Novel, Highly Symmetrical Halogen-Centered Polynuclear Lanthanide Complexes: $[Cp_6Yb_6Cl_{13}]^-$ and $[Cp_{12}Sm_{12}Cl_{24}]$**

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We recently discovered that numerous monocyclopentadienyllanthanide dihalides $[CpLnX_2(thf)_3]$ ($Cp = \eta^5$-C_5H_5) can be readily synthesized as very pure compounds in good yields by using trimethylsilylcyclopentadiene as the alkylating agent [Eq. (a)].[1] In contrast to the metathesis or synpropor-

$$Me_3SiCp + [LnX_3(thf)_n] \xrightarrow[2)\ thf]{1)\ toluene,\ -Me_3SiX,\ -thf} [CpLnX_2(thf)_3] \qquad (a)$$

Ln = La (X = Br, $n = 4$), Ce (Br, 4), Sm (Cl, 3), Yb (Cl, 3)]

tionation reactions reported to date, no coordination of a salt (LiCl, NaCl) nor the often observed multiple alkylation take place.[2,3]

The occurrence of distinct color changes during the synthesis (e.g. colorless →violet →orange in the case of ytterbium) indicated the presence of intermediates. Similar color changes were also observed earlier, in the synthesis of $[CpYbCl_2(thf)_3]$.[4] Recrystallization of the sparingly soluble residues, obtained after alkylation in toluene, led to compounds **1** and **2**, which contain very little or no THF, respectively. Single crystals of **1** and **2** could be reproducibly obtained by treating the THF adducts $[CpLnCl_2(thf)_3]$ (Ln = Sm, Yb) with hot toluene and simultaneous removal of the evolved tetrahydrofuran by distillation.

$[CpYbCl_2] \cdot {}^1/_3\,thf \cdot {}^2/_9\,toluene$ **1**

$[CpSmCl_2] \cdot {}^1/_6\,toluene$ **2**

Complex **1** exhibits an ionic structure, $[Cp_3Yb_3(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_3(thf)_3][Cp_6Yb_6(\mu_6\text{-}Cl)(\mu\text{-}Cl)_{12}] \cdot 2\,C_7H_8$, built up of trinuclear cations and hexanuclear anions (Figure 1).[5] The cation consists of an equilateral triangle of Yb atoms which are connected by doubly bridging Cl atoms over the edges ($\bar{d}$(Yb – Cl) 2.662 Å) and by triply bridging Cl atoms on either side of the triangular plane ($\bar{d}$(Yb – Cl) 2.764 Å). Three cyclopentadienyl ligands ($\bar{d}$(Yb – Cp_z) 2.29 Å) on one side of the plane and three THF ligands ($\bar{d}$(Yb – O) 2.25 Å) on the other side result in pseudooctahedral coordination for each Yb atom.[6] Thus, the cation can be assigned the quite common M_3X_{11} constitution.[7] The six Yb atoms of the anion in **1**

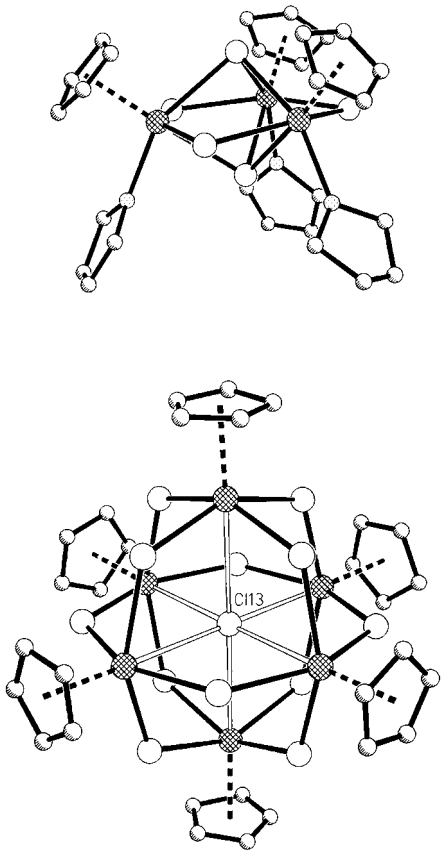

Figure 1. Crystal structure of the trinuclear cation $[Cp_3Yb_3Cl_5(thf)_3]^+$ (top) and the Cl-centered octahedral anion $[Cp_6Yb_6Cl_{13}]^-$ (bottom) of **1**.

delineate an almost regular octahedron, the edges of which are bridged by 12 Cl atoms with nearly equal Yb – Cl bond lengths of 2.61 – 2.67 Å. An additional Cl(13) atom with markedly longer Yb – Cl bond lengths of 3.14 – 3.28 Å lies at the center of the octahedron. The sixth coordination site of each Yb atom is occupied by a cyclopentadienyl ligand ($\bar{d}$(Yb – Cp_z) 2.29 Å). Thus, the anion exhibits uncommon high symmetry. In contrast, other hexanuclear complexes obtained from solutions, such as $[Cp^*_6Sm_6Se_{11}]$ ($Cp^* = \eta^5$-C_5Me_5) and $[\{Nd_3(\mu_3\text{-}OR)(\mu\text{-}OR)_3\}_2(OR)_3(\mu_6\text{-}Cl)]$ exhibit strongly distorted skeletons,[8,9] whereas the symmetrical octahedron in $[K(thf)_4]_2[Cp^s_6Yb_6I_8]$ ($Cp^s = \eta^5$-$C_5Me_4(SiMe_2$-tBu)) is not centered by a halogen and contains divalent Yb ions.[10]

An even greater degree of oligomerization than that attained in **1** is displayed by complex **2** $[Cp_{12}Sm_{12}(\mu_3\text{-}Cl)_{24}] \cdot 2\,C_7H_8$, which is built up from neutral molecules.[11] An X-ray crystal structure analysis showed that twelve $[CpSmCl_2]$ units are linked to produce the whole molecule, whereby the Sm atoms take up an icosahedral arrangement (Figure 2). The total molecular skeleton has 222 crystallographic symmetry with three twofold axes which intersect at the center of the molecule. As a result, only three Sm and six Cl atoms as well as three Cp ligands are crystallographically independent. Each Sm atom has a strongly distorted pentagonal-bipyramidal coordination sphere made up of six Cl atoms and one Cp ligand. Each Cl atom caps a triangle of samarium atoms, so that 20 Cl atoms form an "outer" pentagonal-dodecahedral

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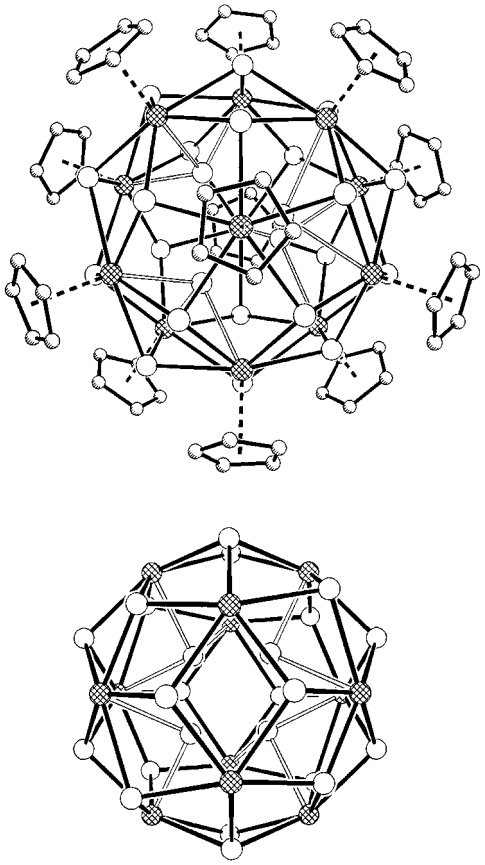

Figure 2. Top: Molecular structure of $[Cp_{12}Sm_{12}Cl_{24}]$ viewed along one of the six fivefold pseudoaxes. Bottom: Structure of the $Sm_{12}Cl_{24}^{-}$ skeleton of **2** with 20 outer and four inner Cl atoms viewed along one of the three twofold axes. The Sm atoms are represented as hatched circles, the Cl atoms as open circles, and the inner Sm–Cl bonds as double lines.

envelope (Sm–Cl_o distances in the range of 2.67–3.09 Å), and the other four Cl atoms form an "inner" tetrahedron(Cl_i–Cl_i 3.29 Å) at the center of the Sm icosahedron (Sm–Cl_i 2.95 Å). The arrangement of the 60 C atoms of the 12 Cp ligands ($\bar{d}$(Sm–Cp_z) 2.36 Å) corresponds to a truncated icosahedron, and is somewhat analogous to the C_{60} fullerene. The overall structure makes the Sm icosahedron unique—not only in lanthanide chemistry.

A comparison of the two complexes very effectively demonstrates the influence of the analogous reactivity of lanthanides with differing ionic radii on the structure. Thus, a pseudooctahedral environment (CN = 6) is a structural feature of monomeric $[CpLnCl_2(thf)_3]$ complexes, and is independent of the ionic radius.[12] If the bulky THF ligands are exchanged for the smaller μ-Cl atoms with a simultaneous elongation of the bond lengths, this leads to an increase in the coordination number from six to seven. This is the case in the analogous π-arene complexes $[(\eta^6\text{-arene})Ln(AlCl_4)_3]$, in all of which the Ln atom has a pentagonal-bipyramidal coordination sphere consisting of six μ-Cl atoms (between Ln and Al) and one arene ligand.[13] However, the coordination number seven can only be attained by the $[CpLnCl_2]$ complexes if each terminal Cl atom of the monomer becomes a μ_3-Cl atom in the oligomer. These conditions are excellently fulfilled in the Sm icosahedron, which, along with the pentagonal symmetry, also provides a cavity large enough to accommodate four Cl atoms. On the other hand, the smaller Yb ions ($r_{Yb} = 0.925$ Å, $r_{Sm} = 1.020$ Å for CN = 7)[14] prefer an octahedral Yb_6 arrangement with CN = 6.

The new compounds **1** and **2** prove very impressively, that in spite of analogous reactivity the lanthanides are capable of a rich and novel structural chemistry. It is expected that a systematic investigation of the removal of THF from the mononuclear monocyclopentadienyl compounds should lead to the isolation of new types of multinuclear complexes for the whole series of lanthanides.

Experimental Section

All the preparative work was carried out under an N_2 atmosphere.

1: A suspension of $[YbCl_3(thf)_3]$ (2.73 g, 5.5 mmol) and $C_5H_5SiMe_3$ (0.84 mL, 5 mmol) in toluene (50 mL) was heated at reflux for 24 h. After removal of the solvent under vacuum, the residue was washed with toluene until it was only slightly colored and then recrystallized from toluene. Slow cooling of the solution to room temperature gave violet prisms, which were filtered and dried under vacuum. Yield: 0.90 g (51 %). Elemental analysis $C_{71}H_{85}Cl_{18}O_3Yb_9$: calcd (found) C 26.80 (27.01), H 2.67 (2.78); IR (KBr, Nujol): $\tilde{\nu}$ [cm^{-1}] = 3097, 3081, 1688, 1681, 1673, 1651, 1038, 1012 (vs), 919, 854 (vs), 794 (vs), 788 (vs), 736, 694, 464.

2: A suspension of $[CpSmCl_2(thf)_3]$ (0.20 g, 0.4 mmol) in toluene (20 mL) was heated at reflux for 24 h with simultaneous removal of the solvent by distillation. The residue was repeatedly extracted with toluene (10 mL) at 80 °C until orange crystals formed. The liquid was decanted, and the crystals washed with a little toluene and dried under vacuum. Yield: 0.044 g (35 %).

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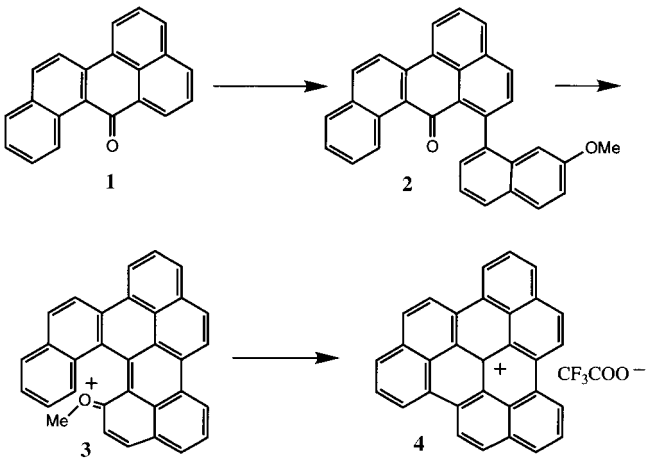
[1] W. P. Kretschmer, S. I. Troyanov, A. Meetsma, J. H. Teuben, *Proc. 31st Int. Conf. Coordination Chemistry, 18–23 Aug. 1996, Vancouver, Canada,* **1996**, abstr. p. 176.
[2] Review on lanthanide complexes: H. Schumann, J. A. Meese-Marktscheffel, L. Esser, *Chem. Rev.* **1995**, *95*, 865–986.
[3] Review on monocyclopentadienyl complexes: R. Poli, *Chem. Rev.* **1991**, *91*, 509–551.
[4] M. Adam, X.-F. Li, W. Oroschin, R. D. Fischer, *J. Organomet. Chem.* **1985**, *296*, C19–C22.
[5] Crystal data for **1**: monoclinic, $P2_1/c$, $a = 16.262(1)$, $b = 26.376(1)$, $c = 21.742(1)$ Å, $\beta = 101.027(5)^\circ$, $V = 9153.5(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.309$ g cm^{-3}, $T = 295$ K, $1.5 < 2\theta < 48^\circ$ ($Mo_{K\alpha}$, $\lambda = 0.71073$ Å), CAD-4 (Enraf-Nonius); of 14655 reflections, 11333 were independent. The structure was solved by direct methods (SHELXS-86) and refined against $|F^2|$ (SHELXL-93) with 9563 reflections ($F_o^2 \geq 0$) and 912 parameters, wR_2(all) = 0.1070 and R_1(observed) = 0.0641.[11b]
[6] Here and throughout the definition of the coordination polyhedron refers to the arrangement of the σ ligands and the centers of the π ligands. See, for example, *Encyclopedia of Inorganic Chemistry, Vol. 2* (Ed.: R. B. King), Wiley, New York, **1994**, p. 819.
[7] Examples of M_3X_{11}: a) D. L. Clark, J. C. Gordon, J. C. Huffman, J. G. Watkin, B. D. Zwick, *New J. Chem.* **1995**, *19*, 495–502; b) W. J. Evans, M. S. Sollberger, T. P. Hanusa, *J. Am. Chem. Soc.* **1988**, *110*, 1841–1850.
[8] W. J. Evans, G. W. Rabe, M. A. Ansari, J. W. Ziller, *Angew. Chem.* **1994**, *106*, 2200–2201; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2110–2111.
[9] R. A Andersen, D. H. Templeton, A. Zalkin, *Inorg. Chem.* **1978**, *17*, 1962–1965.

  1433-7851/98/3701-0089 $ 17.50+.50/0

[10] S. P. Constantine, G. M. De Lima, P. B. Hitchcock, J. M. Keates, G. A. Lawless, *Chem. Commun.* **1996**, 2421 – 2422.
[11] a) Crystal data for **2**: tetragonal, $I4_1/acd$, $a = 26.822(3)$, $c = 28.071(2)$, $V = 20195(4)$ Å^3, $Z = 8$, $\rho_{calcd} = 2.281$ g cm^{-3}, $T = 273$ K, $3.0 < 2\theta < 39.0^\circ$ ($Mo_{K\alpha}$, $\lambda = 0.71073$ Å), IPDS (Stoe); of 12239 reflections, 2160 were independent. The structure was solved by direct methods (SHELXS-86) and refined against $|F^2|$ (SHELXL-93) with 1568 reflections ($F_o^2 \geq 0$) and 160 parameters, wR_2(all) = 0.1233 and R_1(observed) = 0.0659. b) 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-100593. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code + (44)-1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).
[12] X. Zhou, Z. Wu, H. Ma, Z. Xu, X. You, *Polyhedron* **1994**, *13*, 375 – 378.
[13] a) F. A. Cotton, W. Schwotzer, *J. Am. Chem. Soc.* **1986**, *108*, 4657 – 4658. b) Review: G. B. Deacon, Q. Shen, *J. Organomet. Chem.* **1996**, *506*, 1 – 17.
[14] R. D. Shannon, *Acta Crystallogr. Sect.A* **1976**, *32*, 751 – 767.



Scheme 1. Synthesis of **4** · CF_3COO.

Synthesis of the Trinaphthophenalenium Cation**

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The unique feature of odd-alternant hydrocarbons (i.e., polycyclic hydrocarbons with alternating double bonds and an odd number of carbon atoms), is the readily interconvertible redox triad (cation – radical – anion), which has been the subject of many experimental and theoretical studies. Recently we have disclosed a novel synthetic approach[1] to extended phenalenones as potential precursors of the corresponding odd-alternant hydrocarbons. Here we report the application of this method to the synthesis of the hitherto unknown trinaphthophenalenium cation **4**, a cation of a novel C_{3h}-symmetric odd-alternant hydrocarbon.

Treatment[2] of 7*H*-benzo[*hi*]chrysen-7-one (**1**)[3] with 7-methoxy-1-naphthyllithium (prepared from 7-methoxy-1-naphthyl iodide[4, 5] and *n*BuLi in ether at room temperature) and autooxidation of the resulting adduct in the usual workup afforded 6-(7-methoxy-1-naphthyl)-7*H*-benzo[*hi*]chrysen-7-one (**2**)[6] in 75% yield (Scheme 1). This molecule contains the necessary number of carbons for the construction of the desired trinaphthophenalene skeleton. The methoxy group was deliberately introduced to serve as an auxiliary in the following three key steps of the condensation to the target structure. First, it acts as an electron-donating group to make position 8 reactive enough to react with the central carbonyl group to give **3**. Second, it stabilizes the adjacent cationic center as shown in **3** to increase the chance for the ring-closing condensation with the facing benzene ring. Finally, it can leave as methanol to provide the trinaphthophenalenium cation **4**. Our system worked as beautifully as we had originally conceived.

The reaction proceeded in steps and we could isolate the intermediate **3** as a blue-violet solid after heating **2** in 30% HBr/HOAc at 95°C for 1 h. Although **3** was not fully characterized, the presence of 16 different aromatic protons and three methyl protons in the ^{1}H NMR spectrum supports the proposed structure. When the reaction temperature was increased to 110°C, the final transannular condensation occurred very smoothly to furnish trinaphthophenalenium trifluoroacetate **4** · CF_3COO as a dark violet solid (71% from **2**) after chromatographic purification (silica gel, CF_3COOH).

The characteristic absorption of **4** in acetonitrile ($\lambda_{max}(\varepsilon) =$ 568 (10400)) supports its extensively delocalized π system. The ^{1}H NMR spectrum[7] of **4** consists of four doublets at $\delta =$ 9.74, 9.42, 9.05, and 9.02 and one triplet at $\delta = 8.65$ in accord with the expected C_{3h} symmetry. The FAB mass spectrum (**4** in CF_3COOH/*m*-nitrobenzyl alcohol matrix) shows a peak for the trinaphthophenalenium cation at *m*/*z* 387.1172 (calcd for $C_{31}H_{15}$: 387.1174). As a measure of the thermodynamic stability of the trinaphthophenalenium cation, its pK_{R+} value was determined by spectrophotometric titration in buffered 50% aqueous acetonitrile. Although the titration curve was discontinuous[8] between pH 2.65 and 2.96, the preliminary pK_{R+} value was estimated to be roughly 4.2. Therefore, the stability of cation **4** is comparable to that of the tropylium ion ($pK_{R+} = 4.7$).

The electrochemical behavior of **4** was examined by cyclic voltammetry using a microelectrode (Table 1). Two quasi-reversible redox waves were observed. While the first reduction potential is much higher than that of phenalenium ion, the reverse is true with the second reduction potential. The electrochemical properties of the trinaphthophenalenium system are consistent with the results of semiempirical calculations.[11, 12] Thus, while the LUMO energy of cation **4** (−6.04 eV) is higher than that of phenalenium cation

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