

Reviews

New Developments in the Cyclopentadienyl Chemistry of the Alkaline-Earth Metals

Timothy P. Hanusa[†]*Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235**Received February 26, 2002*

Recent developments in the chemistry of cyclopentadienyl derivatives of the alkaline-earth (group 2) metals are reviewed. New complexes and their applications in organometallic and materials synthesis reflect the growing number of ways that can be used to manipulate the alkaline-earth–cyclopentadienyl bond. Complementing the experimental work are computational studies using density functional theory methods. These can now reproduce the geometries of many group 2 molecules with encouraging accuracy and have provided new insight into the energetics of metal–ring bonding. The progress made in group 2 cyclopentadienyl chemistry in the past decade indicates that more expansion can be expected.

1. Introduction

In the 50 years since the discovery of ferrocene,¹ the image of a staggered metallocene with parallel cyclopentadienyl rings has become a universally recognized icon of organometallic chemistry. It is salutary to remember, however, that the classic sandwich geometry represents only one of many structural types known among bis(cyclopentadienyl) compounds, especially those of the main-group (s- and p-block) metals.^{2–4} Even within subsets of these elements, considerable variety exists: the bis(cyclopentadienyl) complexes of the alkaline-earth elements, for example, encompass the slipped beryllocene,⁵ the ferrocene-like magnesocene,⁶ and the polymeric calcocene⁷ (Figure 1). When com-

pounds with substituted cyclopentadienyl rings and those with either one or three rings on the metal center are also considered, the range of accessible complexes enlarges several times.

Cyclopentadienyl derivatives of the group 2 elements are particularly fascinating, in that the structural varieties noted above emerge from what is ostensibly simple electrostatic metal–ligand bonding, i.e., [Cp']-[Ae²⁺][Cp'] (Ae = Be–Ba). Attempts to understand the origins of such structural diversity and the differences in reactivity that accompany it have benefited from a marked expansion in the organometallic chemistry of the alkaline-earth metals in the last 15 years. Newly reported compounds continue to refine our understanding of group 2 chemistry and have highlighted similarities with cyclopentadienyl derivatives of other metal families. The pace of discovery indicates that the potential chemistry available from Cp'_nAeL_{2–n} combinations is far from exhausted.

Several reviews in the past decade have included cyclopentadienyl compounds of the group 2 metals, sometimes as part of larger overviews of main-group

[†] Fax: 615-343-1234. E-mail: t.hanusa@vanderbilt.edu.

(1) Pauson, P. L.; Kealy, T. J. *Nature* **1951**, *168*, 1039–1040.

(2) Jutzi, P.; Burford, N. *Chem. Rev.* **1999**, *99*, 969–990.

(3) Jutzi, P. *Chem. Unserer Zeit* **1999**, *33*, 343–353.

(4) Burkey, D. J.; Hanusa, T. P. *Comments Inorg. Chem.* **1995**, *17*, 41–77.

(5) Nugent, K. W.; Beattie, J. K.; Hambley, T. W.; Snow, M. R. *Aust. J. Chem.* **1984**, *37*, 1601–1606.

(6) Bünder, W.; Weiss, E. *J. Organomet. Chem.* **1975**, *92*, 1–6.

(7) Zerger, R.; Stucky, G. *J. Organomet. Chem.* **1974**, *80*, 7–17.

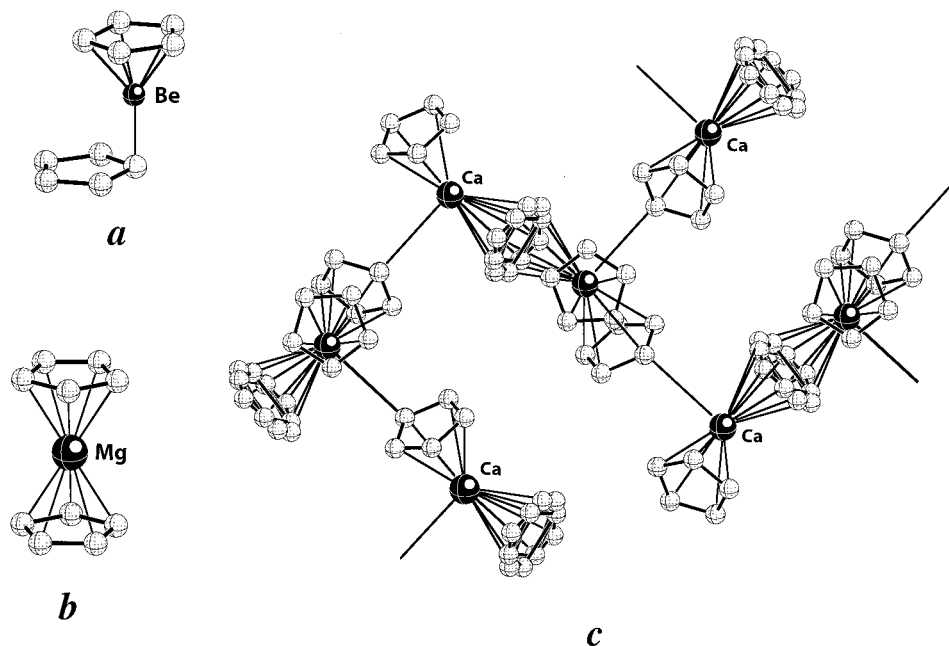


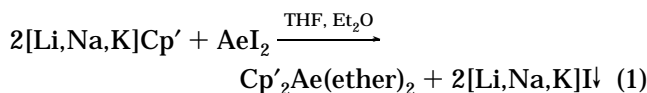
Figure 1. Solid-state structures of the monomeric Cp₂Be (a) and Cp₂Mg (b) and polymeric Cp₂Ca (c).

organometallic complexes.^{2–4,8–10} In this survey, we emphasize compounds reported in the past 5 years, especially when these represent a new category of complex or have helped to refine our understanding of organoalkaline-earth structure and bonding. We begin with a brief summary of general synthetic strategies.

2. Synthesis

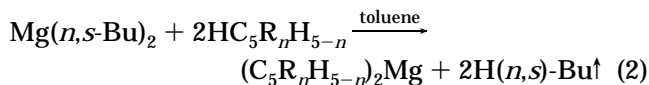
In the preparation of cyclopentadienyl alkaline-earth compounds, the metal sources can take a variety of forms, including the elements themselves (as metal vapor,^{11,12} in the form of finely divided powders,^{13,14} or in solution in liquid ammonia¹⁵), metal hydrides,¹⁶ metal alkyls,¹⁵ anhydrous metal halides, and the bis(trimethylsilyl)amides Ae[N(SiMe₃)₂](THF)_n (Ae = Ca, Sr, Ba).¹⁷

Metallocenes are often made from the metal halides, particularly the iodides, which are reasonably soluble in ethers. Reaction with alkali-metal cyclopentadienides typically gives the metallocenes in high yield (eq 1).^{18,19}

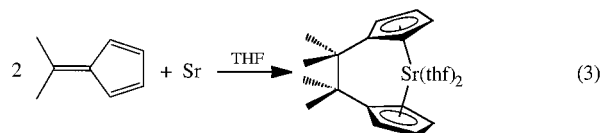


For the synthesis of magnesocenes, the ready avail-

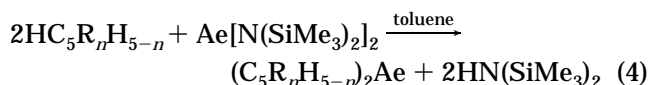
ability of dialkyl species (e.g., (*n*-Bu)₂Mg, (*s*-Bu)₂Mg) have made them commonly used precursors (e.g., eq 2).¹⁵



The use of fulvene-based coupling reactions can lead to *ansa*-bridged metallocenes such as *trans*-Ph₂C₂H₂(η⁵-C₅H₄)₂Ca(THF)₂,²⁰ 1,1'-dicyclopentenylcalocene,²¹ and Me₄C₂(η⁵-C₅H₄)₂Ca(THF)₂ (eq 3).²²



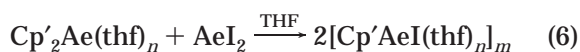
The group 2 metals are typically “hard” metal ions and often strongly bind ethers. In some cases, coordinated THF cannot be removed, even by repeated extraction or sublimation (e.g., from (C₅Me₅)₂Ca(THF)_x).²³ When solvent-free species are desired, synthesis in Et₂O is helpful, but even here, extraction with the “toluene reflux” method is required.¹⁹ In these cases, the toluene-soluble bis(trimethylsilyl)amides are useful; the bulky hexamethyldisilazane byproduct does not bind to the metallocenes (eq 4).²⁴



(8) Hanusa, T. P. *Polyhedron* **1990**, *9*, 1345–1362.
 (9) Hanusa, T. P. *Chem. Rev.* **1993**, *93*, 1023–1036.
 (10) Kwon, O.; McKee, M. L. In *Computational Organometallic Chemistry*; Cundari, T. R., Ed.; Marcel Dekker: New York, 2001.
 (11) Gowenlock, B. G.; Lindsell, W. E.; Singh, B. *J. Chem. Soc., Dalton Trans.* **1978**, 657–664.
 (12) Engelhardt, L. M.; Junk, P. C.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1988**, 1500–1501.
 (13) McCormick, M. J.; Moon, K. B.; Jones, S. R.; Hanusa, T. P. *J. Chem. Soc., Chem. Commun.* **1990**, 778–779.
 (14) Wu, T. C.; Xiong, H.; Rieke, R. D. *J. Org. Chem.* **1990**, *55*, 5045–5051.
 (15) Schumann, H.; Gottfriedsen, J.; Glanz, M.; Dechert, S.; Demtschuk, J. *J. Organomet. Chem.* **2001**, *617–618*, 588–600.
 (16) Fischer, E. O.; Stölzle, G. *Chem. Ber.* **1961**, *94*, 2187–2193.
 (17) Westerhausen, M. *Coord. Chem. Rev.* **1998**, *176*, 157–210.

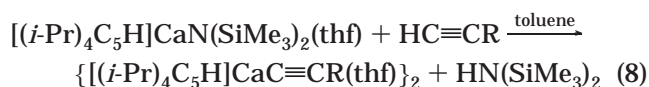
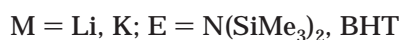
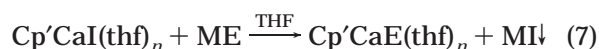
(18) McCormick, M. J.; Williams, R. A.; Levine, L. J.; Hanusa, T. P. *Polyhedron* **1988**, *7*, 725–730.
 (19) Burns, C. J.; Andersen, R. A. *J. Organomet. Chem.* **1987**, 325, 31–37.
 (20) Kane, K. M.; Shapiro, P. J.; Vij, A.; Cubbon, R.; Rheingold, A. L. *Organometallics* **1997**, *21*, 44567–4571.
 (21) Sinnema, P. J.; Shapiro, P. J.; Höhn, B.; Bitterwolf, T. E.; Twamley, B. *Organometallics* **2001**, *20*, 2883–2888.
 (22) Rieckhoff, M.; Pieper, U.; Stalke, D.; Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1079–1081.

Metathetical or conproportionation synthetic routes are required for complexes that cannot be prepared from the elements, such as mono(cyclopentadienyl) halides (eqs 5 and 6).^{25,26} Certain large cyclopentadienyl rings



can give mixtures of metallocenes and mono(cyclopentadienyl) complexes if the reactions are conducted in THF; the use of diethyl ether can minimize this problem.

Derivatization of some mono(cyclopentadienyl) complexes to yield new monosubstituted species can often be accomplished by metathetical exchange (eq 7) or protonation reactions (eq 8).²⁶



Adducts of both metallocenes and mono(cyclopentadienyl) species with Lewis bases can be formed either by synthesis in a donor solvent (e.g., ethers, ammonia) or by admixture with the bases (e.g., various chelating amines,^{27,28} aromatic nitrogen heterocycles,²⁹ phosphines,¹⁹ isocyanides,¹⁹ carbenes,^{15,30} carbon monoxide,³¹ and transition-metal carbonyls³²).

This brief inventory does not exhaust the methods that have been used for the synthesis of cyclopentadienyl alkaline-earth complexes. Other, more specialized approaches will be described below.

3. Bonding Models for Group 2 Cyclopentadienyl Compounds

The low electronegativity of the alkaline-earth elements ($\chi = 1.47$ (Be)– 0.97 (Ba)) means that their bonds to carbon ($\chi = 2.50$) are highly polar. To what extent it is expedient to regard the Ae–C interaction as “ionic”, however, is debatable. It should be stressed that physical properties, such as solubility in hydrocarbon solvents and appreciable volatility, are not reliable criteria for

estimating the covalency of compounds.⁹ These properties depend strongly on intermolecular interactions, which are largely ligand dominated, and they do not provide a direct measure of intramolecular metal–ligand bonding.

An analysis over a decade ago of structurally characterized cyclopentadienyl compounds of the alkaline-earth and f elements suggested that metal–ring centroid distances could be predicted with reasonable accuracy in divalent metal complexes with the formula $r_{\text{M}^{2+}} + 1.61(3) \text{ \AA} = r_{\text{MC}}$, where r is the coordination number adjusted value of the radii³³ and r_{MC} is the metal–ring carbon distance.³⁴ The value of 1.61 \AA can be thought of an “ionic radius” for the Cp^- ligand. This formula is similar to that derived by Raymond for cyclopentadienyl lanthanide complexes (with mainly trivalent metals)³⁵ and presumably has a related origin: i.e., the predominantly electrostatic nature of the bonding in these compounds.

Much more structural data now exist for the group 2 elements than in the late 1980s, but it still appears that it is possible to provide estimates of $\text{Cp}'\text{–M}$ distances for alkaline-earth compounds using a radii addition formula. However, it is also clear that steric influences from bulky ligands and partial covalency in metal–ligand bonds weaken the reliability of such an approach. For example, beryllocene ($(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_5\text{H}_5)\text{Be}$) has an average $\text{Be–C}(\eta^5\text{-Cp})$ bond length of 1.93 \AA and a formal coordination number of 4 ($r = 0.27 \text{ \AA}$) for the metal.⁵ In the more symmetrical decamethylberylloocene ($(\eta^5\text{-C}_5\text{Me}_5)_2\text{Be}$),³⁶ the metal center is formally 6-coordinate ($r = 0.45 \text{ \AA}$): i.e., 0.18 \AA larger. The average bond length in decamethylberylloocene is 2.05 \AA , only 0.12 \AA longer than in the parent complex. Hence, the Be–C distance does not increase as much as the change in ionic radius would suggest. Even when the coordination number for an element remains the same, substantial variations in $\text{M–Cp}'$ distances can be observed in closely related compounds. The average Ba–C distance of $2.997(4) \text{ \AA}$ in $[\eta^5\text{-(}i\text{-Pr)}_5\text{C}_5]_2\text{Ba}$,³⁷ for example, is 0.06 \AA longer than the value in $[\eta^5\text{-(}i\text{-Pr)}_4\text{C}_5\text{H}]_2\text{Ba}$ ($2.94(1) \text{ \AA}$),³⁸ although the only difference between the molecules is a single alkyl group on each ring.

Such examples illustrate that more than just the metal coordination number affects bond distances in group 2 cyclopentadienyl complexes. Consequently, a high degree of predictive accuracy cannot be expected from radii sums alone.

4. Calculations on Organoalkaline-Earth Metallocenes

Attempts to reproduce the structures of alkaline-earth metallocenes provide a severe test for computational methods. The compounds are formally electron deficient and conformationally “floppy,” and only small energies

(23) Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *Organometallics* **1990**, *9*, 1128–1134.

(24) Tanner, P. S.; Burkey, D. J.; Hanusa, T. P. *Polyhedron* **1995**, *14*, 331–333.

(25) McCormick, M. J.; Sockwell, S. C.; Davies, C. E. H.; Hanusa, T. P.; Huffman, J. C. *Organometallics* **1989**, *8*, 2044–2049.

(26) Burkey, D. J.; Alexander, E. K.; Hanusa, T. P. *Organometallics* **1994**, *13*, 2773–2786.

(27) Johnson, C.; Toney, J.; Stucky, G. D. *J. Organomet. Chem.* **1972**, *40*, C11.

(28) Armstrong, D. R.; Herbst-Irmer, R.; Kuhn, A.; Moncrieff, D.; Paver, M. A.; Russell, C. A.; Stalke, D.; Steiner, A.; Wright, D. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1774–1776.

(29) Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *J. Organomet. Chem.* **1992**, *429*, 143–152.

(30) Arduengo, A. J.; Davidson, F.; Krafczyk, R.; Marshall, W. J.; Tamm, M. *Organometallics* **1998**, *17*, 3375–3382.

(31) Selg, P.; Brintzinger, H. H.; Andersen, R. A.; Horváth, I. T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 791–793.

(32) Sockwell, S. C.; Tanner, P. S.; Hanusa, T. P. *Organometallics* **1992**, *11*, 2634–2638.

(33) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751–767.

(34) Sockwell, S. C.; Hanusa, T. P. *Inorg. Chem.* **1990**, *29*, 76–80.

(35) Raymond, K. N.; Eigenbrot, C. W. *Acc. Chem. Res.* **1980**, *13*, 276–283.

(36) Del Mar Conejo, M.; Fernandez, R.; Gutierrez-Puebla, E.; Monge, A.; Ruiz, C.; Carmona, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 1949–1951.

(37) Sitzmann, H.; Dezimmer, T.; Ruck, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 3114–3115.

(38) Williams, R. A.; Tesh, K. F.; Hanusa, T. P. *J. Am. Chem. Soc.* **1991**, *113*, 4843–4851.

Table 1. Density Functional Theory Calculations on Group 2 Metallocenes

	C(Cp)–Ae (Å)	Cp(centroid)–Ae (Å)	Cp–Ae–Cp' (deg)	method (functional/basis set) ^a	ref
Cp ₂ Be	2.055	not given	NA ^b	B3LYP/6-31G(d)	43
	1.92(1)	1.508	NA ^b	exptl (X-ray)	5
Cp ₂ Mg	2.270	1.930	180	VWN/Godbout	122
	2.360	2.040	180	BP86/Godbout	122
	2.357	2.022	180	B3LYP/6-311G(d)(Mg); 6-31G(d)(C,H)	47
	2.339	2.008	180	exptl (elec diff)	123
	2.304	1.977	180	exptl (X-ray)	6
	2.540	2.240	150	VWN/Godbout	122
Cp ₂ Ca	2.580	2.290	150	BP86/Godbout	122
	2.613	2.317	149.6	B3LYP/Wachters+4d(Ca); 6-31G(d)(C,H)	47
	2.609(6)	2.312(6)	154(3)	exptl (elec diff) ^c	39, 51
	2.64(1)	2.354	147.7	exptl (X-ray) ^c	23
	2.600	2.310	145	VWN/Godbout	122
Cp ₂ Sr	2.680	2.440	145	BP86/Godbout	122
	2.750(8)	2.469(6)	149(3)	exptl (elec diff) ^c	40, 41

^a Functional/basis set combination used for geometry optimization; in some cases, larger basis sets were used for energy calculation.

^b Cp₂Be has a slipped-sandwich structure. ^c Value for the decamethylmetallocene, (C₅Me₅)₂Ae.

(often only 1–2 kcal mol⁻¹) are required to alter their geometries. In such cases, the inclusion of electron correlation effects becomes critical to an accurate description of the molecules' structures. Traditional Hartree–Fock approaches are generally inadequate for these complexes; as an example, although the experimentally determined gas-phase and solid-state structures of the alkylated metallocenes of Cp₂Ca and Cp₂Sr have bent rings,^{23,39–41} Hartree–Fock calculations suggest that they should be linear⁴¹ or “quasilinear”.⁴² Even the application of Møller–Plesset corrections to Hartree–Fock calculations in order to account for electron correlation may be insufficient: MP2- and MP4-level calculations on beryllocene still lead to the prediction that a ferrocene-like structure of *D*_{5d} symmetry should be the lowest in energy, contrary to all experimental data.⁴³

Density functional theory (DFT) methods, which implicitly incorporate electron correlation in a computationally efficient form, have found wide use in main-group chemistry.^{44–46} In general, they have been more successful than Hartree–Fock approaches in dealing with organoalkaline-earth molecules (Table 1). The longstanding problem of the structure of beryllocene has recently been addressed with DFT calculations, which determined that the η⁵-η¹-C_s structure found in solution is indeed a minimum on the potential energy surface.⁴³ With some functionals (BP86, B3P86), this conclusion is basis set dependent, and the use of a relatively large basis set (6-311G(d,p)) is required to establish that the C_s structure is in fact the lowest-energy conformer.

In contrast to the other group 2 metallocenes, magnesocene is reasonably well described by Hartree–Fock treatments. A geometry with parallel rings (*D*_{5d}) is predicted to be the lowest energy conformer, although

as is typical for HF computations on cyclopentadienyl compounds, the calculated Mg–C distance slightly overestimates that found in the gas phase (0.037 Å difference).⁴⁷ A DFT treatment using the B3LYP functional reduces the discrepancy to 0.018 Å. The NPA charge^{48,49} on the metal center is +1.76, which suggests that the bonding is largely ionic.¹⁰

The necessity of an adequate treatment for electron correlation and the use of large basis sets is critical also for the heavier group 2 metallocenes. The minimum energy structure of Cp₂Ca is found to be linear with SCF calculations, even with MP2-level corrections applied.⁴² A DFT approach that used the B3LYP functional, an all-electron Watchers-type basis set on calcium supplemented with four additional d functions, and the 6-31G(d) basis on carbon and hydrogen led to the prediction of nonparallel rings (bending angle 149.6°).⁴⁷ Bending was not observed if only the 6-31G set was used on carbon, an indication that the use of polarization functions on the cyclopentadienyl rings is important to the reproduction of the bending.

Bridgeman found that both Cp₂Ca and Cp₂Sr were bent, using the VWN and BP86 functionals and the Godbout basis sets. The latter⁵⁰ are all-electron sets with additional d functions on the metals (four and five sets on Ca and Sr, respectively) The Ca–C and Sr–C bond distances (2.540 and 2.600 Å, respectively) obtained with the VWN functional are considerably shorter than those observed in the gas phase for (C₅Me₅)₂Ca (2.609(6) Å)^{39,51} and (C₅Me₅)₂Sr (2.750(8) Å).^{40,41} This probably reflects the overshooting of bond distances commonly observed with the use of local functionals,⁵² as the use of the nonlocal BP86 functional increased the calculated Ae–C distances to 2.580 and 2.680 Å for calcium and strontium, respectively.

A common thread that appears to unite successful DFT calculations of calcium and strontium metallocenes is the use of all-electron basis sets with polarization

(39) Andersen, R. A.; Blom, R.; Boncella, J. M.; Burns, C. J.; Volden, H. V. *Acta Chem. Scand.* **1987**, *A41*, 24–35.

(40) Andersen, R. A.; Blom, R.; Burns, C. J.; Volden, H. V. *J. Chem. Soc., Chem. Commun.* **1987**, 768–769.

(41) Blom, R.; Faegri, K., Jr.; Volden, H. V. *Organometallics* **1990**, *9*, 373–379.

(42) Kaupp, M.; Schleyer, P. v. R.; Dolg, M.; Stoll, H. *J. Am. Chem. Soc.* **1992**, *114*, 8202–8208.

(43) Mire, L. W.; Wheeler, S. D.; Wagenseller, E.; Marynick, D. S. *Inorg. Chem.* **1998**, *37*, 3099–3106.

(44) Cotton, F. A.; Cowley, A. H.; Feng, X. *J. Am. Chem. Soc.* **1998**, *120*, 1795–1799.

(45) Dunne, J. P.; Fox, S.; Tacke, M. *J. Mol. Struct.-THEOCHEM* **2001**, *543*, 157–166.

(46) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*, 2nd ed.; Wiley: New York, 2001.

(47) Bytheway, I.; Popelier, P. L. A.; Gillespie, R. J. *Can. J. Chem.* **1996**, *74*, 1059–1071.

(48) Reed, A. E.; Weinhold, F. J. *J. Chem. Phys.* **1985**, *83*, 735–746.

(49) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–926.

(50) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmers, E. *Can. J. Chem.* **1992**, *50*, 560.

(51) Andersen, R. A.; Boncella, J. M.; Burns, C. J.; Blom, R.; Haaland, A.; Volden, H. V. *J. Organomet. Chem.* **1986**, *312*, C49–C52.

(52) Matsuzawa, N.; Seto, J.; Dixon, D. A. *J. Phys. Chem. A* **1997**, *101*, 9391–9398.

functions on the cyclopentadienyl rings and the presence of multiple, relatively tightly contracted d functions on the metals. These are similar to the requirements for modeling the bending in the heavy group 2 dihalides as well^{53,54} and point to the important role that polarizing the core electrons⁵⁵ (or, alternatively, reducing antibonding character in the HOMOs⁵⁶) plays in these calculations. There do not appear to be any DFT calculations reported for Cp₂Ba, but it has been predicted to be bent (147°) using HF-SCF methods and an relativistic ECP basis set.⁴² The source of the stabilization gained on bending was ascribed to the polarizability of the Ba²⁺ ion and to d_π orbital participation in the bonding. Since HF methods fail so spectacularly with compounds of the lighter alkaline-earth metals, it is interesting that the bending in organobarium complexes appears easier to model.

Other forces besides polarization of the core electrons have been proposed as contributors to the bending observed in the alkaline-earth metallocenes. Attractive van der Waals forces between the substituents on the ligands have been postulated as the primary stabilizing force for the bent geometries.^{57,58} Using molecular mechanics methods, Bosnich found good agreement between the observed and calculated structures for the (C₅Me₅)₂Ae metallocenes, even when allowing for the perturbing effects of crystal-packing forces in the solid state. The calculated energy difference between the bent and linear structures was always <10 kJ mol⁻¹, with attractive van der Waals forces accounting for at least 90% of the stabilization of the lower energy bent structures. Recently the description of interligand interactions in these molecules has been investigated with a “through space coupling” approach, which recasts van der Waals forces in terms of molecular orbitals.⁵⁹ Such analyses emphasize that the forces required to reorient the rings relative to each other are small and, hence, that the formulation of “definitive” descriptions of the bonding in group 2 cyclopentadienyl compounds will remain a challenge for some time.

5. Case Studies

In this section, several recently reported classes of complexes are reviewed that have refined our understanding of structure, bonding, and reactivity in cyclopentadienyl alkaline-earth chemistry.

5.1. Substituted Beryllocenes. The small Be²⁺ cation³³ is compatible with cyclopentadienyl rings as large as C₅Me₅, at least when only mono(cyclopentadienyl) complexes are considered (e.g., (C₅Me₅)BeE(^tBu)₂ (E = P,⁶⁰ As⁶¹) and (Me₅C₅)₂Yb(*μ*-Me)Be(C₅Me₅)⁶²).

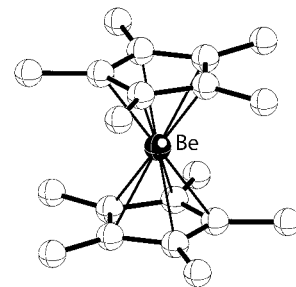


Figure 2. Solid-state structure of the ferrocene-like (C₅Me₅)₂Be.

Considering that beryllocene itself has a slipped-sandwich structure, however, the preparation of substituted beryllocene derivatives with sterically demanding rings could be expected to be difficult. In fact, the failure of attempts to prepare the permethylated derivative of beryllocene, (C₅Me₅)₂Be,^{19,63} was at one point ascribed to the “steric oversaturation” of the metal center that would be present in a sandwich compound with such bulky rings.⁹ Thus, it was surprising when both octamethylberyllocene ((C₅Me₄H)₂Be) and, even more remarkably, decamethylberyllocene ((C₅Me₅)₂Be) were reported as stable, isolable complexes.³⁶ They were prepared by the reaction of BeCl₂ and either K[C₅Me₄H] or K[C₅Me₅] in diethyl ether. The octamethyl compound could be prepared at room temperature, whereas the synthesis of the permethylated derivative required 3.5 days with an ether–toluene mixture refluxing at 115 °C. Apparently the formation of (C₅Me₅)₂Be is slow; insufficient reaction times and temperatures evidently thwarted earlier attempts to make it.

Like the parent beryllocene, (C₅Me₄H)₂Be adopts a η⁵/η¹ slip sandwich structure in the solid state. The distances between the Be atom and the η⁵ ring centroid (1.471(7) Å) and its carbon atoms (average 1.90(7) Å) are close to those in beryllocene itself (1.505 and 1.92 Å, respectively).⁵ Rather than adopt a structure that is at least as slipped as the octamethyl derivative, however, (C₅Me₅)₂Be exhibits a ferrocene-like η⁵/η⁵ parallel-sandwich structure, as indicated by X-ray crystallography (Figure 2). The Be–C₅Me₅ centroid distance (1.655(1) Å) and the Be–C_{ring} distance (average 2.049 Å) is noticeably longer than in Cp₂Be, but not as much as the increase in the coordination number of the metal would suggest (see section 2).

There is some spread in the Be–C bond lengths in (C₅Me₅)₂Be (Δ = 0.15 Å), and there are inter-ring Me–Me′ contacts are as close as 3.63 Å (cf. the sum of the van der Waals radii of 4.0 Å⁶⁴). Although steric repulsions may be influencing the ring orientations, there are interesting parallels between the structures of (C₅Me₅)₂Be and decamethylsilicocene, (C₅Me₅)₂Si.⁶⁵ Calculations on the parent Cp₂Si have indicated that the molecule should be appreciably slipped (e.g., Δ_{Si–C} = 0.6 Å),⁶⁶ but

(53) Hassett, D. M.; Marsden, C. J. *J. Mol. Struct.* **1995**, *346*, 249–263.

(54) Hargittai, M. *Chem. Rev.* **2000**, *100*, 2233–2301.

(55) Kaupp, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 3535–3565.

(56) Lee, E. P. F.; Soldan, P.; Wright, T. G. *Inorg. Chem.* **2001**, *40*, 5979–5984.

(57) Hollis, T. K.; Burdett, J. K.; Bosnich, B. *Organometallics* **1993**, *12*, 3385–3386.

(58) Timofeeva, T. V.; Lii, J.-H.; Allinger, N. L. *J. Am. Chem. Soc.* **1995**, *117*, 7452–7459.

(59) Sapunov, V. N.; Kirchner, K.; Schmid, R. *J. Organomet. Chem.* **2001**, *214*, 143–185.

(60) Atwood, J. L.; Bott, S. G.; Jones, R. A.; Koschmieder, S. U. *J. Chem. Soc., Chem. Commun.* **1990**, 692–693.

(61) Battle, S. L.; Cowley, A. H.; Decken, A.; Jones, R. A.; Koschmieder, S. U. *J. Organomet. Chem.* **1999**, *582*, 66–69.

(62) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 5853–5855.

(63) Pratten, S. J.; Cooper, M. K.; Aroney, M. J. *J. Organomet. Chem.* **1990**, *381*, 147–153.

(64) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(65) Jutzli, P.; Holtmann, U.; Kanne, D.; Kruger, C.; Blom, R.; Gleiter, R.; Hylakrystin, I. *Chem. Ber.* **1989**, *122*, 1629–1639.

(66) Smith, J. D.; Hanusa, T. P. *Organometallics* **2001**, *20*, 3056–3062.

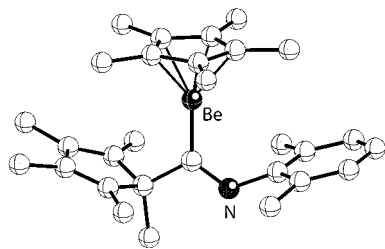


Figure 3. (Iminoacyl)beryllium product formed from $(C_5Me_5)_2Be$ and $CNXyl$.

the near-parallelism of the rings found in $(C_5Me_5)_2Si$ cannot be solely a steric effect, as the closest $Me \cdots Me'$ contacts in its linear form are $>4.5 \text{ \AA}$. Calculations on $(C_5Me_5)_2Si$ do predict that a more regular structure is preferred,⁶⁷ so that even without steric influence a regularizing effect by the C_5Me_5 ring is observed on the metallocene framework; such "regularization" may be operative in the beryllocene case also.

Even at low temperature, only a single resonance is observed in the ^{13}C NMR for the ring carbons of $(C_5Me_5)_2Be$. This does not confirm that the structure is symmetrical in solution, however, as the compound might be subject to an exceptionally facile rearrangement process. Reactions with bases have been used to provide a chemical probe of this question. Neither $(C_5Me_5)Be$ nor $(C_5Me_4H)_2Be$ reacts with CO , however, and 1,3,4,5-tetramethylimidazol-2-ylidene and pyridine do not react with $(C_5Me_5)_2Be$. Both beryllocenes do react with the isonitrile $CNXyl$ ($Xyl = C_6H_3-2,6-Me_2$), to form the (iminoacyl)beryllium compounds $Cp'BeC(=NXyl)-Cp'$, in which the isonitrile has inserted into a $Be-C$ bond (Figure 3).⁶⁸ The process is reversible with $(C_5Me_5)_2Be$, and depending on the temperature, two different isomers are formed from $(C_5Me_4H)_2Be$, which differ by the carbon of the Cp' ring to which the isonitrile carbon has coupled (either at the CH unit of the Cp' ring or β to it). The formation of the iminoacyl complexes is proposed to occur by direct attack of the $CNXyl$ on a $Be-\eta^1-Cp'$ bond. A migratory insertion reaction, involving precoordination of the isonitrile unit, is probably unlikely, given the steric crowding around the metal center and the lack of available orbitals on the metal center. In solution, therefore, η^5/η^1 conformers may exist and undergo facile exchange between themselves.

5.2. Charged Cyclopentadienyl Complexes. In comparison to their neutral analogues, charged group 2 cyclopentadienyl complexes are relatively rare. To some extent this is an artifact of the greater ease in isolating and purifying neutral complexes (e.g., by extraction into hydrocarbons), but examples of well-characterized cationic and anionic compounds have started to appear, with sometimes-unexpected reactivity or structures.

The gas-phase coordination chemistry of $[CpMg]^+$ cations with small inorganic ligands (NH_3 , H_2 , H_2O , CO , NO , O_2 , CO_2 , N_2O , NO_2 , N_2) and saturated hydrocarbons (C_nH_{2n+2} ; $n = 1-7$) has been measured with the selected-ion flow-tube technique.⁶⁹⁻⁷¹ Relative binding

energies and standard enthalpies of formation were computed with density functional theory calculations, and single-point energy calculations were completed with large basis sets at both the DFT and MP4 levels of theory. It was typically observed that ligation of one Cp to the Mg metal center substantially enhances the efficiency of coordination of most small molecules but ligation of a second Cp dramatically reduces it; no coordination of any type is seen to $[Cp_2Mg]^+$.

For example, the ligation of ammonia to the Mg^+ cation is slow ($k = 4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), but the initial addition of NH_3 to the $[CpMg]^+$ cation is 3 orders of magnitude faster ($k > 5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Ammonia is not observed to form an adduct with the $[Cp_2Mg]^+$ cation but, rather, displaces a Cp ring ($[Cp_2Mg]^+ + NH_3 \rightarrow [CpMg(NH_3)]^+ + Cp$).⁷⁰ Similar behavior is observed with H_2O , but not with H_2 , N_2 , or any of the gaseous oxides or saturated hydrocarbons. The presence of one cyclopentadienyl group stabilizes the coordinated cation, but the second one saturates the coordination sphere of the metal, so that binding is inhibited. Interestingly, among the structures proposed for the adducts is a C-bound carbonyl species, $[CpMg(CO)_2]^+$; its formulation is based on analogy with the $[Mg-CO]^+$ system, for which calculations indicate that C-bound CO is preferred over the O-bound variety by $>3 \text{ kcal mol}^{-1}$.⁷²

A cationic cyclopentadienyl complex of calcium ($[(C_5Me_5)Ca(OPPh_3)_3]^+I^-$) has been obtained by the displacement of an iodide from $(C_5Me_5)CaI(THF)_2$ with the basic donor ligand triphenylphosphine oxide.⁷³ The latter's ability to substitute for I^- and THF but not $(C_5Me_5)^-$ on calcium is consistent with the approximate pK_b values of the bases (i.e., -12 ($[C_5Me_5]^-$), ~ 8 ($OPPh_3$), $\lesssim 12$ (THF), $\lesssim 24$ (I^-)).⁷⁴ The organometallic cation is stable in air for up to 6 h; this is remarkable stability compared to other known $Cp'CaX$ species ($Cp' = C_5Me_5$, $C_5(i-Pr)_4H$, $C_5(SiMe_3)_3H_2$), which degrade within minutes in air.^{25,26,75} The reduced air sensitivity of the cation evidently stems from the heavy shielding of the metal center by the ligands.

The cationic complex crystallizes as a monomeric species with the calcium coordinated by an $\eta^5-C_5Me_5$ ring and the three triphenylphosphine oxide ligands in a classic "piano stool" arrangement (Figure 4). The average $Ca-C$ distance of $2.684(4) \text{ \AA}$ is longer than that usually observed in complexes with a formally six-coordinate Ca^{2+} center.^{12,25,76} The longer than expected $Ca-C$ distance was modeled with density functional theory calculations on the compound $[(C_5H_5)Ca(OPMe_3)_3]^+$, which indicated that the distance in the cation reflects the strong electron donor properties of the $OPPh_3$ ligands.

(70) Milburn, R. K.; Baranov, V. I.; Hopkinson, A. C.; Bohme, D. K. *J. Phys. Chem. A* **1999**, *103*, 6373-6382.

(71) Milburn, R. K.; Baranov, V. I.; Hopkinson, A. C.; Bohme, D. K. *J. Phys. Chem. A* **2000**, *104*, 3926-3932.

(72) Bauschlicher, C. W., Jr.; Partridge, H. *Chem. Phys. Lett.* **1991**, *181*, 129-133.

(73) Jayaratne, K. C.; Fitts, L. S.; Hanusa, T. P.; Young, V. G., Jr. *Organometallics* **2001**, *20*, 3638-3640.

(74) *Handbook of Chemistry and Physics*; Weast, R. C., Ed.; Chemical Rubber Co.: Cleveland, OH, 1986; Vol. 67th, pp F-161-F-162.

(75) Harvey, M. J.; Hanusa, T. P. *Organometallics* **2000**, *19*, 1556-1566.

(76) Jutzli, P.; Leffers, W.; Müller, G.; Huber, B. *Chem. Ber.* **1989**, *122*, 879-884.

(67) Schoeller, W. W.; Friedrich, O.; Sundermann, A.; Rozhenko, A. *Organometallics* **1999**, *18*, 2099-2106.

(68) del Mar Conejo, M.; Fernandez, R.; Carmona, E.; Gutierrez-Puebla, E.; Monge, A. *Organometallics* **2001**, *20*, 2434-2436.

(69) Milburn, R. K.; Baranov, V. I.; Hopkinson, A. C.; Bohme, D. K. *J. Phys. Chem. A* **1998**, *102*, 9803-9810.

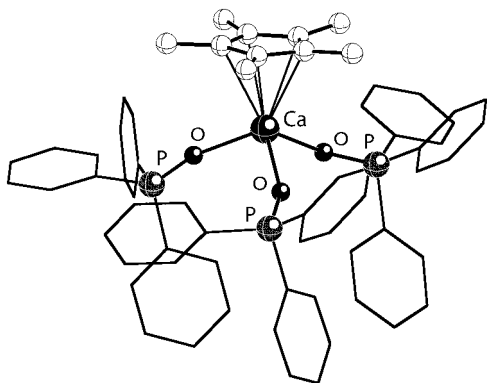


Figure 4. Solid-state structure of the non-hydrogen atoms of the $[(C_5H_5)Ca(OPPh_3)_3]^+$ cation. The phenyl rings are rendered as sticks.

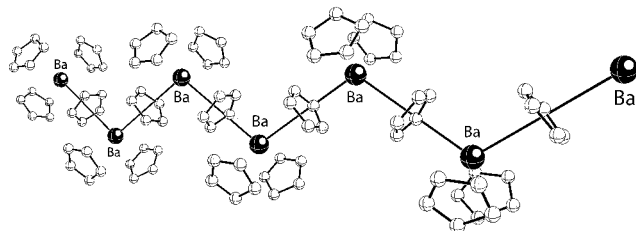
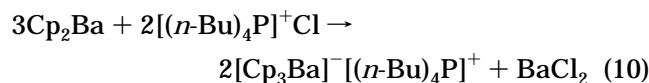
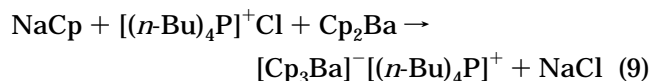


Figure 5. Portion of the coordination polymer of the non-hydrogen atoms of $[Cp_3Ba]^-$. For clarity, the $[Ph_4P]^+$ cations and lattice THF molecules are not shown.

The first isolated organobarate complex, $[Cp_3Ba]^-$, was formed in the reaction of Cp_2Ba with a free Cp^- anion generated in situ from $NaCp$ in refluxing THF/pyridine (eq 9).⁷⁷ The same product is obtained from the reaction of 3 equiv of Cp_2Ba with $[(n-Bu)_4P]^+Cl^-$ (eq 10).



The compound consists of a linear coordination polymer of Cp^- anions tetrahedrally surrounding each barium cation (Figure 5). All Cp rings are η^5 -bound to the Ba, and the Ba–Cp distances are surprisingly similar for both the terminal (3.047(7)–3.184(6) Å) and the bridging ligands (3.123(7)–3.220(7) Å). Complexes of the form $[Cp_nBa]^{2-n}[X]^+$ have also been isolated but not yet structurally characterized.

The search for ligands with steric profiles different from those of individual $[C_5R_nH_{5-n}]^-$ rings has led to investigations of bridged R_nECp_2 species. Neutral complexes with dialkyl, diarylsilyl, and various hydrocarbyl bridges are known among organoalkaline-earth complexes,^{20–22,78} but phosphonium-bridged species (i.e., the diylides $[R_2PCp_2]^-$)⁷⁹ are attractive ligands for group 2 elements, as they simultaneously provide a bulky metallocene-like framework yet still carry only a uninegative charge. Brintzinger has isolated several phosphonium-bridged group 2 species, including $[Me_2P(2-Me-$

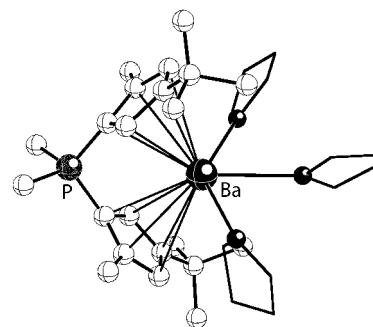
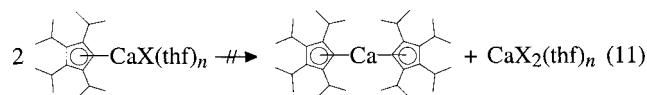


Figure 6. Solid-state structure of the non-hydrogen atoms of the $[Me_2P(2-Me-4-t-Bu-C_5H_2)_2Ba(THF)_3]^+$ cation. The THF rings have been rendered as sticks.

$4-t-Bu-C_5H_2)_2]_2Ba$ and $[Me_2P(2-Me-4-t-Bu-C_5H_2)_2Ba(THF)_3]^+$ (Figure 6).⁸⁰ The latter has been structurally authenticated, and its average Ba–C distance (3.06 Å) is that expected for a complex containing a formally 9-coordinate Ba^{2+} center;³⁴ the *ansa* bridge appears to place no geometric constraint on the metal–ligand distances.

5.3. Mono(cyclopentadienyl) Complexes. Much of the interest in mono(cyclopentadienyl) complexes of the group 2 elements stems from their intrinsic flexibility. A compound of the general form $Cp^+AeEX(L)_n$ ($X =$ monoanionic ligand; $L =$ optional neutral Lewis base(s)) can be derivatized by exchanging X , and the addition or removal of ligands L (ethers, amines) allows adjustment of the coordination environment. A persistent challenge with studying heteroleptic alkaline-earth compounds has been the operation of Schlenk-type equilibria, which leads to the rearrangement of unsymmetrical species into their symmetrical counterparts (i.e., $2MX \rightleftharpoons MX_2 + MY_2$). Nevertheless, it is possible to construct kinetically stabilized complexes if careful attention is given to blocking exchange reactions.

As an example, when two of the heavily substituted $C_5(i-Pr)_4H$ cyclopentadienyl rings (Cp^{4i}) are bound to calcium, the isopropyl groups sterically restrict access to the metal, and the resulting $(Cp^{4i})_2Ca$ metallocene cannot form adducts with Lewis bases such as ethers and amines. In solution, coordinated THF would have to dissociate from the mono(ring) complex $(Cp^{4i})CaI(THF)_n$ before the necessarily base-free $(Cp^{4i})_2Ca$ could form (eq 11). Since the loss of THF is disfavored by the



strong $Ca \leftarrow OC_4H_8$ interaction, ligand redistribution is blocked.²⁶ It is consequently possible to predict the stability of a *mono(ring)* complex by determining whether the associated *metallocene* will bind Lewis bases or not. Metallocenes that cannot form adducts with bases should have kinetically stable *mono(ring)* counterparts.

Compounds with cyclopentadienyl ligands other than Cp^{4i} support this analysis. For example, all three $(Cp^{3Si})_2Ae$ metallocenes ($Cp^{3Si} = 1,2,4$ -tris(trimethylsilyl)cyclopentadienyl; $Ae = Ca, Sr, Ba$) can be isolated as base-free species from the reaction of $K[Cp^{3Si}]$ and

(77) Harder, S. *Angew. Chem., Int. Ed.* **1998**, *37*, 1239–1241.

(78) Harder, S.; Lutz, M.; Straub, A. W. G. *Organometallics* **1997**, *16*, 107–113.

(79) Cristau, H.-J. *Chem. Rev.* **1994**, *94*, 1299–1313.

(80) Leyser, N.; Schmidt, K.; Brintzinger, H.-H. *Organometallics* **1998**, *17*, 2155–2161.

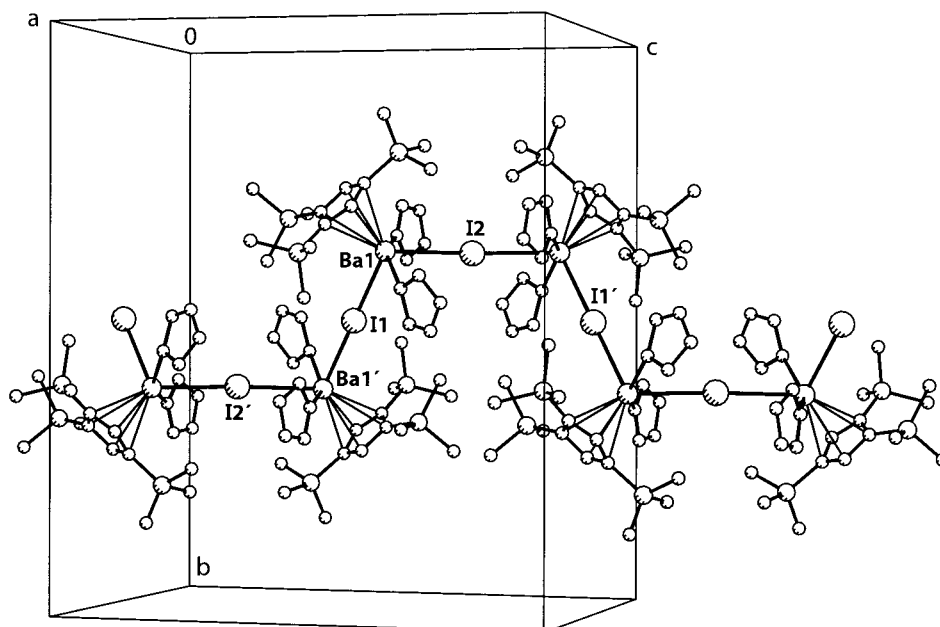


Figure 7. Packing diagram of the non-hydrogen atoms of $(\text{Cp}^{3\text{Si}})\text{BaI}(\text{THF})_2$, indicating the coordination polymer chains that run parallel to the crystallographic c axis. (Reproduced with permission from *Organometallics* **2000**, *19*, 1556–1566. Copyright 2000 American Chemical Society.)

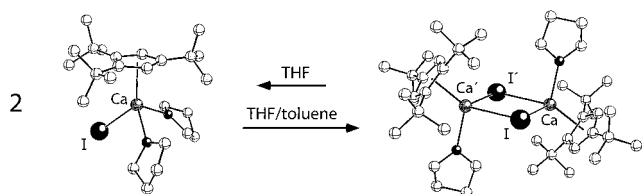
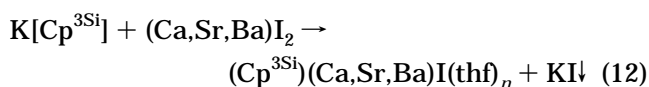


Figure 8. Interconversion of the structures of the monomeric $(\text{Cp}^{3\text{T}})\text{CaI}(\text{THF})_2$ and dimeric $[(\text{Cp}^{3\text{T}})\text{CaI}(\text{THF})]_2$ by the addition or removal of coordinated THF.

the group 2 diiodides in ether,⁸¹ and the related mono-(ring) complexes $(\text{Cp}^{3\text{Si}})\text{AeI}(\text{THF})_n$ are indeed isolable. They can be prepared as crystalline solids by halide displacement reactions (eq 12). The calcium and stron-

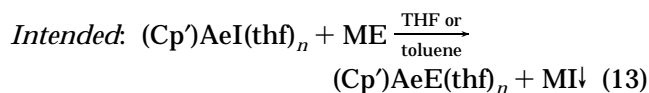


tium iodide complexes are dimers with bridging iodide ligands: i.e., $[(\text{Cp}^{3\text{Si}})\text{Ae}(\mu\text{-I})(\text{THF})_n]_2$.⁷⁵ Unlike the two lighter homologues, the organobarium complex $(\text{Cp}^{3\text{Si}})\text{BaI}(\text{THF})_2$ crystallizes from THF/toluene as a coordination polymer with both linear and near-linear (177.8°) Ba–I–Ba' links in a zigzag motif (Figure 7).

Another cyclopentadienyl ring that has been found to function similarly to Cp^{4i} and $\text{Cp}^{3\text{Si}}$ is the 1,2,4-*tert*-butyl derivative $\text{Cp}^{3\text{T}}$. The mono(ring) compound $(\text{Cp}^{3\text{T}})\text{CaI}(\text{THF})_n$ can be isolated from the 1:1 reaction of $\text{K}[\text{Cp}^{3\text{T}}]$ and CaI_2 in THF.⁸² Like Cp^{4i} and $\text{Cp}^{3\text{Si}}$, the $\text{Cp}^{3\text{T}}$ ring is able to suppress ligand redistribution reactions in mono(cyclopentadienyl)calcium complexes, presumably by a similar encapsulation effect.

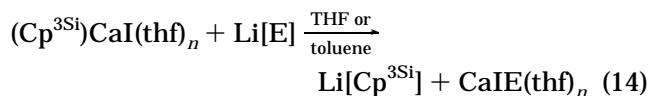
The $(\text{Cp}^{3\text{T}})\text{CaI}(\text{THF})_n$ complexes can be isolated from THF solution as a monomer with two THF molecules or from THF/toluene as a dimer with only one THF per calcium atom (Figure 8); the calcium in the hypothetical monomeric “ $(\text{Cp}^{3\text{T}})\text{CaI}(\text{THF})$ ” structure is apparently so coordinately unsaturated that dimerization occurs upon the loss of one THF.

In principle, the iodide ligands of $(\text{Cp}')\text{AeI}(\text{THF})_n$ complexes should be derivatizable to yield new mono-substituted species (eq 13). In practice, the product



M = Li, Na, K; E = hydrocarbyl, alkoxide, amide

obtained depends strongly on the identity of the alkali-metal cations present. When M = K, the reactions occur largely as expected, but when M = Li, the results are completely different. Treatment of $(\text{Cp}^{3\text{Si}})\text{CaI}(\text{THF})$ with various reagents (e.g., LiI, CH_3Li , $\text{Li}[\text{N}(\text{SiMe}_3)_2]$) yields mainly the lithium cyclopentadienide ($\text{Li}[\text{Cp}^{3\text{Si}}]$): i.e., ring transfer occurs from Ca^{2+} to Li^+ (eq 14). Density



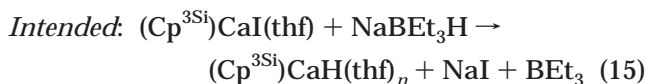
functional theory (DFT) calculations on base-free model compounds (E = iodide) suggest that such ring transfer on unsolvated species would in fact be slightly endoergic. When THF-solvated species are used, however, the calculated reaction becomes exoergic (high solvation of $\text{CaI}_2(\text{THF})_n$ is the principal driving force for the reaction). These experiments and calculations clearly highlight the important, but generally underappreciated, role of neutral bases in controlling the direction of reactions of the heavy alkaline-earth metals.

An attempt to convert an organocalcium iodide to a hydride complex was modeled on successful routes used with cyclopentadienyl lanthanide halides (eq 15).^{83,84}

(81) Harvey, M. J.; Hanusa, T. P.; Young, V. G., Jr. Manuscript in preparation.

(82) Harvey, M. J.; Hanusa, T. P.; Young, V. G., Jr. *J. Organomet. Chem.* **2001**, *626*, 43–48.

(83) Baudry, D.; Dormond, A.; Lachot, B.; Visseaux, M.; Zucchi, G. *J. Organomet. Chem.* **1997**, *547*, 157–165.



The product of the reaction is not a hydride complex, however, but rather the triethylborohydride species $(\text{Cp}^{3\text{Si}})\text{Ca}(\text{HBEt}_3)(\text{THF})_2$. Spectroscopic data indicate that the $[\text{HBEt}_3]^-$ anion is involved in a bridging interaction (IR, ν_{BH} 1935 cm^{-1} ; ^{11}B NMR, $J_{\text{B-H}} = 50$ Hz). The X-ray crystal structure of the complex provides the first details of the bonding of the triethylborohydride anion to a species other than a group 1 cation.⁸⁵ The compound crystallizes from THF with the calcium center surrounded by a $(\text{Cp}^{3\text{Si}})$ ring, two THF molecules, and the $[\text{HBEt}_3]^-$ ligand (Figure 9). The last ligand displays a bidentate coordination mode, in which the hydride on the boron atom and one hydrogen atom of a methylene group are in contact with the metal center. The isolation of the calcium complex sets it apart from formally analogous lanthanide compounds, which are not stable in the solid state.^{83,84} The BEt_3 moiety resists removal from the calcium center; no reaction is observed with PMe_3 , and refluxing a solution in toluene leads to decomposition and the formation of the metallocene $(\text{Cp}^{3\text{Si}})_2\text{Ca}$.

5.4. Carbene Complexes. The remarkably stable Wanzlick-type carbenes isolated by Arduengo⁸⁶ form robust adducts with many main-group-element compounds⁸⁷ and organolanthanide species.⁸⁸ Several alkaline-earth metallocenes complexed to 1,3,4,5-tetramethylimidazol-2-ylidene have also been isolated and structurally characterized. One equivalent of the carbene reacts with the metallocenes $(\text{C}_5\text{Me}_5)_2\text{Mg}$, $(\text{C}_5\text{Me}_5)_2\text{Ca}(\text{OEt}_2)$, $(\text{C}_5\text{Me}_5)_2\text{Sr}(\text{OEt}_2)$, and $(\text{C}_5\text{Me}_5)_2\text{Ba}(\text{THF})_2$ to generate $(\text{C}_5\text{Me}_5)_2\text{Ae}(1,3,4,5\text{-Me}_4\text{-C}_3\text{N}_2)$ adducts.³⁰ The magnesium, calcium, and barium species have been structurally characterized and display bent-metallocene geometries with the carbene occupying the wedge between the rings. In the magnesium complex ($\text{Mg}-\text{C}_{\text{carbene}} = 2.194(2)$ Å), one ring is bound in an η^5 manner, with an average $\text{Mg}-\text{C}$ distance of 2.48(2) Å. The other ring has slipped to an η^3 configuration, in which the bound ring carbons are at an average distance of 2.46(9) Å from the magnesium and the nonbonded carbons display $\text{Mg}\cdots\text{C}$ contact distances of 3.108(3) and 3.184(3) Å (Figure 10). As the η^5/η^3 ring arrangement is absent in the calcium and barium analogues, the driving force for the distortion is probably steric crowding around the metal center, rather than interaction with the carbene p orbital. The coordination environment around the magnesium can be regarded as trigonal planar, as the sum of the angles around Mg of the two ring centroids and the carbene is 359.9°.

When 2 equiv of the carbene reacts with $(\text{C}_5\text{Me}_5)_2\text{Sr}(\text{OEt}_2)$ and $\text{Ba}(\text{C}_5\text{Me}_5)_2(\text{THF})_2$, dicarbene adducts are formed.³⁰ The strontium complex $(\text{C}_5\text{Me}_5)_2\text{Sr}(1,3,4,5\text{-}$

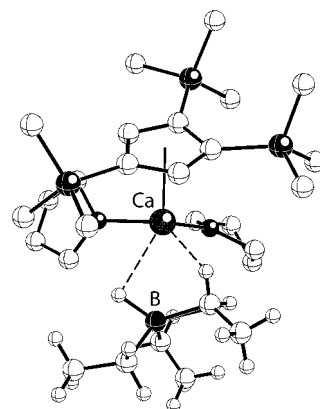


Figure 9. Solid-state structure of $(\text{Cp}^{3\text{Si}})\text{Ca}(\text{HBEt}_3)(\text{THF})_2$. For clarity, hydrogen atoms have been removed from the cyclopentadienyl ring and the THF ligands.

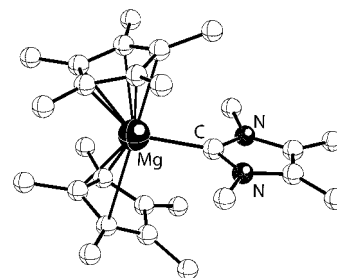


Figure 10. Solid-state structure of $(\text{C}_5\text{Me}_5)_2\text{Mg}(1,3,4,5\text{-Me}_4\text{-C}_3\text{N}_2)$, with both η^5 and η^3 rings.

$\text{Me}_4\text{-C}_3\text{N}_2)_2$ has been crystallographically characterized, and the two ring centroids and the *ipso* carbon atoms of the carbene ligands define a distorted tetrahedron (twist between tetrahedral edges is 76.8°).

A related series of carbene adducts of alkaline-earth metallocenes containing 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (*i*-Pr-carbene) has been reported.¹⁵ In some cases, close contacts between the metal centers and isopropyl groups of the coordinated carbene are observed. In such cases, the carbene carbon resonances in the ^{13}C NMR spectra shift upfield (ca. 7–17 ppm), indicating that the close approaches are not simply a consequence of crystal packing.

The nucleophilicity of the carbenes toward the group 2 metallocenes is remarkable, in that ammonia, Et_2O , and THF can be displaced from the metal centers in favor of the carbon donor ligand. This is particularly noteworthy in the case of calcium species, which usually bind THF tenaciously. The effect on metal–Cp' distances is essentially the same, however, whether THF, NH_3 , pyridine, or a carbene is involved.

5.5. Barocene Complexes. The effect that sterically bulky ligands exert on the structures of group 2 compounds is dramatically illustrated by the metallocenes of barium. The parent barocene has not been structurally characterized but is insoluble in all but the most polar solvents (e.g., DMSO) and presumably has a polymeric structure like that of $(\text{Cp}_2\text{Ca})_x$.⁷ The steric bulk of pentamethylcyclopentadiene is able to block most of the intermolecular interactions in $(\text{C}_5\text{Me}_5)_2\text{Ba}$, but the large size of Ba^{2+} still allows for some contacts between the metal and neighboring C_5Me_5 (3.35, 3.36 Å), thereby producing a coordination polymer in

(84) Visseaux, M.; Baudry, D.; Dormond, A.; Qian, C. *J. Organomet. Chem.* **1999**, *574*, 213–218.

(85) Harvey, M. J.; Hanusa, T. P.; Pink, M. *Chem. Commun.* **2000**, 489–490.

(86) Arduengo, A. J.; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530–5534.

(87) Kuhn, N.; Kratz, T.; Blaeser, D.; Boese, R. *Chem. Ber.* **1995**, *128*, 245–250.

(88) Arduengo, A. J., III; Tamm, M.; McLain, S. J.; Calabrese, J. C.; Davidson, F.; Marshall, W. J. *J. Am. Chem. Soc.* **1994**, *116*, 7927–7928.

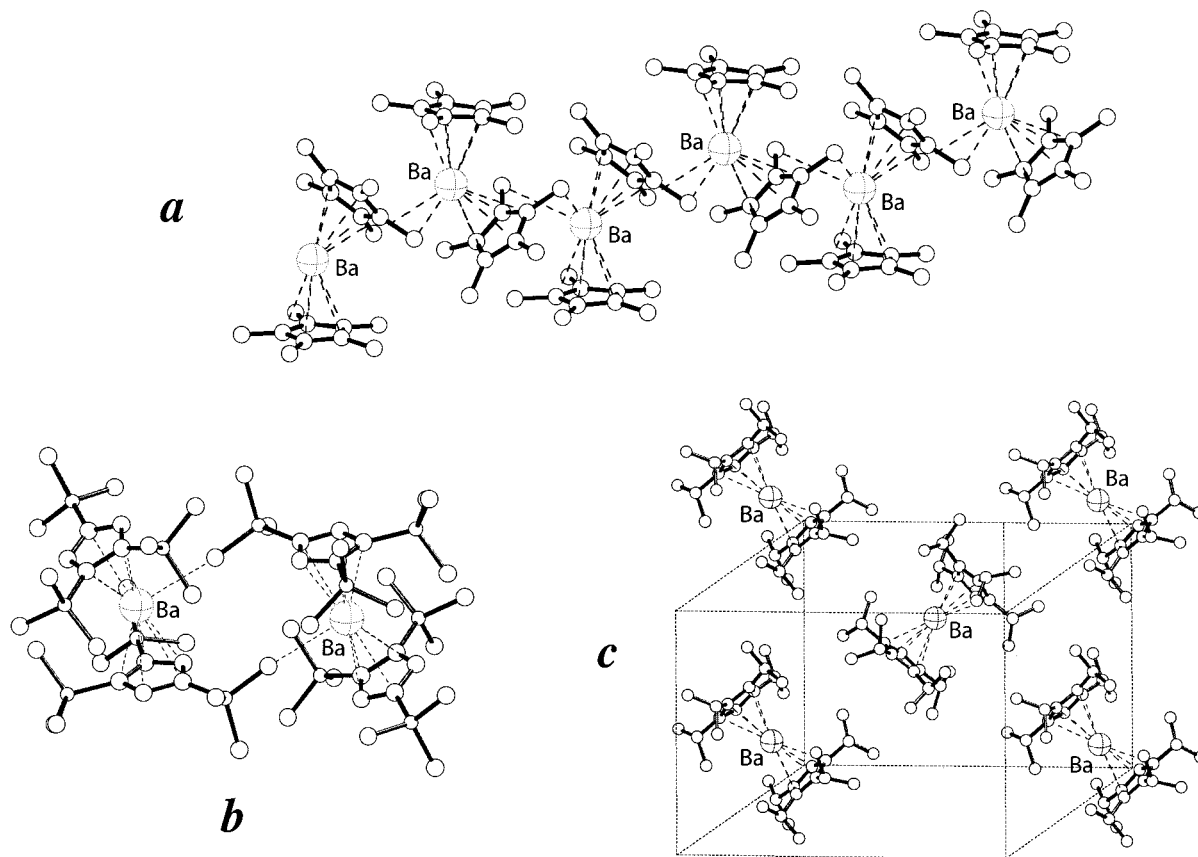


Figure 11. Solid-state structures of the oligomeric $(\text{Me}_5\text{C}_5)_2\text{Ba}$ (a), dimeric $[(1,2,4\text{-}(\text{SiMe}_3)_3\text{C}_5\text{H}_2)_2\text{Ba}]_2$ (b), and monomeric $(\text{Cp}^{41})_2\text{Ca}$ (c).

the solid state (Figure 11a).⁸⁹ Nevertheless, these interactions are relatively weak, and decamethylbarocene is soluble in aromatic solvents and is easily sublimed.

Extremely bulky rings are required to enforce mononuclearity on barocenes. Even the use of the 1,2,4- $(\text{SiMe}_3)_3\text{C}_5\text{H}_2$ ligand produces a metallocene that forms coordination dimers in the solid state, linked with 3.27 Å contacts between a Ba and the methyl carbon of a neighboring SiMe_3 group (Figure 11b).⁹⁰ The contact is only 0.19 Å longer than the longest intramolecular Ba–C(ring) bond (3.07 Å) and is associated with a 0.33 Å displacement of the trimethylsilyl group out of the C_5 ring plane. True mononuclearity can be achieved with the use of the 1,2,3,4- $(i\text{-Pr})_4\text{C}_5\text{H}$ ligand, which is so sterically crowded that the isopropyl groups must orient themselves so that they are nearly perpendicular to the C_5 ring plane.²⁶ When two of the rings are incorporated into a metallocene, they effectively encapsulate the metal center (Figure 11c).

It is possible to take encapsulation a step further with the use of the pentaisopropylated ring 1,2,3,4,5- $(i\text{-Pr})_5\text{C}_5$. Metallocenes of Ca, Sr, and Ba have been made by the reaction of the pentaisopropylcyclopentadienyl radical⁹¹ with the metals in liquid ammonia and isolated by hydrocarbon extraction.³⁷ The $[(i\text{-Pr})_5\text{C}_5]_2\text{Ae}$ species display exceptional levels of air stability (weeks for the

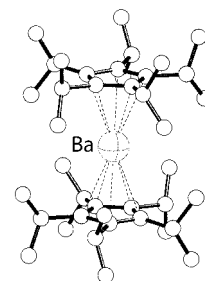


Figure 12. Solid-state structure of the ferrocene-like $[(i\text{-Pr})_5\text{C}_5]_2\text{Ba}$.

calcium and strontium derivatives), undoubtedly a result of the complete enclosure of the metal centers. The ΔG value for isopropyl group rotation in the complexes is ca. 17 kcal mol⁻¹, comparable to the value found in metallocenes of tin, lead, and cobalt containing the pentaisopropylcyclopentadienyl ligand.

The barium complex has been crystallographically characterized, and it is notable precisely for what would ordinarily be considered a pedestrian geometry: i.e., a simple ferrocene-like system with two parallel η^5 rings (Figure 12). It is, however, the only known metallocene of Ca, Sr, or Ba that is *not* bent, and it confirms a prediction based on molecular mechanics calculations made 5 years before its discovery: i.e., that the $[(i\text{-Pr})_5\text{C}_5]_2\text{Ba}$ framework would be parallel owing to steric crowding from the isopropyl substituents.⁵⁷ The amount of steric bulk that is required to “force” the rings to be parallel is remarkable, considering that simple electrostatic analyses of bonding would not have predicted them to be bent at all. The average Ba–C distance of

(89) Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1988**, 1045–1046.

(90) Harvey, M. J.; Hanusa, T. P. Unpublished results.

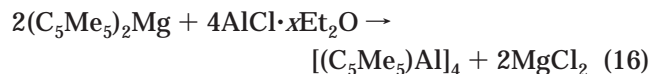
(91) Sitzmann, H.; Bock, H.; Boese, R.; Dezember, T.; Havlas, Z.; Kaim, W.; Moscherosch, M.; Zanathy, L. *J. Am. Chem. Soc.* **1993**, *115*, 12003–12009.

2.997(4) Å is also 0.06 Å longer than the value in [(*i*-Pr)₄C₅H]₂Ba, another illustration of the steric pressure exerted by the rings on the complex.

6. Applications

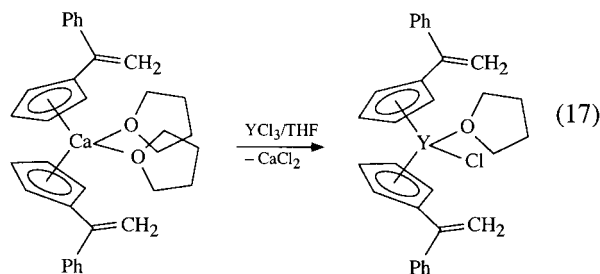
Three properties of the cyclopentadienyl complexes of the alkaline-earth metals have provided the basis for most of their applications: the lability of their rings, their volatility, and their Lewis acidity. The use of each of these features is examined in turn.

6.1. Ring Exchange. Magnesocene and its ring-substituted derivatives have long served as sources of the cyclopentadienyl anion; the reaction in eq 16 exemplifies this use,⁹² but there are many other cases

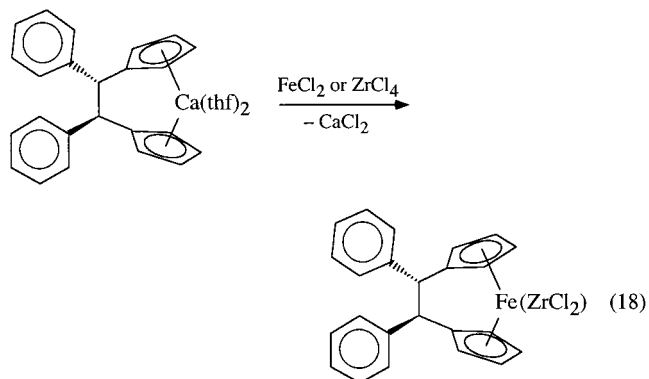


that could be cited (e.g., the synthesis of [Cp₃Mn]⁻,⁹³ (C₅H₅)M(O₂CNEt₂)₃ (M = Zr, Hf),⁹⁴ and (Me₅C₅)M(acac) (M = Co, Ni)⁹⁵).

A recent example of ring transfer involving complexes of the heavier alkaline-earth metals was demonstrated with 1,1'-bis(1-phenylethen-1-yl)calcocene, formed from the metalation of 6-methyl-6-phenylfulvene with Ca-[N(SiMe₃)₂]₂(THF)₂. The calcocene in turn reacts with YCl₃ and SnCl₂ to yield the corresponding ytrocene chloride and stannocene (eq 17).⁹⁶ *ansa*-bridged cal-



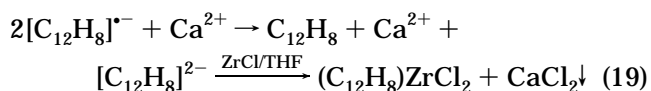
cocenes have also been used as precursors to transition-metal cyclopentadienyl complexes. In some cases, it is possible to monitor changes in stereochemistry that occur during ligand transfer. For example, the reductive coupling of phenylfulvene with activated calcium in THF gives nearly quantitative yields of a mixture of *cis*- and *trans*-diphenylethanediy-bridged *ansa*-calcocenes. The *cis* isomer can be removed by recrystallization, yielding the C₂-symmetric *trans*-Ph₂C₂H₂(η⁵-C₅H₄)₂Ca(THF)₂. Subsequent reaction with FeCl₂ and ZrCl₄ gives the C₂-symmetric transition-metal *ansa*-metallocene complexes in high yield (eq 18).²⁰ In contrast, reductive coupling of 1-(*E*)-benzylidene-4,7-dimethylindene with activated calcium forms the two isomers *trans*-Ph₂C₂H₂-*rac*-(η⁵-4,7-Me-2-C₉H₄)₂Ca(THF)₂ and *cis*-Ph₂C₂H₂-*meso*-



(η⁵-4,7-Me-2-C₉H₄)₂Ca(THF)₂ in approximately equal amounts. Reaction of the calcium compounds with FeCl₂ produces a mixture of the corresponding *trans-rac* and *cis-meso* ferrocenophanes along with another ferrocenophane isomer that is apparently either the *trans-meso* or *cis-rac* isomer. Partial loss of stereochemical integrity occurs during ligand transfer to iron; complete loss occurs on formation of zirconium complexes from the reaction of the calcium metallocenes with ZrCl₄(SMe₂)₂ or ZrCl₄(THF)₂.⁹⁷

ansa-Calcocene compounds are also effective reagents for the synthesis of *ansa*-chromocene complexes from CrCl₂ in the presence of trapping ligands such as CO and RNC. A variety of carbonyl and *tert*-butyl isocyanide complexes (e.g., 1,2-(3,4-(CH₃O)₂C₆H₃)₂C₂H₂{η⁵-C₅H₄})₂-Cr(CO, *t*-BuNC) have been prepared in this manner.⁹⁸

In an unusual twist on the *ansa*-calcocene saga, reductive coupling of acenaphthylene with activated calcium forms the yellow complex (C₁₂H₈)₂Ca(THF)₂ in high yield.⁹⁹ Although not structurally characterized, its NMR spectrum is consistent with the presence of η⁵-C₁₂H₈ rings. On reaction with ZrCl₄ in THF, the *ansa*-biacenyl ligand is decoupled, generating dark green (C₁₂H₈)₂ZrCl₂(THF)₃. Alternatively, reaction of (C₁₂H₈)₂-Ca(THF)₂ with Me₃SiCl in THF generates the 1,2-bis(trimethylsilyl)-substituted acenaphthene (Me₃Si)₂C₁₂H₈. Both of these reactions (which also occur when the metal center in the original complex is ytterbium(II) rather than calcium) apparently originate from an equilibrium between the *ansa*-metallocene, decoupled acenyl radical anions, and metal dications (i.e., (C₁₂H₈)₂M(THF)₂ ⇌ [C₁₂H₈]⁻ + M²⁺). Subsequent disproportionation of [C₁₂H₈]⁻ to the acenyl dianion and neutral acenaphthylene then sets the stage for addition of ZrCl₄ or Me₃SiCl and elimination of the metal dichloride (e.g., eq 19). These reactions highlight the fragility of the bond linking the coupled acenaphthylenes.



The lability of calcocenes can be used in a convenient path to mixed-ring organolanthanide compounds, which are otherwise not available via general routes.²⁴ Hy-

(92) Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. *Angew. Chem.* **1991**, *103*, 594–595.

(93) Bond, A. D.; Layfield, R. A.; MacAllister, J. A.; McPartlin, M.; Rawson, J. M.; Wright, D. S. *Chem. Commun.* **2001**, 1956–1957.

(94) Abis, L.; Calderazzo, F.; Maichle-Mossmer, C.; Pampaloni, G.; Strahle, J.; Tripepi, G. *J. Chem. Soc., Dalton Trans.* **1998**, 841–845.

(95) Smith, M. E.; Andersen, R. A. *J. Am. Chem. Soc.* **1996**, *118*, 11119–11128.

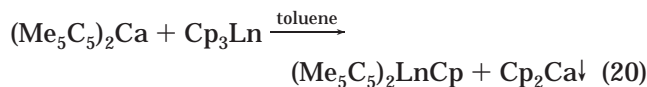
(96) Westerhausen, M.; Hartmann, M.; Makropoulos, N.; Wieneke, B.; Wieneke, M.; Schwarz, W.; Stalke, D. *Z. Naturforsch.* **1998**, *53b*, 117–125.

(97) Shapiro, P. J.; Kane, K. M.; Vij, A.; Stelck, D.; Matare, G. J.; Hubbard, R. L.; Caron, B. *Organometallics* **1997**, *18*, 3468–3473.

(98) Matare, G. J.; Foo, D. M.; Kane, K. M.; Zehnder, R.; Wagoner, M.; Shapiro, P. J.; Concolino, T.; Rheingold, A. L. *Organometallics* **2000**, *19*, 1534–1539.

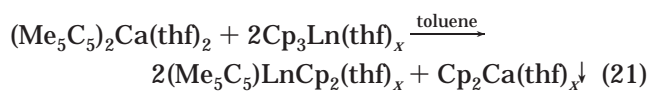
(99) Fedushkin, I. L.; Petrovskaya, T. V.; Bochkarev, M. N.; Dechert, S.; Schumann, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2474–2477.

drocarbon-soluble $(\text{Me}_5\text{C}_5)_2\text{Ca}$ undergoes cyclopentadienyl ring metathesis reactions with Cp_3Ln to yield $(\text{Me}_5\text{C}_5)_2\text{LnCp}$ complexes (eq 20). Adjustments to the



$\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$

reaction stoichiometry with solvated precursors lead to $(\text{Me}_5\text{C}_5)_2\text{LnCp}_2(\text{THF})_x$ complexes instead (eq 21).¹⁰⁰ Pre-



$\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$

cipitation of the toluene-insoluble Cp_2Ca drives the reactions; the exchange reaction does not occur with $(\text{Me}_5\text{C}_5)_2\text{Mg}$, which would generate the hydrocarbon-soluble Cp_2Mg .

6.2. Chemical Vapor Deposition. A new field of use for organoalkaline-earth compounds has emerged in chemical vapor deposition (CVD) technology.^{101,102} The gas-phase decomposition of volatile metallocenes is useful in the preparation of thin films of alkaline-earth-containing materials and as doping reagents for semiconductors. For example, beryllocene has been used to dope group 13/15 semiconductors by molecular beam epitaxy¹⁰³ and has been explored as a precursor for coating capsules with beryllium metal for use as targets in experiments with inertial confinement fusion.¹⁰⁴ Magnesium has been used to deposit MgO by atomic layer epitaxy¹⁰⁵ and is a commonly employed *p*-type dopant for semiconductors, particularly GaAs,¹⁰⁶ GaN,^{107,108} and AlGaIn.¹⁰⁹ In GaN, Mg doping induces a blue 2.8 eV photoluminescence band arising from donor–acceptor (D–A) pair recombination.¹¹⁰ The identity of the donors and acceptors has been much discussed, but it is likely that isolated Mg ions serve as the acceptors, while Mg/nitrogen vacancy complexes are the donors.^{111,112}

(100) (a) Tanner, P. S.; Overby, J. S.; Henein, M. M.; Hanusa, T. P. *Chem. Ber./Recl.* **1997**, *130*, 155–159. (b) Tanner, P. S. Ph.D. Dissertation, Vanderbilt University, 1995.

(101) Wojtczak, W. A.; Fleig, P. F.; Hampden-Smith, M. J. *Adv. Organomet. Chem.* **1996**, *40*, 215–340.

(102) Matthews, J. S.; Rees, W. S., Jr. *Adv. Inorg. Chem.* **2000**, *50*, 173–192.

(103) Mitsuhashi, M.; Ogasawara, M.; Sugiura, H. *J. Cryst. Growth* **1998**, *183*, 38–42.

(104) Salazar, K. V.; Pattillo, S. G.; Trkula, M. *Fusion Technol.* **2000**, *38*, 69–73.

(105) Putkonen, M.; Sajavaara, T.; Niinisto, L. *J. Mater. Chem.* **2000**, *10*, 1857–1861.

(106) Kuech, T. F.; Wang, P. J.; Tischler, M. A.; Potemski, R.; Scilla, G. J.; Cardone, F. *J. Cryst. Growth* **1988**, *93*, 624–630.

(107) Leem, J.-Y.; Lee, C.-R.; Lee, J.-I.; Noh, S. K.; Kwon, Y.-S.; Ryu, Y.-H.; Son, S.-J. *J. Cryst. Growth* **1998**, *193*, 491–495.

(108) Hacke, P.; Nakayama, H.; Detchprohm, T.; Hiramatsu, K.; Sawaki, N. *Appl. Phys. Lett.* **1996**, *68*, 1362–1364.

(109) Suzuki, M.; Nishio, J.; Onomura, M.; Hongo, C. *J. Cryst. Growth* **1998**, *189/190*, 511–515.

(110) Lim, P. H.; Schineller, B.; Schon, O.; Heime, K.; Heuken, M. *J. Cryst. Growth* **1999**, *205*, 1–10.

(111) Kwon, Y.-H.; Shee, S. K.; Gainer, G. H.; Park, G. H.; Hwang, S. J.; Song, J. *J. Appl. Phys. Lett.* **2000**, *76*, 840–842.

(112) Kaufmann, U.; Kunzer, M.; Maier, M.; Obloh, H.; Ramakrishnan, A.; Santic, B.; Schlotter, P. *Appl. Phys. Lett.* **1998**, *72*, 1326–1328.

The vapor-phase reaction of $(\text{C}_5\text{Me}_5)_2\text{Ca}$ with SiF_4 or NF_3 at 150 °C will deposit polycrystalline films of CaF_2 on glass and Si(100) surfaces.¹¹³ Depending on the deposition conditions, such films can be varied in thickness from 10 to 100 μm .

Atomic layer epitaxy has been used to form films of the dielectric heterometallic oxides SrTiO_3 and BaTiO_3 from organoalkaline-earth precursors.¹¹⁴ Titanium isopropoxide, water, and either $((i\text{-Pr})_3\text{C}_5\text{H}_2)_2\text{Sr}$ or $(\text{C}_5\text{Me}_5)_2\text{-Ba}$ can be used to form films of the oxides at temperatures of 325 °C (for SrTiO_3) and 275 °C (for BaTiO_3). Annealing in the air at 500 °C leaves polycrystalline films that display excellent conformal coverage of patterned silicon surfaces and have relative permittivities of 180 and 165 for the Sr and Ba oxides, respectively.^{115,116} Experiments using D_2O demonstrated that the principal volatile decomposition product during the deposition of SrO or SrTiO_3 was $\text{C}_5(i\text{-Pr})_3\text{H}_2\text{D}$;¹¹⁷ low residual carbon was found in the SrTiO_3 films.¹¹⁸

6.3. Catalysis. Metallocenes and mono(cyclopentadienyl) complexes of the group 2 elements have been explored for their potential use as catalysts. An early report describing the formation of poly(methyl methacrylate) (PMMA) using Cp_2Ca ¹¹⁸ has been reinvestigated using both Cp_2Ca and the more soluble $(\text{C}_5\text{Me}_5)_2\text{-Ca}$.¹¹⁹ The claim of high syndiotacticity (*rr* = 94% at 0 °C) could not be reproduced in the new experiments; lower conversions and syndiotacticity were consistently found. The percentage of *rr* is better than that produced by free radical polymerization, but problems with the conversion rates and the broad polydispersity of the polymer make Cp_2Ca unattractive as a catalyst for this system. The use of $(\text{C}_5\text{Me}_5)_2\text{Ca}$ produces higher conversions but even lower syndiotacticity than does $\text{Cp}_2\text{-Ca}$.

A procatalyst for ethylene and propene polymerization has been developed from CpMgCl .¹²⁰ The mono(ring) complex can be treated directly with TiCl_4 , or it can be allowed first to react with *n*-BuLi, followed by TiCl_4 . In either case, subsequent activation with MAO or $(\text{C}_2\text{H}_5)_3\text{-Al}$ generates catalytically active species. There is little evidence for ligand exchange between CpMgCl and TiCl_4 (the use of CpTiCl_3 , which would form if ring exchange had occurred, does not produce an active catalyst), and the $\text{CpMgCl/TiCl}_4/\text{MAO}$ combination shows more than 70% greater reactivity in ethylene polymerization than does a standard mixture of $\text{MgCl}_2/\text{TiCl}_3/(\text{C}_2\text{H}_5)_3\text{Al}$. Isotactic indices of the polymer obtained from the CpMgCl -supported systems appear to be similar to those from the magnesium halide mixtures.

(113) Benac, M. J.; Cowley, A. H.; Jones, R. A.; Tasch, A. F., Jr. *Chem. Mater.* **1989**, *1*, 289–290.

(114) Ritala, M.; Kukli, K.; Vehkamäki, M.; Hanninen, T.; Hatanpää, T.; Raisanen, P. I.; Leskela, M. *Proc.-Electrochem. Soc.* **2000**, *2000-13*, 597–604.

(115) Vehkamäki, M.; Hatanpää, T.; Hanninen, T.; Ritala, M.; Leskela, M. *Electrochem. Solid-State Lett.* **1999**, *2*, 504–506.

(116) Vehkamäki, M.; Hanninen, T.; Ritala, M.; Leskela, M.; Sajavaara, T.; Rauhala, E.; Keinonen, J. *Chem. Vap. Deposition* **2001**, *7*, 75–80.

(117) Rahtu, A.; Hanninen, T.; Ritala, M. *J. Phys. IV: Proc.* **2001**, *11*, 923–930.

(118) Allen, K. A.; Gowenlock, B. G.; Lindsell, W. E. *J. Polym. Sci.* **1974**, *12*, 1131.

(119) Li, Y.; Deng, H.; Brittain, W.; Chisholm, M. S. *Polym. Bull. (Berlin)* **1999**, *42*, 635–639.

(120) Mortara, S.; Fregonese, D.; Bresadola, S. *Macromol. Chem. Phys.* **2001**, *202*, 2630–2633.

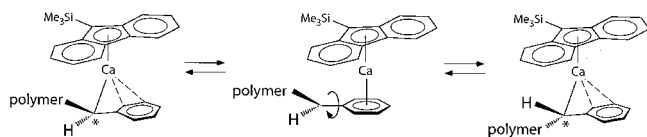


Figure 13. Possible mechanism for the introduction of stereoerrors during the polymerization of styrene with (2-Me₂N- α -Me₃Si-benzyl)(9-Me₃Si-fluorenyl)Ca(THF)₂.

If the coordination sphere around calcium could be controlled by the proper cyclopentadienyl-type ligand, the high polarity of the Ca–R bond might be exploited to produce a living catalyst for syndiotactic polystyrene. This possibility was examined with the fluorenyl calcium benzyl complex (2-Me₂N- α -Me₃Si-benzyl)(9-Me₃Si-fluorenyl)Ca(THF)₂, which does not display Schlenk equilibrium with its symmetrical counterparts (bis-(fluorenyl)calcium and bis(benzyl)calcium).¹²¹ Living polymerization is in fact observed with this compound at room temperature (10% styrene in cyclohexane or benzene), but the resulting material is largely atactic. The stereoerrors apparently arise from configurational rearrangements of the anionic chain end: inversion of the chain end involving rotation around the *ipso*-C α bond is possible without breaking the cation–anion bond (Figure 13). Interestingly, polymerization in pure styrene produces highly syndiotactic polymer, with less than 2% of the isotactic material. The higher concentration of styrene increases the rate of insertion, which is

(121) Harder, S.; Feil, F.; Knoll, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 4261–4264.

(122) Bridgeman, A. J. *J. Chem. Soc., Dalton Trans.* **1997**, *17*, 2887–2893.

(123) Haaland, A.; Lusztyk, J.; Brunvoll, J.; Starowieyski, K. B. *J. Organomet. Chem.* **1975**, *85*, 279–285.

evidently highly stereospecific. Loss of stereochemical control occurs after the insertion step.

7. Conclusions

Compared to the paucity of information that existed about alkaline-earth cyclopentadienyl complexes just two decades ago, the field today has grown to encompass over 100 structurally characterized compounds that display a wide variety of physical properties. The use of sterically bulky cyclopentadienyl rings has markedly increased the solubility and volatility of the complexes, making them convenient and, in some cases, the preferred sources of the alkaline-earth elements for use in materials synthesis. The subtleties of bonding present in these compounds are only beginning to be understood, and further study of this area could be expected to provide more information about the chemical consequences of weak inter- and intramolecular covalent interactions. It may be expected that greater understanding of group 2 cyclopentadienyl complexes will contribute to the development of a more unified view of structure and reactivity in organomain-group chemistry than currently exists.

Acknowledgment for support of research from my laboratory is made to the National Science Foundation. Members of my current research group are also thanked for their assistance in the literature searching and the initial summaries of several sections.

OM0201680