Mono(alkylcyclopentadienyl) Complexes of Barium and Strontium

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The mono(ring) complexes $[\{(C_5H_2R_3\text{-}1,2,4)BaI(THF)_2\}_\infty]$ (**1-Ba**; R = CMe$_3$) and $[\{(C_5HR_4)\text{-}BaI(THF)_2\}_2]$ (**2-Ba**; R = CHMe$_2$) have been synthesized from BaI$_2$ and the corresponding sodium cyclopentadienides. **2-Sr** has been obtained both from SrI$_2$ and NaC$_5$HR$_4$ (R = CHMe$_2$) or by ligand redistribution between octaisopropylstrontocene (**3-Sr**) and SrI$_2$. The chloro-bridged calcium complex $[\{(C_5H_2R_3\text{-}1,2,4)CaCl(DME)\}_2]$ (**4-Ca**, R = CMe$_3$) is available from CaCl$_2$ and NaC$_5$H$_2$R$_3$-1,2,4. The crystal structures of **1-Ba**, **2-Ba**, and **4-Ca** have been determined.

Introduction

Organometallic compounds of heavy alkaline earth metals are attracting interest as synthetic reagents in organic synthesis[1] or as initiators of anionic styrene polymerization.[2] There is still a need for MOCVD precursors of these elements with sufficient volatility and stability for growth of thin films with high-temperature superconducting (HTS) or ferroelectric properties.[3] Basic research has focused primarily on metallocenes[4] and related compounds.[5]

The development of synthetically useful half-sandwich complexes of these large cations as precursors for a variety of follow-up products still presents a challenge. Introduction of the tris(trimethylsilyl)cyclopentadienyl ligand recently enabled the crystallographic characterization of dimeric $[\{(C_5H_2(SiMe_3)_3)Ca(\mu\text{-I})(THF)\}_2]$ (**A**), the strontium derivative $[\{(C_5H_2(SiMe_3)_3)Sr(\mu\text{-I})(THF)_2\}_2]$ (**B**), and the barium chain polymer $[\{C_5H_2(SiMe_3)_3)Ba(\mu\text{-I})(THF)_2\}_\infty]$ (**C**).[6]

Tris(trimethylsilyl)cyclopentadienide loss upon attempted nucleophilic substitution of the halide in these complexes[6] hampers their possible use as starting compounds. Nucleophilic substitution has, however, been successful with mono(alkylcyclopentadienyl)calcium halide complexes and yielded amide and phenoxide derivatives.[7,8]

Scheme 1. Formation of the Chain Polymer 1-Ba

1-Ba
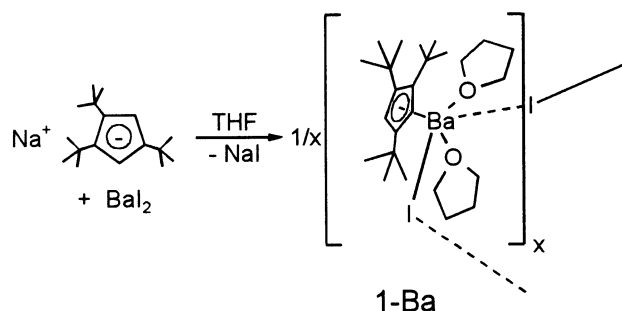
While organometallic chemistry is still underdeveloped for calcium, it is even more so for strontium and barium, and the failure of tetraisopropylcyclopentadienide to stabilize comparable mono(ring) complexes of strontium and barium has been stated in ref 6.

We therefore set out to address this problem by dealing with barium complexes in the first place. In this paper we report on the first mono(alkylcyclopentadienyl) complexes of barium and we included some strontium chemistry as well as the first chloro-bridged calcium compound of this type.

Results and Discussion

Sodium tri-*tert*-butylcyclopentadienide (**1-Na**) reacts with 1 equiv of barium diiodide to furnish the desired mono(ring) complex $[(C_5H_2(CMe_3)_3\text{-}1,2,4)Ba(\mu\text{-I})(THF)_2]_\infty$ (**1-Ba**) in fair yields (Scheme 1). Proton NMR spectra in deuteriobenzene show the typical signal pattern of the tri-*tert*-butylcyclopentadienyl ligand with three singlets of intensity ratio 2:9:18 for the two ring protons at about 6 ppm and the two CMe$_3$ signals between 1.3 and 1.6 ppm. Complex **1-Ba** could be crystallized as single crystals suitable for X-ray diffraction from tetrahydrofuran.

1-Ba is a chain polymer (Figure 1), like its tris(trimethylsilyl)cyclopentadienyl analogue, and features

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(1) Yanagisawa, A.; Habaue, S.; Yasue, K.; Yamamoto, H. *J. Chem. Soc., Chem. Commun.* **1996**, 367−368.

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(3) Neumayer, D. A.; Belot, J. A.; Feezel, R. L.; Reddy, C.; Stern, C. L.; Marks, T. J.; Liable-Sands, L. M.; Rheingold, A. L. *Inorg. Chem.* **1998**, *37*, 5625−5633 and literature cited therein.

(4) (a) Jutzi, P.; Burford, N. In *Metallocenes*; Togni, A., Halterman, R., Eds.; Wiley-VCH: Weinheim, Germany, 1998; pp 3−54. (b) Hanusa, T. P. *Chem. Rev.* **1993**, *93*, 1023−1036.

(5) Westerhausen, M.; Digeser, M. H.; Gckel, C.; Nöth, H.; Knizek, J.; Ponikwar, W. *Organometallics* **1999**, *18*, 2491−2496.

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(7) McCormick, M. J.; Sockwell, S. C.; Hanusa, T. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 3393−3399.

(8) Burkey, D. J.; Alexander, E. K.; Hanusa, T. P. *Organometallics* **1994**, *13*, 2773−2786.
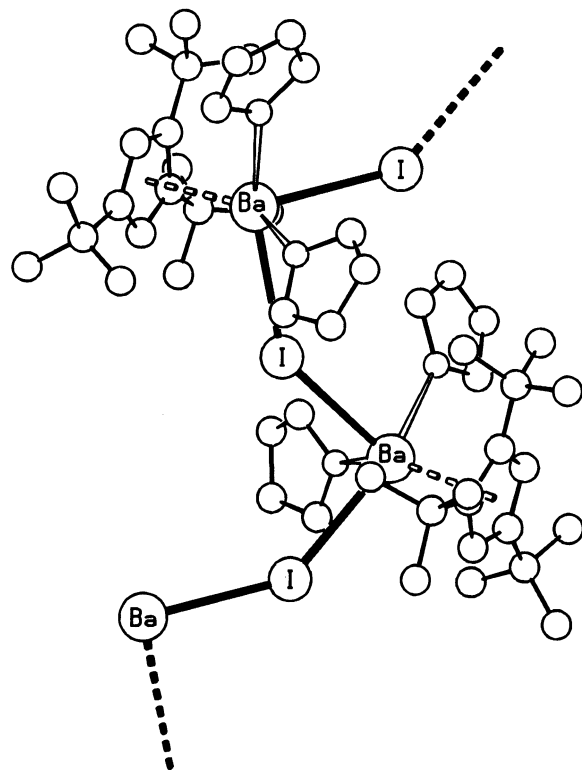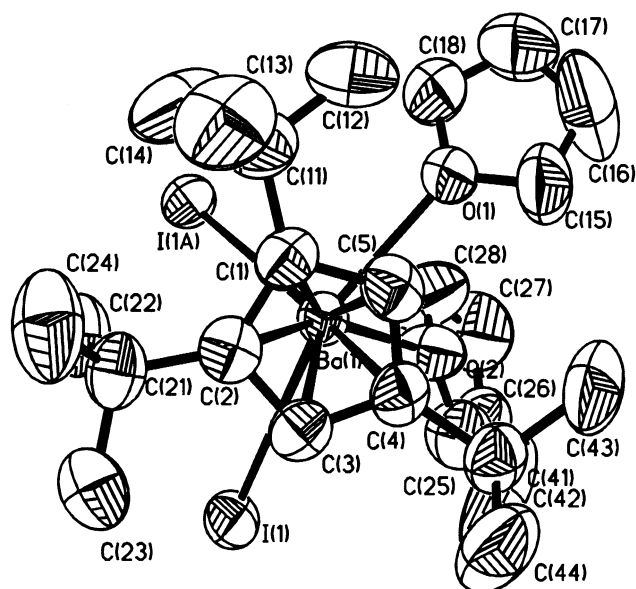
Figure 1. Crystal structure of the chain polymer **1-Ba**. Selected distances (Å) and angles (deg): Ba1−I1 = 3.4720-(7), Ba1−I1A = 3.4458(5), Ba1−O1 = 2.797(4), Ba1−O2 = 2.810(4), Ba1−C1 = 3.023(6), Ba1−C2 = 3.029(5), Ba1−C3 = 2.988(6), Ba1−C4 = 3.022(5), Ba1−C5 = 3.006(5), Ba1−ring plane = 2.762, Ba1···C42 = 3.671, Ba1···C22 = 3.642; I1−Ba1−I1A = 90.173(10), Ba1−I1−Ba1A = 144.460-(16), O1−Ba1−O2 = 70.65(15), O1−Ba1−I1 = 149.41(11), O1−Ba1−I1A = 86.85(9), O2−Ba1−I1 = 78.86(10), O2−Ba1−I1A = 88.92(11). Probability ellipsoids are shown at the 50% level.

two crystallographically independent zigzag chains with iodo bridges and I−Ba−I angles of 90.17(1)° at Ba1 and 89.12(1)° at Ba2 as well as Ba−I−Ba angles of 144.46-

Scheme 2. Formation of the Dimers 2-Ba and 4-Ca
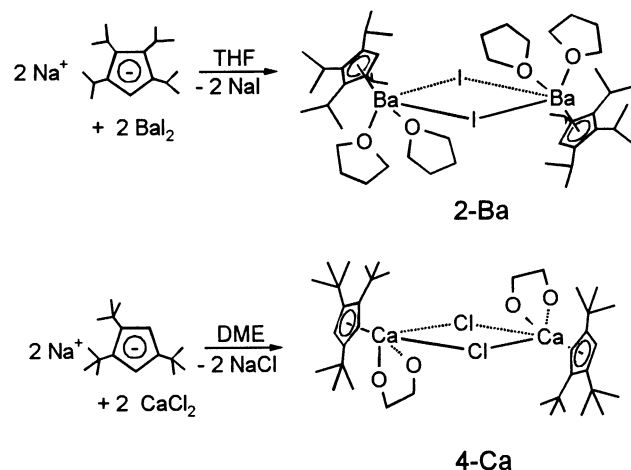
(2)° at I1 and 147.50(2)° at I2. Three out of four Ba−I distances are almost identical within a range from 3.4457(5) to 3.4466(6) Å; the distance Ba1−I1 is 3.4720-(6) Å. There are two short contacts between Ba1 and the methyl groups of the 1,2,4-tri-*tert*-butylcyclopenta-dienyl ligand (C22 at 3.642(6) Å and C42 at 3.671(7) Å). For the *tert*-butyl group C21−C24 at ring C2 (C2 is connected to Ba1) the deviation of the α-C atom (C21) out of the ring plane toward the metal by 0.02 Å is indicative of some attractive interaction between the methyl group represented by C22 and Ba. Whereas the α-C atoms C61 and C71 (ring C6−C10 is connected to Ba2) are bent outward significantly (the average devia-tion from the ring plane is 0.09 Å), C91 is right in the ring plane (its deviation from the ring plane is smaller than the esd value) and is connected to the methyl group represented by C92, which displays a C···Ba distance of 3.497(6) Å.

From sodium tetraisopropylcyclopentadienide and barium diiodide the barium compound $[(C_5HR_4)Ba(\mu\text{-}I)(THF)_2]_2$ (**2-Ba**) could be obtained in good yield (Scheme 2). Colorless crystals of **2-Ba** have been grown from THF solution at −38 °C. **2-Ba** contains 1 equiv of THF in the crystal lattice in excess of the two THF molecules coordinated to the metal atom.

The crystal structure of **2-Ba** reveals a dimer with two crystallographically independent molecules located on centers of symmetry of the triclinic unit cell. The dimer **2-Ba** contains a Ba_2I_2 ring with almost equal Ba−I bond lengths, acute I−Ba−I angles (80.5°, mean value), and Ba−I−Ba angles of about 99.5° (mean value; for details see Figure 2). The Ba−ring plane distance is 2.72 Å for Ba1 and 2.73 Å for Ba2; the Ba−O distances vary from 2.759(4) to 2.860(5) Å within dimer 1 and are closer together for dimer 2 at 2.772(5) and 2.825(4) Å. These distances are close to the values found for the polymeric tris(trimethylsilyl)cyclopentadienyl derivative $[\{(C_5H_2(SiMe_3)_3)Ba(\mu\text{-}I)(THF)_2\}\cdot^1/_2C_7H_8]$ (**D**) (Ba−ring centroid = 2.76(1) Å, Ba−O = 2.73(1), 2.74(1) Å [6]), as are the Ba−I bond lengths (3.4282(7)/3.4718(6) Å for **2-Ba** and 3.390(1)/3.475(2) Å for **D**). Unlike **1-Ba**, **2-Ba** contains no Ba···C contacts shorter than 3.9 Å.

Similar experiments with strontium diiodide gave **2-Sr** in 83% yield (see Experimental Section). A crystal structure analysis[9] of **2-Sr** showed dimeric molecules of $[(C_5HR_4)Sr(\mu\text{-}I)(THF)]_2$, but refinement of the data

Table 1. Crystal Data and Summary of X-ray Data Collection[a] for Complexes 1-Ba, 2-Ba, and 4-Ca[a]

	1-Ba	2-Ba	4-Ca
formula	$C_{27}H_{49}BaIO_{2.50}$	$C_{25}H_{45}BaIO_2$	$C_{60}H_{96}Ca_2 Cl_2O_4$
fw	677.90	641.85	1032.43
cryst size (mm)	$0.40 \times 0.28 \times 0.20$	$0.45 \times 0.40 \times 0.18$	$0.64 \times 0.24 \times 0.16$
space group	$P2_1$	$P\bar{1}$	$P2_1/n$
lattice params			
a (Å)	15.5313(16)	13.7251(12)	17.2240(15)
b (Å)	9.3356(6)	14.2198(13)	9.5618(5)
c (Å)	21.671(2)	15.3657(13)	20.2703(15)
α (deg)	90	102.389(10)	90
β (deg)	93.748(12)	92.239(10)	107.197(9)
γ (deg)	90	97.855(11)	90
V (Å^3)	3135.4(5)	2878.9(4)	3189.1(4)
Z	4	4	2
T (K)	293(2)	293(2)	293(2)
D_{calcd} (g cm^{-3})	1.436	1.481	1.075
μ (cm^{-1})	22.71	24.68	3.02
transmissn factors	0.476 17–0.686 71	0.336 76–0.644 39	0.854 46–0.963 57
θ limits (deg)	2.236–25.98	2.74–25.68	2.73–25.68
total no. of rflns	43 393	40 690	43 457
no. of unique rflns	11 954	10 365	5938
structure soln	direct methods	direct methods	direct methods
program used	SIR97	SHELXS-97	SHELXS-97
refinement	SHELXL-97	SHELXL-97	SHELXL-97
no. of data/restraints/params	11 954/21/561	10 365/0/539	5938/9/307
R1, wR2 ($I > 2\sigma(I)$)	0.273, −0.173	0.0382, 0.0700	0.0459, 0.0957
R1, wR2 (all data)	0.0491, 0.0636	0.0752, 0.0774	0.1096, 0.1106
GOF (all data)	0.891	0.825	0.814
max/min diff peak (e Å^{-3})	0.389/−0.366	0.659/−0.632	0.273/−0.173

[a] For all crystal structure determinations Mo Kα radiation ($\lambda = 0.710\ 73$ Å) has been used.
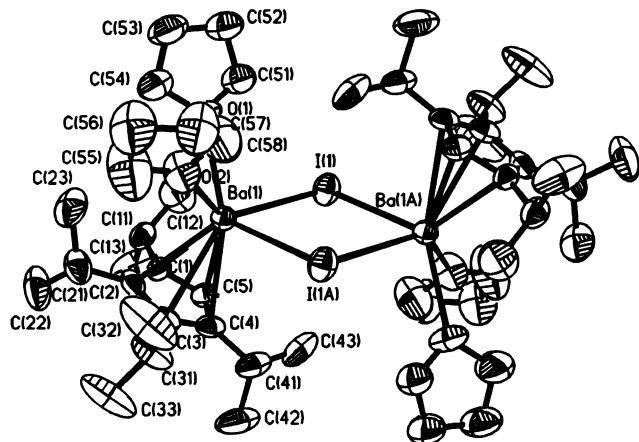
Figure 2. Crystal structure of the dimer **2-Ba**. Selected distances (Å) and angles (deg): Ba1–I1 = 3.4718(6), Ba1–I1A = 3.4282(7), Ba1–O1 = 2.759(4), Ba1–O2 = 2.860(5), Ba1–C1 = 2.974(5), Ba1–C2 = 2.993(5), Ba1–C3 = 2.982-(5), Ba1–C4 = 2.969(5), Ba1–C5 = 2.944(6), Ba1–ring plane = 2.7197, Ba2–ring plane = 2.7304, Ba1···C42 = 3.671, Ba1···C22 = 3.642; I1–Ba1–I1A = 90.1739(10), Ba1–I1–Ba1A = 144.460(16), O1–Ba1–O2 70.65(15), O1–Ba1–I1 = 149.41(11), O1–Ba1–I1A = 86.85(9), O1–Ba1–I1 = 78.86(10), O2–Ba1–I1A = 88.92(11), interplanar angle between ring plane C1–C5 and Ba2I2 25.3. Probability ellipsoids are shown at the 50% level.

did not proceed well and a detailed discussion of the structure is not warranted.

Because the literature on octaisopropylstrontocene (**3-Sr**)[10] was not available to us, we prepared **3-Sr** from strontium diiodide and sodium tetraisopropylcyclopentadienide in tetrahydrofuran and recorded its NMR data in deuteriobenzene as well as in octadeuteriotetrahy-

drofuran (see Experimental Section) for comparison with the mono(ring) complex **2-Sr**. The colorless metallocene **3-Sr** is thermally stable, like octaisopropylcalcocene and -barocene,[12] can be heated well above the melting point (151–153 °C) without decomposition, and sublimes readily above 100 °C/10^{-3} mbar. Crystallization of the strontocene **3-Sr** by sublimation or from solution was rather frustrating, and both methods gave only poor crystals. Optical microscopy and X-ray diffraction are in accordance with multiply twinned crystals. The structure solution[11] is in accord with expectation on the basis of the structures of octaisopropylcycalcocene and -barocene,[5] but refinement did not proceed well and the result is therefore not suitable for a detailed discussion.

Calcium chloride dissolves slowly in a mixture of DME and **1-Na** at ambient temperature with formation of a finely divided precipitate of sodium chloride. Dimeric [{(C$_5$H$_2$R$_3$-1,2,4)Ca(DME)(μ-Cl)}$_2$] (**4-Ca**) was the only detectable product and could be crystallized from DME as a dimer located on a center of symmetry (Table 1, Figure 3). The Ca–centroid distance of 2.435 Å is longer than those found in the calcium complexes mentioned before[7,8] (the bis(trimethylsilyl)amide [(C$_5$-HR$_4$)Ca(OC$_4$H$_8$)(N(SiMe$_3$)$_2$)] is next with 2.397 Å[8]). The relatively small Ca$_2$Cl$_2$ core (average Ca–Cl distance 2.746 Å, compared to 3.094 Å for Ca–I in **I**) results in methyl···methyl distances below 4 Å, e.g. 3.716 Å for C13(isopropyl)···C64(DME) for **4-Ca**.

Crystallization of **4-Ca** from a saturated solution in hexadeuteriobenzene occurred at room temperature and

(9) Cell data for **2-Sr**: triclinic, space group $P\bar{1}$, $a = 9.700(2)$ Å, $b = 11.948(2)$ Å, $c = 14.477(2)$ Å, $\alpha = 80.61°$, $\beta = 79.13°$, $\gamma = 75.42°$.

(10) Burkey, D. J. Ph.D. Thesis, Vanderbilt University, August 1995. Cited in: Hays, M. L.; Hanusa, T. P. *Adv. Organomet. Chem.* **1996**, *40*, 117–170.

(11) Cell data for **3-Sr**: monoclinic, space group $C2/c$, $a = 34.2249$-(21) Å, $b = 12.5025(8)$ Å, $c = 16.6232(8)$ Å, $\beta = 111.845(7)°$.

(12) Williams, R. A.; Tesh, K. F.; Hanusa, T. P. *J. Am. Chem. Soc.* **1991**, *113*, 4843–4851.
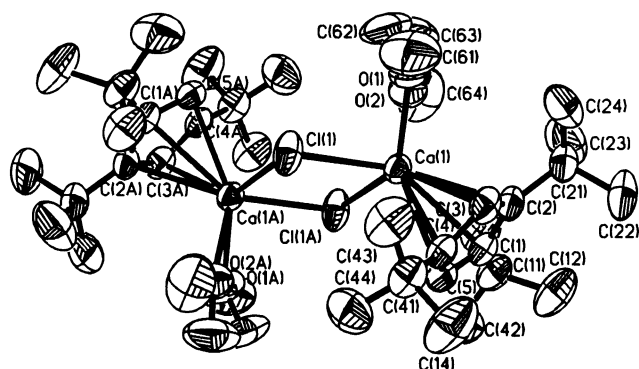
Figure 3. Crystal structure of the dimer **4**-**Ca**. Selected distances (Å) and angles (deg): Ca1−Cl1 = 2.7425(9), Ca1−Cl1A = 2.7494(9), Ca1−O1 = 2.475(2), Ca1−O2 = 2.456-(2), Ca1−C1 = 2.754(3), Ca1−C2 = 2.748(2), Ca1−C3 = 2.693(2), Ca1−C4 = 2.695(3), Ca1−C5 = 2.687(3), Ca1−ring plane = 2.434; Cl1−Ca1−Cl1A = 80.12(3), Ca1−Cl1−Ca1A = 99.88(3), O1−Ca1−O2 = 65.48(11), O1−Ca1−Cl1 = 79.53(7), O1−Ca1−Cl1A = 136.04(6), O2−Ca1−Cl1 = 103.78(6), O2−Ca1−Cl1A = 82.33(7), interplanar angle between C_5 ring and Ca_2Cl_2 ring 40.6. Probability ellipsoids are shown at the 50% level.

yielded crystals of the same DME adduct [{$(C_5H_2R_3$-1,2,4)Ca(DME)$(\mu$-Cl)}$_2$] (**4**-**Ca**, R = CMe$_3$), which contained C_6D_6 in the crystal lattice. The dimeric complex molecules show little deviation from the structure discussed above.

In solution the mono(ring) complexes **1**-**Ba**, **2**-**Ba**, and **2**-**Sr** are expected to be subject to ligand redistribution reactions according to Schlenk equilibria, e.g. eq 1.

$$2Cp' \, MI \rightleftharpoons Cp'_2 \, M + MI_2 \qquad (1)$$
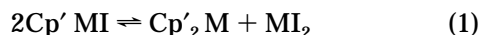
According to NMR studies the equilibrium in tetrahydrofuran solution strongly favors the mono(ring) complexes, however. In octadeuteriotetrahydrofuran solutions of **2**-**Sr** the signals of the metallocene **3**-**Sr** or any other complex containing the tetraisopropylcyclopentadienyl ligand could not be detected by ^{1}H NMR spectroscopy at ambient temperature, and this situation did not change upon heating the sample to 330 K.

Evidence for redistribution reactions such as that expressed in eq 1, however, can be gathered from attempts to dissolve **2**-**Sr** in solvents other than tetrahydrofuran. If nonpolar solvents are used, which are not capable of salt solvation, precipitation of MI$_2$ will occur and shift the equilibrium toward metallocene formation. Extraction of the solid mono(ring) complex **2**-**Sr** with pentane, hexadeuteriobenzene, or toluene resulted in nearly quantitative yields of octaisopropylstrontocene **3**, identified by ^{1}H NMR spectroscopy.

In aromatic solvents such as benzene or toluene the mono(ring) complexes of strontium and barium are stable if tetrahydrofuran is added. This observation has been useful for an efficient workup procedure: the crude reaction solutions obtained from strontium diiodide and sodium tetraisopropylcyclopentadienide in tetrahydrofuran containing sodium iodide are diluted with toluene to precipitate the sodium salt, which can be removed by centrifugation. The solution is then concentrated and stored at low temperature for crystallization.

When **2**-**Ba** was washed with pure pentane at ambient temperature and exposed to a vacuum for several minutes, subsequent addition of deuteriobenzene caused a ligand redistribution with formation of octaisopropylbarocene (identified by its proton NMR signals[12]) and barium diiodide. If the pentane contains about 10% of tetrahydrofuran and washing as well as a short vacuum-drying procedure are carried out in an ice bath, **2**-**Ba** can be dissolved in a mixture of hexadeuteriobenzene and octadeuteriotetrahydrofuran (ca. 10:1) for NMR investigation and has been found free of octaisopropylbarocene.

Hanusa has argued that dissociation of THF ligands from [(C_5HR_4)CaI(THF)$_2$] (R = CHMe$_2$) is a necessary prerequisite for octaisopropylcalcocene formation, because the metallocene is too crowded to accept even one THF ligand.[13] This argument explains the relative stability of calcium complexes with one bulky alkylcyclopentadienyl ring toward ligand redistribution and metallocene formation. For strontium and barium complexes the situation is different, because octaisopropylstrontocene crystallizes from tetrahydrofuran with one THF ligand[14] and hexa-*tert*-butylstrontocene does the same.[15] As a consequence, mono(ring) complexes of calcium with bulky alkylcyclopentadienyl ligands are stable as long as one THF ligand is cordinated to the central atom, whereas strontium or barium mono(ring) complexes apparently need two THF ligands to be protected against ligand redistribution and metallocene formation. Since the mono(ring) calcium complex keeps its last THF ligand more tightly bound than the strontium or barium counterpart keeps its second last THF donor, the latter compounds need more attention to prevent THF loss and ring redistribution. This can be achieved by addition of THF to solutions in aromatic solvents.

Apart from coordinated THF, iodide ions in solution could also provide some stabilization of mono(ring)-complexes according to eq 1. Although the amount of sodium iodide collected by centrifugation of toluene-diluted strontium diiodide/sodium tetraisopropylcyclopentadienide/tetrahydrofuran reaction solutions was quantitative, we cannot rule out the possibility of traces of sodium iodide remaining in solution and helping to stabilize the desired mono(ring) complexes. The same probably applies to a clear solution of equimolar amounts of strontium diiodide and octaisopropylstrontocene **3**-**Sr** in octadeuteriotetrahydrofuran, which displayed the ^{1}H NMR signals of **2**-**Sr** without showing any signal of residual **3**-**Sr**.

Conclusion

Extremely bulky alkylcyclopentadienides such as 1,2,4-tri-*tert*-butylcyclopentadienide and tetraisopropylcyclopentadienide are well suited for the synthesis of mono(alkylcyclopentadienyl) halides of the heavy alkaline earth metals with additional tetrahydrofuran donor ligands, if prolonged treatment of such complexes with nonpolar solvents is avoided or tetrahydrofuran is added to prevent ligand redistribution reactions. This could be demonstrated for strontium and barium com-

(13) Harvey, M. J.; Hanusa, T. P.; Young, V. G., Jr. *J. Organomet. Chem.* **2001**, *626*, 43−48.
(14) Sitzmann, H.; Weber, F.; Wolmershäuser, G. Unpublished data.
(15) Weber, F.; Sitzmann, H.; Schultz, M.; Sofield, S. D.; Andersen, R. A.; *Organometallics* **2002**, *21*, 3139−3146.

pounds, despite a recent report to the contrary.[6] The novel strontium and barium complexes are more sensitive to loss of donor solvent and ring redistribution than their calcium counterparts. The formation of novel triple decker sandwich complexes from **2-Ba** and **2-Sr** with disodium cyclooctatetraeninde[16] is a first example of possible follow-up reactions. The potential of calcium chloride for the synthesis of mono(ring) complexes has been shown.

Experimental Section

All synthetic operations were performed under a dry dinitrogen atmosphere following conventional Schlenk techniques or using a drybox from MBraun Co., Garching, Germany. Tetrahydrofuran and petroleum ether (boiling range 40−60 °C) were distilled from potassium metal. NMR spectra were taken on a Bruker AMX 400 MHz spectrometer. Chemical shifts are given in ppm and refer to the appropriate solvent signals. Mass spectra were taken on a Finnigan MAT 90 mass spectrometer.

Low carbon values have been obtained in this work and elsewhere for other alkylcyclopentadienyl complexes of the heavy alkaline earth metals: e.g., refs 6 and 7 and literature cited therein (refs 8 and 13). The low carbon values are probably a combination of extreme air sensitivity, partial THF loss during sample preparation, and incomplete combustion. Metal analyses have been carried out by atomic absorption spectroscopy, and halide has been determined by volumetric precipitation analysis.

[{(C₅H₂(CMe₃)₃)BaI(THF)₂}∞] (1-Ba). A suspension of 0.76 g (3 mmol) of sodium 1,2,4-tri-*tert*-butylcyclopentadienide and 1.17 g (3 mmol) of barium iodide in 20 mL of tetrahydrofuran was stirred for 2 days at ambient temperature and evaporated to dryness. The solid residue was extracted with three 15 mL portions of toluene, and the filtered extracts were evaporated to yield 0.95 g (1.48 mmol, 49%) of a colorless microcrystalline powder. Analytically pure samples and single crystals suitable for X-ray diffraction were obtained by recrystallization from THF.

Anal. Calcd for $C_{25}H_{45}BaIO_2$: C, 46.81; H, 7.01. Found: C, 46.04; H, 6.74. ¹H NMR (C_4D_8O, 400 MHz): δ 5.80 (s, 2H, ring C*H*), 3.58 (br, residual OCD*H*), 1.71 (br, residual CD*H*) 1.43 (s, 18 H, 6 C*H₃*), 1.26 (s, 9 H, 3 C*H₃*). ¹³C{¹H} NMR (C_4D_8O, 400 MHz): δ 130.2 (1C, ring *C*CMe₃), 129.6 (2C, ring *C*CMe₃), 107.6 (2C, ring C*H*), 67.4 (q, O*C*D₂ solvent), 35.1 (2C, *C*Me₃), 33.8 (6C, *C*H₃), 33.4 (1C, *C*Me₃), 32.4 (3C, *C*H₃), 25.2 (q, OCD₂*C*D₂).

[{(C₅H(CHMe₂)₄)BaI(THF)₂}₂] (2-Ba). A suspension/solution of 1.17 g (3 mmol) of barium iodide and 0.77 g (3 mmol) of sodium tetraisopropylcyclopentadienide in 20 mL of tetrahydrofuran was stirred for 3 days at ambient temperature and then evaporated to dryness. Extraction with three 15 mol portions of toluene, filtration, and evaporation gave 1.17 g (1.82 mmol, 61%) of white microcrystalline product. Analytically pure samples and single crystals suitable for X-ray diffraction were obtained by recrystallization from THF.

Anal. Calcd for $C_{25}H_{45}BaIO_2$: C, 46.81; H, 7.01; Ba, 21.40; I, 19.77. Found: C, 44.88; H, 6.90; Ba, 21.50; I, 20.00. ¹H NMR (mixture of C_6D_6 and C_4D_8O, 400 MHz): δ 5.90 (s, 1H, ring C*H*), 3.46 ("sep", 2H, C*H*Me₂), 3.34 ("sep", 2H, C*H*Me₂), 1.68 (d, 6H, J_{HH} = 7.2 Hz, C*H₃*), 1.62 (d, 6H, J_{HH} = 7.2 Hz, C*H₃*), 1.52 (d, 6H, J_{HH} = 5.9 Hz, C*H₃*), 1.40 (d, 6H, J_{HH} = 6.6 Hz, C*H₃*).

[{(C₅H(CHMe₂)₄)SrI(THF)₂}₂] (2-Sr). A mixture of strontium diiodide (0.55 g, 1.6 mmol) and sodium tetraisopropyl-

cyclopentadienide (0.41 g, 1.6 mmol) and tetrahydrofuran (20 mL) was stirred at ambient temperature for 2 days. Addition of toluene (2 mL) precipitated a white solid, which was removed by centrifugation. The supernatant solution was evaporated to ca. 5−6 mL and stored at 5 °C. After 3 days the product was isolated as a colorless microcrystalline powder (0.79 g, 1.3 mmol, 83%).

Anal. Calcd for $C_{25}H_{45}SrIO_2$: C, 50.71; H, 7.66; Sr, 14.80; I, 21.43. Found: C, 45.66; H, 7.11; Sr, 14.90; I, 21.60. ¹H NMR (C_4D_8O, 400 MHz): δ 5.57 (s, 1H, ring C*H*), 3.12 ("sep", 2H, C*H*Me₂), 3.07 ("sep", 2H, C*H*Me₂), 1.39 (d, 6H, J_{HH} = 6.6 Hz, C*H₃*), 1.29 (d, 6H, J_{HH} = 5.5 Hz, C*H₃*), 1.25 (d, 6H, J_{HH} = 6.4 Hz, C*H₃*), 1.04 (d, 6H, J_{HH} = 5.8 Hz, C*H₃*). ¹³C NMR (C_6D_6, ambient temperature): δ 126.8 (s, 2C, ring *C*R), 122.8 (2, 2C, ring *C*R), 99.6 (d, 1C, ring C*H*, $^1J_{CH}$ = 150 Hz), 28.1 (d, 2C, *C*HMe₂, $^1J_{CH}$ = 131 Hz), 27.8 (4C, *C*H₃*), 27.5 (q, 4C, *C*H₃, $^1J_{CH}$ = 123 Hz), 26.0 (2C, *C*HMe₂*). The asterisks note signals where coupling constants were not determined because of superposition with alkyl or solvent signals.

Synthesis of Octaisopropylstrontocene (3-Sr). A solution of 1.54 g (6.01 mmol) of sodium tetraisopropylcyclopentadienide in 30 mL of tetrahydrofuran was stirred at ambient temperature with 0.98 g (2.87 mmol) of strontium iodide for 3 days. The solvent was removed in vacuo, and the solid residue was extracted with two 15 mL portions of pentane. Evaporation to dryness yielded 1.31 g (2.36 mmol, 82%) of product with a melting point of 151−153 °C.

Anal. Calcd for $C_{34}H_{58}Sr$: C, 73.65; H, 10.54; Sr, 15.80. Found: C, 70.85; H, 10.54; Sr, 15.56. ¹H NMR (C_6D_6, 400 MHz): δ 5.72 (s, 2H, ring C*H*), 3.13 ("sep", 4H, C*H*Me₂), 2.99 ("sep", 4H, C*H*Me₂), 1.36 (d, 12H, J_{HH} = 7.1 Hz, C*H₃*), 1.29 (d, 12H, J_{HH} = 6.7 Hz, C*H₃*), 1.28 (d, 12H, J_{HH} = 6.7 Hz, C*H₃*), 1.15 (d, 12H, J_{HH} = 7.1 Hz, C*H₃*). ¹³C NMR (C_6D_6, ambient temperature): δ 128.5 (s, 4C, ring *C*R), 123.2 (s, 4C, ring *C*R), 100.5 (dt, 2C, ring C*H*, $^1J_{CH}$ = 155, $^3J_{CH}$ = 5), 27.3 (q, 4C, *C*H₃, $^1J_{CH}$ = 125), 27.3 (q, 4C, *C*H₃, $^1J_{CH}$ = 125), 26.8 (d, 4C, *C*H₃, $^1J_{CH}$ = 124), 25.0 (d, 4C, *C*H₃, $^1J_{CH}$ = 123), 24.6 (q, 4C, *C*H₃, $^1J_{CH}$ = 124), 24.3 (q, 4C, *C*H₃, $^1J_{CH}$ = 125). ¹H NMR (C_4D_8O, 400 MHz): δ 5.59 (s, 2H, ring-C*H*), 3.09 ("sep", 4H, C*H*Me₂), 3.05 ("sep", 4H, C*H*Me₂), 1.35 (d, 12H, J_{HH} = 7.2 Hz, C*H₃*), 1.26 (d, 12H, J_{HH} = 6.7 Hz, C*H₃*), 1.17 (d, 12H, J_{HH} = 7.1 Hz, C*H₃*), 1.04 (d, 12H, J_{HH} = 6.7 Hz, C*H₃*). ¹³C{¹H} NMR (C_4D_8O, ambient temperature): δ 127.6 (s, 4C, ring *C*R), 123.9 (s, 4C, ring *C*R), 101.2 (s, 2C, ring C*H*), 28.0 (s, 4C, *), 27.6 (s, 4C, *), 27.1 (s, 4C, *), 26.0 (s, 4C, *), 25.7 (s, 4C, *), 25.4 (s, 4C, *). CI-MS (methane, 120 eV, m/z (%)): 554.3 (88, M⁺), 320.9 (8, M⁺ − $C_{17}H_{29}$), 234.3 (100, $C_{17}H_{30}$⁺), 219.3 (69, $C_{16}H_{27}$⁺), 191.3 (41, $C_{14}H_{23}$⁺), 177.2 (35, $C_{13}H_{21}$⁺), 149.2 (41, $C_{11}H_{17}$⁺), 107.2 (14, C_8H_{11}⁺).

The asterisk denotes C*H*Me₂ or C*H₃*; the signal was not assigned.

Synthesis of [{(C₅H₂(CMe₃)₃)CaCl(THF)}₂] (4-Ca). A suspension of 1.03 g (4.02 mmol) of sodium 1,2,4-tri-*tert*-butylcyclopentadienide and 0.44 g (3.97 mmol) of calcium chloride pellets in 15 mL of dimethoxyethane was stirred for 2 days at ambient temperature and subjected to centrifugation. Extraction of the solid residue with another 14 mL portion of DME, centrifugation, and evaporation of the combined extracts to 10−15 mL volume resulted in formation of a microcrystalline precipitate of product. The precipitate was dissolved completely by warming to 40 °C with stirring, and the warm solution was cooled to ambient temperature. Colorless crystals up to several millimeters in diameter were obtained in 0.48 g yield. From the concentrated mother liquor a second crop of crystals could be harvested, for a total yield of 1.12 g (1.40 mmol, 70.5%). Anal. Calcd for $C_{21}H_{39}CaClO_2$: C, 63.52; H, 9.39; Ca, 10.04; Cl, 8.88. Found: C, 61.89; H, 9.35; Ca, 9.95; Cl, 8.81. ¹H NMR (C_6D_6, 400 MHz): δ 6.23 (s, 2H, ring C*H*), 3.17 (br s, 10H, OC*H₂* and OC*H₃*), 1.70 (s, 18 H, 6 C*H₃*), 1.51 (s, 9 H, 3 C*H₃*).

(16) (a) Sitzmann, H.; Walter, M. D.; Wolmershäuser, G. *Angew. Chem.* **2002**, *41*, 2315−2316. (b) Walter, M. D.; Wolmershäuser, G.; Sitzmann, H., manuscript submitted for publication.

Supporting Information Available: Tables giving details of crystallographic studies, atomic positions and aniso- tropic thermal parameters, bond lengths and angles, and least squares planes for each structure. This material is available free of charge via the Internet at http://pubs.acs.org. Structure factor tables are available from the authors.

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