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An Efficient Access to Organocerium(iv) Complexes: Synthesis and Structure of Bis[1,3,6-tris(trimethylsilyl)cyclooctatetraene]cerium(iv)**
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Dedicated to Professor Wolfgang Lüttke on the occasion of his 75th birthday

The synthesis of stable organometallic compounds containing tetravalent cerium is one of the challenges in the field of preparative organo-f-element chemistry.** The main reason why numerous attempts at the synthesis of organocerium(iv) complexes have failed is the strong oxidizing effect of the cerium(iv) ion (E° for Ce⁴⁺/Ce⁴⁺ = 1.28 V) in HCl: + 1.28 V; in 8 M HClO₄: + 1.87 V[12]. Thus, in reactions with organometallic reagents such as Na₅C₅H₅, the cerium(iv) reagents (NH₄)₂[Ce(NO₃)₄] or [pyH]₂[CeCl₄] are readily accessible by metalation of 1,4-bis(trimethylsilyl)cyclooctadiene.[14] The starting material can be obtained in a one-pot reaction from 1,5-cyclooctadiene.[15] The reaction of 3 with anhydrous cerium trichloride in a molar ratio of 2:1 leads to the bright green anionic sandwich complex 4, which because of its extreme sensitivity to oxidation was not isolated but immediately converted to the neutral cerium(iv) derivative. The desired oxidation to yield 5 occurs smoothly and under mild conditions with an excess of silver iodide as oxidizing agent. Bis[1,4-bis(trimethylsilyl)cyclooctatetraene]cerium(iv) (5) is the first readily accessible derivative of I, which is sufficiently soluble to allow reactivity studies. Spectroscopically pure, diamagnetic 5 is obtained as a deep purple oil, which thermally decomposes only above 226 °C. In contrast to the pyrophoric parent compound 1,[11] compound 5 can be handled in air for short periods of time. In the EI mass spectrum the molecular ion appears as the highest mass peak with 6% relative intensity.

** This work was supported by the Fonds der Chemischen Industrie, by the Deutsche Forschungsgemeinschaft, and by the BASF AG.

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[2] This work was supported by the Fonds der Chemischen Industrie, by the Deutsche Forschungsgemeinschaft, and by the BASF AG.

[3] Ce⁴⁺/Ce⁴⁺: 1.28 V; in 8 M HClO₄: + 1.87 V[12].

[4] The starting material can be obtained in a one-pot reaction from 1,5-cyclooctadiene.[15] The reaction of 3 with anhydrous cerium trichloride in a molar ratio of 2:1 leads to the bright green anionic sandwich complex 4, which because of its extreme sensitivity to oxidation was not isolated but immediately converted to the neutral cerium(iv) derivative. The desired oxidation to yield 5 occurs smoothly and under mild conditions with an excess of silver iodide as oxidizing agent.

[5] Bis[1,4-bis(trimethylsilyl)cyclooctatetraene]cerium(iv) (5) is the first readily accessible derivative of I, which is sufficiently soluble to allow reactivity studies. Spectroscopically pure, diamagnetic 5 is obtained as a deep purple oil, which thermally decomposes only above 226 °C. In contrast to the pyrophoric parent compound 1,[11] compound 5 can be handled in air for short periods of time.

[6] In the EI mass spectrum the molecular ion appears as the highest mass peak with 6% relative intensity.
equivalents of chlorotrimethylsilane in Et₂O/THF selectively to give 1,3,6,6-tetrakis(trimethylsilyl)cyclooctatetraene (6) which can be isolated as colorless, sublimable needles in 52% yield. The substitution pattern of 6 is confirmed unequivocally by the NMR data. The presence of two trimethylsilyl groups on one carbon atom of the cycle initially made the desired derivatization to give the substituted cyclooctatetraene dianion appear impossible (1,2,4,4-tetrakis(trimethylsilyl)cyclopentadiene cannot be metalated at the cyclopentadiene ring).

Indeed, 6 proved to be completely inert towards n-butyllithium. Surprisingly, the metalation was achieved with potassium hydride; however, a notable reaction was only observed in boiling THF. In addition to the expected deprotonation, a trimethylsilyl group is eliminated in the form of trimethylsilane. This leads to the dipotassium salt of the 1,3,6-tris(trimethylsilyl)cyclooctatetraene dianion 7 (37%). The latter is isolated as a colorless, microcrystalline powder of the composition \([K₂(thf)₃][C₅H₅(SiMe₃)₂]\) and spectroscopically characterized. Subsequent reaction with cerium triflate (molar ratio 2:1) led to the extremely air-sensitive dark green anionic complex 8, which was oxidized in situ with silver iodide to give bis[1,3,6-tris(trimethylsilyl)cyclooctatetraene]cerium(IV) (9). This forms permanganate-colored crystals with a low melting point (m.p. = 38 °C), which are stable in air for a short period of time and very soluble in nonpolar solvents such as pentane, hexane, or toluene. Complex 9 can be vaporized without decomposition; in the EI mass spectrum it exhibits the molecular peak with 14% relative intensity.

Deep purple single crystals of 9 were obtained from acetonitrile. The single-crystal X-ray structure analysis confirms the presence of a neutral cerium(IV) complex (Fig. 1). The two annulene rings are \(η^6\)-coordinated to the cerium atom. The Ce-C distances range from 267.0 to 275.1 pm and are comparable with those of related complexes. The two Ce-C rings in 9 are not coplanar. The ring centroid-Ce-ring centroid angle is 176.1° and is thus almost identical with the corresponding value in the anionic Yb²⁺ derivative \([Yb(C₅H₅(SiMe₃)₂)]^²⁺\). The nonlinear coordination of the metal atom in 9 is probably due to steric reasons. The more open side of 9 is the one at which the Me₃Si groups of Si1 and Si3 (Fig. 1 right) are closest to each other (521.4 pm). In comparison, for example, the Si1···Si4 distance on the closed side is 30 pm longer. All other Si···Si distances range from 570 to 590 pm.

The high solubility of 9 can be attributed to the Me₃Si groups, which interlock like a set of cog wheels (Fig. 2) and surround the metal atom with an organic shell.

In order to determine the rotation barrier in sandwich complexes with the 1,3,6-(Me₃Si)₃C₅H₅ ligand, the uranium complex 10, analogous to 9, was synthesized and its variable-temperature \(^{1}H\) NMR spectra were analyzed. Dark green 10 is readily obtained from the reaction of anhydrous uranium tetrachloride with two equivalents of 7. This complex is also stable in air for a short period of time, whereas the unsubstituted parent compound \([U(C₅H₅)]\) is highly pyrophoric. In the EI mass spectrum of 10 the molecular peak appears with 100% relative intensity. The energy barrier for the rotation of the two sub-


The further development of the redox chemistry of 5 and 9 as well as possible applications of these complexes as soluble oxidizing agents in organic synthesis are currently under investigation.

Experimental Procedure

Synthesis and characterization: All work was carried out under a purified N₂ atmosphere.

5: (6.1 g, 24.4 mmol) [14] in THF (50 mL) was treated dropwise with nBuLi (48.8 mmol) at -30 °C. The mixture was allowed to warm to room temperature and stirred for 1 h. To the resulting brown solution was added a suspension of CeCl₃ (2.0 g, 12.4 mmol) in Et₂O (150 mL) at -10 °C. The mixture was allowed to react at room temperature, filtered carefully, and the filtrate was evaporated to dryness under vacuum. The crude product was treated with dry MeOH (250 mL) and filtered while hot to remove the insoluble material. Cooling to ca. 30 °C afforded pale yellow, needle-like crystals of 5 (2.4 g, 52%), m.p. 87 °C, correct elemental analysis; m.p. 87 °C. Correct elemental analysis; m.p. 87 °C. Correct elemental analysis; m.p. 87 °C.

6: nBuLi (239.6 mmol) was added dropwise to a solution of 2 (30 g, 119.8 mmol) [14] in THF (200 mL) at -30 °C. Subsequently the solution was allowed to warm to room temperature and stirred for a further 12 h. The resulting deep brown solution was washed with water (3 x 239 mL) and extracted with Et₂O (2 x 150 mL) at -10 °C. The mixture was allowed to react at room temperature, filtered carefully, and the filtrate was evaporated to dryness under vacuum. The crude product was treated with dry MeOH (250 mL) and filtered while hot to remove the insoluble material. Cooling to ca. 30 °C afforded pale yellow, needle-like crystals of 6 (2.4 g, 52%), m.p. 87 °C, correct elemental analysis; m.p. 87 °C.
Mixed-Valence, Tetranuclear Iron Chelate Complexes as Endoreceptors: Charge Compensation Through Inclusion of Cations**

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Dedicated to Professor Helmut Ringsdorf on the occasion of his 65th birthday

An essential prerequisite for the rapid development of endohedral chemistry, that is chemistry within cages, is easy access to host molecules of variable internal diameter. In this context we have recently reported the tetranuclear adamantanoid Fe"*** spacer-complex [Fe4L"2]11** Complex I is endowed with a substantial cavity, which should, in principle, be suitable for the uptake of guest molecules. Our attempts to obtain the spacer-free metallospherand core unit [Fe4L"2] in analogous manner have thus far given rise to products which could not be characterized unambiguously.

In contrast, we have obtained for the first time, the tetranuclear, mixed-valence ammonium inclusion complexes [NH4+<Fe4L"2>]2 and [NH4+<Fe4L"2>]3 in a one-pot reaction [3] Complexes 2 and 3 are formed by spontaneous self-assembly[14, 47] from the reaction of dialkyl malonates with methyl-lithium/iron(n) chloride and oxalyl chloride at -78 °C in tetrahdrofurarn, followed by workup with aqueous ammonium

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**[**] "Adamantanoid" Chelate Complexes, Part 4. This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie. We thank Prof. Dr. F. Vögtle and Dr. S. Schuh, Universität Bonn, and Prof. Dr. K.-P. Zeller, Universität Tübingen for the measurement of the FAB mass spectra. Part 3: ref. [3].

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