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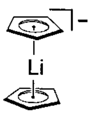
$[Cp_3Ba]^-$: The First Structurally Characterized Barate Complex**

Sjoerd Harder*

In 1994 we reported that the in situ generation of "free" cyclopentadienyl (Cp) anions in the presence of CpLi resulted in the formation of the lithocene anion (**1**).[1] The structure of this complex is remarkably similar to that of its diagonally related neighbor magnesocene (**2**). Analogously, the treatment of Cp_2M (M = alkaline earth metal) with Cp anions could yield a $[Cp_3M]^-$ species. A thorough structural study on such compounds is justified for several reasons.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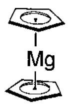
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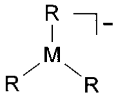
1. Although a few magnesium complexes of the type $[R_3Mg]^-$ have been structurally characterized,[2] at present no structural data are available for heavier alkaline earth metal complexes $[R_3Ca]^-$, $[R_3Sr]^-$, or $[R_3Ba]^-$.
2. How do the structures of $[Cp_3M]^-$ species (M = alkaline earth metal) compare to those of the isovalent Group 3 and Group 13 neighbors?
3. The divalent metallocenes of the heavier alkaline earth metal complexes have an unexpected preference for bent geometries, a structural feature that has attracted and still attracts much attention.[3] A similar trend may be found for the $[Cp_3M]^-$ complexes of the heavier alkaline earth metals. Will the metal center then prefer a planar (**3**) or a pyrimidal (**4**) coordination geometry?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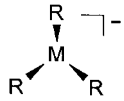
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First results of our studies on $[Cp_3M]^-$ complexes of the alkaline earth metals are presented here: the synthesis and structure elucidation of $[Cp_3Ba]^-$ in the presence of a weakly coordinating cation.

$[Cp_3Ba]^-$ can be synthesized simply by treating Cp_2Ba with a free Cp anion. Accordingly, several synthetic strategies can be employed. Free Cp anions can be generated in situ from CpNa and Ph_4PCl[4] and then treated with Cp_2Ba [Eq. (1)]. Another possibility is the direct reaction of Cp_2Ba with a stoichiometric quantity of Ph_4PCl [Eq. (2)].

$$CpNa + Ph_4PCl + Cp_2Ba \rightarrow [Cp_3Ba]^-[Ph_4P]^+ + NaCl \qquad (1)$$

$$3\,Cp_2Ba + 2\,Ph_4PCl \rightarrow 2\,[Cp_3Ba]^-[Ph_4P]^+ + BaCl_2 \qquad (2)$$

A drawback of both methods is the possible formation of side products such as $[Cp_2Na]^-$, $[Cp_2BaCl]^-$, $[CpBaCl_2]^-$, and other mixed compounds containing a variety of ions (Ba^{2+}, Na^+, Cp^-, and Cl^-). Therefore, a new method for the generation of Cp anions was developed: a Wittig reagent is mixed with cyclopentadiene to give $[Cp]^-[R_4P]^+$, which can be directly treated with Cp_2Ba [Eq. (3)].

$$Bu_3P{=}CHCH_2CH_2CH_3 + CpH + Cp_2Ba \rightarrow [Cp_3Ba]^-[Ph_4P]^+ \qquad (3)$$

The crystals obtained from this reaction mixture[5] had the composition $[Cp_3Ba]^-[Ph_4P]^+[thf]$.[6] The $[Cp_3Ba]^-$ units form a linear coordination polymer (Figure 1) in which the Ba^{2+} cations are tetrahedrally surrounded by four Cp anions. Both the terminal and the bridging Cp anions are bound in an η^5 fashion to the barium centers. The Ba–C distances of the terminal and bridging Cp rings are remarkably similar. The barate $[Cp_3Ba]^-$ is the first structurally characterized unsubstituted Cp–Ba complex. The average Ba–Cp_c distance (Cp_c

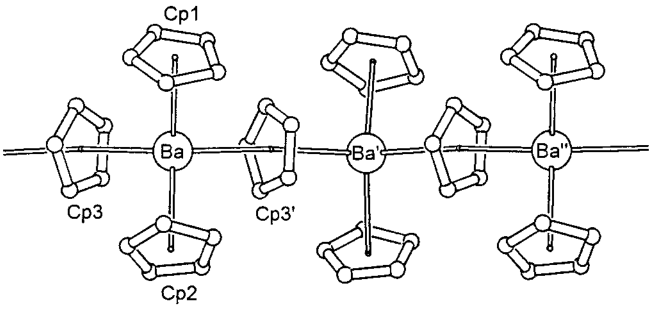

Figure 1. Structure of the linear $[Cp_3Ba]^-_\infty$ chain. All Cp rings are bound to Ba in an η^5 fashion. For the following Ba–C distances [Å] to the rings Cp1, Cp2, Cp3, and Cp3′, the range of Ba–C distances, the mean Ba–C distances, and the Ba–Cp_C distances are given. Cp1: 3.067(5)–3.184(6), 3.123(6), 2.898(6); Cp2: 3.047(7)–3.159(6), 3.096(6), 2.876(6); Cp3: 3.091(7)–3.168(7), 3.129(6), 2.916(6); Cp3′: 3.123(7)–3.220(7), 3.169(7), 2.969(6). The Cp_c-Ba-Cp_c' angles lie in the range 106.4(3)–114.6(3)°.

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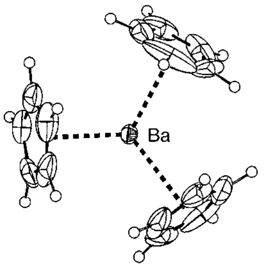


Figure 2. ORTEP plot of the $[Cp_3Ba]^-$ unit (50% probability ellipsoids). The large ellipsoids indicate the rotational disorder around the Ba–Cp$_c$ axes.

represents the geometrical center of the Cp ring) of 2.915(7) Å is considerably longer than that of the decamethyl-substituted barocene Cp^*_2Ba (av. Ba–Cp$_c$ 2.733(6) Å).[3f] Rotational disorder of the Cp rings around the Cp$_c$–Ba axis (Figure 2) indicates a low barrier for rotation of the Cp rings. This was also observed in the structures of the lithocene[1] and sodocene[4] anions.

The parallel $[Cp_3Ba]^-_\infty$ chains are bridged by intervening Bu_4P^+ cations, of which the most acidic PCH_2 protons exhibit short intermolecular CH···Cp$^-$ distances to the terminal Cp anions (Figure 3). These interactions can be regarded as CH···Cp hydrogen bonds between the $C^{\delta-}$–$H^{\delta+}$ dipole and the negatively charged π-electron system of the Cp ring.[7] The shortest CH···Cp distances of 2.65 and 2.68 Å are much shorter than the sum of the van der Waals radii of C and H (2.90 Å) and also shorter than the CH···Cp hydrogen bond of 2.72 Å in the crystal structure of $[Cp]^-[Ph_4P]^+$.[4] This is due to the much higher acidity of a tetrabutylphosphonium group compared to a tetraphenylphosphonium group.[8] In addition, a THF molecule interacts with two other PCH_2 protons (Figure 3). The short H–O distances of 2.65 and 2.66 Å of the intermolecular CH···O$_{THF}$ interactions are in the range observed for other CH···O hydrogen bond interactions.[9]

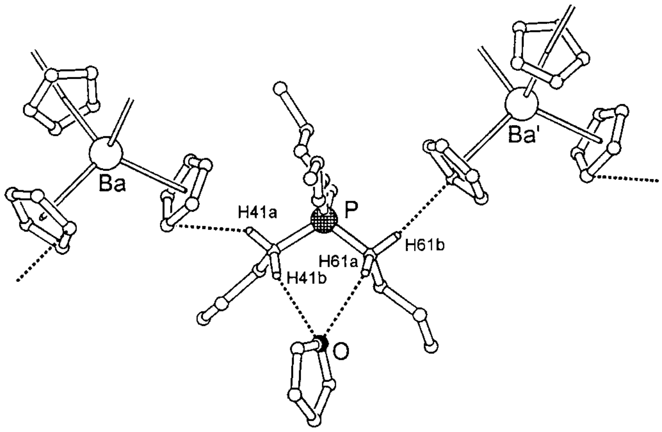
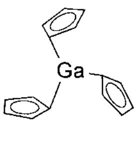


Figure 3. View of the $[Bu_4P]^+$ ion and its interaction with the barate chains. The linear $[Cp_3Ba]^-_\infty$ chains are bridged by $[Bu_4P]^+$ units. The shortest CH···C hydrogen bonds (distances [Å]; angles [°]) are C–H41a···C (C–C 3.529(8), H–C 2.65; C-H-C 147) and C–H61b···C (C–C 3.536(8), H–C 2.68; C-H-C 144). Short CH···O hydrogen bonds: C–H41b···C (C–O 3.586(9), H–O 2.66; C-H-O 153) and C–H61a···O (C–O 3.454(9), H–O 2.65; C-H-O 138). All carbon atoms of the THF molecule are disordered over two positions (the average positions are shown).

How does the structure of the barate anion $[Cp_3Ba]^-$ compare to those of its isovalent Group 3 and Group 13 neighbors? The compound Cp_3Ga (**5**) is a monomer with three η^1-Cp groups and trigonal-planar coordination geometry at the metal center.[10] The complex Cp_3In (**6**) forms a linear polymer chain with a tetrahedral arrangement of ligands. The Cp rings are bound to the metal center with a total hapticity of four.[11] The analogous Group 3 Cp_3M complexes **7**–**9** form coordination polymers in which the total hapticity at the metal center increases with increasing ionic radius of the metal cation: $Cp_3Sc^{[12]} < Cp_3Y^{[13]} < Cp_3La$.[14] Therefore, the polymeric structure of $[Cp_3Ba]^-$ with fourfold η^5-Cp–Ba coordination is not unexpected (the Ba^{2+} cation is, apart from the unstable isotopes Fr^+ and Ra^{2+}, the second largest cation in the periodic table).



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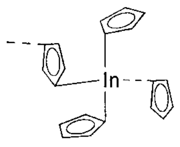

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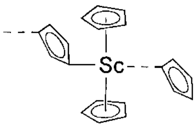

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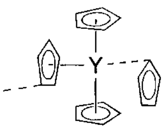

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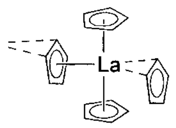

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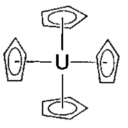
The η^{20} coordination sphere of the Ba^{2+} ion is similar to that in monomeric $[Cp_4U^{IV}]$ (**10**), in which the uranium atom is tetrahedrally surrounded by four η^5-Cp ligands.[15] In solution the $[Cp_3Ba]^-_\infty$ polymer chain is probably broken into solvated monomers. Such solvated monomers could resemble the monosolvates **11**[16] or disolvates **12**[17] (S = solvent) of structurally characterized Cp_3M lanthanide complexes.



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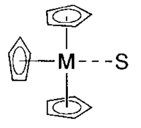

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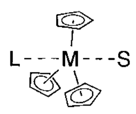

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High-level ab initio calculations[18] on $[Ba(H_2O)_3]^{2+}$ suggest a preference for a pyramidal coordination geometry at the metal center, although the energy difference to the planar geometry is only 0.4 kcal mol^{-1}. At the same level of theory, a bent $[Ba(H_2O)_2]^{2+}$ complex is 1.0 kcal mol^{-1} more stable than its linear form. The calculations on $[Ba(H_2O)_3]^{2+}$ and $[Ba(H_2O)_2]^{2+}$[18] indicate that the energy difference between a pyramidal and a planar barate is even smaller than that between a bent and a linear barocene. Experimental verification of the preferred coordination geometry at a three-coordinate Ba^{2+} ion will probably be difficult. The occurrence of $[Cp_3Ba]^-$ as a polymeric solid structure does not allow any discussion of the preferred ligand arrangement in a barate anion (planar or pyramidal).

The fourfold η^5-Cp–Ba coordination in $[Cp_3Ba]^-_\infty$ suggests that a dianionic species $[Cp_4Ba]^{2-}$ possibly could be isolated as well. Although under certain conditions $[Cp_4Ba]^{2-}[X]^+_2$ complexes can be isolated, many attempts to determine their crystal structures have hitherto failed owing to twinning problems. Even the use of the less symmetric MeCp anion as a ligand only yielded twinned crystals.[19]

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[6] Crystal structure analysis of $[(Cp_3Ba)(Bu_4P)(thf)]$: orthorhombic, $a = 9.6826(8)$, $b = 25.276(2)$, $c = 29.742(4)$ Å, $V = 7279.0(1)$ Å^3, space group *Pbca*, $[(C_{15}H_{15}Ba)(C_{16}H_{36}P) \cdot (C_4H_8O)]$, $M_r = 664.1$, $Z = 8$, $\rho_{calcd} = 1.212$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.158$ mm^{-1}, 7110 reflections were measured on a Enraf Nonius CAD4 diffractometer ($Mo_{K\alpha}$, graphite monochromator, $T = -105$°C), 7110 unique reflections, 4201 observed reflections with $F > 4.0\sigma(F)$, empirical absorption correction (ψ scans). Solution by direct methods with the DIRDIF program.[20] Refinement with the SHELXL-93 program[21] to $R1(F) = 0.041$ and $wR2(F) = 0.075$ (382 parameters; hydrogen atoms in calculated positions). The carbon atoms of the THF molecule were severely disordered and refined as a split model in a 0.55/0.45 ratio. Residual electron density around the THF molecule probably also arises from the presence of small amounts of pyridine instead of THF at this site. The compound was crystallized from THF/pyridine, and NMR analyses in CD_3OD shows that the crystals contain 5–10% pyridine. Geometry calculations and plots were made with the EUCLID package.[22] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100832.

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Solid-Phase Supported Synthesis of the Branched Pentasaccharide Moiety That Occurs in Most Complex Type *N*-Glycan Chains**

Jörg Rademann, Armin Geyer, and
Richard R. Schmidt*

N-glycosylation is a well-known feature of many natural polypeptides in eukaryotic organisms that contributes to their structural as well as functional properties.[1] It determines among others the stability, folding, and intracellular transport of proteins, and is required for cellular adhesion in events such as inflammation, immunogenicity, and metastasis. Unfortunately, naturally occurring *N*-glycans display a high degree of structural diversity, and an array of different carbohydrate isoforms are synthesized even on one type of protein. Varied glycan patterns are expressed in different types of tissues and at different stages of embryonic development. Consequently, for the chemical synthesis of these compounds[2] an approach is needed that intrisically permits a high degree of variation and the application of combinatorial[3] as well as split-synthesis techniques to supply a broad array of natural and

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