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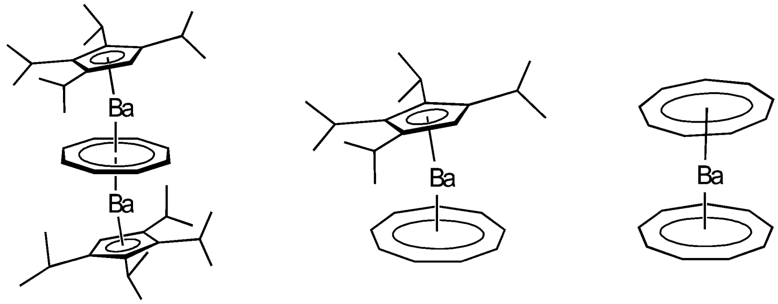
J. Am. Chem. Soc., **2005**, 127 (49), 17494-17503• DOI: 10.1021/ja0550071 • Publication Date (Web): 12 November 2005



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Calcium, Strontium, Barium, and Ytterbium Complexes with Cyclooctatetraenyl or Cyclononatetraenyl Ligands[1]

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Abstract: Neutral triple-decker complexes of the heavy alkaline earth metals and ytterbium with tetraisopropylcyclopentadienide anions as terminal ligands and a cyclooctatetraene dianion as a middle deck have been synthesized from tetraisopropylcyclopentadienyl metal halide precursors and disodium cyclooctatetraenide. The pentaisopropylcyclopentadienyl analogue $[\{(C_5{}^iPr_5)Yb\}_2(C_8H_8)]$ was prepared from ytterbium metal, cyclooctatetraene, and the free pentaisopropylcyclopentadienyl radical. X-ray crystal structure determinations for the barium and the calcium derivative show an almost linear arrangement of ring centers and metal atoms in both cases with metal−ring center distances of 2.33 Å (Ca−Cp), 1.99/1.98 Å (Ca−COT) and 2.71 Å (Ba−Cp), 2.40 Å (Ba−COT). The geometrical features of these molecules could be modeled quite accurately with density functional calculations. With potassium cyclononatetraenide, sparingly soluble bis(cyclononatetraenyl)barium could be prepared and characterized by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. Cyclononatetraenyl(tetraisopropylcyclopentadienyl)barium was obtained from $[(C_5HiPr_4)BaI(THF)_2]_2$ and KC_9H_9 as a 1:1 mixture with octaisopropylbarocene. Density functional calculations predict sandwich structures with parallel rings and a 2.37 Å Ba−ring distance for $[Ba(C_9H_9)_2]$ and a 174° bending with metal−ring distances of 2.72 Å (Ba−Cp) and 2.35 Å (Ba−CNT) for $[(C_5HiPr_4)Ba(C_9H_9)]$. All alkaline earth sandwich and triple-decker complexes mentioned above have been heated to 250 °C without decomposition and have been sublimed in oil pump vacuum.

Introduction

Much of the development of soluble and well-behaved organometallic compounds of the heavy alkaline earth metals known today is owed to the favorable properties of sterically bulky hydrocarbyl ligands such as tris-[2] or bis(trimethylsilyl)-methyl,[3] triphenylsilylethynyl,[4] silylated allyl[5] or benzyl ligands[6] or benzyl ligands with a nitrogen donor function in the side chain,[7] open pentadienyl ligands such as 2,4-di(*tert*-butyl)-pentadienyl,[8] or cyclopentadienyl ligands with bulky substituents, e. g., C_5Me_5 (Cp*),[9−11] $C_5H_2(SiMe_3)_3$-1,2,4,[12−14] $C_5H(CHMe_2)_4$ (^{4}Cp),[15] $C_5H_2(CMe_3)_3$-1,2,4 (Cp‴),[16,17] or $C_5(CHMe_2)_5$ (^{5}Cp).[18]

Organometallic compounds of the heavy alkaline earth metals are attracting interest as synthetic reagents in organic synthesis or as initiators of anionic styrene polymerization.[6,7,19−22] Furthermore, they may function as MOCVD precursors with sufficient volatility and stability for growth of thin films with high-temperature superconducting (HTS) or ferroelectric properties.[23] Basic research has focused primarily on metallocenes and related compounds.[24]

The development of synthetically useful half-sandwich complexes of these large cations as precursors for a variety of functionalized derivatives presents a challenge and a synthetic goal. Introduction of the sterically demanding tris(trimethylsilyl)-

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10.1021/ja0550071 CCC: $30.25 © 2005 American Chemical Society

cyclopentadienyl ligand recently allowed the crystallographic characterization of dimeric calcium and strontium iodo complexes, $[\{(C_5H_2(SiMe_3)_3)Ca(\mu\text{-}I)(THF)\}_2]$ and $[\{(C_5H_2(SiMe_3)_3)Sr(\mu\text{-}I)(THF)_2\}_2]$, and the barium chain polymer $[\{(C_5H_2(SiMe_3)_3)Ba(\mu\text{-}I)(THF)\}_\infty]$.[13] Tris(trimethylsilyl)cyclopentadienide loss upon attempted nucleophilic substitution of the halide in these complexes hampers their possible use as starting materials. The only accessible substitution product to date is the borate complex, $[(C_5H_2(SiMe_3)_3)Ca(HBEt_3)(THF)_2]$.[14] However, nucleophilic substitution has been successful with mono(alkylcyclopentadienyl)calcium halide complexes and has yielded amide and aryloxide derivatives.[25,26]

In our laboratory, extremely bulky alkylcyclopentadienides such as 1,2,4-tri-*tert*-butylcyclopentadienide and tetraisopropylcyclopentandienide have been able to kinetically stabilize mono(cyclopentadienyl) halides of the heavy alkaline earth metals with additional tetrahydrofuran or dimethoxyethane donor ligands.[27] This was demonstrated for strontium and barium compounds, despite a recent report to the contrary.[13]

This work was started within an attempt to create steric bulk with carbocycles possessing more than five ring atoms, whose ring planes have to approach the central atom closer than those of a five-membered ring in order to allow for proper metal−carbon distances and should thus give rise to sandwich compounds with relatively short inter-ring distances. For this purpose, we directed our attention toward the cyclooctatetraene dianion and the cyclononatetraenyl anion as complex ligands. In this context, we previously reported a successful synthesis of a neutral barium triple-decker complex with cyclooctatetraenyl middle deck in a short communication.[28] The extension of this work to similar complexes of calcium, strontium, and ytterbium and to cyclononatetraenyl complexes of barium is the subject of this paper.

Results and Discussion

The most promising starting compounds for the synthesis of mono(cyclopentadienyl) complexes of the heavy alkaline earth metals are monohalides of the $[CpMX(solvent)_m]_n$ type (M = Ca, Sr, Ba; X = Cl, Br, I; $m = 1-3$; $n = 1, 2, \infty$). The only halide substitution reactions in this context have been reported for the introduction of anionic nucleophiles into calcium compounds almost exclusively carrying penta- or tetraalkylated cyclopentadienyl ligands.[14,25,26,29] To extend the feasibility of such substitution reactions to strontium and barium, recently the iodo complexes $[\{(C_5HR_4)BaI(THF)_2\}_2]$ (**1-Ba**; R = $CHMe_2$) and $[\{(C_5HR_4)SrI(THF)_2\}_2]$ (**1-Sr**; R = $CHMe_2$) have been prepared,[27] which could be used as starting compounds for reactions with disodium cyclooctatetraenide (Figure 1).

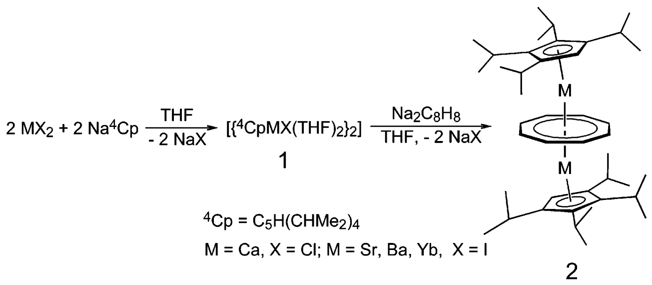

Figure 1. Synthesis of triple-decker sandwich complexes **2**.

Stirring of tetraisopropylcyclopentadienyl calcium chloride **1-Ca** or tetraisopropylcyclopentadienyl strontium iodide **1-Sr**, both generated in situ, or tetraisopropylcyclopentadienyl barium iodide **1-Ba** with disodium cyclooctatetraenide in tetrahydrofuran at ambient temperature for a few days affords the triple-decker sandwich complexes $[(C_5HR_4)M(\mu,\eta^8{:}\eta^8\text{-}C_8H_8)M(C_5HR_4)]$ (R = $CHMe_2$, M = Ca, Sr, Ba[28]) as colorless powders in good yield. **2-Ca**, **2-Sr**, and **2-Ba** are readily soluble in tetrahydrofuran, moderately soluble in toluene, and sparingly soluble in pentane, and they can be crystallized from saturated benzene solution. Compound **2-Yb** behaves differently: the solubility in aliphatic solvents (like *n*-hexane) is fairly good, and this product can be crystallized from a saturated *n*-hexane solution. In an oil pump vacuum, the heavy alkaline earth compounds can be sublimed without decomposition at 130 °C (**2-Ca**), 175 °C (**2-Sr**), 215 °C (**2-Ba**), and unchanged melting points have been found after heating **2-Ca**, **2-Sr**, or **2-Ba** to 250 °C under an argon atmosphere. In air, the compounds turn yellow immediately and orange-red within seconds. Finally, a pale yellow residue is obtained, and a strong COT smell is developed.

In EI mass spectra, the molecular ion as well as signals for the fragments $[^4CpM(COT)M]^+$ (parent peak for M = Ca) and $[^4CpM]^+$ (parent peak for M = Ba) could be detected and shown to exhibit correct isotope patterns for all three heavy alkaline earth derivatives. However, for **2-Yb** no metal containing fragment was detected under these conditions.

In NMR spectra, one set of signals for the tetraisopropylcyclopentadienyl ligand and one signal for the cyclooctatetraene ligand have been observed, and the ^{13}C NMR signals have been recorded at 89.6 ppm for **2-Ca**, 91.6 ppm for **2-Sr**, 95.3 ppm for **2-Ba**, and 89.8 ppm for **2-Yb**, with almost identical $^1J_{C,H}$ coupling constants of 157, 157, 158, and 163 Hz, respectively. For comparison, $\{[(Me_3Si)_2N]Yb(thf)\}_2(\mu\text{-}C_8H_8)$ shows the COT signal at 90.8 ppm in the ^{13}C NMR.[30]

Structure determinations have been carried out by X-ray crystallography on monoclinic crystals of the triple-decker sandwich complexes **2-Ca** and **2-Ba**, the latter including 1 equiv of C_6D_6 in the crystal lattice (Figures 2 and 3).

The Ca−C(^{4}Cp) distance average of 2.62 Å, and the Ba−C(^{4}Cp) distance of 2.96 Å are comparable to the values found for the respective octaisopropylmetallocenes of calcium (2.64 Å) or barium (2.94 Å)[15] and for the tetraisopropylcyclopentadienyl iodide dimer of barium (2.97 Å)[27] and slightly shorter than the value found for $[\{^4CpCa(\mu\text{-}I)(THF)\}_2]$ (2.67 Å).[29] The metal−C(COT) distances are longer: for **2-Ca** the respective distance range is 2.660(3)−2.703(3) Å (2.683 Å average), and for **2-Ba** values between 2.994(5) and 3.016(6) Å (3.006 Å average) have been observed. Despite the longer metal−carbon distances, the metal approaches the cyclooctatetraene plane much closer than the cyclopentadienyl plane because of the large diameter of the eight-membered ring.

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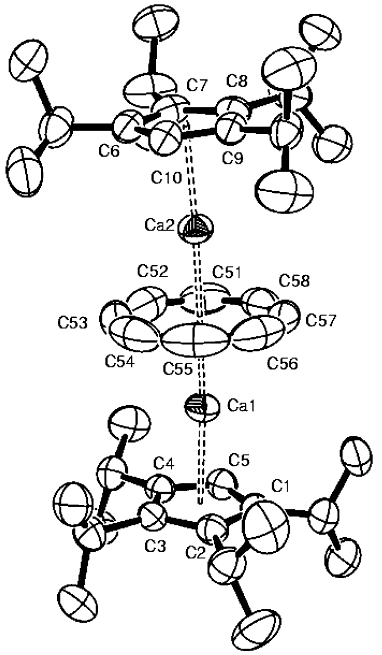

Figure 2. ORTEP diagram of **2-Ca** (50% probability ellipsoids). Selected distances (Å) and angles (deg): Ca1−C1 2.626(3), Ca1−C2 2.645(2), Ca1−C3 2.629(2), Ca1−C4 2.606(2), Ca1−C5 2.589(2), Ca1−C51 2.680(3), Ca1−C52 2.686(3), Ca1−C53 2.692(3), Ca1−C54 2.703(3), Ca1−C55 2.692(4), Ca1−C56 2.682(3), Ca1−C57 2.684(3), Ca1−C58 2.677(3), Ca2−C6 2.637(2), Ca2−C7 2.640(3), Ca2−C8 2.627(2), Ca2−C9 2.600(2), Ca2−C10 2.592(2), Ca2−C51 2.684(3), Ca2−C52 2.669(3), Ca2−C53 2.658(3), Ca2−C54 2.660(4), Ca2−C55 2.677(4), Ca2−C56 2.696(3), Ca2−C57 2.695(3), Ca2−C58 2.699(3), Ca1−Cp$_{\mathrm{cent}}$ 2.33, Ca2−Cp$_{\mathrm{cent}}$ 2.33, Ca1−COT$_{\mathrm{cent}}$ 1.99, Ca2−COT$_{\mathrm{cent}}$ 1.98, Cp$_{\mathrm{cent}}$−Ca1−COT$_{\mathrm{cent}}$ 173.0, Cp$_{\mathrm{cent}}$−Ca2−COT$_{\mathrm{cent}}$ 175.8.

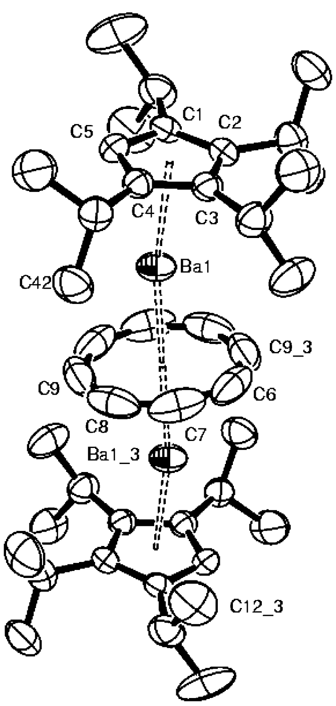

Figure 3. ORTEP diagram of **2-Ba** (50% probability ellipsoids). C_6D_6 incorporated in the crystal lattice was omitted for clarity. Symmetry related positions ($-x + 1$, y, $-z + 2$) are labeled with _3. Selected distances (Å) and angles (deg): Ba1−C1 2.945(4), Ba1−C2 2.982(4), Ba1−C3 2.993(4), Ba1−C4 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), Ba1−C6 3.003(5), Ba1−C7 3.015(6), Ba1−C8 3.016(6), Ba1−C9 3.007(5), Ba1−Cp$_{\mathrm{cent}}$ 2.71, Ba1−COT$_{\mathrm{cent}}$ 2.40, Cp$_{\mathrm{cent}}$−Ba1−COT$_{\mathrm{cent}}$ 169.5, C12···Ba1 3.56, C42···Ba1 3.57; angles between ^{4}Cp plane/C1−C11 0.7, ^{4}Cp plane/C2−C21 3.1, ^{4}Cp plane/C3−C31 2.1, ^{4}Cp plane/C4−C41 0.2.

For **2-Ca** the Ca−^{4}Cp$_{\mathrm{cent}}$ distance is 2.33 Å, whereas the Ca−COT$_{\mathrm{cent}}$ values are 1.99 Å (Ca1) and 1.98 Å (Ca2).Compound **2-Ba** shows the same tendency with 2.71 Å for Ba−^{4}Cp$_{\mathrm{cent}}$ versus 2.40 Å for Ba−COT$_{\mathrm{cent}}$. These numbers show a larger difference for the smaller calcium atom as expected. While the diameters of the C_5 rings are 2.402/2.404 Å (**2-Ca**) and 2.406 Å (**2-Ba**), respectively, the eight carbon atoms of the COT ring are situated on a circle with a 3.613 Å (**2-Ca**) or 3.626 Å (**2-Ba**) diameter, calculated as an average of five or eight C−(ring center) distances. Although the synthesis of heavy alkaline earth compounds of the general formula [$(C_8H_8)ML_n$] (M = Yb, Ca, Sr, Ba, L = THF, pyridine) by metal co-condensation with cycloctatetraene and solvent extraction has been reported, their low solubility, high air sensitivity, and their microcrystalline nature precluded a structural analysis.[31] However, the ytterbium(II) derivative, [(C_8H_8)Yb(pyridine)$_3$], has been crystallographically characterized and shows geometrical features of the Yb(C_8H_8) substructure comparable to those of **2-Ca** with Yb−C distances of 2.57−2.69 Å and a Yb−ring distance of 1.91 Å.[32] Yb−C distances from 2.71 to 2.78 Å have been found for the dipotassium salt [K(dme)]$_2$[(η^8-C_8H_8)$_2$Yb(II)],[33] and the Yb−C(COT) average distances found for the triple-decker [(C_5Me_5)-Yb(μ,η^8:η^8-C_8H_8)Yb(C_5Me_5)] are 2.65 Å (Yb1) and 2.67 Å (Yb2).[34] Streitwieser et al. have also reported the synthesis of [K(dme)]$_2$[(η^8-C_8H_8)$_2$Ca(II)], which is presumably isostructural to its ytterbium analogue, but no single crystal data are available.[33] The short contacts between two methyl groups (C12, C42) and the barium central atom of **2-Ba** (3.56/3.57 Å) correspond to almost complete absence of outward bending of the respective methyne carbon atoms C11 and C41 as well as rotation of the respective isopropyl groups toward the barium center. These features have not been observed in **2-Ca**, where the closest C···Ca contacts are still larger than 3.6 Å (3.65/3.67 Å for Ca2···C82 and Ca1···C12).

Complexes **2** are the only neutral species among the few triple-decker sandwich complexes known with main group central atoms and show a very low degree of bending with ^{4}Cp$_{\mathrm{cent}}$−M−COT$_{\mathrm{cent}}$ angles of 173.0°/175.8° (**2-Ca**) and 168.5° (**2-Ba**), compared to the Cp$_{\mathrm{cent}}$−M−Cp$_{\mathrm{cent}}$ angles of 155°/152° for [$(C_5Me_5)_3Sn_2$]$^+$,[35] 134° for [Cp_3Tl_2]$^-$,[36] 124/130° for [(η^6-C_7H_8)$_2$(μ,η^5:η^5-C_5Me_5)In$_2$]$^+$,[35] or 116° for [Cp_3Cs_2]$^-$.[37] Even octaisopropylmetallocenes of calcium (162°) or barium (154°)[15] are more strongly bent than **2-Ca** or **2-Ba**.

It has been demonstrated that divalent lanthanide and alkaline earth metallocenes prefer bent sandwich structures in gas as well as condensed phases.[9,11,38−41] Different models have been

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Table 1. Comparison of Structural Parameters in Solid Cyclopentadienyl Complexes of Lanthanides and Heavy Alkaline Earth Metals

complex	ionic radius, Å	av M–C, distance, Å	closest M–CH_3, Å	cent–metal–cent, deg	solid state/gas phase
CN = 6					
Cp^*_2Ca	1.00	2.62(2)	2.98	148	s
Cp^*_2Yb	1.02	2.665(4)	2.94	146	s
Cp^*_2Sm	1.17	2.79(1)	3.22	140	s
Cp^*_2Eu	1.17	2.79(1)	3.19	140	s
Cp^*_2Ba	1.35	2.99(2)	3.35	131	s
Cp^*_2Sr	1.18			149	g
Cp^*_2Ca	1.00			154	g
Cp^*_2Ba	1.35			148	g
Cp^*_2Mg	0.72			180	s, g
CN = 8					
$[Cp^*Sm]_2(C_8H_8)$	1.27	2.78; 2.83		149	s
$[Cp^*Eu]_2(C_8H_8)$	1.25	2.79; 2.82		148	s
$[Cp^*Yb]_2(C_8H_8)$	1.14	2.63; 2.65		160	s
$[Cp'Sm]_2(C_8H_8)$	1.27	2.75; 2.77	3.53	158	s
Cp*Sm(COT)	1.079	2.67; 2.56	3.54	164	s
Cp*Yb(COT)	0.985	2.54; 2.43	3.55	177	s
Cp*Er(COT)	1.004	2.61; 2.55		169	s
^{4}CpNd(COT)	1.109			165	s
^{4}CpSm(COT)	1.079			170	s
CN = 6					
$^4Cp_2Ca$	1.00	2.64		162	s
$^4Cp_2Sr$	1.18	2.81	3.62	158	s
$^4Cp_2Ba$	1.35	2.94	3.58	154	s
$^4Cp_2Sm$	1.17	2.78	3.54	152	s
$^4Cp_2Eu$	1.17	2.79	3.57	154	s
$^4Cp_2Yb$	1.02	2.68	3.68	157	s
$[C_5H_2(CMe_3)_3]_2Mg$	0.72	2.39		173	s
$[C_5H_2(CMe_3)_3]_2Ca$	1.00	2.64	3.60	171	s
$[C_5H_2(CMe_3)_3]_2Sm$	1.17	2.79	3.44	164	s
$[C_5H_2(CMe_3)_3]_2Eu$	1.17	2.78	3.29	165	s
$[C_5H_2(CMe_3)_3]_2Yb$	1.02	2.51	3.40	166	s
CN = 8					
$[^4CpBa]_2(C_8H_8)$	1.42	2.96; 3.01	3.56	170	s
$[^4CpCa]_2(C_8H_8)$	1.12	2.62; 2.68		174	s

proposed to rationalize this geometrical behavior, including a molecular orbital model,[42−44] an electrostatic (polarized-ion) model,[45,46] and a model based on attractive van der Waals forces.[47,48] No single explanation has been generally accepted so far. Limits to the extent of bending of ML_2 molecules originated from a repulsion as the ligands approach each other closer than their sum of van der Waals radii. This repulsion is related to the metal radius, as larger metals are capable of increased bending before ligand collision is encountered. Because bending energies are quite small, on the order of 1−5 kcal/mol, no experiment to date has been able to rule out any of these hypotheses.[43,44,49]

To describe this trend empirically, Hanusa et al. followed an analysis by Raymond and Eigenbrot[50] and correlated the available data on bending angles with the ionic radii for decamethylmetallocenes of the lanthanides and heavy alkali metals.[39,51] Evans et al. provided more information on bending angles in triple-decker complexes of Eu, Sm, and Yb with Cp* ligands.[52] The discussion on the origin of steric bending has been addressed in a review article dealing also with alkaline earth complexes with extremely bulky alkylcyclopentadienyl ligands,[39] but a detailed correlation has not been available for sterically even more demanding ligands such as tetraisopropyl- or tri(*tert*-butyl)cyclopentadienide (Table 1). Although only two triple-decker complexes have been structurally characterized, they will most probably also follow the linear relationship between metal radius and bond angle as observed in related metallocene complexes, with a greater tendency toward parallel planes for smaller metals. Furthermore, the replacement of a Cp unit for a COT deck does increase the tendency toward a more linear arrangement by a constant additional increment of roughly 13°, as demonstrated by almost parallel linear fits for $(C_5Me_5)_2M$ and $[(C_5Me_5)M]_2(COT)$ and $^4Cp_2M$ and $(^4CpM)_2(COT)$, respectively (Figure 4).

Furthermore, it has been suggested that short M···CH_3 contacts cause the rings to move toward a more parallel orientation. This kind of interaction served to increase the bonding area of the cyclopentadienyl ligand, and the larger ligand leads to a more linear structure.[53] However, the crystal

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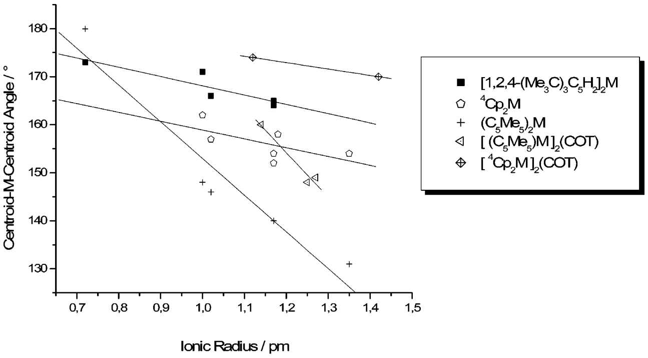

Figure 4. Graph of ionic radii vs (ring centroid)−M−(ring centroid) angle.

structure data available for metallocenes and triple-decker complexes with bulky cyclopentadienyl ligands do not corroborate this hypothesis: ^{4}Cp$_2$Ba has two independent molecules in the asymmetric unit, one of which exhibits a short Ba···CH$_3$ contact, whereas the other molecule does not. However, the bending angle is nearly identical in both cases.[15] The influence of agostic interactions should not be discounted, but these interactions appear to be very weak and therefore they cannot be a dominant factor governing the bending angle.

Computational Studies

Compounds of the heavy alkaline earth metals attracted some interest, because Gagliardi and Pyykkö recently suggested for systems of the type MN$_7$M′, where M is an alkaline metal (K, Rb, Cs) and M′ is an alkaline earth metal (Ca, Sr, Ba), that the N$_7$−M′ interaction is increasing with increasing d character along the series M′ = Ca−Ba. This is pronounced in the Cs or Ba systems, where a quintuple bond between Ba and N$_7$ was predicted. One σ, two π, and two δ bonding MOs are identifiable, with a substantial 5d Ba character in the δ bonds. Also, it was suggested that a similar bonding mechanism might explain the short Ba−C bonds found in **2-Ba**.[54]

Density functional theory (DFT) calculations account for electron correlation effects in large molecules of low symmetry with less computational expense than that required by other post-Hartree−Fock methods,[55−57] and they have been shown to provide experimentally relevant geometries in main group and lanthanide molecules.[58−60] In particular, they have been used to explore the orbital origins of bending in the alkaline earth metallocenes Cp$_2$Ca and Cp$_2$Sr,[45] a structural feature that is not always reproducible with HF/MP2-level calculations.[61]

Accordingly, DFT calculations were performed on a variety of model compounds with various DFT functionals. The studies focused on optimizing the geometry of the complexes compared to the X-ray crystallographic results and on the investigation of the molecular orbitals/NBO charges to give an insight into the bonding situation. Geometry optimizations were carried out without symmetry restrictions (C_1 symmetry). The nature of the minima was verified by analytical frequency calculations, and the zero-point energy (ZPE) was estimated within the harmonic potential approximation. The ^{4}Cp ligand was modeled by C$_5$H$_5$. Although there is a large difference in steric size between these ligands, which is a severe approximation especially when some significant geometrical reorganization can occur,[60,62] Hanusa et al. pointed out that three different cyclopentadienyl ligands (Cp, C$_5$Me$_5$, and 1,2,4-(Me$_3$Si)$_3$C$_5$H$_2$) are virtually interchangeable in their contributions to the geometric parameters (especially distances) and to the reaction enthalpy.[13]

Table 2. Selected Bond Distances (Å) and Angles (deg) of Calculated (B3PW91, 6-311G for C, H, and Ca, SDD for Ba and Sr) and Experimental Structures

	calcd	expt	delta	% error
Cp(cent)1−Ba1	2.739	2.71	0.029	1.1
Ba1−COT(cent)	2.424	2.397	0.027	1.1
COT(cent)−Ba2	2.424			
Ba2−Cp(cent)2	2.738			
Cp1(cent)−Ba1−COT(cent)	175.47	168.46	7.01	4.2
Cp2(cent)−Ba2−COT(cent)	176.27			
Cp(cent)1−Sr1	2.540			
Sr1−COT(cent)	2.206			
COT(cent)−Sr2	2.203			
Sr2−Cp(cent)2	2.548			
Cp1(cent)−Sr1−COT(cent)	179.10			
Cp2(cent)−Sr2−COT(cent)	174.61			
Cp(cent)1−Ca1	2.341	2.327	0.014	0.60
Ca1−COT(cent)	1.998	1.989	0.009	0.45
COT(cent)−Ca2	1.997	1.979	0.018	0.91
Ca2−Cp(cent)2	2.340	2.328	0.012	0.52
Cp1(cent)−Ca1−COT(cent)	178.52	172.99	5.53	3.20

Geometry

Geometry optimization of [(C$_5$H$_5$)M]$_2$(COT) (M = Ca, Sr, Ba)[63] revealed structural parameters that agree favorably with structures of **2-Ca** and **2-Ba** determined by X-ray crystallography (Table 2).

Even the bend angles agree surprisingly well with the experimental values. Due to the smaller size of C$_5$H$_5$ relative to ^{4}Cp, a more dramatic difference in the Cp(centroid)−M−COT(centroid) angle has been anticipated on the basis of comparisons of C$_5$H$_5$ and Me$_5$C$_5$ lanthanide derivatives.[60,64] The molecular geometry of **2-Sr** optimized at the B3PW91/6-311G (C, H) and SDD (Sr) level is shown in Figure 5.

Ligand Redistribution

The triple-decker complexes **2** are remarkably stable toward ligand redistribution; to evaluate this stability, the energetics of this reaction in the gas phase have been calculated in the case of [(C$_5$H$_5$)Ba]$_2$(COT). As the largest of the nonradioactive group 2 elements, it is the most prone to this kind of Schlenk equilibrium (Figure 6).

The ligand redistribution is endothermic by an energy difference of + 211.63 kJ/ mol, supporting the experimental results. However, one might argue that this ligand redistribution energy obtained from a gas phase calculation is substantially

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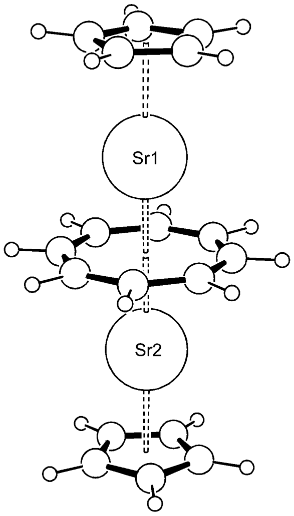

Figure 5. Molecular geometry of **2-Sr** optimized at the B3PW91/6-311G (C, H) and SDD (Sr) level.

too high, because no consideration is given to stabilization due to solvation of the $(C_8H_8)Ba$ species. This is probably true for ether solvents; however, it is experimentally known that the $(C_8H_8)_2Ba$ is insoluble in aromatic solvents such as toluene or benzene,[31] and therefore the perturbation due to solvation is expected to be less dramatic.

Mulliken and NBO Population Analysis

It was suggested that the Mulliken population analysis is an appropriate measurement of the d character of the heavier MN_7M' systems.[54] The Mulliken partial charge on metal in the system $[(C_5H_5)M]_2(COT)$ (M = Ca, Sr, Ba) decreases from Ba to Ca with the smallest partial charge of +1.02 at Ca, instead of the formal value of +2 (Table 3). That is in contrast to Gagliardi and Pyykkö's MN_7M' system, suggesting that the influence of d orbitals on the overall bonding in the COT triple decker is minor. The natural electron configuration on the metal cations is more or less constant as well as the contribution of d orbitals to the bonding, as also reflected in a nearly constant NPA net charge consistent with a mostly ionic bonding in these complexes.

Table 3. Natural Electron Configuration of the Metal Cations and Their Natural Charges at the B3PW91/6-311G (H, C, Ca), SDD (Sr, Ba) Level[a]

		natural population			net charge	
system	point group	ns	(n – 1)d	(n + 2)p	NPA	MPA
$[(C_5H_5)Ca]_2(C_8H_8)$	C_1	0.05	0.15	0.01	1.7929	1.0240
$[(C_5H_5)Sr]_2(C_8H_8)$	C_1	0.03	0.12	0.01	1.8389	1.2050
$[(C_5H_5)Ba]_2(C_8H_8)$	C_1	0.02	0.13	0.01	1.8439	1.3255

[a] Charges predicted by Mulliken population analysis (MPA) are also shown.

Alternative Synthesis for Neutral Triple-Decker Complexes

The synthesis of metallocenes from cyclopentadienyl radicals and metal is probably the most convenient, and conceptually the simplest, synthesis. This synthetic method was realized by the successful synthesis of decaisopropylmetallocenes $[(C_5R_5)_2M]$ (M = Ca, Sr, Ba,[18] Sm, Eu Yb;[65] R= $CHMe_2$) from the elements

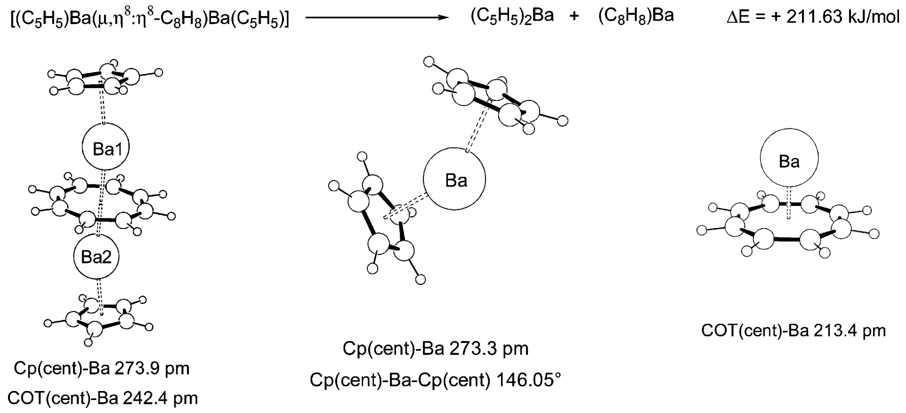

Figure 6. Barium complexes involved in the Schlenk equilibrium.

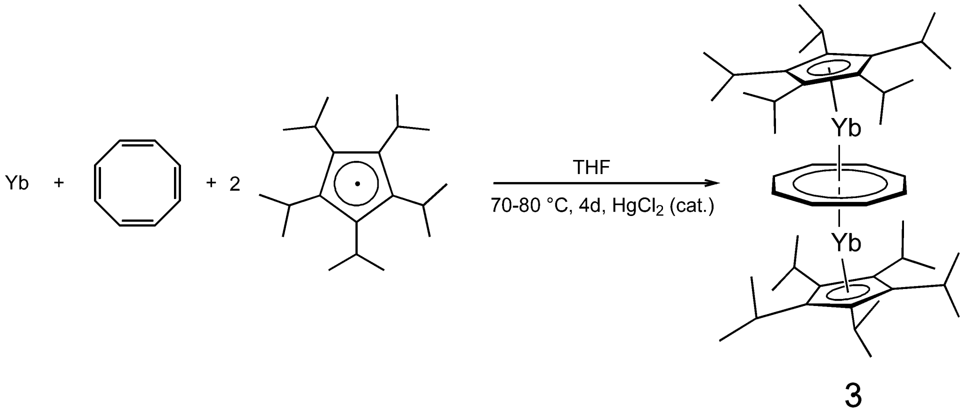

Figure 7. Synthesis of triple-decker sandwich complex **3**.

and 2 equiv of the stable pentaisopropylcyclopentadienyl radical. A salt-free synthesis was also employed for the preparation of (1,4-$(Me_3Si)_2C_8H_6$)Yb[$Me_3CNCHCHNCMe_3$].[66]

An experimental challenge would be the assembly of a triple-decker complex by a similar synthetic methodology (Figure 7).

Ytterbium metal, pentaisopropylcyclopentadienyl radical, and cyclooctatraene react smoothly in tetrahydrofuran at 70−80 °C to yield **3-Yb** as blue-purple powder in moderate yield. It is very soluble in tetrahydrofuran, moderately soluble in aromatic hydrocarbons, and sparingly soluble in aliphatic solvents (like *n*-hexane). The solubility is significantly higher than usually observed for pentaisopropylcyclopentadienyl complexes. On crystallization from saturated *n*-hexane, toluene, or benzene solutions, blue-purple crystals are obtained. Unfortunately, they are not suitable for an X-ray structure analysis. The compound does not melt nor decompose, if heated to 250 °C under an argon atmosphere.

In NMR spectra, one set of signals for the pentaisopropylcyclopentadienyl ligand and one signal for the cyclooctatetraene ligand are observed, and the corresponding ^{13}C NMR signal is recorded at 90.1 ppm with a $^1J_{C,H}$ coupling constant of 163 Hz, which compares well with the NMR data observed for its tetraisopropylcyclopentadienyl analogues, **2-Yb**.

Reactivity

It has recently been reported that [Cp*Yb]$_2$(C_8H_8) reacts in a formal two-electron oxidative addition with C_8H_8 to a [Cp*Yb-(COT)] unit indicating that the reduction potential of this complex is at least −1.83 V (vs SCE), the measured potential for $(C_8H_8)/(C_8H_8)^{2-}$ reduction.[67] This is larger than usually expected for Yb(II) complexes.

However, complex **3** does not react with C_8H_8 in benzene at room temperature, suggesting that the sterically encumbered pentaisopropylcyclopentadienyl ligand is able to effectively shield the redox active Yb(II) center and therefore prevents this oxidative addition process, in contrast to the pentamethylcyclopentadienyl ligand.

Cyclononatetraenyl Barium Complexes

Although the cyclononatetraenyl anion ($C_9H_9^-$, CNT) and its alkali metal salts have been known for many years, authentic η^9-$C_9H_9^-$ containing organometallic compounds are unknown.[68−73] The only reported organometallic complex (C_5H_5)-Ti(C_9H_9) is best described as (η^5-C_5H_5)Ti((η^7-C_9H_9) on the basis of IR and ^1H NMR studies.[74] The synthesis of neutral main group triple-decker complexes employing the $C_8H_8^{2-}$ (COT) ligand, also a 10 π- electron system,[28] spurred the interest in this ligand. To accommodate such a demanding ring system (diameter = ca. 4.1 Å), a reasonable ionic radius is an absolute requirement, and metals of choice are either heavy main group metals (like Ba, Pb, or Bi), lanthanides, or actinides. Interestingly, the failed synthesis of $(C_8H_8)Ce(C_9H_9)$ resulted in the development of a new class of cyclooctatetraene dianion containing lanthanide complexes, [$(C_8H_8)LnCl(thf)_2]_2$.[75]

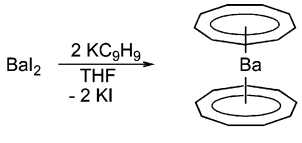

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Figure 8. Synthesis of complex **4**.

KC_9H_9 is synthesized according to literature procedures,[72,73] and it reacts with BaI_2 in tetrahydrofuran at ambient temperatures. $Ba(C_9H_9)_2$ (**4**) is isolated in moderate yield as a colorless, thermally stable, sublimable solid (see Figure 8). The product is readily soluble in polar solvents (like THF), moderately soluble in hot aromatic solvents (like benzene or toluene), and sparingly soluble to insoluble in aliphatic solvents (like pentane or *n*-hexane). ^1H and $^{13}C\{^1H\}$ NMR in THF-d_8 exhibits one signal for the magnetically equivalent cnt ligand at $\delta = 6.96$ ppm (^1H) and $\delta = 110.1$ ppm (^{13}C) with a $^1J_{C,H}$ coupling constant of 151 Hz, which is close to values observed in the COT complexes **2**, but bigger than the value of 137 Hz in K(cnt).[73] On the other hand, Anastassiou has reported a $^1J_{C,H}$ coupling constant of 152.5 Hz for $C_9H_9^-$,[71] which is in good agreement with the value obtained in this study.

EI mass spectra show a signal corresponding to a monomeric $[Ba(C_9H_9)_2]^+$ ion with the correct isotope pattern as well as *m*/*e* values for the fragments $[Ba(C_9H_9)]^+$ and $[(C_9H_9)]^+$. In a capillary sealed under argon, the Ba(cnt)$_2$ complex does neither melt nor decompose up to 250 °C. However, it can be sublimed without decomposition between 210 and 215 °C in oil pump vacuum. Crystallization attempts were rather frustrating, and single crystals suitable for X-ray diffraction studies could not obtained by crystallization from toluene or benzene solution nor by sublimation.

An alternative approach to structurally characterize an authentic cyclononatetraenyl compound of barium was the reaction of [^{4}CpBaI(thf)$_2$]$_2$[27] and K(cnt) in analogy to the triple-decker synthesis. Furthermore, heteroleptic compound **5** should exhibit a better solubility than **4**. However, under all conditions examined, ligand redistribution could not be prevented, and a mixture of homo- and heteroleptic compounds was obtained (Figure 9).

Although it was possible to separate [Ba(cnt)$_2$] (**4**) by extraction with a toluene/*n*-hexane mixture (because of its low solubility), [(^{4}Cp)Ba(cnt)] (**5**) and [(^{4}Cp)$_2$Ba] could not be separated by sublimation at 170 °C in oil-pump vacuum. Resublimation of the obtained 1:1 mixture did not allow enrichment of one species (see Experimental Section for details).

Computational Studies

DFT calculations have been shown to be a very useful tool to evaluate bonding and geometry in triple-decker complexes, and they might also provide interesting details for cyclononatetraenyl complexes. Therefore, the species involved in ligand redistribution process (Figure 9) have been investigated.

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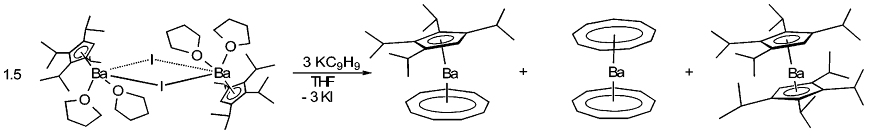

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Figure 9. Reaction of **1-Ba** with potassium cyclononatetraenide.

Chart 1. Calculated Energies of Formation

$$Ba^{2+} + 2\ C_9H_9^- \longrightarrow Ba(C_9H_9)_2 \qquad \Delta E = -1724.96\ kJ/mol$$

$$Ba^{2+} + 2\ C_5H_5^- \longrightarrow Ba(C_5H_5)_2 \qquad \Delta E = -1765.86\ kJ/mol$$

$$Ba^{2+} + C_9H_9^- + C_5H_5^- \longrightarrow Ba(C_9H_9)(C_5H_5) \qquad \Delta E = -1785.09\ kJ/mol$$

$$2\ Ba(C_9H_9)(C_5H_5) \longrightarrow Ba(C_9H_9)_2 + Ba(C_5H_5)_2 \qquad \Delta E = +20.72\ kJ/mol$$

$$2\ Ba^{2+} + C_8H_8^{2-} + 2\ C_5H_5^- \longrightarrow [(C_5H_5)Ba]_2(C_8H_8) \qquad \Delta E = -4162.35\ kJ/mol$$

Gas phase reactions of barium cations with various anions, $C_9H_9^-$, $C_5H_5^-$, and $C_8H_8^{2-}$, are all exothermic (Chart 1). The value for $Ba(C_5H_5)_2$ is comparable with the data reported previously.[49] The $[(C_5H_5)Ba]_2(C_8H_8)$ formation and the ligand redistribution process of $Ba(C_9H_9)(C_5H_5)$ have been included for comparison. It is obvious that the mixed barocene, $Ba(C_9H_9)(C_5H_5)$, is less stable toward ligand redistribution than the triple complex $[(C_5H_5)Ba]_2(C_8H_8)$, consistent with the experimental observations.

In contrast to $[(C_5H_5)M]_2(COT)$ (M = Ca, Sr, Ba), it was possible to obtain fully optimized structures with no imaginary vibrational frequencies for $[(\eta^5\text{-}C_5H_5)Ba(\eta^9\text{-}C_9H_9)]$, $[(\eta^5\text{-}C_5H_5)_2Ba]$, and $[(\eta^9\text{-}C_9H_9)_2Ba]$, whose geometries are depicted in Figure 10. The geometry obtained for $(C_5H_5)_2Ba$ at the DFT-B3PW91 level of theory agrees well with the values of Schleyer et al. employing MP2 calculations,[49] providing further confidence in the appropriate choice of method and basis set.

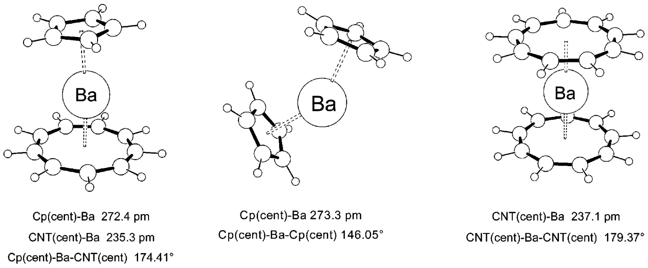

Figure 10. Fully optimized geometries (C_1 symmetry) of $[(\eta^9\text{-}C_9H_9)_2Ba]$, $[(\eta^5\text{-}C_5H_5)_2Ba]$, and $[(\eta^5\text{-}C_5H_5)Ba(\eta^9\text{-}C_9H_9)]$.

Conclusions

Tetraisopropylcyclopentadienyl halides of the heavy alkaline earth metals are suitable starting compounds for nucleophilic substitution reactions. With a ring as large as the cyclooctatetraene dianion coming close to the dications of calcium, strontium, or barium, steric bulk at least comparable to that of a tetraisopropylcyclopentadienyl ligand can be achieved without bulky substituents, bending of $^4Cp_{cent}-M-COT_{cent}$ angles can effectively be restricted to values close to linearity, and thermally stable structures can be established. In extension of earlier studies by Sitzmann et al., the concept of cyclopentadienyl radicals as synthons in the metallocene synthesis has been successfully transferred to triple-decker systems as demonstrated in the synthesis of $[(C_5(CHMe_2)_5)Yb(\mu,\eta^8{:}\eta^8\text{-}C_8H_8)Yb(C_5(CHMe_2)_5)]$, **3**. The synthetic approaches used in this work may be generally useful for the synthesis of neutral triple-decker sandwich compounds with other main group central atoms.

Although the reaction of $[^4CpBaI(thf)_2]_2$ with KC_9H_9 failed to produce pure, mixed barocenes, bis(cyclononatetraenyl)-barium, $Ba(C_9H_9)_2$, can be synthesized in moderate yield as thermally stable, sublimable material, whose molecular structure has been evaluated by DFT calculations.

Experimental Section

All synthetic operations were performed under a dry argon atmosphere using a drybox from MBraun company, Garching, or by using standard Schlenk techniques. Tetrahydrofuran and *n*-hexane were distilled from potassium metal, toluene from sodium metal. $Na[C_5H(CHMe_2)_4]$,[76] $[\{(C_5H(CHMe_2)_4)BaI(THF)_2\}_2]$ (**1-Ba**),[27] $K(C_9H_9)$,[72] and $[C_5(CHMe_2)_5]$ radical[77] were prepared according to published procedures. NMR spectra were taken on a Bruker DPX 400 NMR 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. We were unable to get reasonable C,H analyses for compounds **2-Ca**, **-Sr**, **-Ba**. Especially the carbon values were very low as a result of carbide and carbonate formation during the combustion.[12,27] Calcium analysis has been carried out by atomic absorption spectrometry.

2-Ca. A suspension of calcium chloride (222 mg, 2.0 mmol) and sodium tetraisopropylcyclopentadienide (512 mg, 2.0 mmol) in tetrahydrofuran (10 mL) was stirred at room temperature. The suspension turned brown-green after 5 min, and stirring was continued for 2 h until the calcium chloride was completely dissolved. Disodium cyclooctatetraenide (152 mg, 1.0 mmol) was added, and the suspension was stirred for 4 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 of the orange solution, gave a solid, which was washed with three 5 mL portions of *n*-hexane to yield 370 mg (0.57 mmol, 57%) of a colorless powder, which could be obtained as single crystals suitable for X-ray diffraction from a saturated hexadeuteriobenzene solution. Mp 188−189 °C, sublimation temperature 130 °C (oil pump vacuum). Anal. Calcd for $C_{42}H_{66}Ca_2$: C,77.47; H, 10.22; Ca, 12.31. Found: C, 68.80; H, 9.92; Ca 12.04. ^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 6.04 (s, 8H, COT), 5.21 (s, 2H, ring H (^{4}Cp)), 2.87 (m, 4H, C*H*Me$_2$), 2.72 (m, 4H, C*H*Me$_2$), 1.24 (d, ^3J(HH) = 7.1 Hz, 12 H, C*H*$_3$), 1.20 (d, ^3J(HH) = 6.8 Hz, 12 H, C*H*$_3$), 1.19 (d, ^3J(HH) = 7.2 Hz, 12 H, C*H*$_3$), 1.09 (d, ^3J(HH) = 6.7 Hz,

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12 H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ = 127.6 (s, ring-*C*), 123.3 (s, ring-*C*), 98.1 (dt, ring *C*H (^{4}Cp), ^1J(CH) = 156 Hz, ^4J(CH) = 5 Hz), 89.6 (d, ^1J(CH) = 157 Hz, COT), 26.8 (*C*HMe$_2$), 26.7 (*C*HMe$_2$), 26.5 (CH_3), 25.2 (CH_3), 24.6 (CH_3), 23.9 (CH_3). EI-MS (70 eV): *m*/*z* (%) 650.3 (45) [M$^+$], 417.1 (100) [M$^+$ − $C_5H(CHMe_2)_4$], 273.1 (45) [Ca{$C_5H(CHMe_2)_4$}$^+$].

2-Sr. A suspension of strontium iodide (341 mg, 1.0 mmol) and sodium tetraisopropylcyclopentadienide (256 mg, 1.0 mmol) in tetrahydrofuran (20 mL) was stirred at room temperature. The suspended material was dissolved to a yellow solution within 5 min. Disodium cyclooctatetraenide (75 mg, 0.5 mmol) was added, and stirring was continued for 24 h at ambient temperature. A 2 mL portion of *n*-hexane was added with formation of a white precipitate and stirring was continued for another 24 h. Removal of the precipitate by centrifugation and evaporation of the solvent in vacuo gave a light yellow residue, which was extracted with toluene (3 × 10 mL). Centrifugation and evaporation of the light yellow solution gave a light yellow powder, which was washed with three 5 mL portions of *n*-hexane and sublimed to yield 260 mg (0.35 mmol, 70%) of a colorless solid. **2-Sr** was heated to 250 °C without melting or decomposition; in oil pump vacuum, sublimation was observed at 175 °C. Anal. Calcd for $C_{42}H_{66}Sr_2$: C, 67.60; H, 8.91. Found: C, 57.58; H, 8.83. ^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 6.00 (s, 8H, COT), 5.22 (s, 2H, ring H (^{4}Cp)), 2.93 (m, 4H, C*H*Me$_2$), 2.78 (m, 4H, C*H*Me$_2$), 1.22 (d, ^3J(HH) = 6.9 Hz, 12 H, CH_3), 1.18 (d, ^3J(HH) = 6.8 Hz, 12 H, CH_3), 1.12 (d, ^3J(HH) = 7.3 Hz, 12 H, CH_3), 1.08 (d, ^3J(HH) = 6.8 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ = 127.6 (s, ring-*C*), 124.3 (s, ring-*C*), 99.1 (dt, ring *C*H (^{4}Cp), ^1J(CH) = 155 Hz, ^4J(CH) = 5 Hz)), 91.6 (d, ^1J(CH) = 157 Hz, COT), 26.7 (*C*HMe$_2$), 26.5 (*C*HMe$_2$), 25.9 (CH_3), 24.9 (CH_3), 24.3 (CH_3), 23.9 (CH_3). EI-MS (70 eV): *m*/*z* (%) 746 (<1) [M$^+$], 513 (2) [M$^+$ − $C_5H(CHMe_2)_4$], 321.1 (9) [Sr{$C_5H(CHMe_2)_4$}$^+$].

2-Ba.[28] To a solution of **1-Ba** (642 mg, 0.5 mmol) in a mixture of tetrahydrofuran (20 mL) and *n*-hexane (5 mL) was added solid $Na_2C_8H_8$ (75 mg, 0.5 mmol), and the suspension was stirred for 2 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 190 mg (0.22 mmol, 45%) of an ivory powder, which could be obtained as colorless single crystals suitable for X-ray diffraction from hexadeuteriobenzene solution. Mp 224−227 °C, sublimation temperature 215 °C in oil-pump vacuum. C,H-analysis gave completely unsatisfactory results due to the reasons outlined above. ^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 6.02 (s, 8H, COT), 5.11 (s, 2H, ring H (^{4}Cp)), 2.94 (m, 4H, C*H*Me$_2$), 2.84 (m, 4H, C*H*Me$_2$), 1.24 (d, ^3J(HH) = 7.2 Hz, 12 H, CH_3), 1.21 (d, ^3J(HH) = 7.2 Hz, 12 H, CH_3), 1.16 (d, ^3J(HH) = 6.8 Hz, 12 H, CH_3), 1.02 (d, ^3J(HH) = 6.8 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ = 127.5 (s, ring-*C*), 123.4 (s, ring-*C*), 101.7 (dt, ring *C*H (^{4}Cp), ^1J(CH) = 155 Hz, ^4J(CH) = 5 Hz), 95.3 (d, ^1J(CH) = 158 Hz, COT), 26.9 (*C*HMe$_2$), 26.6 (*C*HMe$_2$), 25.7 (CH_3), 25.3 (CH_3), 24.1 (CH_3), 23.7 (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{$C_5H(CHMe_2)_4$}$^+$].

2-Yb. A suspension of $YbI_2(thf)_4$ (717 mg, 1.0 mmol) and sodium tetraisopropylcyclopentadienide (256 mg, 1.0 mmol) in tetrahydrofuran (40 mL) was stirred at room temperature. Disodium cyclooctatetraenide (75 mg, 0.5 mmol) was added, and stirring was continued for 2 days at ambient temperature. During this time, the mixture turned green-brown. The solvent was removed in vacuo and the residue extracted with hexane (3 × 10 mL). Centrifugation and evaporation of the dark red solution yielded a red powder. ^{1}H NMR spectra of the crude product revealed a mixture of **2-Yb** and $[C_5H(CHMe_2)_4]_2Yb$. The $[C_5H(CHMe_2)_4]_2Yb$ contamination was removed by sublimation in oil pump vacuum (110−120 °C). **2-Yb** was recrystallized from a saturated *n*-hexane solution at −20 °C to yield 254 mg (0.28 mmol, 56%) as blue-red microcrystalline powder. Anal. Calcd for $C_{42}H_{66}Yb_2$: C, 55.0; H, 7.04. Found: C, 53.22; H, 6.90. ^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 5.88 (s, 8H, COT), 5.20 (s, 2H, ring H (^{4}Cp)), 2.87 (m, 4H, C*H*Me$_2$), 2.73 (m, 4H, C*H*Me$_2$), 1.25 (d, ^3J(HH) = 7.06 Hz, 12 H, CH_3), 1.24 (d, ^3J(HH) = 6.98 Hz, 12 H, CH_3), 1.21 (d, ^3J(HH) = 7.35 Hz, 12 H, CH_3), 1.11 (d, ^3J(HH) = 6.66 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ = 126.9 (s, ring-*C*), 122.9 (s, ring-*C*), 98.4 (dt, ring *C*H (^{4}Cp), ^1J(CH) = 156 Hz, ^4J(CH) = 5 Hz), 89.8 (d, ^1J(CH) = 163 Hz, COT), 26.8 (*C*HMe$_2$), 26.4 (*C*HMe$_2$), 26.7 (CH_3), 25.1 (CH_3), 24.6 (2 × CH_3).

3-Yb. Ytterbium chips (173 mg, 1.00 mmol), $HgCl_2$ (7 mg), and a few glass splitters were suspended in tetrahydrofuran (ca. 10 mL). The clear THF solution turned cloudy within 10 min. After 20 min, pentaisopropycyclopentadienyl radical (275 mg, 1.00 mmol) dissolved in tetrahydrofuran (5 mL) was added and resulted in color change of tetrahydrofuran solution to dark brown within a few minutes. At this point, cyclooctatetraene (52 mg, 0.5 mmol) was added to the reaction mixture. After 15 h, the tetrahydrofuran solution changed color to deep blue, and it was heated at 70−80 °C for 4 days. During this time, the solution color changed again to red-violet. Insoluble materials were separated by centrifugation, and the solvent was removed in dynamic vacuum leaving behind a deep blue-purple powder (287 mg, 0.287 mmol, 57.3%). It is very soluble in tetrahydrofuran and moderately soluble in aromatic hydrocarbons. Crystallization from a concentrated toluene and *n*-hexane solution yielded an analytically pure microcyrstalline blue-purple powder. Mp > 250 °C. Anal. Calcd for $C_{48}H_{78}Yb_2$: C, 57.58; H, 7.85. Found: C, 57.91; H, 8.68. ^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 6.06 (s, 8H, COT), 3.01 (m, 10H, C*H*Me$_2$), 1.34 (d, ^3J(HH) = 7.4 Hz, 30 H, CH_3), 1.22 (d, ^3J(HH) = 6.83 Hz, 30 H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ = 123.3 (s, ring-*C*), 90.1 (d, ^1J(CH) = 163 Hz, COT), 26.8 (*C*HMe$_2$), 26.6 (d, ^1J(CH) = 123 Hz, *C*HMe$_2$), 25.1 (q, ^1J(CH) = 125 Hz, CH_3), 25.1 (q, ^1J(CH) = 127 Hz CH_3).

4-Ba. Solid KC_9H_9 (332 mg, 2 mmol) was added to a suspension of BaI_2 (341 mg, 1 mmol) in 20 mL of tetrahydrofuran. The brown mixture was stirred for 10 min at ambient temperature. Removal of the solvent in vacuo, washing of the remaining off-white solid with ca. 10 mL cold pentane, and extraction into 3 × 15 mL toluene, followed by filtration and evaporation, gave an ivory powder, which was further purified by sublimation (210−215 °C in oil pump vacuum) to yield a colorless powder (156 mg, 0.42 mmol, 42%). Anal. Calcd for $C_{18}H_{18}Ba$ (371.67): C, 58.17; H, 4.88; Ba, 36.95. Found: C, 57.05; H, 5.04; Ba, 36.3. ^{1}H NMR (400 MHz, 298 K, d_8-THF): 6.96 ppm (s, cnt). ^{13}C NMR (100 MHz, 298 K, d_8-THF): 110.1 ppm (d, $^1J_{CH}$= 151 Hz, cnt). EI-MS (70 eV): *m*/*z* (%) 372 (6) [M]$^+$, 346 (<1) [M − C_2H_2]$^+$, 320 (<1) [M − $2C_2H_2$]$^+$, 234 [$C_{18}H_{18}$]$^+$, 117 (100) [C_9H_9]$^+$, 91 (55) [C_7H_7]$^+$, 55 (33) [C_5H_5]$^+$. Mp > 280 °C.

5-Ba. Crystalline [^{4}CpBaI(thf)$_2$]$_2$ (642 mg, 0.5 mmol) was dissolved in 15 mL of tetrahydrofuran, and solid KC_9H_9 (156 mg, 1 mmol) was added. The brown suspension was stirred at ambient temperature for 10 min. Solvent was removed in vacuo, and the dark residue extracted with 3 × 15 mL hexane−toluene (10:1); filtration and evaporation gave a yellow solid. The yellow solid was sublimed at 170 °C in oil pump vacuum to yield a colorless solid. NMR as well as MS-EI analysis confirmed a 1:1 mixture of ^{4}Cp$_2$Ba and (^{4}Cp)(C_9H_9)Ba; Ba(cnt)$_2$ is not present in the mixture (as shown by EI-MS and NMR).

^{1}H NMR (400 MHz, 298 K, C_6D_6) data follow.

Signal set for ^{4}Cp$_2$Ba: 5.68 (ring-C*H*), 3.19 (m, 4H, C*H*Me$_2$), 2.96 (m, 4H, C*H*Me$_2$), 1.31 (d, ^3J(HH) = 6.9 Hz, 12 H, CH_3), 1.27 (d, ^3J(HH) = 7.2 Hz, 12 H, CH_3), 1.23 (d, ^3J(HH) = 6.7 Hz, 24 H, CH_3).

Signal set for ^{4}CpBa(cnt): 7.28 (C_9H_9), 5.03 (ring-C*H*), 2.77 (m, 4H, C*H*Me$_2$), 1.13 (d, ^3J(HH) = 7.2 Hz, 6 H, CH_3), 1.12 (d, ^3J(HH) = 6.6 Hz, 6 H, CH_3), 1.09 (d, ^3J(HH) = 7.0 Hz, 12 H, CH_3).

^{13}C NMR (100 MHz, 298 K, C_6D_6) follow.

Signal set for ^{4}Cp$_2$Ba: one ring-*C*(^{i}Pr) overlayed by the solvent signal, 123.6 (ring-*C*(^{i}Pr)), 101.3 (ring-*C*H), 27.2 (*C*HMe$_2$), 26.8 (*C*HMe$_2$), 27.1 (CH_3), 25.0 (CH_3), 24.0 (CH_3), 23.7 (CH_3).

Signal set for ^{4}CpBa(cnt): 129.0 (ring-*C*(^{i}Pr)), 123.8 (ring-*C*(^{i}Pr)), 111.6 (CNT, $^1J_{CH}$= 151 Hz), 101.9 (ring-*C*H), 26.7 (*C*HMe$_2$), 26.4 (*C*HMe$_2$), 25.6 (*C*H$_3$), 25.2 (*C*H$_3$), 24.0 (*C*H$_3$), 23.9 (*C*H$_3$).

Calculational Details

The calculations were carried out at the density functional (DFT) level, using the B3PW91 functional, which incorporates Becke's three-parameter exchange functional[78] with the 1991 gradient-corrected correlation functional of Perdew and Wang;[79] this hybrid functional has previously been shown to provide realistic geometries for organometallic species.[58] On carbon, hydrogen, and calcium, a 6-311G basis set was used, and for barium and strontium the effective core potentials (ECPs) provided by the Stuttgart−Dresden group (SDD) was employed. A full geometry optimization was carried out without any symmetry restrictions. The calculations were performed using the ultrafine (99, 590) grid having 99 radial shells and 590 angular points per shell. The nature of the optimized extrema was verified by analytical frequency calculations. All calculations have been carried out with the Gaussian 98 suite of programs.[80]

Acknowledgment. M.D.W. thanks the state Rhineland-Palatinate for a scholarship, and H.S. is grateful to Professor O. J. Scherer for his support. The authors thank Professor O. Eisenstein for helpful discussions and Dr. G. Hornung for mass spectra.

Supporting Information Available: Crystallographic data, labeling diagrams, tables giving atomic positions, anisotropic thermal parameters, bond distances, bond angles, SDD basis sets for Sr and Ba (Gaussian input), and Cartesian coordinates of selected fully optimized structures. Complete list of authors for the Gaussian 98 program in ref 80. This material is available free of charge via the Internet at http://pubs.acs.org. Structure factor tables are available from the authors. Crystallographic data are also deposited with Cambridge Crystallographic Data Centre. Copies of the data (CCDC 182290,[28] CCDC 278390) can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB 1EZ, UK; fax +44 1223 336033.

JA0550071

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