Metal

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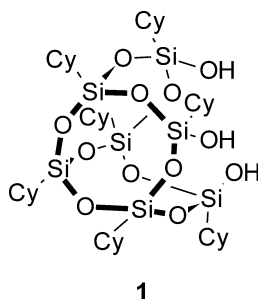
Abstract. $\{[\mu\text{-Cy}_8\text{Si}_8\text{O}_{13}]_2\text{Ca}(\text{DME})\text{Ca}(\text{THF})_2\}$ (**2**), the first metallasilsesquioxane derivative of a heavier alkaline earth metal, has been prepared by a reaction of $\text{Cy}_7\text{Si}_7\text{O}_9(\text{OH})_3$ (**1**) with metallic Ca in liquid ammonia / THF followed by recrystallization from DME. In the course of the reaction ligand rearrangement under formation of the $(\text{Cy}_8\text{Si}_8\text{O}_{13})^{2-}$ dianion takes place. In the dinuclear calcium

complex **2** the anionic silsesquioxane cages act as bridging ligands. The Ca^{2+} ions are unsymmetrically coordinated by THF and DME molecules.

Keywords: Calcium; Silsesquioxanes; Metallasilsesquioxanes; Crystal structure

Introduction

Polyhedral oligosilsesquioxanes of the general formula $(\text{RSiO}_{1.5})_n$ form an unusual and interesting class of organosilicon compounds which currently have a strong impact on both catalysis research [1, 2] and materials science [3]. In accordance with several unique properties, the polyhedral silsesquioxanes have been termed the “smallest particles of silica possible” [4] or “small soluble chunks of silica” [2]. With respect to catalysis research the chemistry of metallasilsesquioxanes also receives considerable current interest [1, 2, 5, 6]. Incompletely condensed silsesquioxanes such as $\text{Cy}_7\text{Si}_7\text{O}_9(\text{OH})_3$ (**1**, Cy = cyclohexyl) share astonishing structural similarities with β -tridymite and β -cristobalite and are thus quite realistic models for the silanol sites on silica surfaces [1, 2, 6–11]. Metal complexes derived from **1** are therefore commonly regarded as “realistic” models for industrially important metal catalysts immobilized on silica surfaces [1, 2, 7].



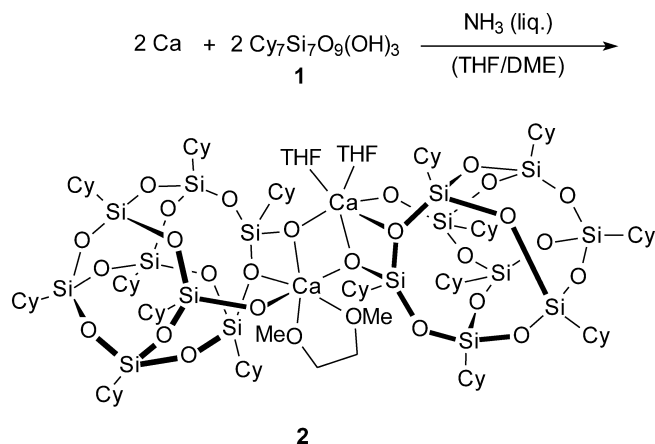
Metallasilsesquioxanes containing alkaline earth metals remain a little investigated class of compounds. Until now,

the lighter beryllium and magnesium are the only elements of Group 2 which have been successfully incorporated into silsesquioxane cages. The structurally characterized compound $[\text{Cy}_7\text{Si}_7\text{O}_9(\text{OLi})_3]_2 \cdot 2\text{THF}$ was prepared from $[\text{Cy}_7\text{Si}_7\text{O}_9(\text{OLi})_3]$ and anhydrous BeCl_2 in THF [12]. The only other alkaline earth metal for which metallasilsesquioxanes have been reported is magnesium. The first Mg derivative was reported in 1996 [13, 14]. Butylethylmagnesium reacts with **1** to give $[\text{Cy}_7\text{Si}_7\text{O}_9(\text{OH})\text{O}_2\text{Mg}]_n$ ($n = 1, 2$). A polymeric magnesiasilsesquioxane material was made by *Lichtenhan* et al. from a silsesquioxane disilanol and dialkylmagnesium derivatives [15], and another magnesium silsesquioxane has been used as an intermediate in reactions with epoxides [16]. The reaction of the cyclopentyl analogue of **1** with MeMgCl led to an unprecedented tetranuclear magnesium silsesquioxane complex [17]. Catalytically active microporous Mg-Si-O materials have been obtained from the controlled calcination of magnesium silsesquioxane complexes [18]. Simple calcium siloxides such as $[(\text{Ph}_3\text{SiO})_2\text{Ca}(\text{THF})_4]$ have recently been reported to be promising precursors for the production of fine calcium ceramic nanoparticles [19a], and calcium silsesquioxanes have been discussed as intermediates in the formation of organosiloxane-based inorganic-organic hybrid materials [19b]. We report here the preparation and characterization of $\{[\mu\text{-Cy}_8\text{Si}_8\text{O}_{13}]_2\text{Ca}(\text{DME})\text{Ca}(\text{THF})_2\}$ (**2**), the first metallasilsesquioxane derivative of a heavier alkaline earth metal. It is also a rare example of a metallasilsesquioxane containing the $(\text{Cy}_8\text{Si}_8\text{O}_{13})^{2-}$ dianion formed by ligand rearrangement.

Results and Discussion

Initial studies showed that the preparation of a calcium silsesquioxane complex is not straightforward. A metathetical reaction between $[\text{Cy}_7\text{Si}_7\text{O}_9(\text{OLi})_3]$ [20] and CaI_2 failed to give a well-defined product. We therefore decided to try a

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Scheme 1 Preparation of $[\{\mu\text{-Cy}_8\text{Si}_8\text{O}_{13}\}_2\text{Ca}(\text{DME})\text{Ca}(\text{THF})_2]$ (**2**).

preparative route starting directly from Ca metal. It is well established in the previous literature that the formation of organocalcium compounds or calcium amides, alkoxides, and siloxides can be greatly accelerated through the presence of ammonia [21]. This can be achieved either by using liquid ammonia or by saturating ethereal organic solvents with ammonia. In our case, an excess of calcium was dissolved in dry liquid ammonia and treated with a solution of **1** in THF. The ammonia was allowed to evaporate, and the crude product obtained after removing the THF was recrystallized from DME to afford a colorless crystalline material. The ^1H NMR spectrum indicated the presence of both THF and DME in the product. Quite surprisingly, the ^{29}Si NMR spectrum displayed eight distinct signals, which is in contrast to the C_{3v} symmetry of the starting material **1** and the presence of only seven Si atoms. An informative

mass spectrum of the product could not be obtained. Fortunately, the crystals obtained by slow cooling of a DME solution were suitable for X-ray diffraction. The single-crystal X-ray structural analysis revealed the presence of the first calcium metallasilsesquioxane which unexpectedly contains difunctional $(\text{Cy}_8\text{Si}_8\text{O}_{13})^{2-}$ dianions as bridging ligands. Thus the overall reaction can be formulated as illustrated in Scheme 1.

Figure 1 shows the molecular structure of **2**. Crystal and structure refinement data are summarized in Table 1, while selected bond lengths (\AA) and angles ($^\circ$) for **2** are listed in Table 2. Similar to previously reported metallasilsesquioxanes *e.g.* of beryllium [12] and indium [22], compound **2** is a dinuclear complex in which the two Ca^{2+} ions are bridged by two silsesquioxane cages. The X-ray study confirms the presence of both THF and DME as additional ligands completing the coordination sphere of calcium. However, the most surprising structural feature of **2** is the presence of difunctional $(\text{Cy}_8\text{Si}_8\text{O}_{13})^{2-}$ dianions acting as bridging ligands despite the fact that pure $\text{Cy}_7\text{Si}_7\text{O}_9(\text{OH})_3$ (**1**) was used as starting material. There is only one report in the literature on the formation of the same *octasilsesquioxane* ligand starting from **1** [23]. Treatment of $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3$ with two equivalents of **1** in diethyl ether in the presence of an excess of pyridine afforded the diamagnetic cerium(IV) complex $[\{\text{Cy}_8\text{Si}_8\text{O}_{13}\}_2\text{Ce}(\text{py})_3]$ in low yield. The same compound could also be prepared in a more deliberate way [23] by reaction of either $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3$ or anhydrous CeCl_3 with two equivalents of the “correct” precursor $\text{Cy}_8\text{Si}_8\text{O}_{11}(\text{OH})_2$ [24] in a THF/pyridine mixture. In both the cerium and the calcium case it is not clear how the octasilsesquioxane ligand $(\text{Cy}_8\text{Si}_8\text{O}_{13})^{2-}$ is formed during the course of the reaction. However, in the case of the Ca com-

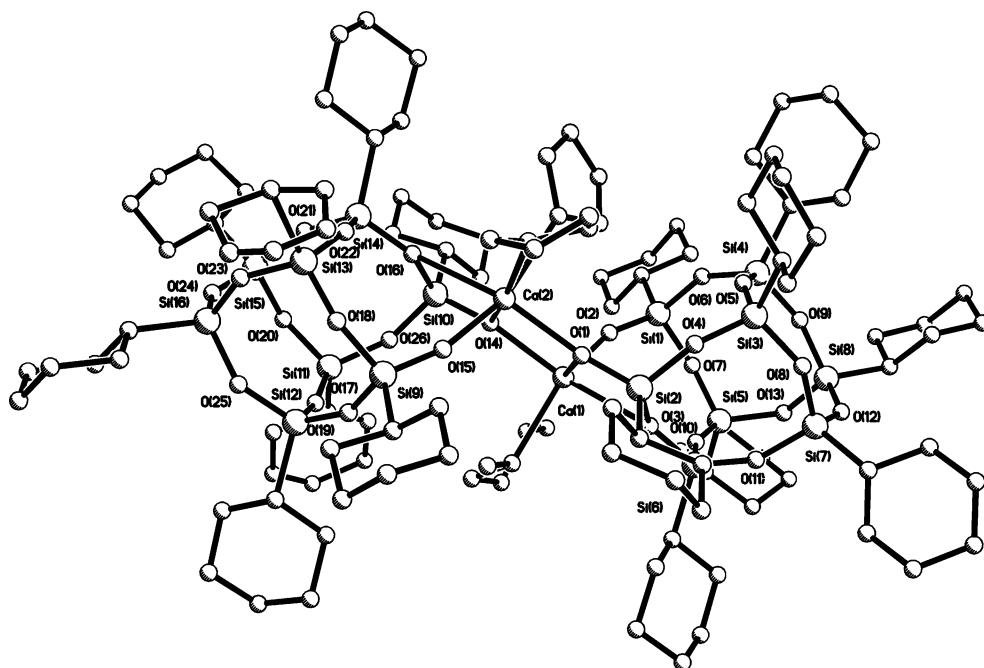


Figure 1 Molecular structure of **2**.

plex **2** it is plausible to assume a cage rearrangement reaction under the chosen reaction conditions as the compound is not just a minor by-product but can be isolated in about 50–60 % yield (the exact yield cannot be precisely calculated due to the silsesquioxane cage rearrangement). Notable in both cases is the fact that the reactions are accompanied by oxidation of the metal atoms (Ce³⁺ → Ce⁴⁺, Ca⁰ → Ca²⁺). Despite that, the mechanism of the silsesquioxane cage rearrangement remains unknown.

Table 1 Crystal data and structure refinement for [μ -C₈Si₈O₁₃]₂-Ca(DME)Ca(THF)₂ (**2**)

Empirical formula	C ₁₁₂ H ₂₁₀ Ca ₂ O ₃₁ Si ₁₆
Formula weight	2582.40
Temperature / K	180(2)
Wavelength / Å	0.71073
Crystal system, space group	monoclinic, P2 ₁ (1)
Unit cell dimensions	<i>a</i> = 14.281(3) Å <i>b</i> = 25.509(5) Å <i>c</i> = 20.440(4) Å β = 107.16(3)°
<i>V</i> / Å ³	7115(2)
<i>Z</i> , Calculated density / g cm ⁻³	2, 1.205
Absorption coefficient / mm ⁻¹	0.280
F(000)	2788
Crystal size	0.50 x 0.40 x 0.40 mm
θ range for data collection	3.18° to 28.08°
Limiting indices	-17 ≤ <i>h</i> ≤ 18, -33 ≤ <i>k</i> ≤ 33, -26 ≤ <i>l</i> ≤ 26
Reflections collected	58630
Reflections unique	33616 [<i>R</i> (int) = 0.0820]
Completeness to θ = 28.08	98.3 %
Absorption correction	None
Max. and min. Transmission	0.8962 and 0.8726
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	33616 / 1 / 1489
Goodness-of-fit on F ²	0.834
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0648, <i>wR</i> ₂ = 0.1295
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1345, <i>wR</i> ₂ = 0.1516
Absolute structure parameter	0.53(4)
Largest diff. peak and hole / e · Å ⁻³	0.776 and -0.312

The coordination around both calcium ions in **2** is highly distorted octahedral, with the calcium atom being bonded to oxygen atoms only. Hexacoordination results from bonding of two siloxide oxygen atoms (one bridging and one terminal), two O atoms of the solvent ligands, and one cage oxygen atom. Interactions of cage oxygen atoms with the metal atoms in metallasilsesquioxanes is not uncommon and has for example been observed in structurally characterized lithium and potassium derivatives of **1** [20, 25]. With Ca-O distances in the range of of 2.233(4)–2.349(4) Å the bonding to the bridging siloxide oxygen atoms is slightly unsymmetrical, as was observed in a calcium β -diketiminato complex containing (Me₃SiO)⁻ bridging ligands [21b]. These distances can also favorably be compared to the Ca-O bond lengths in the structurally characterized calcium triphenylsiloxide derivative [(Ph₃SiO)₄Ca(NH₃)₄(toluene)_{0.5}] (Ca-O: 2.252(5), 2.334(5), and 2.462(5) Å). In this compound three of the siloxide anions act as bridging ligands [26]. With Ca(1)-O(2) 2.174(4) Å and Ca(2)-O(15) 2.165(4) Å the Ca-O distances to the siloxide functions of the silsesquioxane ligands are significantly shorter. All other distances and angles within the silsesquioxane framework are in the normal range.

Table 2 Selected bond lengths/Å and angles/° for [μ -C₈Si₈O₁₃]₂-Ca(DME)Ca(THF)₂ (**2**)

Bond lengths			
Ca(1)-O(2)	2.174(4)	Ca(2)-O(4L)	2.439(5)
Ca(1)-O(14)	2.233(4)	Ca(2)-O(3L)	2.443(4)
Ca(1)-O(1)	2.349(4)	Ca(2)-O(16)	2.844(4)
Ca(1)-O(1L)	2.417(5)	Si(1)-O(2)	1.556(4)
Ca(1)-O(2L)	2.521(4)	Si(1)-O(6)	1.634(4)
Ca(1)-O(3)	2.635(3)	Si(1)-O(7)	1.667(4)
Ca(2)-O(15)	2.165(4)	Si(2)-O(1)	1.575(4)
Ca(2)-O(1)	2.254(4)	Si(2)-O(4)	1.630(4)
Ca(2)-O(14)	2.318(4)	Si(2)-O(3)	1.675(4)
Si(9)-O(15)	1.556(5)		
Si(9)-O(18)	1.640(5)		
Si(9)-O(17)	1.642(5)		
Si(10)-O(14)	1.582(4)		
Si(10)-O(26)	1.623(4)		
Si(10)-O(16)	1.659(4)		
Bond angles			
O(2)-Ca(1)-O(14)	105.7(1)	O(15)-Ca(2)-O(1)	107.6(1)
O(2)-Ca(1)-O(1)	117.0(1)	O(15)-Ca(2)-O(14)	107.7(1)
O(14)-Ca(1)-O(1)	79.0(1)	O(1)-Ca(2)-O(14)	79.3(1)
O(2)-Ca(1)-O(1L)	88.6(1)	O(15)-Ca(2)-O(4L)	87.5(1)
O(14)-Ca(1)-O(1L)	100.9(1)	O(1)-Ca(2)-O(4L)	105.4(1)
O(1)-Ca(1)-O(1L)	153.8(1)	O(14)-Ca(2)-O(4L)	162.2(1)
O(2)-Ca(1)-O(2L)	152.2(1)	O(15)-Ca(2)-O(3L)	158.5(1)
O(14)-Ca(1)-O(2L)	91.2(1)	O(1)-Ca(2)-O(3L)	89.5(1)
O(1)-Ca(1)-O(2L)	87.4(1)	O(14)-Ca(2)-O(3L)	87.7(1)
O(1L)-Ca(1)-O(2L)	66.3(1)	O(4L)-Ca(2)-O(3L)	75.3(1)
O(2)-Ca(1)-O(3)	96.8(1)	O(15)-Ca(2)-O(16)	89.2(1)
O(14)-Ca(1)-O(3)	140.1(1)	O(1)-Ca(2)-O(16)	137.8(1)
O(1)-Ca(1)-O(3)	61.4(1)	O(14)-Ca(2)-O(16)	58.7(1)
O(1L)-Ca(1)-O(3)	112.4(1)	O(4L)-Ca(2)-O(16)	114.0(1)
O(2L)-Ca(1)-O(3)	83.0(1)	O(3L)-Ca(2)-O(16)	86.3(1)

In summarizing the results reported here, the reaction of Ca metal in liquid ammonia with the incompletely condensed silsesquioxane trisilanol **1** provided an access to the first metallasilsesquioxane derivative of calcium. This is only the second example of a metal complex containing the difunctional (C₈Si₈O₁₃)²⁻ dianion as ligand. It can be expected that related metallasilsesquioxanes of strontium and barium are accessible in a similar manner.

Experimental Section

The reaction was carried out in an atmosphere of dry nitrogen with the use of standard Schlenk techniques. THF and DME were dried over Na/benzophenone and freshly distilled under nitrogen prior to use. The IR spectrum was recorded on a Perkin Elmer FT-IR Spectrometer System 2000. NMR spectra were recorded on a Bruker DPX 400 NMR spectrometer (¹H 400.13 MHz, ¹³C 101.62 MHz, ²⁹Si 79.49 MHz). Chemical shifts are reported in ppm and referenced to residual solvent resonances (¹H, ¹³C) or an internal standard (²⁹Si: TMS = 0 ppm). The elemental analysis was performed at the Chemistry Department of the Otto-von-Guericke-Universität using a Leco CHNS 932 apparatus. The starting material Cy₇Si₇O₉(OH)₃ (**1**) was prepared according to a literature procedure [27].

Preparation of 2: A solution of 2.0 g (2.05 mmol) Cy₇Si₇O₉(OH)₃ (**1**) in 100 ml THF was added to 0.3 g (7.32 mmol) of Ca metal, dissolved in liquid NH₃ at -40 °C. The reaction mixture was allowed to warm up to room temperature and was stirred for 12 h. Insoluble particles were filtered off, and the solvent was evaporated in vacuum. The solid residue was recrystallized from DME to afford 1.35 g of [μ -C₈Si₈O₁₃]₂Ca(DME)Ca(THF)₂ (**2**) as colorless crystals. These crystals contain one additional equivalent of THF which is lost upon thorough drying in vacuum. Analysis calcd for

$C_{112}H_{210}Ca_2O_{31}Si_{16}$ ($M = 2582.4 \text{ g}\cdot\text{mol}^{-1}$): C 52.09, H 8.20; found C 51.64, H 7.87 %.

^1H NMR (400.1 MHz, THF- d_8 , 22 °C): 3.56 (br s, 8H, $-\text{CH}_2\text{O}-$, THF), 3.36 (s, 4H, $-\text{CH}_2\text{O}-$, DME), 3.20 (s, 6H, $\text{CH}_3\text{O}-$, DME), 1.90–1.50 (br m, 80H, CH_2 , $c\text{-C}_6\text{H}_{11}$); 8H, $-\text{CH}_2-$, THF), 1.35–1.00 (br m, 80H, CH_2 , $c\text{-C}_6\text{H}_{11}$), 0.75–0.55 (br m, 16H, $-\text{CH}-\text{Si}$, $c\text{-C}_6\text{H}_{11}$) ppm. ^{13}C NMR (100.6 MHz, THF- d_8 , 22 °C): 72.7 ($-\text{CH}_2\text{O}-$, DME), 68.1 ($-\text{CH}_2\text{O}-$, THF), 58.9 ($\text{CH}_3\text{O}-$, DME), 30.0–27.4 ($-\text{CH}_2-$, $c\text{-C}_6\text{H}_{11}$) 26.3 ($-\text{CH}_2-$, THF), 25.8–24.0 ($-\text{CH}-\text{Si}$, $c\text{-C}_6\text{H}_{11}$) ppm. ^{29}Si NMR (79.5 MHz, THF- d_8 , 22 °C): -64.5 , -65.2 , -69.5 , -69.6 , -69.7 , -72.1 , -72.4 , -73.3 ppm. IR (KBr): 2919vs, 2849vs, 2666w, 1494m, 1448s, 1268s, 1196vs, 1119vs, 894s, 848m, 825m, 739w, 687w, 515vs, 466m, 415m cm^{-1} .

The X-ray crystallographic study of **2** was carried out on a Stoe IPDS 2T with MoK_α -radiation ($\lambda = 0.71073 \text{ \AA}$) and graphite monochromator. Data were collected at 180(2). The structure was solved by direct methods using SHELXS-97 [28a] and refined using SHELXL-97 [28b]. Refinement was by full-matrix least-squares on F^2 . Anisotropic thermal parameters were refined for all non-hydrogen atoms. The structure was refined in the chiral space group $P2_1$ as a racemic twin. All treatments to refine it in the centrosymmetric spacegroup $P2_1/m$ failed. Furthermore the program PLATON [28c] did not suggest additional obvious symmetry. Crystallographic data for the crystal structures reported in this paper can be obtained from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or [www.http://ccdc.cam.ac.uk](http://ccdc.cam.ac.uk)) by referring to the CIF deposition code CCDC 654593 for **2**.

References

- Recent review articles: a) V. Lorenz, A. Fischer, S. Gießmann, J. W. Gilje, Yu. Gun'ko, K. Jacob, F. T. Edelmann, *Coord. Chem. Rev.* **2000**, 206–207, 321; b) R. Duchateau, *Chem. Rev.* **2002**, 102, 3525; c) R. W. J. M. Hanssen, R. A. van Santen, H. C. L. Abbenhuis, *Eur. J. Inorg. Chem.* **2004**, 675; d) V. Lorenz, F. T. Edelmann, *Adv. Organomet. Chem.* **2005**, 53, 101.
- H. C. L. Abbenhuis, *Chem. Eur. J.* **2000**, 6, 25.
- P. G. Harrison, *J. Organomet. Chem.* **1997**, 542, 141.
- J. D. Lichtenhan, *Comments Inorg. Chem.* **1995**, 17, 115.
- F. J. Feher, D. A. Newman, J. F. Walzer, *J. Am. Chem. Soc.* **1989**, 111, 1741.
- M. G. Voronkov, V. L. Lavrentyev, *Top. Curr. Chem.* **1982**, 102, 199.
- F. J. Feher, T. A. Budzichowski, R. L. Blanski, K. J. Keller, J. W. Ziller, *Organometallics* **1991**, 10, 2526.
- F. J. Feher, T. A. Budzichowski, *Polyhedron* **1995**, 14, 3239.
- J. R. Severn, R. Duchateau, R. A. van Santen, D. D. Ellis, A. L. Spek, G. P. A. Yap, *Dalton Trans.* **2003**, 2293.
- R. Murugavel, A. Voigt, M. G. Walawalkar, H. W. Roesky, *Chem. Rev.* **1996**, 96, 2205.
- T. W. Hambley, T. Maschmeyer, A. F. Masters, *Appl. Organomet. Chem.* **1992**, 6, 253.
- V. Lorenz, A. Fischer, F. T. Edelmann, *Inorg. Chem. Commun.* **2000**, 3, 292.
- J.-C. Liu, *Chem. Commun.* **1996**, 1109.
- J. C. Liu, *Appl. Organomet. Chem.* **1999**, 13, 295.
- T. S. Haddad, J. D. Lichtenhan, *J. Inorg. Organomet. Polym.* **1995**, 5, 237.
- P. Smet, J. Riondato, T. Pauwels, L. Moens, L. Verdonck, *Inorg. Chem. Commun.* **2000**, 3, 557.
- R. W. J. M. Hanssen, A. Meetsma, R. A. van Santen, H. C. L. Abbenhuis, *Inorg. Chem.* **2001**, 40, 4049.
- N. Maxim, P. C. M. M. Magusin, P. J. Kooyman, J. H. M. C. van Wolput, R. A. van Santen, H. C. L. Abbenhuis, *Chem. Mater.* **2001**, 13, 2958.
- a) T. J. Boyle, B. A. Hernandez-Sanchez, C. M. Baros, L. N. Brewer, M. A. Rodriguez, *Chem. Mater.* **2007**, 19, 2016; b) S. Katayama, Y. Nonaka, K. Iwata, Y. Kubo, N. Yamada, *Adv. Mater.* **2005**, 17, 2596.
- V. Lorenz, S. Gießmann, Yu. K. Gun'ko, A. K. Fischer, J. W. Gilje, F. T. Edelmann, *Angew. Chem.* **2004**, 116, 4703; *Angew. Chem. Int. Ed.* **2004**, 43, 4603.
- a) S. R. Drake, D. J. Otway, *J. Chem. Soc., Chem. Commun.* **1991**, 517; b) J. A. Darr, S. R. Drake, M. B. Hursthouse, K. M. A. Malik, *Inorg. Chem.* **1993**, 32, 5704; c) I. Baxter, J. A. Darr, S. R. Drake, M. B. Hursthouse, K. M. A. Malik, D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.* **1997**, 2875.
- V. Lorenz, A. Fischer, K. Jacob, F. T. Edelmann, *Inorg. Chem. Commun.* **2003**, 6/7, 795.
- Yu. K. Gun'ko, R. Reilly, F. T. Edelmann, D. Stalke, *Angew. Chem.* **2001**, 113, 1319; *Angew. Chem. Int. Ed.* **2001**, 40, 1279.
- a) F. J. Feher, D. Soulivong, A. G. Eklund, *Chem. Commun.* **1998**, 399; b) F. J. Feher, R. Terroba, D. Soulivong, A. G. Nguyen, *Chem. Commun.* **1998**, 1279; c) F. J. Feher, R. Terroba, J. W. Ziller, *Chem. Commun.* **1999**, 2309.
- V. Lorenz, F. T. Edelmann, *Z. Anorg. Allg. Chem.* **2004**, 630, 1147, and references cited therein.
- A. G. Avent, M. R. Crimmin, M. S. Hill, P. B. Hitchcock, *J. Organomet. Chem.* **2006**, 691, 1242.
- F. J. Feher, D. A. Newman, J. F. Walzer, *J. Am. Chem. Soc.* **1989**, 111, 1741.
- a) G. M. Sheldrick, *SHELXS-97 Program for Crystal Structure Solution*, Universität Göttingen (Germany) **1997**; b) G. M. Sheldrick, *SHELXL-97 Program for Crystal Structure Refinement*, Universität Göttingen (Germany) **1997**; c) A. L. Spek, *PLATON A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, Netherlands, **2007**.