

Summary: Metalloccen Compounds of Barium

The present paper describes syntheses and characterizations of barium metallocene compounds with the anionic ligands cyclopentadienyl (C_5H_5), indenyl (Ind), fluorenyl (Fl) and pentamethylcyclopentadienyl (Cp^*). Neutral base adducts of the mentioned complexes were synthesized by the use of macrocyclic polyethers like crown ethers and cryptands. Structure determinations were done by single crystal X-ray analysis (RSA) and by comparative X-ray powder diffraction. As a precursor for the production of barium metallocene complexes, barium-bis(hexamethyldisilazide) ($Ba[N(SiMe_3)_2]_2$) was synthesized by a metalation process with barium metal and hexamethyldisilazane ($HN(SiMe_3)_2$) in the presence of ammonia^[29]. Metalation reactions of the strong Brønstedt-base $Ba[N(SiMe_3)_2]_2$ with the CH-acids cyclopentadiene, indene and fluorene led to the above-mentioned π -complexes bis(cyclopentadienyl)barium, $Ba(C_5H_5)_2$, bis(indenyl)barium, $BaInd_2$ and bis(fluorenyl)barium, $BaFl_2$. The half-sandwich compound pentamethylcyclopentadienyl-barium hexamethyldisilazide could be obtained by a reaction of pentamethylcyclopentadiene (Cp^*H) with the precursor $Ba[N(SiMe_3)_2]_2$, which could be attributed to nearly the same pK_a -values (about 26) of the two H acids Cp^*H and $HN(SiMe_3)_2$.

The structure determination of barocene, $Ba(C_5H_5)_2$, succeeded in single crystal X-ray analysis of the compound $Ba(C_5H_5)_2 \cdot DMSO$ (**1c**, fig. 1 left). Although the complex contains the solvent DMSO, these molecules do not show any coordination to the barium atoms but are located in voids of the three-dimensional polymeric array of $Ba(C_5H_5)_2$ (average distance $Ba \leftrightarrow DMSO$: 584.5 pm). A comparative X-ray powder diffraction analysis could demonstrate the same solid state structure in a crystal powder of $Ba(C_5H_5)_2$ (**1b**), which was synthesized from a THF solution. Monomeric barocene could be obtained as the crown ether complex $[Ba(C_5H_5)_2(18-crown-6)]$. A crystal powder **2** presented the same structure in solid state as the single crystals **2a**.

The complex $BaInd_2(18-crown-6)(py)_2$ (**5a**) crystallized as a novel type of structure: The compound **5a** is a salt and contains the complex cation $[BaInd(18-Krone-6)(py)]^+$, a non-coordinated (“naked”) indenyl anion and a free pyridine molecule as a crystal solvent. Within the complex single positive charged barium cation, the center of the barium atom is located approximatively in the plane of the cyclic polyether and is coordinated axially by η^5 -contacts of an indenyl anion as well as by a nitrogen-metal coordinative bond of a pyridine ligand (fig. 1, right). Alltogether the complex cation and the “naked” indenyl anion are existent as a solvent separated ion pair (SSIP) in the solid state. The complex bis(indenyl)barium-

sesqui(dibenzo-18-crown-6)-dipyridine(**7a**) is in accordance with this type of structure and crystallized with an additional non-coordinated crown ether molecule in the asymmetric unit. Two crown ether complexes of bis(fluorenyl)barium were synthesized as $\text{BaFl}_2(18\text{-crown-6})(\text{py})_2$ (**12a**) and as $\text{BaFl}_2(\text{dibenzo-18-crown-6})(\text{py})_3$ (**13a**). Structure determinations were done by single crystal X-ray analysis (RSA) and showed the same structural array like the mentioned complex **5a** (fig. 1).

The dimeric complex 2-(η^5 -indenyliden-pentaethoxy)-phenolatobarium-dipyridine ($[(\text{-(CH}_2\text{CH}_2\text{O)}_5\text{-PhO)BaInd}] \cdot 2 \text{ Py}$, **6a**) was produced by a decomposition of the crown ether monobenzo-18-crown-6 and represents a new type of an *ansa*-compound. Within the monomeric formula unit, an indenylidene anion is coordinated by η^5 -contacts to the barium cation, while the bridged pentaethoxy-phenolate anion ($\text{-(CH}_2\text{CH}_2\text{O)}_5\text{-PhO}^-$) is bound to the central atom.

The compound **8a** exists as a salt, which is composed of a complex bis(benzo-15-crown-5)barium(2+) cation and two complex tris(indenyl)pyridine-barate(1-) anions. The aggregation of $[\text{Ba}(\text{benzo-15-crown-5})_2][\text{BaInd}_3(\text{py})_2]$ corresponds to an “at-complex”. This is the first mentioned structure of an indenyl barate.

The complex $[\text{BaFl}_2(\text{py})_3] \cdot \text{Py}$ (**10a**) crystallized as an intensive bent sandwich structure in monomeric aggregation with two η^5 -coordinated fluorenyl anions at the barium atom. As a Lewis-base three additional pyridine solvent molecules are bound with coordinative nitrogen bonds to the central atom. The monomeric solvate complex $[\text{BaCp}^*_2(\text{py})_3]$ (**17a**) is arranged as a sandwich-structure like the described compound **10a** above.

Further structure determinations of two mixed fluorenylhydroxobarium compounds were accomplished: The complex $[[\text{Ba}(\text{cryptand 222})_2(\text{OH})][\text{Fl}]_3 \cdot \text{Py}$ (**14a**) contains a salt-like array, which is composed of a complex cation $[[\text{Ba}(\text{Kryptand 222})_2(\text{OH})]^{3+}$, three “naked” fluorenyl anions and a pyridine solvent molecule. The complex $[\text{Ba}(\text{OH})(\text{benzo-18-crown-6})_4[\text{Fl}]_4 \cdot 9 \text{ Py}$ (**15a**) is salt, consisting of a tetramer complex cation $[\text{Ba}(\mu_3\text{-OH})(\text{benzo-18-crown-6})_4]^{4+}$, four non-coordinated fluorenyl anions and nine pyridine molecules as crystal solvent.

This thesis ends with experiments related to the topic anionic polymerisation of styrene to polystyrene catalyzed by bis(fluorenyl)barium compounds (BaFl_2).

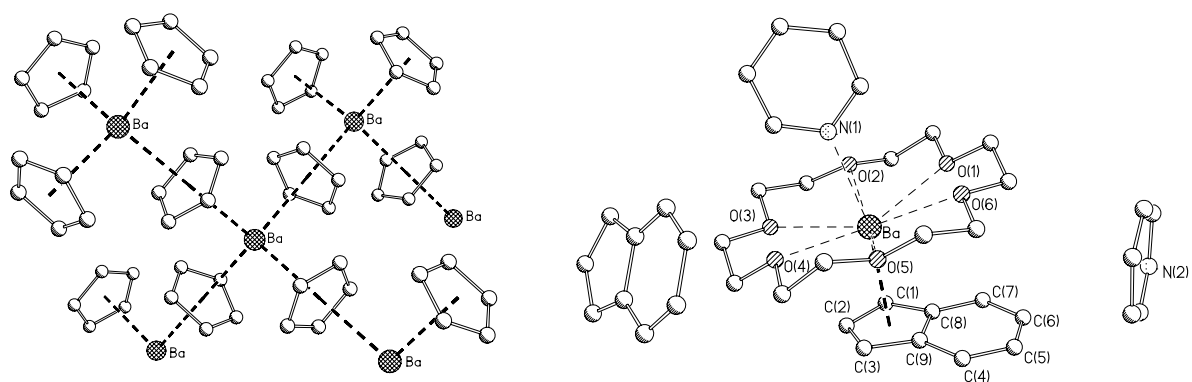


Fig. 1: Polymeric barocene: $\text{Ba}(\text{C}_5\text{H}_5)_2 \cdot \text{DMSO}$ (**1c**, left) without H atoms and DMSO molecules; structure of $\text{BaInd}_2(18\text{-crown-6})(\text{py})_2$ (**5a**, right) without H atoms