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Structural Lessons from Main-Group Metallocenes

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The metallocenes of the Group 2 and Group 14 elements display a higher degree of structural and chemical similarity than would be expected based on the differences in their electronic configurations alone. A comparison of their structures suggests that the interplanar ring angles in both are primarily determined by the size and shape of the cyclopentadienyl ligands; the two additional valence electrons in the Group 14 compounds exert little stereochemical influence. Although the two metallocene families display differences in reactivity, the presence or absence of metal valence electrons is not always a useful criterion for distinguishing between them. In Group 14 metallocenes, the electrons are not efficient donors to electrophiles, and sufficiently bulky cyclopentadienyl rings can interfere with the extent of redox reactions. Examination of main-group metallocene melting points reveals a trend based on the symmetry and flexibility of the cyclopentadienyl ring. In rigorously monomeric species, compounds with longer metal–carbon bonds have lower melting points.

Key Words: *metallocene, main group, alkaline earth, Group 14 elements, structures, redox reactions, melting points*

INTRODUCTION

In our search for ligand-centered methods to influence the chemistry of organoalkaline-earth complexes, we recently described the proper-

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ties of calcium, strontium, and barium metallocenes containing tetraisopropylcyclopentadienyl rings ($(i\text{-Pr})_4C_5H$ = Cp^{4i}).[1,2] These compounds are crystalline solids that display greater oxidative stability than less heavily substituted analogs (e.g., air stability of minutes rather than seconds), and despite the high Lewis acidity of the metals, they do not form adducts with Lewis bases. We attribute this behavior to an "encapsulation" of the metal center by the isopropyl substituents.

To determine whether this protective effect would exist in metallocenes with slightly less substituted cyclopentadienyl rings, we synthesized the triisopropylcyclopentadienyl derivatives $(Cp^{3i})_2Ae$ (Cp^{3i} = $(i\text{-Pr})_3C_5H_2$; Ae = Ca, Sr, Ba). Unexpectedly, these compounds display properties completely unlike those of the $(Cp^{4i})_2Ae$ compounds.[3,4] For example, the moderate air stability of the $(Cp^{4i})_2Ae$ compounds is lost in the $(Cp^{3i})_2Ae$ derivatives, and they now form adducts with ethers without difficulty. Furthermore, rather than being easily crystallized solids, the calcium compound is initially isolated as an oil that requires several weeks to solidify, and the strontium species remains an oil indefinitely at room temperature. Adding to these differences, freshly sublimed $(Cp^{3i})_2Ba$ is a low-melting wax that hardens to a powdery solid over several days. It is remarkable that the removal of a single isopropyl group from a cyclopentadienyl ring induces such large changes in the chemical reactivity and physical properties of the resulting metallocenes; the unique effects of metal encapsulation are almost lost.

Considering how striking the changes were in alkaline-earth metallocenes, we then began to investigate whether such differences could be induced in analogous compounds of other main-group metals. Stannocenes were chosen first for study, as the ionic radius of Sn^{2+} is the same as Sr^{2+} (1.18 Å)[5] and the literature on stannocenes is extensive.[6,7] Both $(Cp^{4i})_2Sn$ and $(Cp^{3i})_2Sn$ were readily prepared, and their properties differed as sharply from each other as did those of their Group 2 counterparts: e.g., $(Cp^{4i})_2Sn$ is a highly crystalline solid, air stable for weeks, whereas $(Cp^{3i})_2Sn$ is an air-sensitive oil that shows no signs of crystallizing even after a year.[8] In addition, the crystal structure of $(Cp^{4i})_2Sn$ revealed it to be isostructural with $(Cp^{4i})_2Ca$. The similar manner in which the structures and physical properties of these Group 2 and Group 14 metallocenes could be manipulated, even though they would be thought to have substantially

different metal–ligand covalency and bonding energetics, prompted us to investigate this resemblance further. Detailed below are the results of a representative literature survey on Group 2 and Group 14 metallocenes that stressed three points of comparison: (1) the relative energetics of the bending of the cyclopentadienyl ligands; (2) the degree of difference in their reactivity; and (3) the effects of ligand size and shape on main-group metallocene melting points.

1. BENT METALLOCENES—WITH AND WITHOUT LONE PAIRS

With only a few exceptions, all structurally characterized Group 14 metallocenes are "bent", that is, they have non-parallel rings. The source of bending has generally been ascribed to a "stereochemically active" lone pair of electrons on the metal.[9] There is no equally facile explanation for the fact that all crystallographically characterized monomeric metallocenes of the heavy Group 2 metals (and related compounds of the divalent lanthanides Sm, Eu, and Yb) are also bent.[10,11] The Cp^*_2Ae ($Cp^* = Me_5C_5$) derivatives are bent in the gas phase as well.[12,13] Unlike the situation with the Group 14 species, the noble gas electron configuration of the alkaline-earth metallocenes offers no obvious electronic rationale for the bending of the alkaline-earth metallocenes, and even simple steric considerations would lead to a prediction of parallel rings, a fact that has engendered considerable discussion in the literature (see Section 1.a).

Metal differences aside, Group 2 and Group 14 metallocenes with the same cyclopentadienyl rings display similar structures. At one extreme, if the metal center is large enough relative to the cyclopentadienyl ligands, the metallocenes will spontaneously oligomerize. Structures have been crystallographically established in which either chains (e.g., Cp_2Pb)[14] or a three-dimensional network (Cp_2Ca)[15] are found (Fig. 1). At the other extreme, sterically bulky cyclopentadienyl ligands will enforce monomeric structures that are similar for both Group 2 and Group 14 compounds. For example, both $[(Me_3Si)_3C_5H_2]_2M$ metallocenes (M = Mg,[16] Ge[17]) crystallize with two independent molecules in their unit cells, with the same arrangement of trimethylsilyl groups.

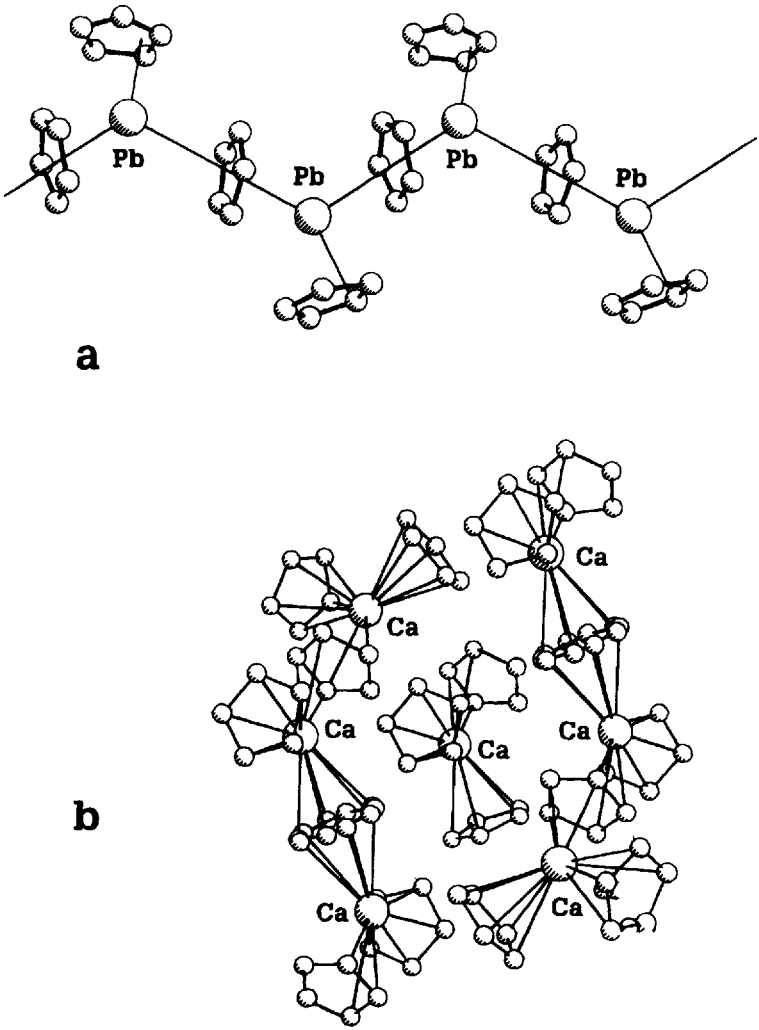

FIGURE 1 Schematics of the polymeric metallocenes Cp_2Pb (a) and Cp_2Ca (b).

The high degree of structural uniformity imposed by bulky cyclopentadienyl rings can be observed in a superposition of the $(Cp^{4i})_2Ca$/$(Cp^{4i})_2Sn$ pair (Fig. 2a), which reveals similar interplanar angles (152.2° [Sn], 158.9° [Ca]) and *i*-Pr group orientations.[8] Even with the less sterically encumbered couple Cp^*_2Sn/Cp^*_2Ca (Fig. 2b), the angles between the rings are nearly the same (144.1° [Sn], 145.3° [Ca]), although there are some differences in the ring staggering.

Several years ago we found a strongly linear correlation between the bending angles and metal radii in solid Cp^*_2M compounds of the Group 2 metals and lanthanides.[11] The relationship suggested that the bending angles were sterically controlled; i.e., complexes with larger metal centers had longer M–C distances, and could bend further before encountering significant repulsion between the methyl groups on the Cp* rings. Intriguingly, the decamethylmetallocenes of Si, Sn, and Pb also follow the same correlation (Fig. 3; we have substituted metal–ring normal distances to sidestep the issue of the

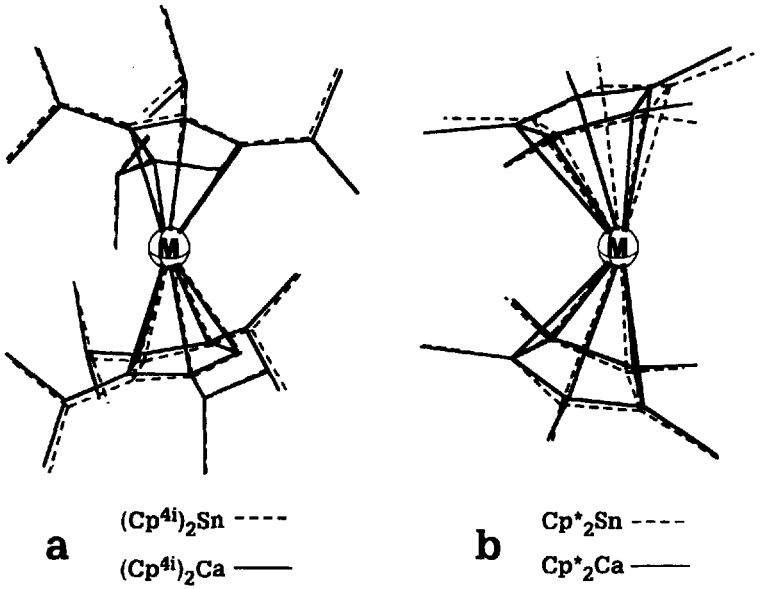

FIGURE 2 Superposition of the solid state structures of (a) $(Cp^{4i})_2Ca$ and $(Cp^{4i})_2Sn$ and (b) Cp^*_2Ca and Cp^*_2Sn.

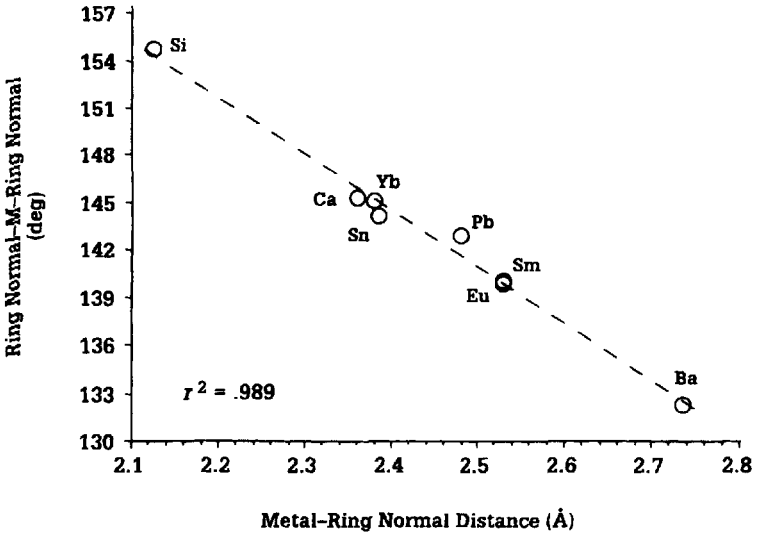

FIGURE 3 Bending in solid base-free main-group and lanthanide decamethylmetallocenes (Cp^*_2M) as a function of the metal to ring-normal distance. Both bent and linear conformers of Cp^*_2Si are found in the solid state; only the value for the bent form is placed on the graph.

proper value of the metal radii to be used). It appears that the steric restrictions on bending imposed on the Group 2 decamethylmetallocenes also apply to their Group 14 counterparts. It should be noted that the linear correlation only holds for the highly symmetrical $[Cp^*]^-$ ligand; with $[Cp^{3i}]^-$ and $[Cp^{4i}]^-$ rings, for example, differences in ring staggering obscure any simple distance/angle correlation.[4]

Despite their similarities, there is a characteristic geometric difference between the two families of metallocenes. The plane of the cyclopentadienyl rings is perpendicular to the metal–ring centroid vectors in the alkaline-earth metallocenes, whereas the rings are substantially tilted relative to these vectors in the bent Group 14 compounds. These structural distortions are illustrated schematically in Fig. 4. The interplanar angles in metallocenes a and b are identical, and the two are thus equally "bent". In metallocene a, however, the metal lies at the intersection of the C_5 axes of each cyclopentadienyl ring, an arrangement typical for Group 2 metallocenes. In metallocene

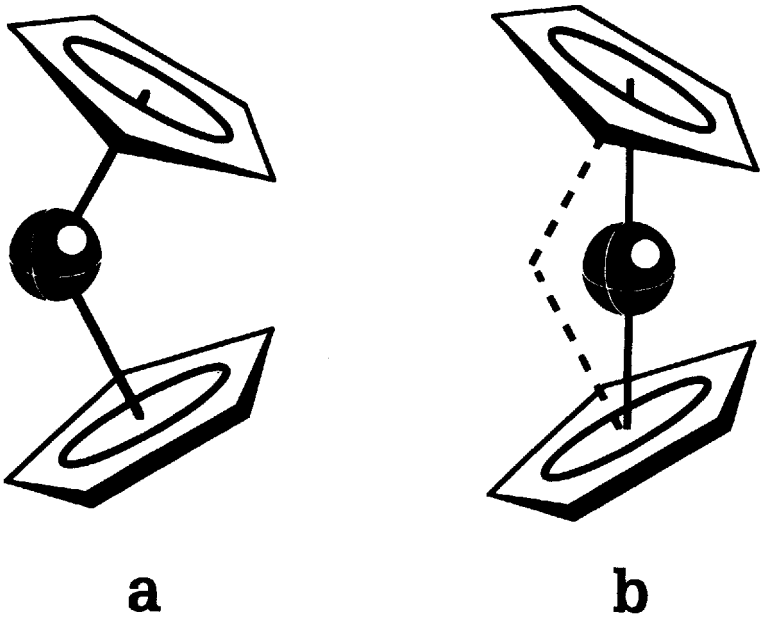

FIGURE 4 Structural characteristics of main-group metallocenes. The bending in (a) is typical for Group 2 metallocenes, whereas a distortion away from symmetrical η^5-ring coordination (b) occurs in Group 14 metallocenes.

b, the metal is displaced toward the "closed" side of the metallocene, a characteristic feature of Group 14 metallocenes.

The geometric differences between the Group 2 and Group 14 metallocenes become evident in a comparison of the ring centroid–M–ring centroid (R_C-M-R_C) and ring normal–M–ring normal (R_N-M-R_N) angles (Table I). With the Group 2 metals, the R_C-M-R_C and R_N-M-R_N angles are nearly always the same (differences $< 3.5°$). In Group 14 species, in contrast, except for the sterically encumbered $(Ph_5C_5)_2Sn$,[18] the R_N-M-R_N angles are substantially less than the R_C-M-R_C values, sometimes by more than 16°. The angular differences are responsible for large spreads in the M–C distances in Group 14 metallocenes; in Cp_2Ge, for example, a range of 2.347(7)–2.730(7) Å (Δ = 0.38 Å; 16%) is observed.[19]

These structural comparisons return us to the question of the relationship between bonding and bending. It is obvious that a metal-

TABLE I

Solid state structural data on unsolvated monomeric Group 14 and heavy Group 2 metallocenes.

Metallocene	Angles (deg) ring centroid–M–ring centroid	Angles (deg) ring normal–M–ring normal	Distances (Å) M–ring centroid	Distances (Å) M–C(ring) (range)	Ref.
Group 2					
Cp^*_2Ca	147.7	146.5	2.358, 2.333	2.597–2.653	11
	146.3	144.0	2.359, 2.354	2.612–2.681	
Cp^*_2Ba	130.9	133.3	2.700, 2.757	2.899–3.030	11
	131.0	131.2	2.699, 2.775	2.915–3.074	
$(Cp^{3i})_2Ca$	169.7	170.2	2.33 (av)	2.587–2.643	4
$(Cp^{4i})_2Ca$	162.3	158.9	2.349, 2.352	2.594–2.682	1
$(Cp^{4i})_2Ba$	154.3	153.2	2.679, 2.676	2.921–2.960	1
	154.1	153.7	2.681, 2.683		
Group 14					
Cp^*_2Si	180.0	180.0	2.114	2.409–2.442	33
	167.4	154.7	2.120, 2.122	2.323–2.541	
Cp_2Ge		129.6		2.347–2.730	19
$[(Me_3Si)_3Cp]_2Ge$	169.48	159.23	2.261, 2.256	2.458–2.661	17
	171.77	165.10	2.252, 2.250	2.490–2.633	
$(Bz_5Cp)_2Ge$	163.1	149	2.240, 2.288	2.429–2.723	78
Cp_2Sn	143.7	134	2.38, 2.45	2.56–2.85	79
	148	133	2.41, 2.41	2.58–2.75	
$[(i\text{-}Pr_2N)_2PC_5H_4]_2Sn$	148.6	133.4	2.38, 2.39	2.527–2.807	74
$(Ph_5C_5)SnCp$	151.1	136.1	2.391 (Cp)	2.541–2.792 (Cp)	80
			2.487 (Ph_5C_5)	2.63–2.92 (Ph_5C_5)	
Cp^*_2Sn	154.8	144.6	2.388, 2.399	2.585–2.77	81
	154.9	143.6	2.400, 2.399	2.57–2.776	
$[(PhCH_2)_5C_5]_2Sn$	155.9	147.2	2.439, 2.415	2.615–2.818	82
$[(Me_3Si)_3C_5H_2]_2Sn$	162	164	not given	not given	83
$(Cp^{4i})_2Sn$	165.0	152.2	2.423, 2.424	2.575–2.821	8
$(Ph_5C_5)_2Sn$	180	180	2.401, 2.401	2.686–2.705	18
Cp^*_2Pb	151	142.9	not given	2.69–2.90	79
$[(PhCH_2)_5C_5]_2Pb$	153.4	146.7	2.507, 2.500	2.680–2.871	82
				2.740–2.818	

centered pair of electrons does not cause the bending in the alkaline-earth metallocenes, and although there is no agreement about what does (see below), the difference in energy between the bent and linear geometries is thought to be small (< 10 kJ mol^{-1}). In spite of the two valence electrons, recent experimental and theoretical work on the bending energetics of Group 14 metallocenes, also summarized below, have indicated that they are remarkably similar to those of their alkaline-earth counterparts. The structural role of the extra valence electrons in the Group 14 metallocenes is thus not as straightforward as it might first appear.

1.a. Bending Energetics in Group 2 Metallocenes

Several arguments have been advanced as explanations for the bending of the cyclopentadienyl ligands in calcium, strontium, and barium metallocenes, including the operation of attractive van der Waals forces between the rings,[20] induced polarization of the metal center by the ligands (as has been proposed to occur with the bent gaseous dihalides[21]), and the involvement of *d* orbitals in the metal–ring bonding.[22]

Which if any of these possibilities might be the dominant contributor to the bending in Group 2 metallocenes has been difficult to establish. There is substantial agreement, however, that the energetic benefits associated with bending are small; for example, the stabilization achieved by bending the decamethylmetallocenes of Ca, Sr, and Ba in the gas phase by 20° away from a linear structure has been estimated to be only 2 to 3.5 kJ mol^{-1}.[13,23] Such small values may be the reason that attempts to reproduce the bent geometries observed in these compounds by molecular orbital calculations have had limited success. Calculations on Cp_2Ca (SCF-HF level)[23] predict a linear structure for the metallocene, and more recent calculations on Cp_2(Ca, Sr, Ba) at the MP2 level also predict a linear structure for Cp_2Ca and a "quasilinear" (i.e., linear, but with a nearly flat potential energy curve for bending) geometry for Cp_2Sr. A bent structure was anticipated for Cp_2Ba with a ring centroid–Ba–ring centroid angle of 147°; the energy required to straighten it (linearization energy) was only 1.5 kJ mol^{-1}, however.[22] The bent structure for Cp_2Ba was obtained only when a large basis set including *d*-functions on both *carbon* and the *metal* was used; the source of the energetic stabilization

gained on bending was ascribed to the polarizability of the Ba^{2+} ion and to slight d_π-orbital participation in the bonding.

The possibility that attractive van der Waals forces between the substituents on the ligands are a primary stabilizing force for the bent geometries is appealing, especially in view of recent molecular mechanics calculations by Bosnich and co-workers on the Cp^*_2M metallocenes of Group 2 and divalent lanthanide metals.[20] They find good agreement between the observed and calculated structures for the compounds, 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 is always small (< 9 kJ mol^{-1}), with attractive van der Waals forces accounting for at least 90% of the stabilization of the lower energy bent structures.[24]

In summary, work to date has consistently found that there are only minor energy differences between bent and linear geometries for Group 2 metallocenes. Considering that the Ae^{2+} ions cannot provide substantial orbital stabilization for either geometry, this is a conclusion that is not likely to change with more detailed theoretical work. It seems appropriate to view the alkaline-earth metallocenes as electronically "floppy" systems, with very shallow potential energy curves relating the orientation of the cyclopentadienyl rings about the metal centers.

1.b. The Origin of Bending in Group 14 Metallocenes

Explanations for the bent geometries observed in almost all Group 14 metallocenes have focused on the two valence electrons possessed by the divalent metals in these compounds. A valence bond (VB) description of the structures was first proposed by Wilkinson in 1959,[25] which has given way to molecular orbital approaches in the more recent research literature. The VB explanation (or a related one employing VSEPR terminology) is still found in textbooks and review articles, however, and it has contributed to a belief that there is a strong energetic preference for bending in these metallocenes. We thus briefly describe the theory and some of its consequences here.

In the VB approach, three regions of electron density exist around the metal center in a Group 14 metallocene; two of these will be associated with the metal–cyclopentadienyl bonds, while the third will represent the non-bonding valence electron density of the metal.

The rings will bend to minimize electron–electron repulsion between bonding electron pairs and the non-bonding, "stereochemically active" valence electrons. The VB/VSEPR approach achieves this electron distribution in Cp_2Sn by considering the metals to be approximately sp^2 hybridized with a lone pair of electrons occupying one hybrid orbital.[25] More generally, the angle between the rings in the metallocenes is diagnostic of the amount of hybridization of the metal center; most of the known metallocenes lie near the center of the continuum of different hybridization possibilities depicted in Fig. 5. As the angle between the rings increases, greater amounts of *p*-orbital character are found in the lone pair orbital, until the limiting case of a linear geometry is reached in which the rings are bound to the metal by *sp* hybrid orbitals and the lone pair is in pure *p* orbitals.

The valence bond approach makes several incorrect predictions about the spectroscopic and chemical properties of Group 14 metallocenes. For example, if the hybridization scheme were followed consistently, a linear metallocene should have the non-bonding electrons in degenerate p_x and p_y orbitals, and thus have a triplet ground state. Contrary to this expectation, however, the linear metallocene $(Ph_3C_5)_2Sn$ is diamagnetic,[18] with a singlet ground state.[26]

A greater difficulty with the VB approach is its implication that the hybridized orbital containing the lone pair of electrons is highly directed, and that consequently these compounds should function as Lewis bases. These expectations are not borne out by experimental

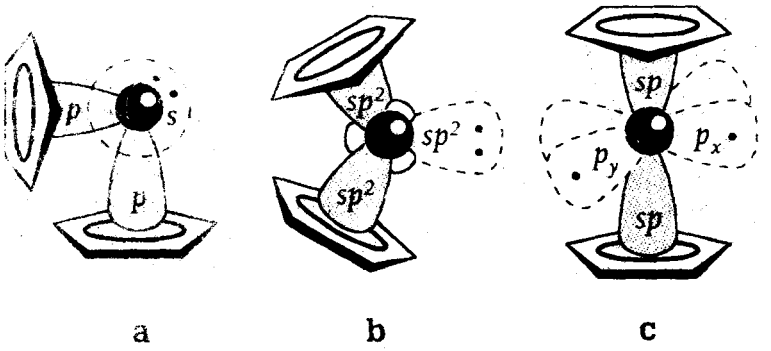

FIGURE 5 Valence bond interpretation of the bending in group 14 metallocenes, in which the hybridization of the metal center varies with the bending angle.

studies. For example, Mössbauer spectra on a variety of stannocenes have consistently supported the confinement of the metal valence electrons to orbitals of high *s* character, which are necessarily nondirectional.[28] Furthermore, as will be examined in Section 2.b, electrophiles generally attack the electron density of the *cyclopentadienyl rings*, rather than the metal centers.

The core idea of the VB analysis of the Group 14 metallocenes, i.e., that the two valence electrons exist in an orbital with sp^x hybrid character, is maintained in the molecular orbital description of the bonding.[29] In an MO analysis of a linear metallocene geometry, the two valence electrons are assigned primarily to an ns^2 orbital of a_1 symmetry that is antibonding with respect to the cyclopentadienyl ligands. On bending of the rings, mixing of the (lone pair) a_1 orbital with a higher-energy unfilled metal-centered n*p* orbital is allowed. The resulting sp^x hybrid MO is stabilized owing to a reduction in metal–ring electron–electron repulsion (Fig. 6). Although this analysis is fundamentally sound, based as it is on group symmetry arguments, its *quantitative* features (i.e., ordering of energy levels, extent of mixing) are not as easily established. It is also worth noting that although both MO and VB approaches correlate stabilization of the bent geometry with some degree of sp^x hybridization of the valence electrons, they reach *opposite* conclusions about the geometries when hybridization does not occur; in the VB case, the metallocene is the most bent (ideally 90° with the use of pure *p* orbitals), whereas in the MO picture, the metallocene is linear.

1.c. Bending Energetics in Group 14 Metallocenes

Both the VB/VSEPR and MO approaches have been used to predict that bent structures for Group 14 metallocenes are electronically preferred to linear geometries. What has still remained unresolved is the amount of stabilization gained by bending in these structures. The original VB/VSEPR approach, with its highly directed orbitals, lead to the expectation of a substantial difference in the energetics of the bent and linear forms. Within the last decade, however, both experimental and theoretical lines of investigation have converged on small values for the energy associated with bending of the cyclopentadienyl rings.

It is interesting to note that the experimentally determined energy associated with bending the cyclopentadienyl ligands in Group 14

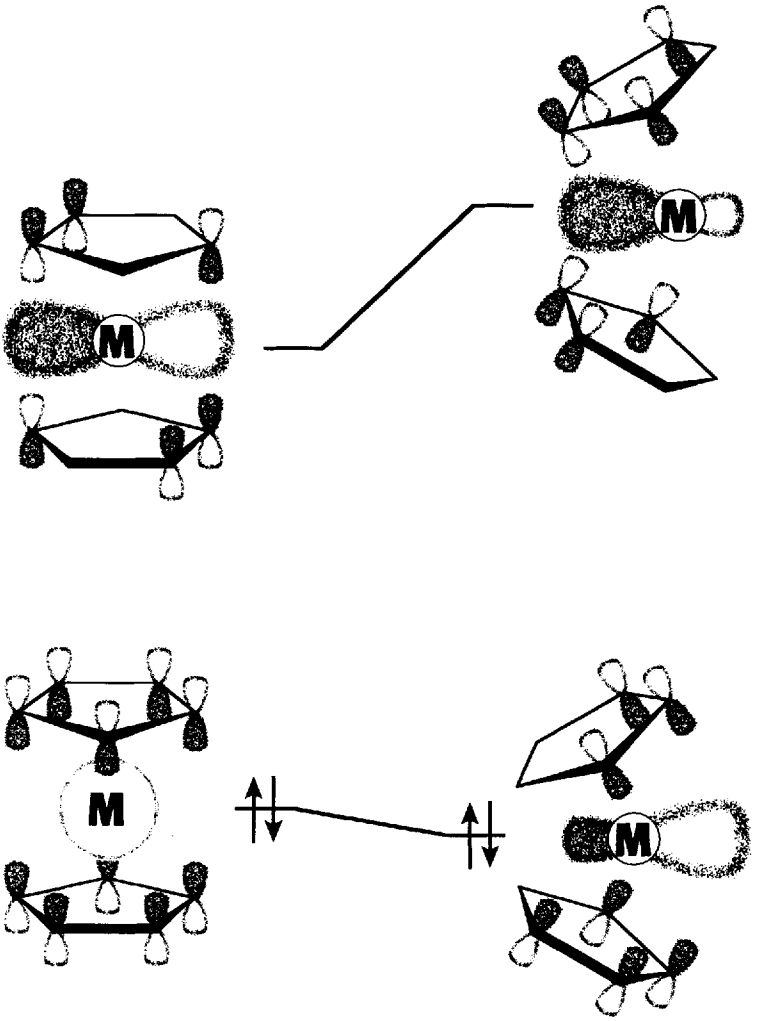

FIGURE 6 Molecular orbital interpretation of the bending in Group 14 metallocenes. The bending angle can be correlated with the mixing of the n*s* orbital containing the valence electrons with an unfilled metal-centered n*p* orbital to create a new non-bonding hybrid sp^x orbital.

metallocenes has always appeared to be low. For example, gas electron diffraction measurements have usually found these compounds to have large amplitude ring–metal–ring bending vibrations, which has been interpreted as reflecting a shallow energy potential for changing the orientation of the cyclopentadienyl rings. The large amplitude vibrations lead to wide error limits on the interplanar ring angles (e.g., the angle in $(MeC_5H_4)_2Ge$ is 146(7)°,[30] while that in Cp_2Pb is 135(15)°[31]).[32,13] Sometimes the bending amplitudes are such that it is not possible to state unequivocally that the equilibrium structure *is* bent (e.g., in Cp^*_2Si).[33]

Consistent with this finding is that linear Group 14 metallocenes can be readily prepared by using bulky cyclopentadienyl rings.[7] If the energetic preference for bent metallocene geometries were truly strong, one might expect difficulties in forming such compounds. In fact, the rigorously linear stannocene $(Ph_5C_5)_2Sn$ is easily synthesized,[18] and is the most thermally stable of the known stannocenes (mp > 370°C), indicating that any preference for a bent structure can be overridden with sufficient inter-ring van der Waals repulsions. In addition, both linear (R_N-M-R_N = 180°) and bent (R_N-M-R_N = 154.7°) forms of Cp^*_2Si are found co-crystallized in the solid state,[7] attesting to the energetic similarity of the two conformers.

Calculations on Group 14 metallocenes have led to different conclusions about the relative stabilities of the possible ground state geometries; they have not even consistently predicted that a sandwich structure (whether linear or bent) is the lowest energy conformation for these systems. For example, depending on the starting geometrical parameters and how rigorous the search of the energy hypersurface is, calculations using MNDO have identified a linear $(\eta^5\text{-Cp})_2Si$ sandwich,[29] the bis(*mono*hapto) structure $(\eta^1\text{-Cp})_2Si$,[34] and the half-sandwich $(\eta^1\text{-Cp})Si(\eta^5\text{-Cp})$ structure as the energy minima.[33] At the HF-SCF (STO-3G*) level, the bent $(\eta^5\text{-Cp})_2Si$ sandwich form is calculated to be the global energy minimum and is lower in energy than the linear form by 48.5 kJ mol^{-1}. At the highest level of theory used to date (DZP-MP2), the bent $(\eta^5\text{-Cp})_2Si$ structure is also more stable than the linear, but by only 11.7 kJ mol^{-1}.[35] It was noted that higher level calculations increasingly favor the linear structures, because greater *d* orbital participation in the bonding is then possible.[36]

The computational situation for the heavier metallocenes has been equally convoluted. Extended-Hückel calculations on Cp_2Ge predict a bent structure that is dramatically more stable than the linear geometry (by 110 kJ mol^{-1}), but these results reverse with *ab initio* calculations, which slightly favor the linear geometry (by ca. 3 kJ mol^{-1}), although the potential energy surface for bending the Cp rings is shallow.[30] Extended-Hückel calculations on Cp_2Sn also heavily favor a bent structure (by ca. 100 kJ mol^{-1}), but an MNDO calculation on Cp_2Sn found the bent structure to be only 6.3 kJ mol^{-1} lower in energy than the linear geometry,[38] although the classical *mono*hapto form (η^1-Cp)$_2$Sn was the global minimum. A recent AM1 calculation placed the difference between the bent and linear sandwiches at 4.0 kJ mol^{-1}; the bent form was now the global minimum.[39] As far as we are aware, plumbocene has been studied by MNDO methods only; as with tin, a bent sandwich was more stable than the linear form (by 2.6 kJ mol^{-1}), but the *mono*hapto configuration (η^1-Cp)$_2$Pb was far more stable than either (over 140 kJ mol^{-1}).[40]

Although not a Group 14 metallocene, the isolated Group 13 anion $[Cp_2Tl]^-$ is isoelectronic with them, and was recently found to have a ring centroid–Tl–ring centroid angle of 156.7° in the structure of [CpMg · PMDETA][Cp_2Tl].[41] *Ab initio* calculations at the DZ-MP4 level found the difference between the linear and bent molecular geometries to be only 3.4 kJ mol^{-1} in favor of the latter. The Group 15 metallocene cations are also isoelectronic with the Group 14 metallocenes, but the structures are harder to compare, as none has a (η^5-Cp)$_2$M sandwich type structure.[42]

Table II summarizes the history of calculations on the bent/linear structure question in Group 14 metallocenes. Evidently, levels of theory above MNDO are necessary to predict that bent sandwich structures with approximately *pentahapto* rings are the global minima. It is also apparent that the trend with higher order theory has been to find small differences ($\lesssim$10 kJ mol^{-1}) between the energies of the bent and linear structures, in line with the previously described experimental results. As a class, therefore, *the Group 14 metallocenes are as structurally flexible as the heavy Group 2 metallocenes.*

1.d. A Pink Slip for the Lone Pair?

Our original interest in studying stannocenes containing "encapsulating" cyclopentadienyl rings was as a method to evaluate the impor-

TABLE II

Molecular orbital calculations on unsubstituted Group 13 and 14 metallocenes.

Element	Year	Method	Bent/Linear Preference (kJ mol^{21})	Global Minimum	Comments	Ref.
Si	1982	MNDO	Linear (35)	Linear sandwich		29
	1985	MNDO		(η^1-Cp)$_2$Si		34
	1989	MNDO	Bent (99)	(η^5-Cp)(η^1-Cp)Si		33
	1989	STO-3G	Bent (20.1)	Bent sandwich	Si–C distances in Cp_2^*Si were used	33
	1989	STO-3G	Bent (74.5)	Bent sandwich	optimized geometry	33
	1989	STO-3G*	Bent (48.5)	Bent sandwich	optimized geometry	33
		DZP-MP2	Bent (11.7)	Bent sandwich	optimized geometry	35
Ge	1983	Extended Hückel	Bent (110)			30
	1983	Ab initio	Linear (3)	Linear sandwich	shallow potential well for ring orientations	30
Sn	1980	Extended Hückel	Bent (100)			81
	1982	SW-Xα			used experimental geometry	29
	1984	MNDO	Bent (6.3)	(η^1-Cp)$_2$Sn	minimum is 154 kJ mol^{21} below sandwiches	38
	1991	AM1	Bent (4.0)	Bent sandwich		39
Pb	1985	MNDO	Bent (2.6)	(η^1-Cp)$_2$Pb	minimum is 140 kJ mol^{21} below sandwiches	40
Tl	1993	DZP-MP4	Bent (3.4)	Bent sandwich	$[Cp_2Tl]^2$ is isoelectronic with Cp_2Sn	41

tance of the steric bulk and shape of the Cp′ ligand to the chemistry of alkaline-earth metallocenes. Not only did we find that small changes in cyclopentadienyl ring substitution could evoke large changes in the properties of both Group 2 and Group 14 metallocenes, but we also discovered that the resemblances between the metallocenes extended to structures (comparable bending angles) and bending energetics (small for both types).

These similarities limit the structural importance of what might at first have seemed the principle difference between the two main-group metallocene families—the presence of the metal valence electrons in the Group 14 compounds. If the bent geometries of the alkaline-earth metallocenes can be stabilized without help from lone pairs, and if the bent geometries of silicocenes, germanocenes, stannocenes and plumbocenes have roughly the same stabilization as the Group 2 compounds, then the possibility must be considered that *the lone pair of electrons in Group 14 metallocenes is stereochemically inactive.*

We were initially uncomfortable with this conclusion, as it seemed counterintuitive to have inactive lone pairs present in compounds that are nevertheless distorted from a symmetrical geometry. Stereochemically inactive lone pairs are known in other main-group compounds, of course (e.g., $SnCl_6^{2-}$ and $TeBr_6^{2-}$), but their classification as "inactive" is justified because of the regular octahedral geometries of these compounds.[45] The bent structures of Group 14 metallocenes, however, seem to *require* stereochemical activity from the lone pair.

Although commonly encountered, the last statement is an unwarranted application of VSEPR rules. From the premise that a stereochemically active lone pair of electrons on a metal center will occupy a distinct coordination site, leading to a bent or distorted geometry, the only proper inference is that if a structure is *not* distorted, a stereochemically active lone pair of electrons is *not* present. It is not correct to deduce that a distorted structure presupposes an active lone pair, as there may be other reasons for the bending. The existence of bent Group 2 and divalent lanthanide metallocenes demonstrates that mechanisms are available for bending largely ionic metallocenes that do not require the operation of metal-centered valence electrons.

Once the similar energetics of the cyclopentadienyl ligand orientations are considered, it becomes reasonable to assume that the same forces involved in the bending of Group 2 metallocenes (e.g., van der Waals attractions) play a dominant role in the bending in Group 14 metallocenes. The importance of van der Waals attractions could be investigated by the use of molecular mechanics (MM), but we are unaware of any systematic application of MM to the Group 14 metallocenes. It is interesting to note, however, that it has been used to explain why $(Ph_5C_5)_2Sn$ is *not* bent,[46] and Jutzi and co-workers studied the conformations of the bent germanocene

$[(Me_3Si)_3C_5H_2]_2Ge$ by MM,[17] and found that attractive interactions between the trimethylsilyl groups on the two rings "may be responsible, in part, for the tilting and bending."

The applicability of bonding schemes such as VB/VSEPR, the distinction between stereochemically "active" and "inactive" electron pairs, and even the relevance of molecular orbital analysis depends upon the existence of substantial covalent interaction between the metal valence electrons and the electrons of the Cp rings. What experimental evidence is available, however, suggests that the metal–ring bonding in Group 14 metallocenes is less covalent than has often been assumed. Photoelectron spectroscopic studies (He(I) and He(II)) of pentamethylgermanocene and -stannocene have found that the metal valence electrons are tightly bound relative to the Cp* ring electrons (up to 1.9 eV), demonstrating that their interaction with the ring electrons is slight; the metal–ring bonding was accordingly described as "almost ionic".[47] Other photoelectron studies have reached similar conclusions about the energy of the metal valence electrons compared to the cyclopentadienyl ring electrons in Cp_2Sn and Cp_2Pb.[29,48]

It is true that a consistent difference exists in the metal–ring orientations between the two metallocene families, namely, a shift of the metal away from the rigorous η^5-ring coordination in the alkaline-earth compounds to a slipped or "tilted" ring binding characteristic of the Group 14 metallocenes (see Introduction). Such shifts could be viewed as incipient distortions toward the classical $(\eta^1\text{-}Cp')_2M$ structures that would be adopted if highly covalent interactions were present. The less electropositive metal centers in the Group 14 metallocenes will allow somewhat greater metal–ring covalency than in the alkaline-earth metallocenes, even if in general the metal–ligand bonding in both types of compounds is fairly similar.

2. THE STRUCTURE/REACTIVITY RELATIONSHIP

Although the extra valence electrons present in Group 14 metallocenes do not dramatically alter the bonding energetics when compared to their Group 2 counterparts, they could still generate differences in reactivity. Specifically, these would involve: (1) the possibility of metal-centered redox reactions; (2) the potential for

the metal to behave as a Lewis base; and (3) decreased reactivity toward nucleophiles. We thus sought to compare Group 2/Group 14 metallocene reactivity to assess the relative importance of these differences. In addition, we were interested in whether the comparison would indicate that the reactivities were consistent with a stereochemically inactive lone pair of electrons in the Group 14 metallocenes.

2.a. Oxidative and Thermal Stability

Nearly all Group 14 metallocenes are air- and moisture-sensitive compounds, although substantial stability (weeks to months) can be had when bulky enough cyclopentadienyl rings are used (e.g., in $(Bz_5C_5)_2Sn$, $(Ph_5C_5)_2Sn$, and $(Cp^{4i})_2Sn$). This stability has been attributed to shielding of the metal center (and therefore of the valence electrons), but large alkyl and aryl groups also protect the electron-rich carbon atoms of the cyclopentadienyl ring, where the HOMO's are concentrated.[9] Air sensitivity increases appreciably once even a moderate amount of access to the metal (or rings) is available; the $(Ph_4C_5H)_2Sn$ and $(Cp^{3i})_2Sn$ derivatives, for example, decompose within minutes in air.

Consistent with the lower electronegativity of their metal centers, Group 2 metallocenes are much more air sensitive than their Group 14 analogues even when they have the same cyclopentadienyl rings. Thus Cp^*_2Ca decomposes with deflagration on contact with air, whereas Cp^*_2Sn decomposes in air, but is not pyrophoric. The most air-stable calcocene reported to date is $(Cp^{4i})_2Ca$, in which the metal center and the external faces of the rings are well shielded from external reagents. Microcrystalline $(Cp^{4i})_2Ca$ is stable in air for brief (<5 min) exposures; large single crystals exhibit only moderate decomposition after 30 min.[1] The corresponding stannocene $(Cp^{4i})_2Sn$, however, is stable for weeks in air.[8] It is worth noting that, as with the analogous stannocene, higher air sensitivity returns on removal of a single *i*-Pr group from each ring (e.g., in $(Cp^{3i})_2Ca$). Some measure of the difference the fourth *i*-Pr group makes on limiting access to the metal center can be gathered from the space-filling drawings of $(Cp^{4i})_2Ba$ and $(Cp^{3i})_2Ba(THF)_2$ in Fig. 7. A truly air-stable Group 2 metallocene has yet to be prepared; unlike the decaphenyl germanocenes, stannocenes and plumbocenes, decaphenyl alkaline-earth metallocenes have resisted attempts at synthesis.[49]

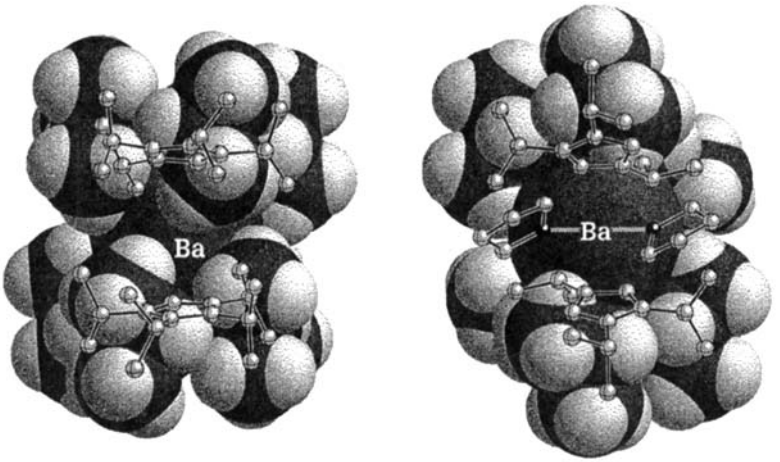

FIGURE 7 Space-filling drawings of $(Cp^{4i})_2Ba$ (left) and $(Cp^{3i})_2Ba(THF)_2$ (right). Ball-and-stick renderings of the molecules have been superimposed on the compounds. The space-filling portions of the THF molecules of $(Cp^{3i})_2Ba(THF)_2$ have been removed to illustrate the greater access to the metal center offered by the $[Cp^{3i}]^-$ ring.

Obviously, only the cyclopentadienyl rings can be oxidized in Group 2 compounds, and direct reaction of Group 2 metallocenes with oxygen generally gives intractable mixtures of organic byproducts. A notable recent exception is the isolation of the triplet biradical species $[\{1,3\text{-}(Me_3Si)_2C_5H_3\}Ca\{\mu\text{-}OC_5H_2\text{-}2,4\text{-}(Me_3Si)_2\}]_2$ (Fig. 8), produced in the controlled oxidation of $[1,3\text{-}(Me_3Si)_2C_5H_3]_2Ca$.[50]

Considering that the metal center can be involved in the oxidation of Group 14 metallocenes, it is somewhat surprising that no well-characterized example of an aerial oxidation product has been reported. Based on Mössbauer data, a solid produced from the air oxidation of stannocene was described as the polymeric compound $[Cp_2SnO]_n$, although this assignment remains tentative.[51] The lack of a well-characterized product from the reaction with oxygen is perhaps an indication that, like the Group 2 species, oxidation in Group 14 metallocenes occurs primarily at the cyclopentadienyl rings.

There are, however, well-characterized oxidative addition products of Group 14 metallocenes with other reagents [e.g., Eqs. (1) and (2)].[52,53]

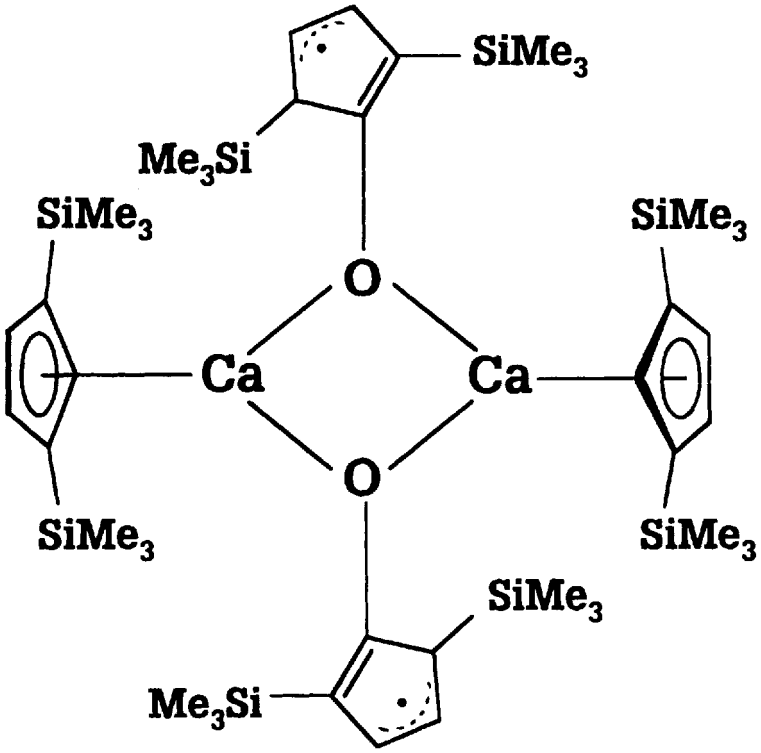

FIGURE 8 Oxidation product of $[1,3\text{-}(Me_3Si)_2C_5H_3]_2Ca$.

$$Cp_2Sn\ 1\ CH_3I \xrightarrow[C_6H_6]{h\nu} (\eta^1\text{-}Cp)_2Sn(CH_3)I \qquad (1)$$

$$Cp^*_2Si\ 1\ HCl \xrightarrow{THF} (\eta^1\text{-}Cp^*)_2Si(H)Cl \qquad (2)$$

The conditions for the success of such addition reactions cannot be easily generalized, as they are particularly sensitive to the size of the cyclopentadienyl rings and to the nature of the addition reagent. Thus, in contrast to the reaction in Eq. (1), replacing CH_3I with $PhCH_2X$ (X 5 Cl, Br) or Ph_3CBr causes ring displacement, rather than oxidation of the metal [e.g., Eq. (3)].[52]

$$Cp_2Sn + PhCH_2Br \xrightarrow{C_6H_6} CpSnBr\downarrow + PhCH_2\text{–}C_5H_5 \quad (3)$$

The use of even a modestly bulky ligand like $[Cp^*]^-$ can prevent a reaction from occurring at all [Eq. (4)], perhaps another indication that the valence electrons do not extend in a highly directed manner from the metal center.

$$Cp^*_2Sn + CH_3I \xrightarrow{\not\quad} NR \quad (4)$$

The outcomes of reactions with protic reagents are also difficult to predict. Although they may add oxidatively to the metal center, as in Eq. (2), such reagents may simply attack and displace the cyclopentadienyl rings [e.g., Eqs. (5) and (6)].[19,53]

$$Cp^*_2Si + HOR \xrightarrow{0°C} NR \xrightarrow{heat} 2\ Cp^*H + \text{decomp. prod.} \quad (5)$$

(R = Me, Et, Pr)

$$2\ Cp_2Ge + 4\ t\text{-BuOH} \xrightarrow{C_6H_6} [Ge(O\text{-}t\text{-}Bu)_2]_2 + 2\ CpH \quad (6)$$

These displacement reactions are typical of the behavior of Group 2 metallocenes with protic reagents [e.g., Eq. (7)].[2]

$$(Cp^{4i})_2Ca + 2\ HOC_6H_2\text{-}t\text{-}Bu_2\text{-}2,6\text{-}Me\text{-}4 \xrightarrow{C_6H_6} Ca(OC_6H_2\text{-}t\text{-}Bu_2\text{-}2,6\text{-}Me\text{-}4)_2 + 2\ HCp^{4i} \quad (7)$$

The limited importance of oxidative addition reactions in Group 14 metallocenes is a strong indication that the metal centers do not function as expected for "carbene-like" analogues (L_2M:).

An interesting point of difference between the thermal stability of Group 2/14 metallocenes recently appeared with the report of the synthesis of octaphenylbarocene, $(Ph_4C_5H)_2Ba$.[49] Unlike all other barocenes (or Group 2 metallocenes) reported to date, octaphenylbarocene has only marginal thermal stability at room temperature, slowly decomposing in the solid state over several weeks' time. At 120°C, complete decomposition occurs within hours. In contrast, the octaphenylmetallocenes of Ge and Sn are thermally stable in the solid state, although they do not maintain this stability in THF solution, decomposing within minutes at room temperature.[54]

2.b. Reactions with Electrophiles

As noted in Section 1.b, the valence bond explanation for the bent Group 14 metallocenes leads to the expectation that the lone pair of electrons in these compounds should be an attractive target for electrophiles. This idea was used to rationalize the reaction of Cp_2Sn with BF_3 [Eq. (8)], which was originally believed to form a simple Lewis acid/base adduct.[55]

$$Cp_2Sn: + BF_3 \xrightarrow{THF} Cp_2Sn: \rightarrow BF_3 \qquad (8)$$

More than a dozen years after this reaction was first reported, the stannocene/BF_3 "adduct" was recharacterized as the polymeric species $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+THF\}_n$ (Fig. 9), formed by attack of the BF_3 on a cyclopentadienyl ring [Eq. (9)].[56]

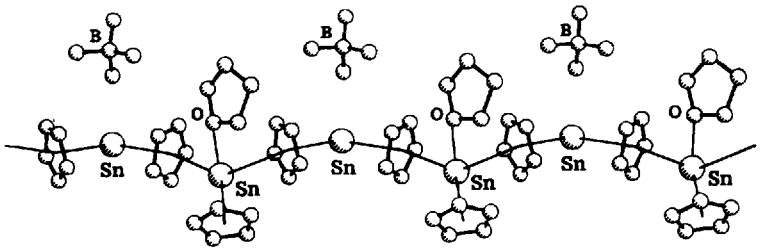

FIGURE 9 Portion of the polymeric species $\{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+THF\}_n$, formed by attack of BF_3 on a cyclopentadienyl ring of Cp_2Sn.

$$2\ Cp_2Sn + 2\ BF_3 \xrightarrow{THF}$$

$$CpBF_2 + \{[BF_4]^-(\mu\text{-}\eta^5\text{-}C_5H_5)_2Sn[\mu\text{-}\eta^5\text{-}C_5H_5Sn]^+THF\}_n \quad (9)$$

With a bulkier cyclopentadienyl ring, a cationic monomeric mono-(ring) species can be isolated [Eq. (10)].[57]

$$2((t\text{-}Bu)C_5H_4)_2Sn + 2\ BF_3 \xrightarrow{THF}$$

$$[((t\text{-}Bu)C_5H_4)_2Sn][BF_4] + \text{“}[(t\text{-}Bu)C_5H_4]_3SnBF_2\text{”} \quad (10)$$

The stability of this and other mono(ring) cations [e.g., Eqs. (11) and (12)][58] has been rationalized with the use of the Wade–Mingos counting rules[59,60]; the compounds are regarded as 8-electron cluster species. The extent to which this analogy is valid suggests that the metal valence electrons are extensively involved in bonding, and consequently that metal–ring covalency is more important here than with the bis(ring) metallocenes.

$$Cp^*_2Sn + CF_3SO_3H \xrightarrow{CH_2Cl_2} [Cp^*Sn][CF_3SO_3] + Cp^*H \quad (11)$$

$$Cp^*_2Sn + AlCl_3 \xrightarrow{C_6H_6} [Cp^*Sn][AlCl_4] + Cp^*AlCl_2 \quad (12)$$

The reluctance of the metal centers to serve as the targets of electrophilic attack by electrophiles is underscored by reactions of Cp_2Sn and Cp_2Pb with the phosphenium cation $[(i\text{-}Pr_2N)_2P]^+$.[61] Rather than reacting to form compounds with $Sn{=}P^+$ or $Pb{=}P^+$ interactions, the phosphenium cation inserts into the *C–H bond* of the cyclopentadienyl ring [Eq. (13)].

$$Cp_2Pb + [(i\text{-}Pr_2N)_2P]^+AlCl_4^- \xrightarrow{CH_2Cl_2}$$

$$\{[(i\text{-}Pr_2N)_2PH\text{–}C_5H_4](H_5C_5)Pb\}[AlCl_4] \quad (13)$$

Both these insertion reactions and all the ring displacement reactions reported to date demonstrate that the *cyclopentadienyl ligands*, and not the metal centers, are the favored sites of electrophilic attack by Lewis acids on Group 14 metallocenes.

Although the reactions of electrophiles with the heavy Group 2 metallocenes have not been systematically investigated, similar results should be expected, since it is the cyclopentadienyl rings that will be the sites of reactivity.

2.c. Reactions with Nucleophiles

The Group 2 metallocenes form adducts with a variety of Lewis bases, ranging from *O*- and *N*-donors such as ethers and amines, to weaker donors such as phosphines and isocyanates.[62,63] So rapacious are the metal centers for electron density that adducts can be formed with extremely weak donors, such as alkynes (as in $Cp^*_2Ca \cdot (Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3)$[63]) or transition metal carbonyls (using isocarbonyl interactions, as in $[Cp^*_2Ca(\mu\text{-}OC)_2(OC)Cr(C_6H_3Me_3)]_2$[64]). Some adducts of Cp^*_2Ca, such as $Cp^*_2Ca(THF)_n$, are so robust that the base cannot be completely removed chemically or by sublimation.[11,65] Total encapsulation of the metal center, as in the $(Cp^{4i})_2Ae$ metallocenes, is required to block adduct formation with oxygen and nitrogen donors.

In contrast, Group 14 metallocenes do not form stable adducts with neutral *O*- and *N*-donors, and are isolated base-free after their synthesis in ethers.[66,67] With stronger nucleophiles, the Group 14 metal center does become the site of attack. For example, Jutzi has reported that the reaction of Cp^*_2Sn with $Li[CH(SiMe_3)_2]$ or LiMe in ether results in total ring replacement [Eq. (14)].[68]

$$Cp^*_2Sn + 2\ LiR \xrightarrow{\text{ether}} R_2Sn + 2\ LiCp^* \downarrow \qquad (14)$$

When only one equivalent of LiR is used, R_2Sn (and not Cp*SnR) is still the final product; half the stannocene is isolated unchanged after the reaction [Eq. (15)].[69]

$$Cp^*_2Sn + LiR \xrightarrow{\text{ether}} {}^1/_2\ R_2Sn + {}^1/_2\ Cp^*_2Sn + LiCp^* \downarrow \qquad (15)$$

Using evidence from trapping experiments, Jutzi proposed that these nucleophilic reactions proceed through the formation of an addition product $(\eta^1\text{-}C_5Me_5)_2Sn(Me)Li$. This organostannate cannot be isolated, however, and rapidly decomposes to give the observed products.

The range of reactions with nucleophiles has recently been expanded by the reports of addition reactions of Cp_2Mg and CpNa to Cp'_2Sn ($Cp' = C_5H_5$, fluorenyl) and Cp_2Pb.[70,71] In these reactions [e.g., Eq. (16)], the metal centers in the Group 14 complexes again function as electron acceptors, rather than as donors.

$$2\ Cp_2Sn + Cp_2Mg \xrightarrow{THF} [Mg(THF)_6][Sn(\eta^3\text{-}C_5H_5)_3]_2 \qquad (16)$$

The organostannates isolated from in these reactions lend plausibility to the existence of an analogous intermediate formed in Eqs. (14) and (15).

Nucleophilic alkyl lithiums react with Group 2 metallocenes the same as they do with the Group 14 compounds. For example, the reaction of LiR with Cp^*_2Ba and Cp^*_2Ca initially leads to addition products, formally related to the stannate intermediate in Eqs. (14) and (15). With Cp^*_2Ba, the organobarates are the final products of the reaction [Eq. (17)].

$$Cp^*_2Ba + LiR \xrightarrow{THF} Li^+[Cp^*_2BaR(THF)_n]^- \qquad (17)$$

$$(R = N(SiMe_3)_2,\ CH(SiMe_3)_2)$$

In contrast, the same reactions with Cp^*_2Ca leave a mono(ring) product following elimination of LiCp* [Eq. (18)].[72]

$$Cp^*_2Ca + LiR \xrightarrow{THF} \text{“}Li^+[Cp^*_2CaR(THF)_n]^-\text{”} \longrightarrow Cp^*CaR(THF)_3 + LiCp^* \downarrow \qquad (18)$$

$$(R = N(SiMe_3)_2,\ CH(SiMe_3)_2)$$

It is notable that unlike the analogous reactions involving tin and

barium, a calcium mono(ring) product is the final product; it may owe its stability to the tight binding of the THF ligands.

2.d. Metallocene Reactivity—Different, Only the Same

The resemblances between the structures of Group 2 and Group 14 metallocenes were traced in Section 1 to the relative inactivity of the metal valence electrons in the latter group, a consequence of the bonding in the two classes of compounds being more similar than might otherwise be supposed. To some extent these parallelisms extend to types of reactivity; the differences between Group 2 and Group 14 metallocenes that were expected because of the valence electrons in the latter (see beginning of Section 2) are not as distinct as anticipated. For example, neither Group 2 nor Group 14 metallocenes behave as Lewis bases, the former because no metal-centered electrons are present, the latter because the valence electrons are evidently not readily accessible to potential Lewis acids. Metal-centered oxidative addition reactions are obviously not possible with the Group 2 metallocenes, and although they are known in Group 14 compounds, sufficiently bulky cyclopentadienyl rings can interfere with their occurrence and extent. Steric shielding modulates the air and moisture sensitivity of both families of metallocenes, although a greater range of reactivity (from decomposition in minutes to indefinite air stability) is displayed by the Group 14 complexes.

Even though reactions with nucleophiles have not been investigated with both classes of metallocenes to the same extent, the Group 14 compounds display a bifunctional mode of reactivity that is not found in their alkaline-earth counterparts. Sufficiently strong nucleophiles (e.g., alkyl lithiums) will react with both families of metallocenes, forming either mono(ring) species or anionic "-ate" complexes. With weaker nucleophiles (e.g., ethers, amines), the Group 2 compounds form stable adducts, whereas the extra electron density at the metal on Group 14 metallocenes serves to repel attack by such nucleophiles. This type of discrimination is not an option for Group 2 metallocenes with their noble gas electron configurations.

3. MELTING POINTS WITH A DIFFERENCE

The transformation of the crystalline $(Cp^{4i})_2M$ (M = Ca, Sr, Ba) metallocenes into the oily or waxy $(Cp^{3i})_2M$ derivatives, and the

parallel behavior of the analogous stannocenes, suggests how dependent physical properties can be on a comparatively small change in a bulky cyclopentadienyl ligand. On the other end of the spectrum, however, the data have long been available to demonstrate that a small change in *un*substituted cyclopentadienyl rings will strongly influence the melting points of main-group metallocenes (Table III). Except for polymeric or presumably polymeric compounds, metallocenes with (mono)alkylated or (mono)silylated cyclopentadienyl rings are low melting solids or liquids at room temperature. Although the extra substituent evidently interferes with the efficient packing of metallocenes into lattices, it appears that its *size* is not critically important: a methyl, *t*-butyl, or trimethylsilyl group, for example, will each lower the melting point of Cp_2Sn from 150°C to below room temperature.[73,74] The melting points of magnesocenes are similarly affected; they drop from 176°C in the parent compound to room temperature or below on monosubstitution of the rings.

It is also notable that the high melting points of the parent metallocenes are restored in the octa- and decasubstituted metallocenes. The melting points of the $(R_4C_5H)_2M$ and $(R_5C_5)_2M$ (M = Mg, Ca, Sr, Ba, Ge, Sn, and Pb) are close to or greater than 100°C, despite the type of substituent (e.g., methyl, phenyl, benzyl). Packing into well-ordered lattices evidently becomes easier with completely or almost completely substituted rings; the higher molecular weight of these complexes compared to the monosubstituted metallocenes likely contributes to the increase in melting points as well.

It is interesting that similar trends are observed with transition metal metallocenes. Ferrocene melts at 173°C, for example, but the monosubstituted $(MeC_5H_4)_2Fe$, $[(t\text{-}Bu)C_5H_4]_2Fe$ and $[(Me_3Si)C_5H_4]_2Fe$ derivatives melt at 38°, 29–30°, and 16°, respectively; octamethyl and decamethylferrocene melt at 153–5°C and 291–5°C, respectively.[75] Evidently the effect of the size and shape of the cyclopentadienyl rings on crystal packing rather than the nature of the metal–ligand bonding is the critical determinant of metallocene melting points.

In this light, it is possible to trace the differences between the crystalline $(Cp^{4i})_2Ae$ metallocenes and their oily/waxy $(Cp^{3i})_2Ae$ counterparts to the conformational flexibility of the respective cyclopentadienyl rings. In both the HCp^{4i} hydrocarbon[76] and in all the

TABLE III

Melting point data for main group metallocenes.

Metallocene	mp (°C)	Ref.
Cp_2Mg	176	84
$(MeC_5H_4)_2Mg$	29–30	84
$[(t\text{-}Bu)C_5H_4]_2Mg$	<25	85
$[(Me_3Si)C_5H_4]_2Mg$	<25	84
$[(Me_3Si)_2C_5H_3]_2Mg$	80–83	84
$[(Me_3Si)_3C_5H_2]_2Mg$	303–4	16
$(Cp^{3i})_2Mg$	92–100	4
$(Cp^{4i})_2Mg$	229–31	2
Cp_2^*Mg	289–292	86
Cp_2Ca	>265	15
$[(t\text{-}Bu)C_5H_4]_2Ca$	301–304	85
$[(Me_3Si)_2C_5H_3]_2Ca$	189	87
$(Cp^{3i})_2Ca$	40–45	3
$(Cp^{4i})_2Ca$	196–200	1
Cp_2^*Ca	207–210	62
Cp_2Sr	>360	88
$[(t\text{-}Bu)C_5H_4]_2Sr$	375–380	85
$[(Me_3Si)_2C_5H_3]_2Sr$	150	87
$(Cp^{3i})_2Sr$	<25	3
$(Cp^{4i})_2Sr$	151–153	2
Cp_2^*Sr	216–218	62
Cp_2Ba	>420	88
$[(t\text{-}Bu)C_5H_4]_2Ba$	320	85
$[(Me_3Si)_2C_5H_3]_2Ba$	222	87
$(Cp^{3i})_2Ba$	92–94	3
$(Cp^{4i})_2Ba$	149–150	1
Cp_2^*Ba	265–268	62
Cp_2Ge	78	19
$[(Me_3Si)C_5H_4]_2Ge$	<25	17
$[(t\text{-}Bu)_2C_5H_3]_2Ge$	85	89
$[(Me_3Si)_2C_5H_3]_2Ge$	72	17
$[(Me_3Si)_3C_5H_2]_2Ge$	98	17
$(Ph_4C_5H)_2Ge$	200	54
Cp_2^*Ge	90–94	81
$(Ph_5Cp)_2Ge$	>370	80
$(Bz_5Cp)_2Ge$	105	78
$[((t\text{-}Bu)Ph)Ph_4Cp]_2Ge$	ca. 295	54

TABLE III—*continued*

Melting point data for main group metallocenes.

Metallocene	mp (°C)	Ref.
Cp_2Sn	105	90
$(MeC_5H_4)_2Sn$	<25	90
$[(t\text{-}Bu)C_5H_4]_2Sn$	<25	57
$[(Me_3Si)C_5H_4]_2Sn$	<25	57
$[(i\text{-}Pr_2N)_2PC_5H_4]_2Sn$	162–164	74
$[(t\text{-}Bu)_2C_5H_3]_2Sn$	<25	89
$[(Me_3Si)_2C_5H_3]_2Sn$	solid	83
$[(Me_3Si)_3C_5H_2]_2Sn$	solid	83
$(Cp^{3i})_2Sn$	ca. 18	8
$(Cp^{4i})_2Sn$	162–163	8
$(Ph_4C_5H)_2Sn$	200	54
Cp^*_2Sn	100–121	81
$(Ph_5C_5)_2Sn$	>370	80
$(Bz_5C_5)_2Sn$	95	82
$[((t\text{-}Bu)Ph)Ph_4C_5H]_2Sn$	340	54
$(Ph_5C_5)SnCp$	150	91
Cp_2Pb	140	92
$(MeC_5H_4)_2Pb$	(low melting solid, readily supercools)	92
$[(t\text{-}Bu)_2C_5H_3]_2Pb$	10	93
$(Ph_4C_5H)_2Pb$	211–213	54
Cp^*_2Pb	100–105	79
$(Ph_5C_5)_2Pb$	ca. 370	91
$(Bz_5C_5)_2Pb$	110	82
$[((t\text{-}Bu)Ph)Ph_4Cp]_2Pb$	360	54

known metallocenes based on it, the isopropyl groups adopt a nearly perpendicular arrangement relative to the ring plane (Fig. 10a).

This restriction is relaxed in $(Cp^{3i})_2Ca$ (Fig. 10b), where the orientation of the isopropyl groups ranges from 12.3° to 82.8° relative to the ring plane. The extra degree of freedom increases the difficulty of finding an optimum arrangement for packing into a crystalline lattice, hence the existence of a persistent (weeks) supercooled phase. In $(Cp^{3i})_2Sn$, the slightly longer distances between the cyclopentadienyl rings reduce any restrictive inter-ring *i*Pr · · · *i*Pr interactions even further, leaving the complex permanently supercooled (i.e., liquid) at room temperature.

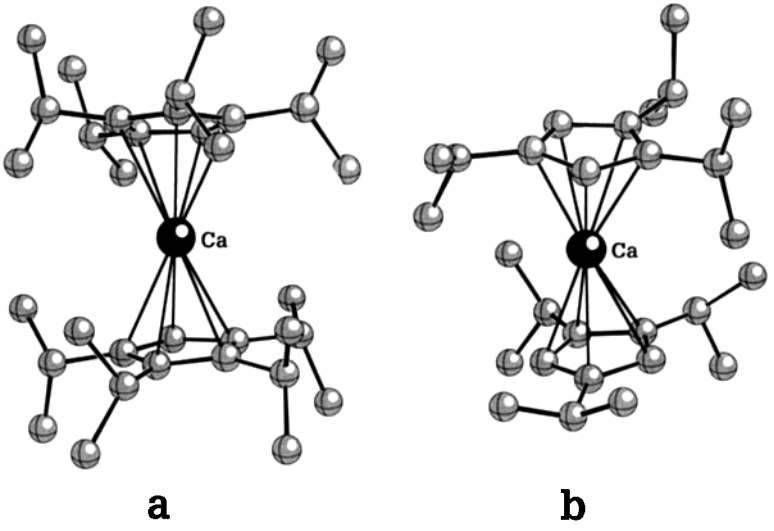

FIGURE 10 (a) Ball-and-stick drawing of solid $(Cp^{4i})_2Ca$, illustrating the roughly perpendicular arrangement of the isopropyl groups relative to the C_5 ring plane; (b) ball-and-stick drawing of solid $(Cp^{3i})_2Ca$, in which the isopropyl groups adopt a greater range of orientations.

The behavior of the main-group metallocenes illustrates how even minor changes in ligand structure can dramatically affect melting behavior. The interest in obtaining compounds with low melting point ranges for organometallic chemical vapor deposition[77] suggests that greater attention should be given to the design of conformationally flexible ligands as an effective strategy for pursuing this goal.

3.a. Metal Trends

Despite what might be suggested from the above discussion, the metal type *can* play an important role in determining the melting point, but this is only clearly observed in special cases. The polymeric metallocenes mentioned in Section 1 (Cp_2Pb, Cp_2Ca) and other species thought to be oligomeric (e.g., Cp_2Sr, Cp_2Ba) have higher melting points than do their monomeric counterparts of similar or higher molecular weight (e.g., Cp_2Pb (337 g mol^{-1}, mp 140°C) vs Cp^*_2Pb (478 g mol^{-1}, mp 100–105°C)).

Only a few types of cyclopentadienyl rings are bulky enough to ensure that monomeric metallocenes are formed across a wide range of metal radii. One case in which this happens involves metallocenes constructed with the $[Cp^{4i}]^-$ligand.[1] As Fig. 11 makes plain, there is a marked decrease in the melting points of the metallocenes with an increase in the metal–carbon distances. The correlation apparently stems from the greater freedom of rotation provided by longer metal–carbon distances, which allows for the generation of a less symmetrical packing environment.

4. CONCLUSIONS

Although the relationship might not have seemed obvious at the beginning, the heavy Group 2 and Group 14 metallocenes share considerable structural and chemical similarities. This is largely a consequence of the confinement of the metal valence electrons of

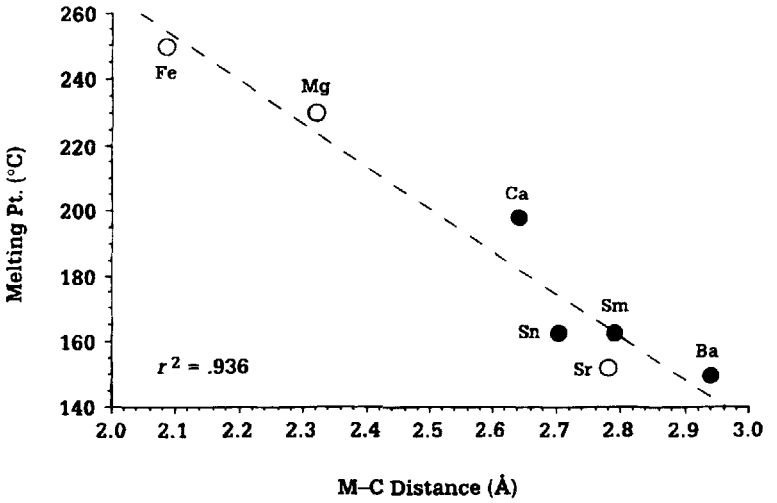

FIGURE 11 Melting points of $(Cp^{4i})_2M$ metallocenes as a function of metal–carbon distances. The filled circles represent experimentally determined M–C distances; the open circles are predicted distances. The value for Fe is based on that for the isoelectronic $[(Cp^{4i})_2Co]^+$ cation (Ref. 2).

the divalent Group 14 metals to non-directional orbitals of high *s*-character; they consequently do not strongly influence the orientation of the cyclopentadienyl ligands about the metal centers or serve as a source of electrons toward most electrophiles. More comparative studies would help to determine whether similar relationships exists between other classes of organo-*s*- and *p*-block compounds, and thus encourage the development of a more unified view of main-group chemistry and reactivity.

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$$Cp^{\sharp}_{2}Sn + LiR \xrightarrow{\text{ether}} LiCp^{*}\downarrow + Cp^{*}SnR \longrightarrow {}^{1}/_{2}\,R_2Sn + {}^{1}/_{2}\,Cp^{\sharp}_{2}Sn$$

or (b) one involving preferential reaction with LiR:

$$Cp^{\sharp}_{2}Sn + LiR \xrightarrow{\text{slow}} Cp^{*}SnR + LiCp^{*}\downarrow$$

$$Cp^{*}SnR + LiR \xrightarrow{\text{fast}} R_2Sn + LiCp^{*}\downarrow$$

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