Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119–124). Water was described by the CHARMm force field of the MSI-CHARMm 25b2 program (QUANTA98, Molecular Simulations, Inc., 9685 Scranton Rd. San Diego, CA 92121. The published results were generated by using the program CHARMm. This program is distributed by Molecular Simulations Inc.). For the coupling between QM and MM parts, a polarized embedding scheme was used (corresponding to model B in: D. Bakowies, W. Thiel, *J. Phys. Chem.* **1996**, *100*, 10580–10594). MD simulations were performed by using the ChemShell program (P. Sherwood, A. H. deVries, *ChemShell - A Shell for Computational Chemistry*, CCLRC Daresbury Laboratory, **1999**, see http://www.dl.ac.uk) for NVT ensembles at approximately 300 K. For the aqueous species, the complexes were placed at the center of a spherical water cluster with a diameter of 30 Å, containing a total of 449 water molecules. After a short minimization (100 steps), the outmost layer to a depth of 5 Å from the surface was completely frozen to avoid evaporation of the minidroplet in the subsequent MD run. The aqueous species were simulated for 4 ps with a time step of 1 fs. Data sampling was started after the first 3 ps, which were taken for equilibration. In addition, the O–H distances in the water monomers were frozen with the SHAKE algorithm. Isolated complexes were simulated (after 0.5 ps of equilibration) for 1 ps with a time step of 0.5 fs.

[7] See for instance: M. Orozco, F. J. Luque, *Chem. Rev.* **2000**, *100*, 4187–4225.

[8] Magnetic shieldings were computed for equilibrium geometries and for snapshots taken from the MD simulations at the GIAO-B3LYP level (see ref. [3a] for details), by employing a medium-sized grid and DZ basis, that is, the augmented Wachters basis on Fe and DZ basis (W. Kutzelnigg, U. Fleischer, M. Schindler in *NMR Basic Principles and Progress*, *Vol. 23*, Springer, Berlin, **1990**, pp. 165–262) on all other atoms. The use of the smaller DZ basis, rather than the larger basis II (that has been employed, for instance, in ref. [3a]) resulted in relatively small changes of the computed δ values, for instance by $\Delta\delta = 40$ ppm for **2**, but makes the large number of NMR computations for the snapshots more tractable. In the chemical-shift calculations, the 20 nearest solvent water molecules were included explicitly. Representative snapshots were taken every 20 fs. Chemical shifts are reported relative to $[Fe(CO)_5]$ (**3**), optimized or simulated at the same respective level (σ_e and σ^{300K} values -3036.6 and -3282.3, respectively, see Figure 1). Neat **3** is the accepted standard in ^{57}Fe NMR spectroscopy. We have only performed a simulation for the gas phase, not for the liquid, which would be a formidable task in itself, but have used the averaged σ^{300K} value from the gas-phase simulation as a reference value also for the solution studies. It should be kept in mind that this procedure could introduce a systematic error for the computed gas-to-liquid shifts, and that more attention should be paid to the trends in the δ values between **1** and **2**, rather than to their actual values.

[9] It should be noted that this value only represents the "classical" thermal effect and is not averaged over the zero-point motion. More than qualitative agreement with experiment is not to be expected anyway, due to the rather limited basis sets employed in the computations.

[10] Obtained by performing NMR computations for a total of four static structures with elongated or compressed Fe–C distances (in steps of 0.02 Å) and a linear fit of the resulting σ values.

[11] A similar value, 35200 ppm Å^{-1}, is obtained when the larger basis II is used for the ligands.

[12] C. J. Jameson, D. Rehder, M. Hoch, *J. Am. Chem. Soc.* **1987**, *109*, 2589–2594; this empirical value has been qualitatively reproduced by using theoretical methods similar to those employed in the present study: N. Godbout, E. Oldfield, *J. Am. Chem. Soc.* **1997**, *119*, 8065–8069.

[13] In typical hydrogen-bonded systems containing O–H⋯O moieties, the O⋯O distance is smaller than 3.5 Å and the O–H bond is directed towards the second oxygen atom such that the O–H⋯O angle is larger than 140° (see for instance: E. Schwegler, G. Galli, F. Gygi, *Phys. Rev. Lett.* **2000**, *84*, 2429–2432); the same criteria have been applied to the O–H⋯X moieties in **1** and **2**.

[14] Counterions, which have not been considered explicitly, are likely to affect the fine structure of the solvation shell, but would probably not change the qualitative picture.

[15] M. Bühl, T. Steinke, P. v. R. Schleyer, R. Boese, *Angew. Chem.* **1991**, *103*, 1179–1180; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1160–1161.

[16] Simple optimization of **2** in a polarizable continuum, as has been done for BH_3NH_3 in ref. [15], also leads to Fe–C bond contraction, but gives much too short Fe–C bond lengths, below 1.90 Å.

[17] For similar pictorial rationalizations of paramagnetic contributions see, for instance: Y. Ruiz-Morales, T. Ziegler, *J. Phys. Chem. A* **1998**, *102*, 3970–3976.

A Triple-Decker Sandwich Complex of Barium

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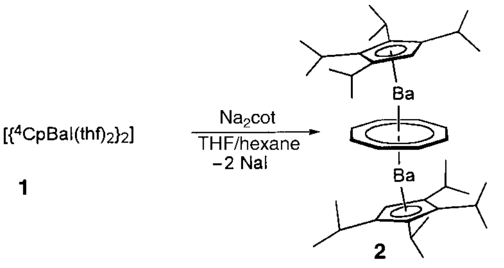
While triple-decker sandwich complexes are common in transition-metal chemistry,[1–8] very few comparable complexes of main-group metals are known that are ionic and show strong bending with centroid-M-centroid angles of 134° ($[Cp_3Tl_2]^-$ ($Cp = C_5H_5$)[9]), 116° ($[Cp_3Cs_2]^-$[10]), 155/152° ($[(C_5Me_5)_3Sn_2]^+$[11]), or 124/130° ($[(\eta^6\text{-}C_7H_8)_2(\mu,\eta^5{:}\eta^5\text{-}C_5Me_5)In_2]^+$[11]). We showed several years ago that bending in sandwich complexes of the heavy alkaline-earth metals can be eliminated with extremely bulky alkylcyclopentadienyl ligands.[12]

Herein we report on the first triple-decker complex of barium. At ambient temperature the half-sandwich complex $[\{^4CpBaI(thf)_2\}_2]$ (**1**; $^4Cp = C_5H(CHMe_2)_4$)[13] reacts slowly with Na_2cot (cot = cyclooctatetraene) in THF/hexane (5:1) [Eq. (1)]. The colorless product is readily soluble in THF, soluble in toluene, and moderately soluble in pentane. ^{1}H and ^{13}C NMR spectra show one set of signals for two magnetically equivalent ^{4}Cp rings (see Experimental Section) and one signal for one cot ligand at $\delta = 6.02$ ppm (^{1}H) and $\delta = 95.3$ ppm (^{13}C). On exposure to air the microcrystalline compound turns intense yellow immediately, then orange-red within seconds, and finally pale yellow with a strong cot smell.



(1)

EI mass spectra show a signal corresponding to a dinuclear $[^4CpBa(cot)Ba^4Cp]^+$ ion with the correct isotope pattern as well as signals for the fragments $[^4CpBa(cot)Ba]^+$ and

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1433-7851/02/4113-2315 $ 20.00+.50/0

$[^4CpBa]^+$. In a sealed capillary under argon the dibarium complex $[^4CpBa(COT)Ba^4Cp]$ (**2**) displays a melting range of 224–227 °C. It remained unchanged even after the melt had been heated to 250 °C and could be sublimed above 215 °C in oil pump vacuum.

Heavy alkaline-earth element cot complexes $[(cot)ML_n]$ (M = Ca, Sr, Ba, L = thf, pyridine[14]) are known, but could not be crystallographically characterized. The analogous ytterbium complex $[(cot)Yb(py)_3]$, however, could be structurally characterized by single-crystal X-ray diffraction.[15]

The crystal structure of **2**[16] shows a centrosymmetric triple-decker sandwich complex with essentially planar C_5 and C_8 rings and an interplanar angle of 169.9° between ^4Cp and cot (Figure 1). The distance Ba–$Cp_{centroid}$ (2.71 Å) is comparable with those found in the half-sandwich complex **1** (2.72/2.73 Å)[13] and slightly longer than the value found for octaisopropylbarocene (2.68 Å).[17] For the Ba–$cot_{centroid}$ distance of 2.40 Å no literature precedent could be found. This appears to be the shortest distance between a Ba center and a ring plane known for molecular compounds. The C12 ⋯ Ba and C42 ⋯ Ba distances of 3.56 and 3.57 Å indicate that two methyl groups of each ^4Cp ligand undergo a $CH_3 \cdots Ba$ interaction. The respective isopropyl groups show significantly smaller outward bending than the two other isopropyl groups and are rotated toward the central atom. These features have not been observed for the half-sandwich complex **1**.

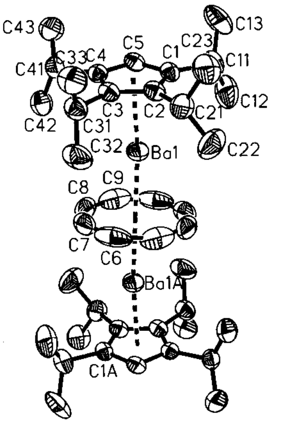

Figure 1. Crystal structure of **2.** Selected distances [Å] and angles [°]: Ba1-C1 2.945(4), Ba1-C2 2.982(4), Ba1-C3 2.993(4), Ba1-C4 2.977(4), Ba1-C5 2.927(4), Ba1-C6 2.998(4), Ba1-C7 2.994(5), Ba1-C8 3.014(4), Ba1-C9 3.000(5), Ba1A-C6 3.003(5), Ba1A-C7 3.015(6), Ba1A-C8 3.016(6), Ba1A-C9 3.007(5), Ba1-$Cp_{centroid}$ 2.71, Ba1-$cot_{centroid}$ 2.40, $Cp_{centroid}$-Ba1-$cot_{centroid}$ 169.5; angles between ^4Cp plane/C1–C11 0.7, ^4Cp plane/C2–C21 3.1, ^4Cp plane/C3–C31 2.1, ^4Cp plane/C4–C41 0.2.

While there are no comparable alkaline-earth metal complexes known, triple-decker complexes of the general formula $[(C_5Me_5)Ln(cot)Ln(C_5Me_5)]$ with a cot middle deck have been structurally characterized for the divalent lanthanides Sm,[18] Yb, and Eu.[19] They are bent with $Cp^*_{centroid}$-Sm-$Cp^*_{centroid}$ = 149.3/148.9°, $Cp^*_{centroid}$-Eu-$Cp^*_{centroid}$ = 147.2/149.5°, $Cp^*_{centroid}$-Yb-$Cp^*_{centroid}$ = 161.2/159.5°. Triple-decker sandwich complexes of the trivalent lanthanides cerium, neodymium, and samarium of general formula $[(cot'')Ln(cot'')Ln(cot'')]$ (cot'' = 1,4-$(SiMe_3)_2\,C_8H_6$) could not yet be structurally characterized.[20]

Experimental Section

Solid Na_2cot (75 mg, 0.5 mmol) was added to a solution of **1** (642 mg, 0.5 mmol) in a mixture of THF (20 mL) and hexanes (5 mL) and the suspension was stirred for two days at ambient temperature. Removal of the solvent in vacuo and extraction of the solid residue with toluene (20 mL), followed by filtration and evaporation gave an ivory powder (190 mg, 0.22 mmol; 45%), which could be obtained as colorless single crystals suitable for X-ray diffraction from $[D_6]$benzene. C,H-analysis gave unsatisfactory results due to the extreme air sensitivity of **2.** ^1H NMR (400 MHz, 298 K, C_6D_6): δ = 6.02 (s, 8H; cot), 5.11 (s, 2H; ring-H (^4Cp)), 2.94 (m, 4H; C*H*Me$_2$), 2.84 (m, 4H; C*H*Me$_2$), 1.24 (d, $^3J(H,H)$ = 7.2 Hz, 12H; CH_3), 1.21 (d, $^3J(H,H)$ = 7.2 Hz, 12H; CH_3), 1.16 (d, $^3J(H,H)$ = 6.8 Hz, 12H; CH_3), 1.02 ppm (d, $^3J(H,H)$ = 6.8 Hz, 12H; CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 127.5 (s; ring-C), 123.4 (s; ring-C), 101.7 (dt; ring-CH (^4Cp), $^1J(C,H)$ = 155, $^4J(C,H)$ = 5 Hz), 95.3 (d, $^1J(C,H)$ = 158 Hz; cot), 26.9 ($CHMe_2$), 26.6 ($CHMe_2$), 25.7 (CH_3), 25.3 (CH_3), 24.1 (CH_3), 23.7 ppm (CH_3); EI-MS (70 eV): m/z (%): 846.2 (6) $[M^+]$, 613.0 (74) $[M^+ - C_5H(CHMe_2)_4]$, 371.1 (100) $[Ba\{C_5H(CHMe_2)_4\}^+]$.

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[16] Crystal structure determination of $2 \cdot 2\,C_6D_6$: IPDS diffractometer with imaging system (Stoe), $Mo_{K\alpha}$ radiation, λ = 71.073 pm, $2\Theta_{max}$ = 51.0°, 359 images with $0° \leq \phi \leq 359°$ and $\Delta\phi = 1.0°$, T = 293(2) K, crystal dimensions 0.48 × 0.40 × 0.16 mm^3, monoclinic, space group $P2(1)/c$ (no. 14), lattice parameters (293 K): a = 14.9481(14), b = 9.0286(6), c = 19.430(2) Å, β = 103.846(12)°, V = 2546.0(4) $Å^3$, Z = 4, ρ_{calcd} = 1.307 $g\,cm^{-1}$, $\mu(Mo_{K\alpha})$ = 15.69 cm^{-1}, absorption correction with the multi-scan method (MULABS/PLATON 98), transmission factors 0.495 to 0.773, structure solution: direct methods (SIR97), full-matrix least-squares refinement based on F_o^2 (SHELXL-97), 34732 reflections, 4729 unique reflections, 261 parameters, $R1(2821\ F_o > 2\sigma(F_o))$ = 0.0345, $wR2$(all) = 0.0781, residual electron density +0.688 to −0.662 $e\,Å^3$, no disorder, CH and CH_3 groups have been refined as rigid groups with variable torsion angles (C–H = 0.96 Å, C-C-H and H-C-H 109.5°). Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-182290.

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