Ligand Influences on Structure and Reactivity in Organoalkaline-Earth Chemistry

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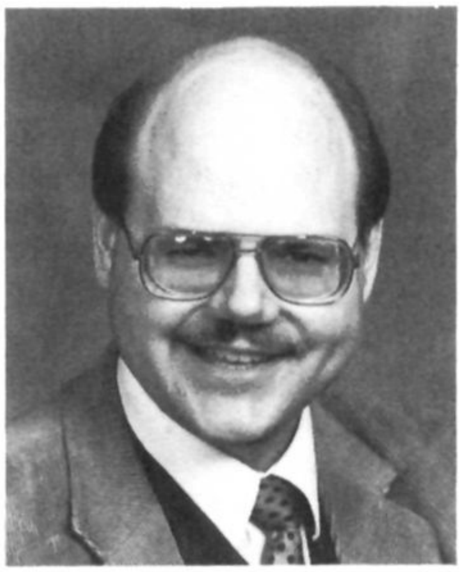
Contents



Timothy P. Hanusa was born in 1956 in Council Bluffs, IA. He received the bachelor's degree in chemistry in 1978 from Cornell College, Mt. Vernon, IA. In 1983 he completed his Ph.D. degree at Indiana University (Bloomington), where he had studied the reactions of metalloheteroboranes under Prof. Lee J. Todd. During the next two years at the University of California (Irvine), he undertook postdoctoral research on organolanthanide complexes with Prof. William J. Evans. In 1985 he joined the faculty at Vanderbilt University in Nashville, TN, as an Assistant Professor. He is currently an Associate Professor at Vanderbilt. His research interests include the synthesis, structures, and reactions of main-group compounds, particularly molecular complexes of the alkali and alkaline-earth metals.

I. Introduction

The extent to which coordinated ligands influence the chemistry of metal complexes varies greatly across the periodic table. The transition metals support a rich variety of ligand systems, including those with multiple M–L bonds,[1] π-donors and acceptors,[2] and oligomers with extensive electron delocalization.[3] Such metal–ligand interactions are much less common among main-group compounds, especially those containing the highly electropositive s-block elements (groups 1 and 2). Complexes of the latter are characteristically ionic species, whose typical ligands are anions such as halides, amides, alkoxides, and alkyls; neutral bases such as ethers and amines are also frequently present. This comparatively limited tableau of substituents has not hindered the synthetic use of compounds such as alkyllithiums and Grignard reagents, which rely on the highly polar nature of the metal–carbon bond for their effectiveness. The lack of ligand control, however, has hindered development of the coordination chemistry of the heavier alkali and alkaline-earth metals.

This situation is now rapidly changing, spurred in part by the search for alkaline-earth precursors to metal oxides and halides for chemical vapor deposition (CVD)[4–7] or sol-gel purposes.[8] Optimum precursors for CVD preparation of thin films would be volatile at low temperatures, readily synthesized and handled, and free of elements (e.g., fluorides) that could interfere with the epitaxy of the deposited layers.[9] For mixed metal oxides, such as the superconducting cuprates, it would be desirable to have access to bi- and even trimetallic precursors, so that the elements could be deposited in stoichiometrically precise ratios.[10] Sol-gel syntheses require materials whose metal–ligand bonds can be hydrolyzed predictably, so that solution stoichiometries and precipitated particle size can be controlled.[11]

Alkaline-earth alkoxides have received considerable study as precursors for CVD and sol-gel work, and several investigations have examined the effects of various solvents and gases on their volatility and reactivity.[12–15] Many alkoxides used in these studies are nonmolecular materials, however, and the absence of adequate structural and spectroscopic data has slowed attempts to rationalize ligand effects on reactivity.[16]

For many years, organometallic compounds of calcium, strontium, and barium were as poorly characterized as the alkoxides and were more difficult to synthesize and handle.[17] The dialkyls (R_2M), Grignard analogues (RMX), and simple metallocenes (Cp_2M) that constituted the organometallic complexes of these elements were consequently unattractive candidates for organic or materials synthesis. Since the mid-1980s, however, new varieties of molecular organometallic species with a diverse range of physical and chemical properties have been synthesized and often structurally characterized.[18] The properties of these compounds have in turn led to a new appreciation of the degree to which calcium subgroup chemistry can be developed by exploiting the geometric and electronic characteristics of coordinated ligands.

Distinctions in bonding between organometallic compounds (containing *C*-donor ligands) and classical coordination complexes (with non-*C*-donor ligands) are not as great in group 2 chemistry as with the transition or posttransition metals. Thus despite the focus of this article on ligand effects in organometallic derivatives of the heavy alkaline earths, comparisons are made with related amides and alkoxides as well. We do not attempt, however, to present a general survey of organoalkaline-earth chemistry; recent reviews on this subject are available.[17-19]

II. Attributes of the Heavy Alkaline-Earth Ions

In examining the effects that ligands can exert on the properties of alkaline-earth (Ae) complexes, it is useful to keep in mind some relatively invariant properties of the metal ions themselves: among these are radii, electron configuration, and charge density.

A. Large Metal Radii

Although the Be^{2+} ion is the smallest dipositive cation (0.27 Å),[20] and the size of Mg^{2+} (0.72 Å) is similar to that of many first-row transition metal ions, the radii of the heavier ions [1.00 Å (Ca^{2+}), 1.18 (Sr^{2+}), 1.35 Å (Ba^{2+}) for CN = 6] are comparable to the largest lanthanide and actinide ions [cf. La^{3+} (1.03 Å), Sm^{2+} (1.17 Å), U^{3+} (1.03 Å)]. With ligands of "average" size (e.g., Et, OMe, Cp), the ions will be coordinately unsaturated; to compensate, they will typically display high coordination numbers (8–12), with values found in the order $Ca^{2+} < Sr^{2+} < Ba^{2+}$.[21] Their compounds often spontaneously oligomerize and form nonmolecular lattices [cf. the alkoxides $[Ae(OR)_2]_x$[22-25] and $[Cp_2Ca]_n$ (section IV.A)].

B. Noble Gas Electron Configurations

Monovalent alkaline-earth species can be stabilized in low-temperature gas matrices,[26] and several organometallic radicals are known in the gas phase (e.g., $Ca–Cp^{\bullet}$, $Ca–CH_3^{\bullet}$, $Sr–CCH^{\bullet}$, $Sr–C_4H_4N^{\bullet}$).[27] Except in these cases, Ae cations have no valence electrons and exhibit only the +2 oxidation state. Their compounds consequently have no metal-centered redox chemistry, and only a few combinations of charged ligands can be accommodated. For example, neutral species must be of the form AeLL′ or AeL″ (L, L′ = uninegative ligands; L″ = dinegative ligand). Well-characterized anionic "ate" complexes, such as $K_2[(C_8H_8)_2Ca(DME)_2]$[28] and $Li[Cp^*{}_2BaR(THF)_2]$[29] are rare. In addition, the lack of valence electrons means that kinetic lability and the possibility of ligand loss will usually be high.

Until recently, it has been accepted as a truism that d orbitals play essentially no role in the chemistry of the alkaline earths. As will be discussed below (section IV.C), there is growing evidence that d electrons may exert structural effects on organometallic complexes that become observable in when sufficiently bulky ligands are present to prevent the formation of oligomeric species.

C. Low Charge/Size Ratios

Although charge/size relationships are a consequence of points A and B, their effects will be considered separately here. The alkaline-earth cations resemble those of the alkali metals in their low Z^+/r ratios[30] and are "hard", relatively nonpolarizable ions.[31] Their metal–carbon bonds are highly polar and sensitive to oxygen and moisture. Solvents for organoalkaline-earth compounds have generally been limited to polar media such as ethers, DMSO, and amines; until recently, few organoalkaline-earth compounds could be prepared in hydrocarbons. Even in THF or pyridine, organobarium compounds exist primarily as contact ion pairs; addition of strongly coordinating solvents such as HMPA or triglyme or cooling of the solutions is required to produce significant numbers of solvent-separated ion pairs.[32,33]

Because of the increasing ionic radii, the metals' charge/size ratios and their Lewis acidities decrease on descending the family. Those properties of complexes that depend upon the degree of metal acidity (e.g., adduct strength) will vary substantially from Ca^{2+} to Ba^{2+}. Adducts of organocalcium complexes, for example, are known for which the corresponding barium derivatives are not isolable (section VI.B).

Considering these metal properties as starting points, the areas of alkaline-earth chemistry that have proven to be the most amenable to ligand influences are (1) control of oligomerization in the solid state and solution and (2) manipulation of the stability of Lewis acid/base adducts. After a brief review of methods used to synthesize organoalkaline-earth complexes, we will discuss ways in which substituents can be used to modify their properties.

III. Synthetic Approaches to Organoalkaline-Earth Complexes

Organoalkaline-earth complexes are often synthesized by direct reaction of the elements with the neutral ligand precursors. The metals might be used in the vapor form,[34-38] but more commonly are employed as bulk solids, used either alone or activated by amalgamation, iodine,[17] or treatment with $NH_3(g)$ (eq 1).[33,39,40] Reduction of the halides by organolithium

$$2Ba \xrightarrow[THF]{NH_3(g)} \text{“}Ba(NH_3)_x\text{”} \tag{1}$$

electron-transfer reagents (eq 2)[41-43] or by potassium (eq 3)[44] will generate highly active powders (Ae*) that are synthetically useful. The activated metals or

$$2Li^+[C_6H_5C_6H_5]^- + (Ca,Ba)I_2 \xrightarrow{THF} (Ca,Ba)^*\downarrow + 2LiI + 2[C_6H_5C_6H_5] \tag{2}$$

$$2K + AeI_2 \xrightarrow{THF} Ae^*\downarrow + 2KI\downarrow \tag{3}$$

powders will directly metalate protonic reagents to generate the respective organoalkaline-earth species

Table I. Structurally Characterized Organocalcium, -strontium, and -barium Complexes

complex	coordination no.	nuclearity	method[a]	ref(s)
$(Cp_2Ca)_n$	9	3-D polymer	X	52
Cp^*_2Ca	6	monomeric	E	101,102
Cp^*_2Ca	6	monomeric	X	53
$Cp^*_2Ca(Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3)$	8	monomeric	X	154
$Cp^*_2Ca(MeC{\equiv}C{-}C{\equiv}CMe)$	8	monomeric	X	86
$(MeCp)_2Ca(DME)$	8	monomeric	X	155
$[(C_3H_7)_3C_5H_2]_2Ca$	6	monomeric	X	84
$[(C_3H_7)_4C_5H]_2Ca$	6	monomeric	X	55
$[C_5H_3\text{-}1,3\text{-}(SiMe_3)_2]_2Ca(THF)$	7	monomeric	X	36
$[Cp^*CaI(THF)_2]_2$	7	dimeric	X	50
$[(C_3H_7)_4C_5H]CaI(THF)]_2$	6	dimeric	X	156
$Ca[CH(SiMe_3)_2]_2(dioxane)_2$	4	monomeric	X	64
$[(C_5H_4(t\text{-}Bu)]_2Ca(THF)_2$	8	monomeric	X	38
$[(Me_4EtC_5)Ca(\mu\text{-}\overline{NSiMe_2CH_2CH_2Si}Me_2)]_2$	5	dimeric	X	29
$Cp^*_2Ca(\mu\text{-}Cl)ClHfCp^*_2$	7	dinuclear	X	51
$[Cp^*_2Ca(\mu\text{-}OC)_2(OC)Cr(C_6H_3(CH_3)_3)]_2$	8	dimeric	X	51
$[Cp^*_2Ca(\mu\text{-}CH_3)_2Al(CH_3)(THF)]_2$	8	dimeric	X	126
$[[C_5H_3\text{-}1,3\text{-}(SiMe_3)_2]_2Ca[\mu\text{-}OC_5H_2\text{-}2,4\text{-}(SiMe_3)_2]]_2$	5	dimeric	X	157
closo-$(MeCN)_4\text{-}1,2,4\text{-}CaC_2B_{10}H_{12}$	7	monomeric	X	158
Cp^*_2Sr	6	monomeric	E	103,104
$[(C_5H_4(t\text{-}Bu)]_2Sr(THF)_2$	8	monomeric	X	38
$[C_5H_3\text{-}1,3\text{-}(SiMe_3)_2]_2Sr(THF)$	7	monomeric	X	36
[*closo*-$(MeCN)_3\text{-}1,2,4\text{-}SrC_2B_{10}H_{12}]_n$	8	1-D polymer	X	159
Cp^*_2Ba	6	monomeric	E	103,104
$[Cp^*_2Ba]_n$	6 (8)	1-D polymer	X	54
$[Cp^*_2Ba]_2(\mu\text{-}pyrazine)$	7	dinuclear	X	56
$[(C_3H_7)_3C_5H_2]_2Ba(THF)_2$	8	monomeric	X	61
$[(C_3H_7)_4C_5H]_2Ba$	6	monomeric	X	55
$(\eta^5\text{-}fluorenyl)_2Ba(NH_3)_4$	10	monomeric	X	112

[a] E = Gas electron diffraction; X = single-crystal X-ray diffraction.

(e.g., eq 4). Protonation reactions can also be accomplished with metal amides, either with those generated in situ (e.g., eq 5)[45] or supplied separately (eq 6).[46]

$$Ae^* + 2(RH,HNR_2,HOR) \rightarrow (R_2Ae,Ae(NR_2)_2,Ae(OR)_2) + H_2\uparrow \quad (4)$$

$$Ca \xrightarrow[-H_2]{NH_3(l)} Ca(NH_2)_2 + 2Cp^*H \xrightarrow{THF,NH_3(l)} Cp^*_2Ca(THF)_2 + H_2\uparrow \quad (5)$$

$$Ba[N(SiMe_3)_2]_2(THF)_2 + 2Ph_4C_5H_2 \xrightarrow{toluene} (Ph_4C_5H)_2Ba + 2HN(SiMe_3)_2 \quad (6)$$

An alternative approach to organoalkaline-earth synthesis employs anhydrous metal halides, which react with the alkali metal salts of organic anions to form the appropriate derivatives (eq 7).[47–49] Halide metathesis lends itself to the formation of asymmetric species, such as monocyclopentadienyl complexes, which can be further derivatized (e.g., eqs 8 and 9).[50,51]

$$2MR + AeX_2 \xrightarrow{ether} R_2Ae + 2MX\downarrow \quad (7)$$
$$M = Li, Na, K; R = amide, Cp; X = Cl, Br, I$$

$$KCp^* + CaI_2 \xrightarrow{THF} Cp^*CaI(THF)_2 + KI\downarrow \quad (8)$$

$$Cp^*CaI(THF)_2 + K(NR_2,OR) \xrightarrow{toluene} Cp^*Ca(NR_2,OR) + KI\downarrow \quad (9)$$

IV. Control of Structure in Alkaline-Earth Systems

A. Sterically Bulky Groups

Among the most dramatic effects exerted by ligands on organoalkaline-earth complexes is the change in coordination environment provided by sterically bulky groups. The high coordination numbers observed in metal salts and oxides can be lowered to CN = 3 or 4 with bulky groups in organometallic complexes, amides, and alkoxides. Often the resulting compounds are monomeric, although low oligomers (especially dimers) are often found (Table I). Depending on the bulk of the anionic ligands, additional coordinating bases, such as NH_3, Et_2O, THF, and DME, may be present as well. Usually, compounds with sufficiently bulky ligands crystallize in molecular arrays, rather than ionic lattices, and it is meaningful to discuss the interaction of specific metal–ligand pairs.

1. Metallocenes

Among the most extensively studied series of organoalkaline-earth complexes, both from a chemical and structural viewpoint, are the metallocenes Cp'_2Ae and their Lewis base adducts.[18] The change in nuclearity accompanying increased ligand size is strikingly demonstrated by the difference in the structure of Cp_2Ca and Cp^*_2Ca ($Cp^* = C_5Me_5$). The former is a polymeric species, in which each calcium atom interacts with as many as four cyclopentadienyl rings (Figure 1); discrete Cp_2Ca units do not exist in the crystal lattice.[52] In contrast, the steric bulk of the Cp^* rings prevents any such close approach of adjacent molecules, and Cp^*_2Ca is consequently monomeric in the solid state (Figure 2).[53] With the larger Ba^{2+} center, the Cp^* ring is not

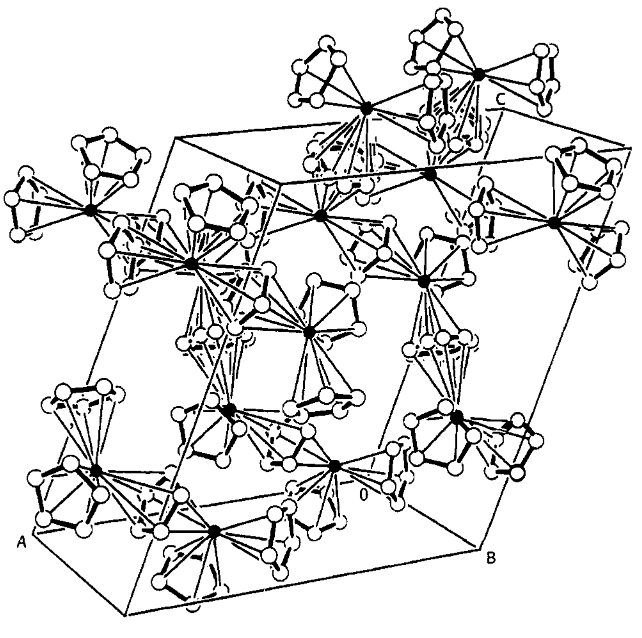


Figure 1. Unit cell of Cp_2Ca (ref 52). The apparent 10-membered Cp rings arise from disorder.

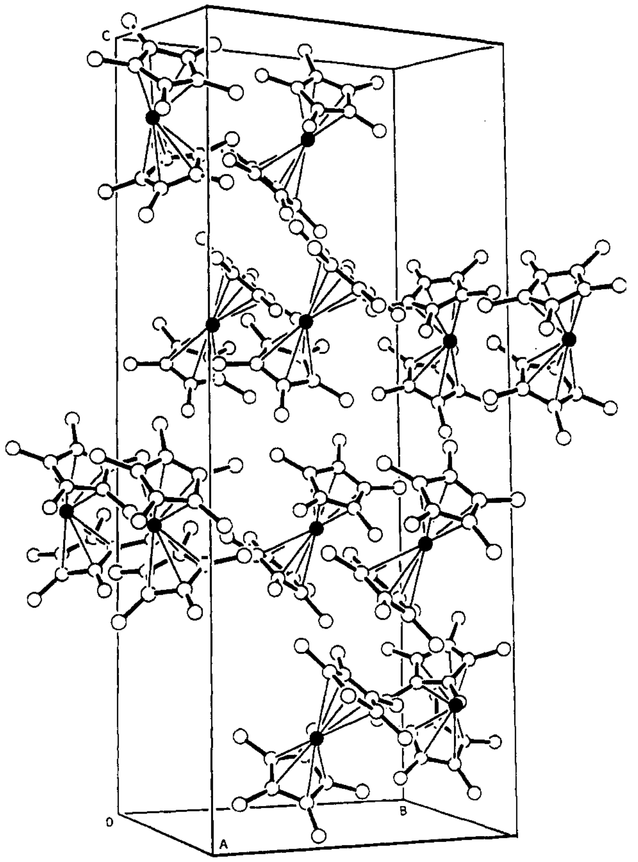


Figure 2. Unit cell of Cp^*_2Ca (ref 53).

bulky enough to prevent neighboring rings from entering the coordination sphere of the metal, and Cp^*_2Ba forms a one-dimensional coordination polymer (Figure 3).[53,54] However, an even larger ligand, such as tetraisopropylcyclopentadiene, will produce a strictly monomeric base-free barocene.[55]

Many monomeric metallocenes have been structurally characterized as adducts with coordinated bases, and sometimes the latter help supply the steric bulk required to reduce or block oligomerization. For instance, unlike the parent chainlike Cp^*_2Ba, its pyrazine adduct $[Cp^*_2Ba]_2(\mu\text{-}C_6H_4N_2)$ is dinuclear.[56] Similarly, the base-free complexes $[C_5H_4(t\text{-Bu})]_2(Ca,Sr)$ are partially associated in the solid state (^{13}C CP/MAS NMR evidence); in contrast, the solvated $[C_5H_4(t\text{-Bu})]_2(Ca,Sr)(THF)_2$ complexes are monomeric.[38]

By using extremely bulky Cp′ rings, such as Cp^{3i}, Cp^{4i} ($Cp^{n}{}_{i} = (i\text{-Pr})_nC_5H_{5-n}$) and Ph_4C_5H,[57-60] a class of monomeric "encapsulated" metallocenes can be formed that display noticeably suppressed reactivity compared to their less encumbered counterparts.[55] The complex $(Cp^{4i})_2Ca$, for example, does not form adducts with neutral donors such as ethers and aromatic amines, and in contrast to the extreme air sensitivity of Cp^*_2Ca, crystalline $(Cp^{4i})_2Ca$ can be handled for several minutes in dry air without obvious decomposition. A space-filling drawing based on the X-ray crystal structure of the complex reveals that the isopropyl groups have rotated perpendicularly to the cyclopentadienyl plane, thus interlocking to form a "cage" around the metal center (Figure 4).[55] Other encapsulated species that display reduced reactivity and could serve as controllable sources of Ae^{2+} ions include $(Cp^{4i})_2(Sr,Ba)$, the $(Cp^{3i})_2Ae$ (Ae = Ca, Sr, Ba) series[61] and $(Ph_4C_4H)_2Ba$.[46]

2. Alkyls

The relationship between oligomerization and steric bulk is reasonably well established for beryllium and magnesium alkyl complexes.[62,63] Much less attention has been given to the structures of alkyls and aryls of the heavy alkaline-earth metals, although many R_2Ae and RAeX compounds have been prepared in situ.[17,40,43] To date, the only structurally characterized dialkyl species is the monomeric tetrahedral solvate $Ca[CH(SiMe_3)_2]_2(dioxane)_2$.[64] Interestingly, its magnesium counterpart forms a dinuclear complex with *p*-dioxane, $\{Mg[CH(SiMe_3)_2]_2\}_2(\mu\text{-dioxane})$.[65] Evidently the presence of a second dioxane molecule supplies enough bulk that oligomerization need not occur in the calcium system.

3. Amides

The primary amides of the alkaline-earth elements, $Ae(NH_2)_2$, are nonmolecular species.[21] When the NH_2 ligand is replaced by the bulky bis(trimethylsilyl)amido group, however, molecular complexes are formed. A complete set of structures has been obtained for Be–Ba (Table II). The barium bis(trimethylsilyl)amides form an interesting progression of compounds that illustrate the relationship between coordination number and metal nuclearity.[39] The base-free compound $\{Ba[N(SiMe_3)_2]\}_2$ exists as a dimer that can add a single THF ligand to each metal center without a gross change in structure (i.e., $\{Ba[N(SiMe_3)_2]_2(THF)\}_2$). Addition of a second THF, however, provides enough steric bulk that the $Ba[N(SiMe_3)_2]_2(THF)_2$ adduct crystallizes as a monomer.

Remarkably, isostructural dimers of the form $\{Ae[N(SiMe_3)_2]_2\}_2$ exist for all the metals Mg–Ba. Even though the metal radii in these compounds vary by more than a factor of 2, the bis(trimethylsilyl)amido ligands accommodate the range of metal–ligand distances without requiring changes in nuclearity.

4. Alkoxides

Historically, the first alkoxides of Ca, Sr, and Ba isolated were those containing sterically compact groups

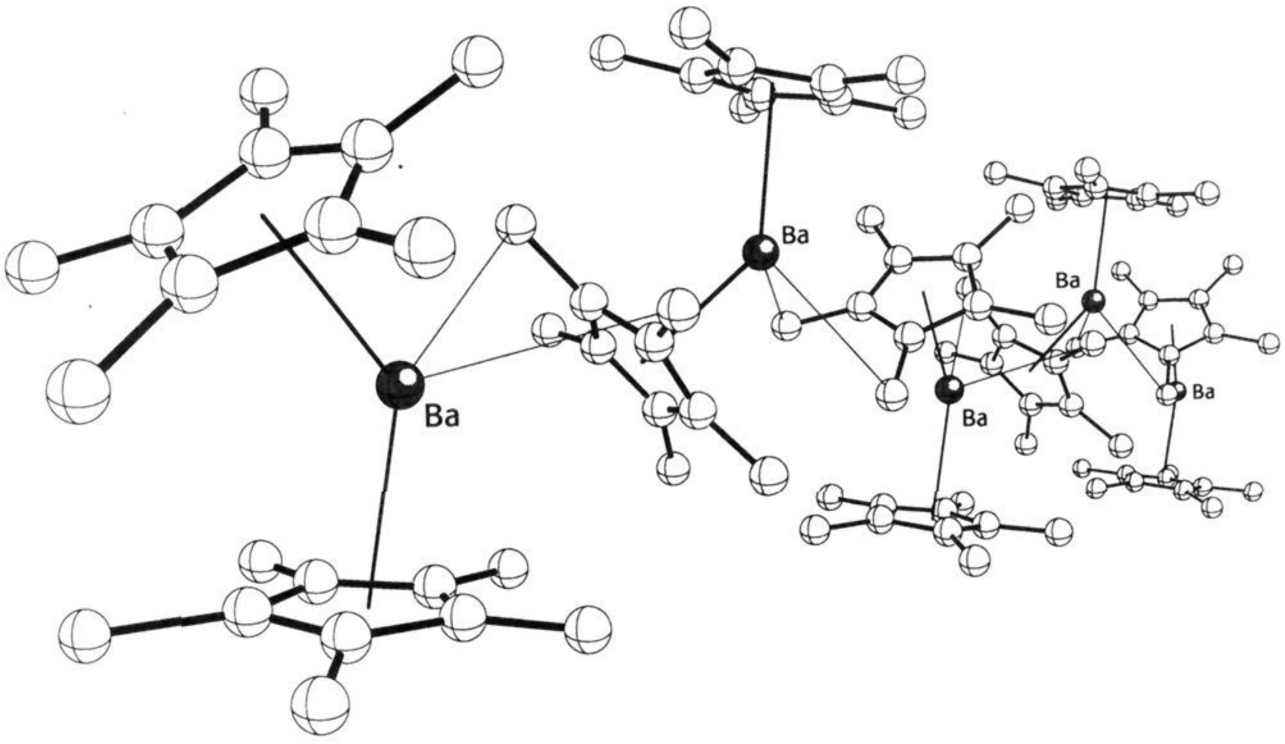


Figure 3. Chaining of Cp$^*_2$Ba in the solid state (ref 54). Within a chain, the shortest intermolecular Ba–C(methyl) distance is 0.28 Å longer than the shortest intramolecular Ba–C distance.

Table II. Structures of Alkaline-Earth Bis(trimethylsilyl)amides and Adducts

complex	coordination number	nuclearity	average Ae–N distance (Å)	method[a]	ref
$Be[N(SiMe_3)_2]_2$	2	monomeric	1.566 (17)	E	160
$\{Mg[N(SiMe_3)_2]_2\}_2$	3	dimeric	1.975 (5) t-N 2.151 (6) μ-N	X	161
$Mg[N(SiMe_3)_2]_2(THF)_2$	4	monomeric	2.021 (7)	X	162
$\{Ca[N(SiMe_3)_2]_2\}_2$	3	dimeric	2.275 (9) t-N 2.47 (1) μ-N	X	163
$Ca[N(SiMe_3)_2]_2(DME)$	4	monomeric	2.271 (3)	X	163
$\{Sr[N(SiMe_3)_2]_2\}_2$	3	dimeric	2.43 (2) t-N 2.63 (2) μ-N	X	164
$Sr[N(SiMe_3)_2]_2(DME)_2$	4	monomeric	2.538 (7)	X	164
$\{Sr[N(SiMe_3)_2]_2(dioxane)\}_n$	4	1-D polymer	2.449 (7)	X	64
$\{Ba[N(SiMe_3)_2]_2\}_2$	3	dimeric	2.576 (3) t-N 2.798 (3), 2.846 (4) μ-N	X	39
$\{Ba[N(SiMe_3)_2]_2(THF)\}_2$	4	dimeric	2.602 (9) t-N 2.834 (9), 2.903 (10) μ-N	X	39
$Ba[N(SiMe_3)_2]_2(THF)_2$	4	monomeric	2.592 (8)	X	39

[a] E = Gas electron diffraction; X = single-crystal X-ray diffraction.

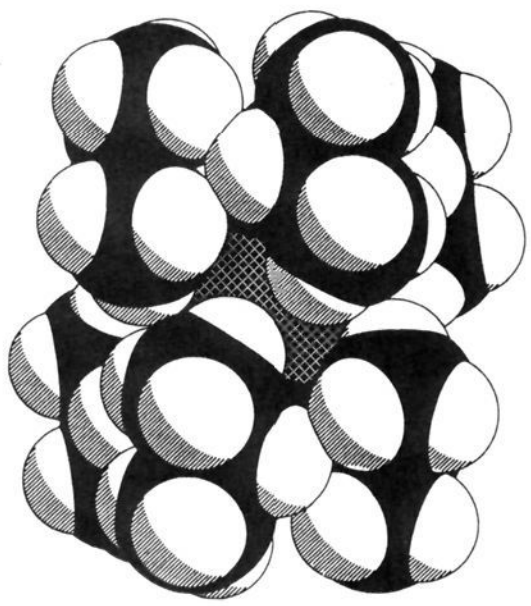


Figure 4. Space-filling view of $(Cp^{4i})_2Ca$ (ref 55), illustrating the minimal exposure of the metal center (crosshatched area).

(OMe, OEt, etc.), which formed $[Ae(OR)_2]_n$ derivatives that are presumably oligomeric or polymeric.[25] The use of somewhat more sterically bulky groups has led in recent years to the isolation of a variety of structurally characterized cluster complexes, such as $Sr_4(OPh)_8(PhOH)_2(THF)_6$,[66] $[Ba_4(\mu_4\text{-}O)(\mu_2\text{-}OC_6H_2\text{-}(CH_2NMe_2)_3\text{-}2,4,6)_6]\cdot 3(toluene)$,[67] $HBa_5(O)(OPh)_9(THF)_8$, $H_3Ba_6(O)(O\text{-}t\text{-}Bu)_{11}(OCEt_2CH_2O)(THF)_3$,[68] $Ba_6O(OC_2H_4OMe)_{10}(HOC_2H_4OMe)_4$,[69] and the siloxide $[Ba_3(OSiPh_3)_6(THF)]\cdot 0.5(THF)$.[70]

The number of crystallographically characterized monomeric or dimeric Ae alkoxides or aryloxides has also expanded and includes complexes with a diverse array of ligand geometries. They include the calcium and barium aryloxides $Ae(BHT)_2(THF)_3\cdot(THF)$,[71,72] the related strontium complex $Sr(OC_6H_2(t\text{-}Bu)_3)_2(THF)_3$,[73] calcium bis(2,4-dinitrophenoxide),[74] barium bis(2,4,6-trinitrophenoxide),[75] hydrogen-bonded $Ba(2,6\text{-}t\text{-}Bu_2C_6H_3O)_2(HOCH_2CH_2NMe_2)_4$,[76] and the alkoxides $Ca(OR)_2(THF)_3\cdot(THF)$, $[Ca(\mu\text{-}OR)(OR)(THF)]_2$ (OR = $OC(C_6H_5)_2CH_2C_6H_4\text{-}Cl\text{-}4$),[72] $Ba[(OC_2H_4)(OHC_2H_4)_2N]_2\cdot 2EtOH$,[77] $Ba_2(OCPh_3)_4(THF)_3$,[78] and the siloxide $Ba_2(OSi\text{-}t\text{-}Bu_3)_4(THF)$.[78] It is noteworthy that the calcium, strontium, and barium $Ae(OAr)_2(THF)_3$ complexes are isostructural; just as with the $\{Ae[N(SiMe_3)_2]_2\}_2$ complexes, the interligand interactions in the aryloxides apparently override the structural differences that might be expected to accompany the ca. 0.35 Å change in metal radius.

B. Steric Oversaturation

The concept of steric over- and undersaturation was developed in organo-f-element chemistry to explain the tendency of certain complexes to extrude coordinated bases spontaneously (e.g., $Cp_2UCl_2L_2$), whereas others (e.g., $CpUCl_3L$) are more stable if additional ligands are bound.[79,80] The idea has been quantified by an extension of the cone-angle concept called "solid angle sums", and ligand sets that would lead to sterically undersaturated, saturated, and oversaturated metal centers have been identified.[81,82] The concept has been applied in a more general way to the reactivity of lanthanide–carbon bonds and used to explain the ability of organolanthanide complexes to activate saturated hydrocarbons.[83]

Steric oversaturation is apparently the reason that no more than one of certain large ligands can be accommodated on group 2 metal centers. There are several examples of this phenomenon among the lighter alkaline earths. For instance, attempts to form the metallocene Cp^*_2Be by halide metathesis are unsuccessful, and a monopentamethylcyclopentadienyl species is isolated instead (eqs 10 and 11).[47] Similarly, use of the large Cp^{4i} ligand prevents isolation of a corresponding magnesocene in THF (eq 12).[84] An analogous situation exists with the *tert*-butyl-substituted tris(pyrazoyl)hydroborates, $[\eta^3\text{-}HB(3\text{-}Bu^tpz)_3]^-$, which will not form bis-species with Mg (i.e., $[\eta^3\text{-}HB(3\text{-}Bu^tpz)_3]_2Mg$);[85] monosubstituted complexes are generated instead.

$$2NaCp^* + BeCl_2 \not\longrightarrow Cp^*_2Be + 2NaCl\downarrow \tag{10}$$

$$\searrow\ Cp^*BeCl + NaCl\downarrow + NaCp^* \tag{11}$$

$$2K(Cp^{4i}) + MgBr_2 \xrightarrow{THF} (Cp^{4i})MgBr(THF)_2 + KBr\downarrow + K(Cp^{4i}) \tag{12}$$

Steric oversaturation is more difficult to achieve with the larger alkaline-earth metals. Steric effects may be involved, however, in the reaction of 2 equiv of KCp′ (Cp′ = Cp^{3i}, Cp^{4i}) with CaI_2 in THF, which does not yield the metallocene exclusively (as would occur with Cp or Cp*; cf. eq 7). Instead, a mixture of the metallocene and a monoring species is produced; the observed ratio of $Cp'_2Ca(THF)_n$ to $Cp'CaI(THF)_2$ (2:1) can be accounted for by eq 13.[61,86] This finding suggests that the bulky Cp′ ring helps kinetically stabilize the monoring species. The steric bulk provided by the coordinated solvent is also critical, since if the reactions are run in diethyl ether a high yield of the base-free metallocene Cp'_2Ca is obtained (eq 14).[55,61]

$$6KCp' + 3CaI_2 \xrightarrow{THF} 2Cp'_2Ca(THF)_n + Cp'CaI(THF)_2 + 5KI\downarrow + KCp' \tag{13}$$

$$2KCp' + CaI_2 \xrightarrow{ether} Cp'_2Ca + 2KI\downarrow \tag{14}$$

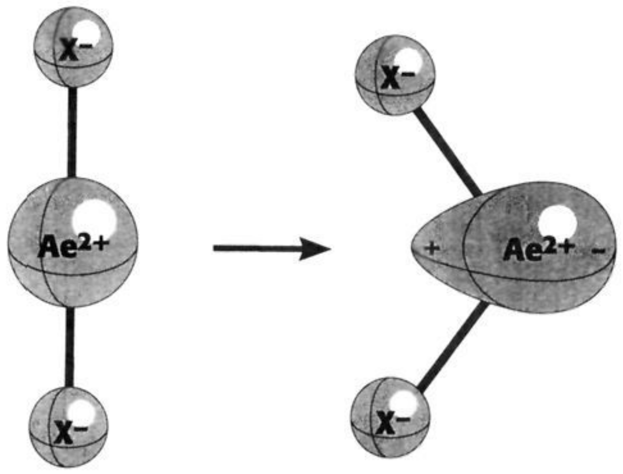


Figure 5. Bending of an alkaline-earth dihalide caused by polarization of the metal ion. The induced dipole on the metal can interact favorably with the negatively charged halide anions.

C. Effects of d Orbitals on Structure

The influence of d electrons on the chemistry of the main-group elements has a long and contentious history.[87] Early rationales for their involvement stemmed from the existence of five-, six-, and higher-coordinate species of the second- and higher-row elements, which were thought to require the use of d orbitals to explain their geometry (cf. the sp^3d and sp^3d^2 bonding schemes of valence bond theory[88]). During the last 20 years, however, the growing acceptance of delocalized bonding schemes[89–91] in group 12–18 chemistry has helped diminish the stress placed on d-electron involvement in their compounds.

It is incongruous, then, that as arguments for d-orbital participation in the chemistry of the *post*transition elements appear increasingly less persuasive, they are becoming more common when describing the bonding in the *pre*transition elements. This is especially ironic since compounds of the alkali and alkaline-earth metals seemed safely out of reach of the d-orbital controversy. Even though d-orbital effects are not induced by ligands per se, we discuss them here since it is monomeric compounds with large, sterically bulky ligands that have provided some of the recent experimental evidence for their operation.

On the basis of molecular beam experiments, Klemperer reported in 1963 that several gaseous Ae dihalides (AeF_2 (Ae = Ca, Sr, Ba); $AeCl_2$ (Ae = Sr, Ba); BaI_2) were bent in the gas phase.[92,93] Similar results were reported for the dihalides trapped in frozen gas matrices.[94,95] This fact is not easily reconciled with a simple ionic model of bonding ($X^-\text{–}Ae^{2+}\text{–}X^-$) or with a valence bond approach involving s, p, or sp hybrid orbitals. Guido and Gigli elaborated a rationale for the bending in the halides based on a "reverse polarization" model.[96] In this approach, an initially linear MX_2 molecule (X = highly electronegative atom) constructed around a polarizable metal center will spontaneously bend, because in so doing a dipole moment is generated that will favorably interact with the negatively charged ligands (Figure 5). The model predicts that bending should occur in the order Ca < Sr < Ba, in agreement with the experimental values. It has been criticized, however, on grounds that the core polarizabilities of the metal centers are not high enough to lead to the magnitude of the observed bending.[97]

In an organometallic context, the problem of rationalizing nonlinear structures of ostensibly "ionic" compounds was raised by the discovery of the f-element metallocenes Cp^*_2Sm and Cp^*_2Eu, which are bent in the solid state (ring centroid–metal–ring centroid angles of ca. 140°).[98,99] Although the metal configurations in

Table III. Distances and Bending Angles in Monomeric Base-free Alkaline-Earth and Lanthanide Metallocenes

complex	average Ae–C distance (Å)	ring centroid–Ae–ring centroid (deg)	method[a]	ref(s)
$Cp^*{}_2Mg$	2.341 (6)	180	E	102
$Cp^*{}_2Ca$	2.609 (6)	154 (3)	E	101,102
$Cp^*{}_2Ca$	2.64 (2)	147.0	X	53
$[(C_3H_7)_3C_5H_2]_2Ca$	2.62 (2)	169.7	X	84
$[(C_3H_7)_4C_5H]_2Ca$	2.64 (1)	162.3	X	55
$Cp^*{}_2Sr$	2.750 (8)	149 (3)	E	103,104
$Cp^*{}_2Ba$	2.898 (17)	148 (6)	E	103,104
$(Cp^*{}_2Ba)_n$	2.99 (2)	131.0	X	54
$[(C_3H_7)_4C_5H]_2Ba$	2.94 (2)	154.2 (av)	X	55
$Cp^*{}_2Sm$	2.79 (1)	140.1	X	98,99
$Cp^*{}_2Eu$	2.79 (1)	140.3	X	99
$Cp^*{}_2Yb$	2.622 (6)	158 (4)	E	102
$Cp^*{}_2Yb$	2.665 (3)	145.4 (av)	X	102

[a] E = Gas electron diffraction; X = single-crystal X-ray diffraction.

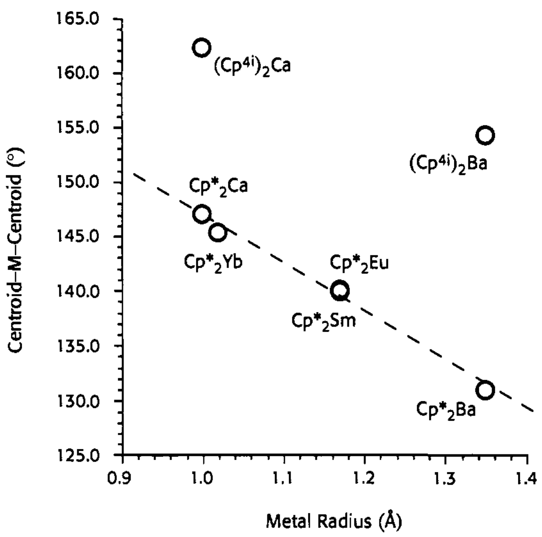


Figure 6. Bending in ionic solid-state base-free decamethylmetallocenes as a function of the metal radius.

the two compounds are [Xe]$4f^6$ and [Xe]$4f^7$, respectively, the f electrons are sufficiently well shielded that the metal ions could be considered analogous to the alkaline earths.[100]

The reports that $Cp^*{}_2Ca$,[101,102] $Cp^*{}_2Yb$,[101] $Cp^*{}_2Sr$,[103,104] and $Cp^*{}_2Ba$[103,104] are bent in the gas phase (GED evidence) confirmed that the bending of decamethylmetallocenes around large electropositive metal centers is a generally observed phenomenon (Table III). The vapor-phase evidence is clouded somewhat by the fact that the geometries determined were thermal average structures and thus could appear to be bent for statistical reasons. $Cp^*{}_2Ca$ and $Cp^*{}_2Ba$ are bent as well in the solid state, however, and a detailed comparison of the available data has found that the bending is not an effect of any readily identifiable crystal packing forces.[53] In the solid-state structures, the degree of bending is observed in the order ($Cp^*{}_2Ca$, $Cp^*{}_2Yb$) < ($Cp^*{}_2Sm$, $Cp^*{}_2Eu$) < ($Cp^*{}_2Ba$), which is also in the order of increasing radii and increasing polarizability (Figure 6). The linearity of the bending angle/metal radii relationship may be due to intramolecular methyl–methyl contacts in the decamethylmetallocenes, but bending is not confined to $Cp^*{}_2M$ complexes; the base-free metallocenes $(Cp^{4i})_2Ca$ and $(Cp^{4i})_2Ba$ are also bent in the solid state, in the order $(Cp^{4i})_2Ca$ < $(Cp^{4i})_2Ba$.[55]

The energy required to bend the metallocenes by 20° is estimated to be only 2–3.5 kJ/mol.[103,104] It is thus not surprising that calculations on Cp_2Sm (extended Hückel level),[105] Cp_2(Eu, Yb) (SW-X_α)[106] and Cp_2Ca (SCF Hartree–Fock)[104] did not identify any effects arising from d-orbital participation; these studies predicted linear or "quasilinear" structures for the metallocenes. Recent ab initio calculations by Schleyer and others, however, have identified bent minima for a variety of alkaline-earth (Ca, Sr, Ba) and lanthanide (Sm, Eu, Yb) species, including MH_2, MLi_2, $M(BeH)_2$, $M(BH_2)_2$, $M(CH_3)_2$, $M(NH_2)_2$, $M(OH)_2$, and MX_2.[94,107–110] A reinvestigation of the ionic metallocenes at the MP2 level has confirmed a linear structure for Cp_2Ca and a "quasilinear" geometry for Cp_2Sr; Cp_2Ba, however, was predicted to have a centroid–Ba–centroid angle of 147 °C, with a linearization energy of 1.5 kJ/mol.[111] The calculated linearization energies for certain compounds can be substantially higher, however; the energy released in bending $Ba(NH_2)_2$, for example, is ca. 28 kJ/mol.[108] It has been suggested that this energy is high enough that the inherent bending in some BaX_2 systems can be identified even when other neutral ligands are present, such as in (η^5-fluorenyl)$_2Ba(NH_3)_4$.[112]

Even as the evidence for a role for d electrons in group 2 structural chemistry is starting to appear compelling, these studies have emphasized the need for very high-level calculations with the alkaline-earth elements, and the sensitivity of the results to the basis sets used. Seijo et al. have suggested that as much attention be given to d orbitals in calculations with the alkaline earth as with the transition metals and that accordingly their valence electrons should be considered as the $(n-1)p\,ns(n-1)d$ set.[94]

V. Effects of Ligands on Physical Properties

A. Solubility

The solubility of a highly polar or ionic compound depends upon several thermodynamic quantities, involving a balance between lattice energies, enthalpies of solution, and entropic forces.[87,113] As lattice forces and nuclearity are lowered by the increasing bulk of ligands, solubility in nonpolar solvents becomes more energetically feasible. Although few quantitative values of solubility have been reported for organoalkaline-earth species, the available qualitative solubility data for metallocenes are summarized in Table IV. In general, for identical ligand sets, solubilities decrease in the order Ca > Sr > Ba. Again the metallocenes provide a striking illustration of the way in which solubilities vary with the size of the coordinated ligands; polymeric Cp_2Ca is soluble only in highly polar solvents such as DMSO and HMPA, for example, whereas mononuclear species such as $Cp^*{}_2Ca$ and $(Cp^{4i})_2Ca$ have at least some solubility in alkanes.

Solubility in hydrocarbons provides practical advantages in organoalkaline-earth chemistry. For those complexes synthesized using halide metathesis or in ethereal solvents, residual halides and ethers can often be removed by extraction of the complexes into hydrocarbons.[48]

Table IV. Solubilities and Melting Points of Base-Free Alkaline-Earth Metallocenes

complex	ethers	aromatics	alkanes	others	mp (°C)	ref(s)
$(Cp_2Ca)_n$	insoluble	insoluble	insoluble	DMSO, HMPA		34
$(MeCp)_2Ca$		insoluble	insoluble			155
$[C_5H_4(t\text{-}Bu)]_2Ca$	soluble	insoluble	insoluble		301–304	38
$[(C_3H_7)_3C_5H_2]_2Ca$	soluble	soluble	soluble			61
$\{1,3\text{-}(SiMe_3)_2C_5H_3\}_2Ca$	soluble	soluble				36
$Cp^*{}_2Ca$	soluble	soluble	moderate		207–210	47
$[(C_3H_7)_4C_5H]_2Ca$	soluble	soluble	soluble		196–200	55
$\{Cp_2Sr\}_n$	insoluble	insoluble	insoluble	DMSO, HMPA		34
$[C_5H_4(t\text{-}Bu)]_2Sr$	soluble	insoluble	insoluble		375–380	38
$[(C_3H_7)_3C_5H_2]_2Sr$	soluble	soluble				61
$[1,3\text{-}(SiMe_3)_2C_5H_3]_2Sr$	soluble	soluble				36
$Cp^*{}_2Sr$	soluble	soluble	slight		216–218	47
$[(C_3H_7)_4C_5H]_2Sr$	soluble	soluble	soluble		151–153	84
Cp_2Ba	insoluble	insoluble	insoluble	DMSO, HMPA		34,48
$[(C_5H_4)(t\text{-}Bu)]_2Ba$	insoluble	insoluble	insoluble		>300	38
$[(C_3H_7)_3C_5H_2]_2Ba$	soluble	soluble	soluble		92–94	61
$[1,3\text{-}(SiMe_3)_2C_5H_3)_2Ba$	soluble	soluble				36
$Cp^*{}_2Ba$	soluble	soluble	slight		265–268	47
$[(C_3H_7)_4C_5H]_2Ba$	soluble	soluble	soluble		149–150	55

An interpretation of the solubility behavior of base adducts of metallocenes is much more difficult than with that of the parent compounds. For adducts that are more soluble than the parent species, such as the pairs Cp_2Ca (THF insoluble)/$Cp_2Ca(THF)_2$ (THF soluble) or $[C_5H_4(t\text{-}Bu)]_2Ca$ (benzene insoluble)/$[C_5H_4(t\text{-}Bu)]_2Ca(THF)_2$ (slight benzene solubility), the increased solubility can be reasonably traced to a reduction in the nuclearity of the solvated complexes (section IV.A).

Many adducts of organoalkaline-earth complexes are substantially less soluble than the parent complex, however. Thus unlike the base-free decamethylmetallocenes, the 2,2′-bipyridine adducts of $Cp^*{}_2Ca$, $Cp^*{}_2Sr$, and $Cp^*{}_2Ba$ are insoluble in hydrocarbons,[47] and their phenazine, pyridazine, and pyrazine adducts are barely soluble enough to permit the acquisition of NMR data.[86] The coordinated bases may lower solubility by allowing the formation of oligomeric species or more stable lattices.[114] In one case, the differences in solid-state structures can be observed macroscopically: hexane-soluble $(Cp^{3i})_2Ba$ is a waxy, paraffin-like solid, whereas the less soluble $(Cp^{3i})_2Ba(THF)_2$ is a highly crystalline material.[61] The presence of the THF evidently makes possible the formation of a stable lattice that is not as easily disrupted by solvents.

Pending the accumulation of additional data from a larger variety of systems, the effect of ligands on the solubility of organoalkaline-earth complexes, especially those with coordinated bases, cannot yet be predicted with reliability.

B. Volatility

The volatility of a compound is a complex function of intermolecular forces, which are affected by molecular weight and geometry, and in solids, lattice structure.[115] The changes that ligands can exert on the intermolecular interactions in organoalkaline-earth complexes should in principle be reflected in their corresponding volatilities. Enthalpies of sublimation have not been reported for heavy organoalkaline-earth species, but relative volatilities in the form of "sublimation temperatures" are known for a number of compounds. In the absence of rate data, comparisons of sublimation temperature must be semiquantitative at best, especially considering the different pressures at which the temperatures have been reported (generally 10^{-2}–10^{-6} Torr). Nevertheless, if these limitations are understood, qualitative comparisons of volatility as a function of ligand sets on the metals are instructive.

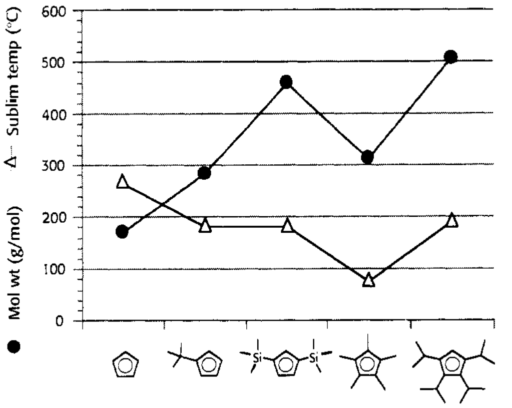


Figure 7. Sublimation temperatures of base-free calcocenes as a function of molecular weight and increasing steric bulk of the cyclopentadienyl ligands.

1. Metallocenes

Figure 7 presents the sublimation temperatures and corresponding molecular weights of a variety of calcocenes. The sublimation temperature drop on going from Cp_2Ca to $Cp^*{}_2Ca$, although molecular weights more than double during that interval. As noted in section IV.A, Cp_2Ca is an extensively oligomerized material (Table I), and $[C_5H_4(t\text{-}Bu)]_2Ca$ is at least partially associated in the solid state; $Cp^*{}_2Ca$ is monomeric. The drop in sublimation temperatures evidently reflects the progressive weakening of the intermolecular forces in the solids, which more than offsets any increase in molecular weight. Once mononuclearity is reached, however, molecular weight increases should become a dominant factor in volatility, and sublimation temperatures indeed rise on going from $Cp^*{}_2Ca$ (311 g/mol) to $(Cp^{4i})_2Ca$ (507 g/mol).

A similar situation exists for barium metallocenes (Figure 8), in that sublimation temperatures drop even as molecular weights are increasing. The decrease in sublimation temperatures again represents the reduction in intermolecular forces as the steric bulk of the ligands increases. Even $Cp^*{}_2Ba$ is not monomeric

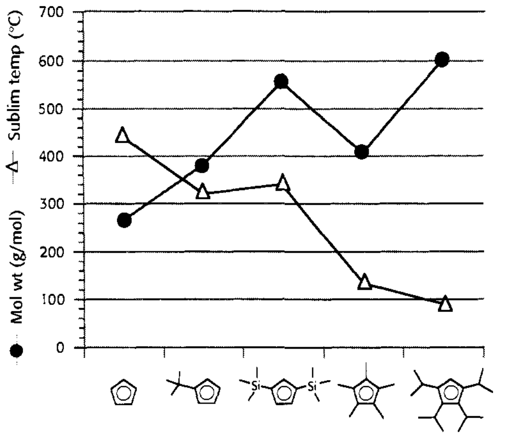


Figure 8. Sublimation temperatures of base-free barocenes as a function of molecular weight and increasing steric bulk of the cyclopentadienyl ligands.

(section IV.A), and mononuclearity is not reached until $(Cp^{4i})_2Ba$. Thus, unlike the calcium analogues, the sublimation temperature of $(Cp^{4i})_2Ba$ is the lowest of the known barocenes. It would prove interesting to prepare other metallocenes with even larger groups than the isopropyl groups of $(Cp^{4i})_2Ba$. With no further change in molecularity and with an increase in molecular weight, sublimation temperatures should rise. The currently available data suggests that the greatest impediment to producing metallocenes of high volatility is the inability of conventionally sized ligands to block intermolecular forces that lead to oligomerization.

2. Alkoxides

Despite the interest in alkoxides and β-diketonates as precursors to metal oxides via CVD routes, systematic studies that correlate their structure and volatility are still few. The solid-state structures of many alkoxides used for CVD work are not known, and the identity of the materials may vary greatly depending on their mode of preparation. The widely used β-diketonate derivative "$Ba(tmhd)_2$" (tmhd = $(CH_3)_3CCOCHCOC(CH_3)_3^-$), for example, has that formula only if prepared under rigorously anhydrous conditions;[116] in the presence of moisture, the pentanuclear cluster $Ba_5(thd)_9(H_2O)_3(OH)$ can form.[117] Such uncertainties make the identification of trends in volatilities difficult.

The sublimation temperatures (onset at 10^{-5} Torr) for a series of barium alkoxides and fluoroalkoxides are plotted with the corresponding formula weights in Figure 9.[118] The greater bulk (and presumably lower oligomerization) associated with the larger alkoxides appears to counterbalance the increases in molecular weight, so that the sublimation temperatures of $Ba(OCMe_3)_2$ and $Ba[OCH(CMe_3)_2]_2$, for example, differ by only 10 °C, despite the latter's nearly 50% greater weight. The two fluoroalkoxides are remarkably volatile for their masses; the perfluoro-*tert*-butoxy derivative sublimes at 10 °C higher than the nonfluorinated compound, although the molecular weight has risen from 284 to 607 g/mol. Increases in the volatility of complexes with fluorinated ligands have been observed in β-diketonate systems as well and presumably stem from the disruption of intermolecular interactions.[119] Interestingly, the barium tetrahydrofurfuroxide decomposes before subliming; the C_4H_8O ring probably binds to adjacent complexes, increasing the effective molecular weight and suppressing volatility.

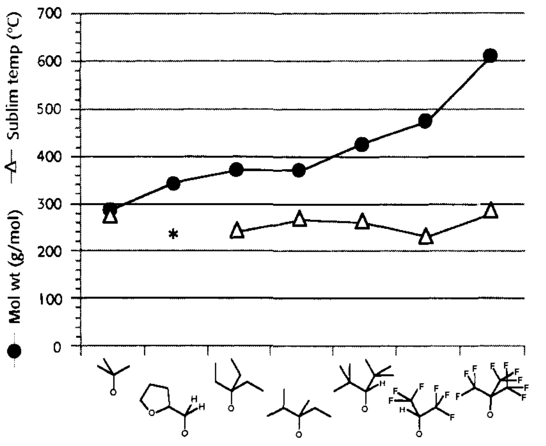


Figure 9. Sublimation temperatures of barium alkoxides and fluoroalkoxides as a function of molecular weight. The 2-tetrahydrofurfuroxy derivative (*) decomposes before subliming. Data is from ref 118.

Comparisons of the volatility of adducts of alkoxides with the relevant unsolvated species are difficult. For example, the volatility of $Ba(thd)_2$ is increased in the presence of excess free ligand, possibly by suppressing ligand loss in the gas phase through adduct formation.[12,117] No actual adducts of the form "$Ba(thd)_2\cdot(Hthd)_n$" have been isolated from these experiments, however. The presence of ammonia has also been found to increase the volatility of $Ba(thd)_2$ under CVD conditions, and the NH_3 adduct $[Ba(thd)_2\cdot 2NH_3]_2$ has been independently prepared and structurally characterized.[16] On sublimation the coordinated NH_3 is lost, however, and the volatility of the parent compound and the adduct are nearly the same. Loss of coordinated neutral ligands on sublimation often renders the stoichiometry of gaseous species uncertain, although mass spectroscopic techniques have been used to identify oligomeric alkoxides and β-diketonates in the gas phase.[117-119]

C. Melting Points

Melting points of solids should vary inversely with the strength of intermolecular interactions, which in turn are affected by ligand bulk. As they are highly dependent on the details of lattice packing, prediction of melting points, or even of melting point trends, is not straightforward. As Table IV suggests, however, the melting points of metallocenes with the bulkiest ligands (and the lowest nuclearity) are generally low, although considerable variations are observed in this property; melting points are obviously not monotonic functions of ligand bulk.

Especially interesting are recently reported complexes that are liquid or semisolid at room temperature. The bis(alkoxides) $Ba[O(CH_2CH_2O)_nCH_3]_2$ ($n = 2, 3$)[120] are liquid at room temperature and solution molecular weight data indicate that the materials are monomeric. The base-free $(Cp^{3i})_2Ca$ and $(Cp^{3i})_2Sr$ metallocenes are viscous oils that either require weeks to crystallize (Ca) or only thicken on long standing (Sr); stirring the former causes it to become oily again.[61] Evidently the relative size and shape of the metal atoms and ligands are such that the formation of well-ordered lattices is difficult.

Further studies to determine what combinations of ligand geometries and metal radii are conducive to forming these ionic liquids would be valuable.

VI. Manipulation of Lewis Acidity

A characteristic feature of organoalkaline-earth complexes is the formation of a variety of adducts with Lewis bases. So pervasive is this tendency that only compounds with ligands that completely envelop the metal center (e.g., the encapsulated metallocenes, section IV.A) are not known to form such species. In the formation of adducts, the coordination number of the metal center will increase, and given that Ba^{2+} can best accommodate such an increase, adduct formation might seem to favor the order $Ca^{2+} < Sr^{2+} < Ba^{2+}$. Yet the inherent acidity of the metal center also must be a determining factor in the stability of acid/base adducts, and acidity varies in the order $Ca^{2+} > Sr^{2+} > Ba^{2+}$. As these two trends lie in opposite directions, it is often the ligands that will determine the stability of adducts.

As we have seen, physical properties such as the volatility and solubility of compounds can change substantially depending on whether coordinated bases are present or not (section V). Two areas where the chemical behavior of adducts has received systematic attention has been the ease of desolvation of metallocenes and the formation of heterometallic alkaline-earth/transition metal complexes.

A. Stability of Acid/Base Adducts

The avoidance of decomposition through premature loss of coordinated ligands is of considerable concern in the design of precursors for CVD applications (section V.B).[10] The thermal instability of many solvated alkoxides and β-diketonates and the often unidentified residues left after their decomposition has hindered attempts to identify the important factors in alkoxide adduct stability.

The desolvation behavior of adducts of alkaline-earth metallocenes has been more amenable to rationalization on the basis of ligand size and metal acidity. The decamethylmetallocenes are normally isolated from their synthesis in THF or diethyl ether as the disolvates ($Cp^*_2Ae(ether)_2$), yet the ease of removal of the base from each differs substantially. Both THFs are removed from $Cp^*_2Ba(THF)_2$ by a single sublimation to yield the unsolvated Cp^*_2Ba, for example; yet THF cannot be completely removed from $Cp^*_2Ca(THF)_2$ by repeated sublimation or by refluxing in toluene.[53] Similarly, the solvated metallocenes $[C_5H_4(t\text{-}Bu)]_2Ae(THF)_n$ become base free at markedly different temperatures; the barium compound at 40 °C; the calcium complex at 180 °C.[38] Although the ability to accommodate high coordination numbers is greater for Ba^{2+} than for Ca^{2+}, the relative acidities of the metal centers apparently dominate the desolvation behavior in these cases; Ba^{2+} would be expected to bind to bases less strongly than Ca^{2+}, thus contributing to their ready loss.

This explanation is not adequate when the stability of adducts involving the same metal is compared. In contrast to the difficulty of desolvating $Cp^*_2Ca(THF)_2$, coordinated THF is readily removed from $Cp_2Ca(THF)_2$ by sublimation to yield the base-free metallocene.[52] What apparently differentiates the behavior of these compounds is that during the condensation to form polymeric Cp_2Ca, negatively charged Cp rings from adjacent molecules can coordinate to the metal center to replace of the departing THF ligands.[52] In contrast, the steric bulk of the Cp* rings prevents such oligomerization, and therefore cannot assist in the desolvation; on removal of the ethers, Cp^*_2Ca (prepared from $Cp^*_2Ca(OEt_2)_2$) remains monomeric in the solid state.

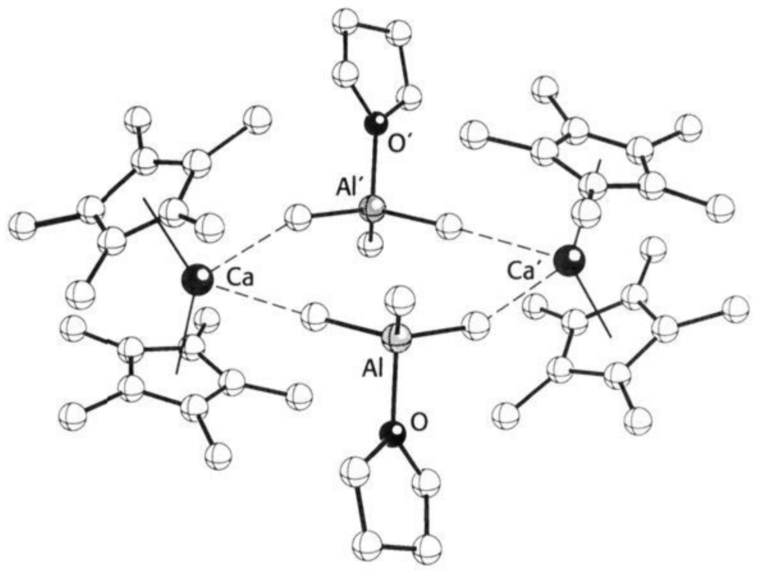


Figure 10. Structure of the methyl-bridged dimer, $[Cp^*_2Ca(\mu\text{-}CH_3)_2AlCH_3(THF)]_2$.

In view of the above, the ease with which $Cp^*_2Ba(THF)_2$ is rendererd base free by sublimation is probably a consequence of both the lowered Lewis acidity of Ba^{2+} vs Ca^{2+} and the larger radius of Ba^{2+}. This permits the approach of adjacent Cp* rings into the coordination sphere of the metal, allowing condensation to form oligomeric chains (Figure 3). Although the solid-state structures of $[C_5H_4(t\text{-}Bu)]_2(Ca,Ba)$ are not known, a similar explanation may apply to their desolvation behavior.[38]

The generation of oligomerized structures during thermal desolvation reactions is not confined to alkaline-earth species; examples are known with organolanthanide complexes (eq 15).[121-124] Similar results can be

$$n\mathrm{Cp'_3Ln(ether)}_m \xrightarrow{\Delta} [\mathrm{Cp'_3Ln}]_n + m\ \mathrm{ether}\uparrow \quad (15)$$

had with chemical desolvation, as in the reaction of $(MeC_5H_4)_3Ce(THF)$ with Me_3Al to yield the base-free tetrameric organocerium complex $[(MeC_5H_4)_3Ce]_4$ (eq 16).[125] Attempted removal of coordinated ethers can

$$4(\mathrm{MeC_5H_4})_3\mathrm{Ce(THF)} + 4\mathrm{Me_3Al} \rightarrow [(\mathrm{MeC_5H_4})_3\mathrm{Ce}]_4 + 4\mathrm{Me_3Al(THF)} \quad (16)$$

generate unusual results when oligomerization of the metallocene *cannot* occur, as with Cp^*_2Ca. Rather than desolvate, $Cp^*_2Ca(THF)_2$ reacts with Me_3Al to form the heterometallic species $[Cp^*_2Ca(\mu\text{-}CH_3)_2AlCH_3(THF)]_2$ (eq 17).[126] The crystal structure of the

$$2\mathrm{Cp^*_2Ca(THF)_2} + 2\mathrm{Me_3Al} \rightarrow [\mathrm{Cp^*_2Ca}(\mu\text{-}\mathrm{CH_3})_2\mathrm{AlCH_3(THF)}]_2 + \mathrm{THF}\uparrow \quad (17)$$

compound (Figure 10) reveals that one THF has been removed from the calcium and transferred to the aluminum. Unlike the base-free organocerium product, however, the calcium remains attached to the $Me_3Al(THF)$ unit through long $Ca\cdots CH_3$ interactions (2.95 (1), 3.00 (1) Å).

B. Formation of Heterometallic Complexes

Interest in heterometallic alkaline-earth materials and alkaline-earth polymetallic complexes dates from Gilman's work in the 1940s on "ate" compounds such as $Ae[ZnR_4]$.[17,127] Since then, many heterometallic alkoxides of the alkaline earths have been described[10] and increasing numbers have been structurally characterized.[128–133] Some of the recent interest in these system stems from attempts to use alkoxides as models of, or precursors to, heterometallic oxides such as the high T_c superconducting cuprates (e.g., $YBa_2Cu_3O_{7-x}$)[134–136] and methane oxidation catalysts [e.g., ABO_3 (A = Ca, Sr, Ba; B = Ti, Zr, Ce)].[137,138]

Rational syntheses of discrete polymetallic group 2–transition-metal complexes have been slow to develop.[129] Not surprisingly, facile ligand exchange or loss can make controlling the composition of these systems difficult. For example, the copper–barium alkoxide cluster $Ba_2Cu_2(OR)_4(acac)_4{\cdot}2HOR$ ($R = CH_2CH_2OCH_3$) (Ba:Cu = 1:1) is isolated from the reaction of $[Cu(acac)(OCH_2CH_2OCH_3)]_2$ with $Ba(OR)_2$ ($R = CH_2CH_2OCH_3$) (Ba:Cu = 1:2) (eq 18).[139] The partial exchange of ligands and resulting precipitation of the copper alkoxide causes the Ba:Cu ratio to change between the starting materials and products.

$$\begin{aligned}2[(acac)Cu(OR)_2]_2 + 2Ba(OR)_2 &\xrightarrow{ROH} 2Cu(OR)_2\downarrow + \\ 2(acac)Ba(OR) + [(acac)Cu(OR)]_2 &\rightarrow \\ &Ba_2Cu_2(OR)_4(acac)_4 \quad (18)\end{aligned}$$

Ligand exchange also complicates attempts to assemble organometallic Ae/transition-metal complexes. Using Cp′ complexes as substrates is especially problematic, as the relative hardness of the Ae^{2+} ions makes them efficient cyclopentadienylating agents. For example, in a manner much like alkali metal cyclopentadienides, Cp_2Ca will react with metal dihalides to form the corresponding Cp_2M derivatives (eq 19).[140]

$$\begin{gathered}Cp_2Ca + MCl_n \xrightarrow{THF} Cp_2MCl_{n-2} + CaCl_2\downarrow \\ M = Fe, Hg\ (n = 2);\ M = Ti\ (n = 4) \qquad (19)\end{gathered}$$

Similarly, Cp^*_2Ca reacts with various metal halides to generate decamethylmetallocenes and the calcium halide (e.g., eqs 20 and 21).[51]

$$\begin{aligned}Cp^*_2Ca + (dppe)NiCl_2 \xrightarrow{toluene} Cp^*_2Ni + CaCl_2\downarrow + \\ Ph_2PCH_2CH_2PPh_2 \quad (20)\end{aligned}$$

$$\begin{aligned}Cp^*_2Ca(THF)_2 + YbI_2(THF)_2 \xrightarrow{THF} Cp^*_2Yb(THF) + \\ CaI_2(THF)_4 \quad (21)\end{aligned}$$

Cp^*_2Ca can even displace Cp from other metallocenes; it will react with Cp_2Pb in toluene to precipitate insoluble Cp_2Ca and generate decamethylplumbocene (eq 22).[86]

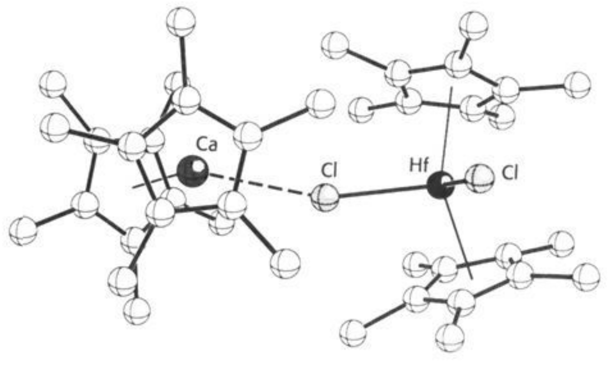


Figure 11. Structure of the chloride-bridged calcium/hafnium adduct, $Cp^*_2HfCl(\mu\text{-}Cl)CaCp^*_2$ (ref 51).

$$Cp^*_2Ca + Cp_2Pb \xrightarrow{toluene} Cp^*_2Pb + Cp_2Ca\downarrow \quad (22)$$

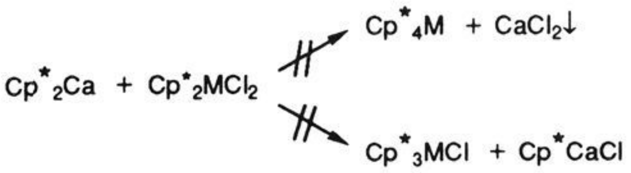
1. Controlling Disproportionation by Degenerate Ligand Exchange

A way to minimize the effects of ligand *exchange* (but not ligand *loss*) in the formation of heterometallic cyclopentadienyl complexes is by providing identical sets of ligands for both the alkaline-earth and transition-metal species, so that any exchange of ligands will be degenerate.

This approach has been used to form a variety of chloride-bridged alkaline-earth/transition-metal species, in which both metals contain Cp* ligands (eq 23):

$$\begin{gathered}Cp^*_2Ca + Cp^*_2MCl_n \xrightarrow{toluene} Cp^*_2Ca(\mu\text{-}Cl)(Cl)_{n-1}MCp^*_2 \\ M = Zr, Hf, Th\ (n = 2);\ M = Y\ (n = 1) \qquad (23)\end{gathered}$$

The structure of the hafnium derivative has been determined, and consists of two bent metallocene units with a single bridging Cl and a terminal Cl on hafnium (Figure 11).[51] The control of stoichiometry in this reaction depends on the steric inability of the transition-metal center to accommodate three or four η^5-Cp* ligands,[141] and therefore net Cp* transfer from Ca does not occur (e.g., eq 24).



$$Cp^*_2Ca + Cp^*_2MCl_2 \not\rightarrow Cp^*_4M + CaCl_2\downarrow; \quad Cp^*_2Ca + Cp^*_2MCl_2 \not\rightarrow Cp^*_3MCl + Cp^*CaCl \quad (24)$$

An interesting point of comparison with these reactions is provided by analogous organomagnesium reagents. Unlike Cp^*_2Ca, Cp^*_2Mg displays no interaction with $Cp^*_2ZrCl_2$,[142] and Cp_2Mg or Cp^*_2Mg is similarly unreactive toward Cp_2MoH_2 or Cp_2WH_2 (eq 25).[143] The lack of reaction with $Cp^*_2ZrCl_2$ may be sterically based, whereas the resistance of the Mg–Cp bond to protolysis by the transition-metal hydrides may be more important in eq 25. As evidence of this, Me_2Mg does react with Cp_2MoH_2 to yield a trimetallic product and methane (eq 26).[143]

$$2Cp_2Mg + Cp_2MH_2 \not\twoheadrightarrow (CpMg)_2MCp_2 + 2C_5H_6 \quad (25)$$

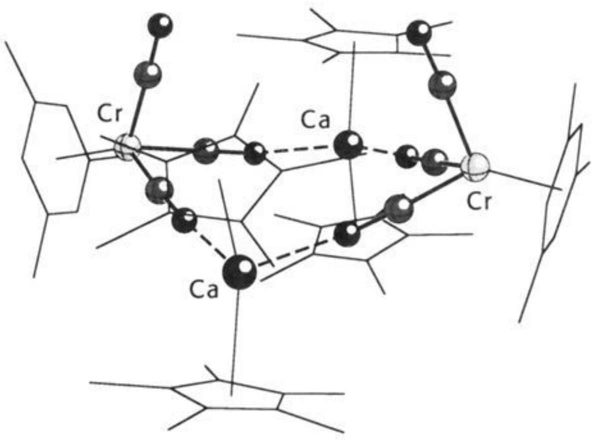


Figure 12. Structure of the isocarbonyl-linked calcium/chromium adduct, $[Cp^*_2Ca(\mu\text{-}OC)_2(OC)Cr(C_6H_3(CH_3)_3)]_2$. (Reprinted from ref 51. Copyright 1992 American Chemical Society.)

$$Me_2Mg + Cp_2MoH \xrightarrow[100\ °C]{C_6H_6,\ tmeda} Mg[Mo(H)Cp_2](tmeda) + 2CH_4\uparrow \quad (26)$$

2. Controlling Ligand Exchange by Hard/Soft Interactions

The hardness of the Ae^{2+} cations could be considered a limitation in the formation of their compounds, since only similarly hard bases will serve as robust ligands. In practice, however, the preference for hard ligands introduces a measure of discrimination in the reactions of organoalkaline-earth species and lifts the necessity of having identical ligand sets on each metal center when forming heterometallic compounds.

This approach has been used to construct heterometallic compounds from transition-metal carbonyl complexes. For example, Cp_2Mg will cyclopentadienylate various transition-metal halides to produce Cp_2M complexes and $MgCl_2$.[144] If elemental Mg reacts with a cyclopentadienyl metal carbonyl complex, however, transfer of Cp rings from the "softer" transition metal to the "harder" Mg does not occur, and stable heterometallic complexes can be isolated (eq 27).[145–150]

$$HgE_2 + Mg \xrightarrow{THF/ether} MgE_2(THF)_n + Hg\downarrow \xrightarrow{pyridine} MgE_2(py)_4$$
$$E = CpM(CO)_3\ (M = Cr, Mo, W);\ CpFe(CO)_2 \quad (27)$$

When Cp^*_2Ca is added to a toluene solution of $Cp^*_2Zr(CO)_2$, a black product is isolated with the formula $Cp^*_2Ca(OC)_2ZrCp^*_2$.[51] On the basis of the reduced carbonyl stretching frequencies, which indicate the presence of an isocarbonyl interaction (i.e., $Ca\cdots O{\equiv}C{-}Zr$), a structure similar to that observed for the chloride-bridged complexes (i.e., $Cp^*_2Ca(\mu\text{-}OC)(OC)ZrCp^*_2$) may be involved. In this case, not only is a direct transfer of Cp* ligands to Zr sterically prohibited (i.e., to form Cp^*_4Zr), but the carbonyl ligands would not be stabilized by calcium alone (eq 28).

$$Cp^*_2Ca + Cp^*_2Zr(CO)_2 \not\twoheadrightarrow [Ca(CO)_2]^{2+} + [Cp^*_4Zr]^{2-} \quad (28)$$

Mixing toluene solutions of Cp^*_2Ca and $(mes)Cr(CO)_3$ (mes = 2,4,6-$C_6H_3Me_3$) produces orange crystals of tetranuclear $[Cp^*_2Ca(\mu\text{-}OC)_2(OC)Cr(mes)]_2$ (Figure 12).[51] The isocarbonyl interactions between the Ca centers and the oxygen atoms of the carbonyls are evident in reduced IR stretching frequencies. Ligand exchange does not occur, again probably because the hard Ca^{2+} center would not support the "soft" arene and CO ligands.

For heterometallic complex formation to succeed, a sufficiently basic transition metal substrate and acidic Ae complex must both be present. No reaction is observed between Cp^*_2Ca and $Cp^*_2HfH_2$, for example, (cf. the inertness of Cp_2Mg and Cp_2MoH_2 noted above) and a mixture of Cp^*_2Ca and Cp^*_2HfHCl in toluene displays only slight shifts in the ^1H NMR resonances of the respective complexes; no bimetallic species has been isolated.[51] Similarly, no complex has been isolated between $Cp^*_2HfCl_2$ and the more weakly acidic Cp^*_2Ba.[151]

VII. Conclusions and Future Directions

Traditional approaches to organoalkaline-earth chemistry have been metal centered and have generally ignored the size, shape, or relative donor properties of coordinated ligands. The recent emphasis on the *isolation* and structural characterization of complexes, rather than simply on their generation and use in situ, has made the opportunities for ligand control of group 2 chemistry more obvious. The possibility that ligands of sufficient bulk might contribute to the kinetic stabilization of reaction products (section IV.B) suggests that mechanistic investigations of compound formation might be feasible; more than simple diffusion-controlled ion-pairing processes may be involved.

Despite the substantial progress that has been made in understanding the effects of ligands on the structures and reactions of organoalkaline-earth compounds, many large gaps in our knowledge remain. For example, how smooth or abrupt is the transition from oligomeric to monomeric structures as the ligand or metal size increases? How sensitive is the solubility or volatility of a compound to the amount of oligomerization in the solid? Are "degrees" of encapsulation of the metal centers in metallocenes possible, so that ligand cages could be constructed to permit coordination of bases of only specific geometries?

To date, the use of large groups has been the primary means for controlling metal nuclearity and blocking condensation reactions in organoalkaline-earth systems. An alternate route to generating complexes of controlled nuclearity is with the use of polydentate ligands, such as oligoethers or oligoamines, which can stabilize high coordination numbers yet still prevent polymerization. There is the possibility that polydentate ligands will affect reactivity in ways different from monodentate ligands with large steric bulk. Known examples have been primarily confined to alkoxide complexes, such as the monomeric bis(alkoxides) $Ba[(OC_2H_4)(OHC_2H_4)_2N]_2\cdot EtOH$ and $Ba[O(CH_2CH_2O)_nCH_3]_2$ noted in sections IV.A and V.C, respectively, and the large molecular aggregates $M_9(OCH_2CH_2OMe)_{18}(HOCH_2CH_2OMe)_2$ (M = Ca,[152] Cd[153]). Polydentate ligands coordinated to organometallic complexes are conceivable as well; this possibility remains to be explored.

The ability to solubilize and transport alkaline-earth ions controllably is central to their expanding use in material science and organic synthesis. Improved understanding of the interactions between metal and ligands in group 2 chemistry will extend our ability to extract useful chemistry from these highly reactive metals.

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