A Homologous Series of Base-Free Organo(alkaline-earth) Metallocenes: Synthesis and Molecular Structures of [1,2,4-$(SiMe_3)_3C_5H_2]_2$(Ca, Sr, Ba)

Melanie J. Harvey,[a] Keith T. Quisenberry,[a] Timothy P. Hanusa,*[a] and Victor G. Young Jr.[b]

Dedicated to the memory of Professor Ronald Snaith

Keywords: Alkaline-earth metals / Metallocenes / Solid-state structures

Bis[1,2,4-tris(trimethylsilyl)cyclopentadienyl] complexes [1,2,4-$(SiMe_3)_3C_5H_2]_2$Ae [$(Cp^{3Si})_2$Ae; Ae = Ca (**1**), Sr (**2**), Ba (**3**)] are isolated from the 2:1 reaction of K[Cp^{3Si}] and AeI_2 in diethyl ether. Under the same reaction conditions used for the heavier metallocenes, the corresponding $(Cp^{3Si})_2$Be compound was not formed, although calculations suggest that the beryllocene would be sterically feasible. Compound **1** crystallizes as a bent monomer from hexanes (ring centroid–Ca–ring centroid = 166.7°) with two η^5-Cp^{3Si} ligands on the calcium atom [Ca–C(av) = 2.63(2) Å]. Metallocene **2**, the first crystallographically characterized example of an unsolvated strontocene, is also isolated as a bent monomer (159.4°) from hexanes with two η^5-Cp^{3Si} ligands on the strontium atom [Sr–C(av) = 2.819(2) Å]. Compound **3** crystallizes on sublimation as a coordination dimer in which each barium atom is flanked by two η^5-Cp^{3Si} rings [Ba–C(av) = 3.01(2) Å] and one methyl group from a neighboring Cp′ ring; the intermolecular Ba···C(methyl)′ distance is 3.275(6) Å. The amount of bending observed in **1**–**3** and other Group-2 metallocenes varies with the metals, the steric bulk of the cyclopentadienyl ligands, and crystal packing effects, and is not easily predictable.

Introduction

A characteristic feature of nearly all base-free metallocenes of the heavy alkaline-earth (Ca, Sr, Ba) and lanthanide (Sm, Eu, Yb) elements is a distinctly "bent" geometry, with ring centroid−metal−ring centroid angles as small as 131°.[1−8] The non-linear structures are found in both the solid state and the gas phase,[9,10] and their origin is not easily explained on steric or electrostatic grounds alone. One analysis of the bending phenomenon found that a strongly linear correlation existed between metal−ring distances and the ring−metal−ring bending angles in decamethylmetallocenes of the alkaline-earth, lanthanide, and p-block elements;[8] larger metals (with longer M−C distances) were associated with greater bending angles. The distance/bending correlation partially reflects the fact that decamethylmetallocenes with long metal−ring distances can bend proportionally farther back before encountering appreciable van der Waals resistance between the methyl groups (Figure 1).

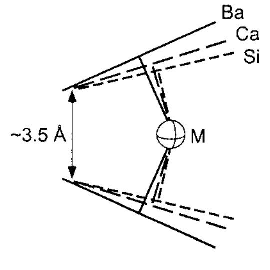

Figure 1. Origin of the strongly linear correlation between metal radius and bending angles in Cp^*_2M (M = Ae, Ln, Group 14) complexes; with longer M−C distances, greater bending is allowed before $CH_3 \cdots CH_3'$ repulsions on the "closed" side of the metallocene prevent further bending

With cyclopentadienyl rings less symmetrical than Cp*, the bending angle/metal radius relationship is less easily modeled. Although it can be expected that metallocenes with bulkier rings, i.e., [$(i\mathrm{Pr})_4C_5H]_2$(Ca, Ba), would be less bent than Cp_2M or Cp^*_2M complexes,[11] it is not simple to compare the relative bulkiness of cyclopentadienyl rings when both the number and sizes of the substituents are different. In addition, there are still many gaps within the series of structurally characterized metallocenes containing a particular cyclopentadienyl ligand; in fact, until this re-

---

[a] Department of Chemistry, Vanderbilt University,
Nashville, TN 37235, U.S.A.
Fax: (internat.) + 1-615/343-1234
E-mail: t.hanusa@vanderbilt.edu
[b] X-ray Crystallographic Laboratory,
Chemistry Department, University of Minnesota,
Minneapolis, MN 55455, U.S.A.
Fax: (internat.) + 1-612/626-7541
E-mail: young@chemsun.chem.umn.edu

port, there were no published crystallographic data for any base-free strontocene.

We have been examining the properties of 1,2,4-tris(trimethylsilyl)cyclopentadiene (HCp^{3Si})[12,13] as a sterically bulky ligand in s-block metal chemistry.[14,15] In conjunction with the previously reported structure of the substituted magnesocene $[1,2,4\text{-}(SiMe_3)_3C_5H_2]_2Mg$ [$(Cp^{3Si})_2Mg$],[16] a homologous series of unsolvated Group-2 metallocenes from Mg to Ba has now been synthesized and crystallographically authenticated. Such data provide a means for testing the strength of the M−C bond length/ring bending relationship when the metal radius is varied by nearly a factor of two (for 6-coordination, $r_{Mg^{2+}} = 0.72$ Å; $r_{Ba^{2+}} = 1.35$ Å).[17]

Results and Discussion

The bis[tris(trimethylsilyl)cyclopentadienyl]alkaline-earth metallocenes, $(Cp^{3Si})_2Ae$ (Ae = Ca, Sr, Ba), can be isolated from the 2:1 reaction of $K[Cp^{3Si}]$ and AeI_2 in diethyl ether [Equation (1)].

$$2\ K[Cp^{3Si}] + AeI_2 \xrightarrow{Et_2O} (Cp^{3Si})_2Ae + 2\ KI\downarrow \qquad (1)$$

Ae = Ca (**1**), Sr (**2**), Ba (**3**)

The metallocenes were characterized with spectroscopic methods and X-ray crystallography, which supported the proposed formulations. The complexes are thermally stable and begin to sublime at temperatures ranging from 125 to 140 °C at between 10^{-5} and 10^{-7} Torr. These complexes must be formed in diethyl ether, since in the presence of even small amounts of THF, the mono(ring) complexes $(Cp^{3Si})AeI(THF)_n$ are isolated as the exclusive products.[15] Once formed, however, the complexes can be recrystallized as base-free metallocenes from THF solution. The hexakis(trimethylsilyl)metallocenes visibly decompose upon exposure to air after only a few seconds, turning from white to dark brown. In contrast, enhanced air stability has been reported for both the octa- and decaisopropylated alkaline-earth metallocenes.[18,19]

The magnesium compound $(Cp^{3Si})_2Mg$ was reported some time ago by Jutzi and co-workers.[16] Of the remaining Group-2 elements, only the radium and beryllium analogues remain unknown. We attempted to synthesize $(Cp^{3Si})_2Be$ with methods similar to those used recently to prepare $(Me_4C_5H)_2Be$ and $Cp^*{}_2Be$;[20] viz., the reaction of $BeCl_2$ and $K[Cp^{3Si}]$ in diethyl ether (3 d at room temperature) or in a 1:1 diethyl ether/toluene mixture at reflux for 3 d. The reaction at room temperature yielded only starting materials; the refluxed reaction mixture produced a black residue from which no metallocene was isolated.

Solid State Structures

$(Cp^{3Si})_2Ca$ (1)

A crystal of **1** grown from hexanes was used to determine its structure with X-ray crystallography. A summary of bond lengths and angles for **1** is given in Table 1. An ORTEP is provided in Figure 2.

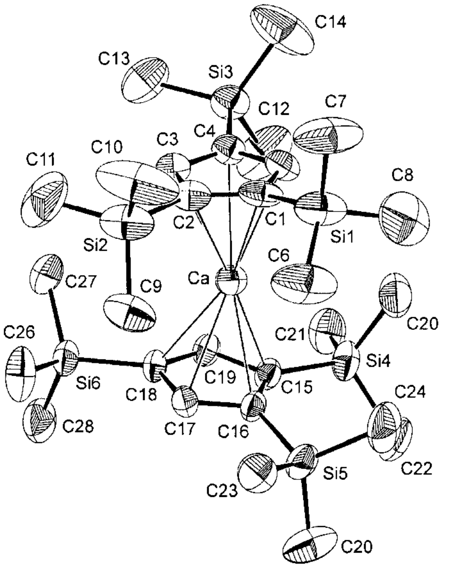

Figure 2. ORTEP of the non-hydrogen atoms of **1**; Ca−C bond lengths [Å] to C1, C2, C3, C4, C5, C15, C16, C17, C18, and C19 are 2.619(7), 2.607(7), 2.618(6), 2.665(6), 2.631(6), 2.625(6), 2.618(6), 2.638(6), 2.650(6), and 2.612(6), respectively

The compound exists as a monomeric species with two nearly eclipsed (twist angle of 8°) η^5-Cp^{3Si} ligands framing a Ca core in a bent geometry. The average Ca−C distance

Table 1. Selected bond lengths [Å] and angles [°] for $(Cp^{3Si})_2Ae$ (Ae = Mg, Ca, Sr, Ba)

	Mg (a)[a]	Mg (b)	**1**	**2**	**3**
Ae−C(ring) (av)	2.37	2.37	2.63(2)	2.812(9)	3.01(2)
Ae−ring centroid (av)	2.03(1)	2.03(1)	2.35	2.54	2.75
Ring centroid−Ae−ring centroid	171.8(2)	170.4(2)	166.7	159.4	162.2
C−C(Cp ring) (av)	1.45(3)	1.44(5)	1.42(3)	1.42(1)	1.42(2)
C(ring)−Si (av)	1.88(2)	1.88(2)	1.86(2)	1.860(7)	1.87(1)
Closest inter-ring Me···Me′ contact	4.0	4.0	4.0	3.8	3.7
Twist angle between rings	1	5	8	18	2
Ref.	[16]	[16]	this work	this work	this work

[a] Two independent molecules (a and b) are found in the unit cell.

in **1** is 2.63(2) Å. This distance is within experimental error of the average Ca−C length observed in the other structurally characterized base-free calcocenes, i.e., $(Cp^{4i})_2Ca$,[18] $(Cp^{3i})_2Ca$ {Cp^{ni} = $[(iPr)_nC_5H_{5-n}]$},[21] and $Cp^*{}_2Ca$[2] [2.64(1) Å, 2.62(2) Å, and 2.64(2) Å, respectively]. Although the two complexes belong to structurally distinct classes of compounds, the Ca−centroid distance of 2.35 Å in **1** is indistinguishable from the analogous distance in $[(Cp^{3Si})Ca(\mu\text{-}I)(THF)]_2$, which also contains a formally six-coordinate calcium center.[15] The ring centroid−Ca−ring centroid angle of 166.7° is more linear than the analogous angles found in $(Cp^{4i})_2Ca$[18] and $Cp^*{}_2Ca$[2] (162.3° and 147.0°, respectively). There is no evidence for excessive steric crowding in the complex, however, as the closest intramolecular methyl···methyl′ contact is at 4.0 Å; this is equal to the sum of the van der Waals radii of two methyl groups.[22] In addition, the greatest silyl group displacement from the cyclopentadienyl ring plane is 8.3°, which is similar to the maximum displacement of 8.7° found in the relatively uncrowded $[(Cp^{3Si})Ca(\mu\text{-}I)(THF)]_2$.[15]

$(Cp^{3Si})_2Sr$ (2)

A crystal of **2** grown from hexanes was used to determine its structure with X-ray crystallography. A summary of bond lengths and angles for **2** is given in Table 1. An ORTEP is provided in Figure 3.

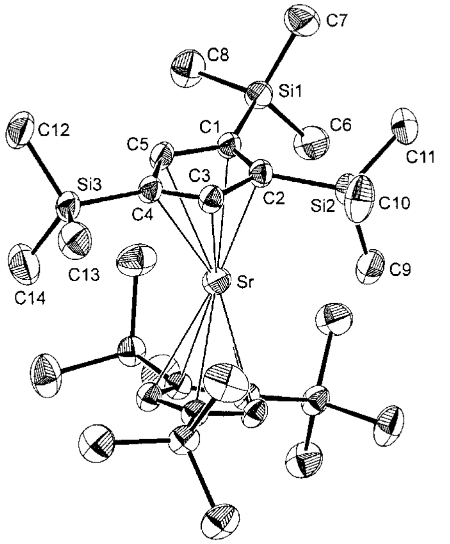

Figure 3. ORTEP of the non-hydrogen atoms of **2**; Sr−C bond lengths [Å] to C1, C2, C3, C4, and C5 are 2.811(4), 2.773(4), 2.784(4), 2.850(4), and 2.841(4), respectively

The compound exists as a monomer in which the strontium atom is coordinated by two partially staggered (twist angle of 18°) Cp^{3Si} rings. The strontium atom resides on a crystallographic C_2 axis, so that only half the molecule is unique. Although no other unsolvated strontocenes exist for direct comparison, useful structural parallels exist with divalent organolanthanide species, as Sm^{2+} and Eu^{2+} have six-coordinate radii (1.17 Å) that are almost identical to that of Sr^{2+} (1.18 Å).[17] The average Sr−C distance of 2.812(9) Å in **2** is similar to the analogous distances observed in $Cp^*{}_2Sm$ and $Cp^*{}_2Eu$ [Ln−C = 2.79(1) Å],[1] or $(Cp^{4i})_2Sm$ (Sm−C = 2.79 Å)[23] and $(Cp^{4i})_2Eu$ [Eu−C = 2.782(6) Å].[24] Giving consideration to the difference between the six- vs. seven-coordinate radii of Sr^{2+} (Δ = 0.03 Å), the Sr−ring centroid distance of 2.54 Å in **2** is also equivalent to the 2.57 Å distance found in $(Cp^{3i})_2Sr(THF)$.[25] The ring centroid−Sr−ring centroid angle of 159.4° represents a substantially more linear structure than is found in $Cp^*{}_2Sm$ and $Cp^*{}_2Eu$ (140.1° and 140.3°).[1] This is not unexpected, given the increase in steric bulk in going from Cp* to Cp^{3Si} ligands. Even so, the closest interring methyl···methyl contact is at 3.78 Å, which is 95% of the sum of the van der Waals radii of two methyl groups,[22] and as with compound **1**, **2** does not display any significant silyl group displacements from the cyclopentadienyl ring planes (maximum of 7.7°; cf. 8.7° in the dimer $[(Cp^{3Si})Sr(\mu\text{-}I)(THF)_2]_2$.[15]

$(Cp^{3Si})_2Ba$ (3)

A crystal of **3**, grown by sublimation, was used to determine its structure with X-ray crystallography. A summary of bond lengths and angles for **3** is given in Table 1. An ORTEP is provided in Figure 4.

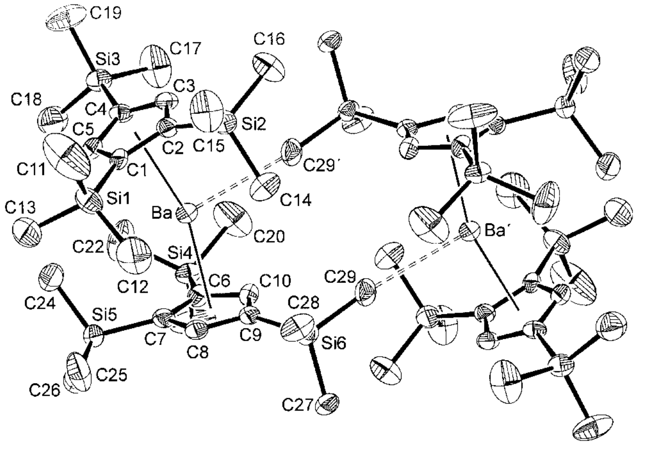

Figure 4. ORTEP of the non-hydrogen atoms of **3**, giving the numbering scheme used in the text; Ba−C bond lengths [Å] to C1, C2, C3, C4, C5, C6, C7, C8, C9, C10, and C29′ are 2.975(5), 2.977(5), 2.988(5), 3.044(5), 3.012(5), 2.981(5), 2.976(5), 3.007(5), 3.076(5), 3.036(5), and 3.275(6), respectively

Unlike the calcium and strontium analogues, **3** crystallizes as a coordination dimer in which each barium atom is surrounded by two nearly eclipsed η^5-1,2,4-tris(trimethylsilyl)cyclopentadienyl rings and one methyl group from a neighboring Cp^{3Si} ring. The average Ba−C(Cp′) distance in **3** of 3.01(2) Å and the Ba−ring centroid distance of 2.75 Å are longer than those observed in the formally six-coordinate $(Cp^{4i})_2Ba$ [2.94(2) Å and 2.68 Å, respectively].[18] The Ba−C distance is similar to that found in the sterically crowded metallocene $[(iPr)_5C_5]_2Ba$ [2.997(4) Å].[19] Based on the additional bridging interaction, however, **3** could be considered a formally seven-coordinate complex; consistent with this, the average Ba−C and Ba−ring centroid distances are indistinguishable from those observed in the seven-coordinate $\{[(Cp^{3Si})BaI(THF)_2]\cdot C_7H_8\}_\infty$ [3.00(2) and 2.76(1), respectively].[18] The ring centroid−Ba−ring centroid angle of 162.2° in **3** is considerably wider than the angle in either $(Cp^{4i})_2Ba$ (154.2°)[18] or $Cp^*{}_2Ba$ (131.0°).[2] In contrast, $(Cp^{5i})_2Ba$ is strictly linear with a ring centroid−Ba−ring centroid angle of 180°.[19]

The intermolecular contact between each barium metal center and a methyl group from an adjacent metallocene unit [Ba(1)−C(29)′] is at 3.275(6) Å, a shorter distance than the sum of the van der Waals radius of a methyl group and the ionic radius of seven-coordinate Ba^{2+} (= 3.4 Å). Similar interactions between cyclopentadienyl ring substituents and neighboring metallocenes have been observed in Group-2 and lanthanide metallocene structures. For example, in $Cp^*{}_2Ba$, there are two methyl groups with $Ba\cdots CH_3'$ distances of 3.35 and 3.36 Å.[2] There is a related interaction observed in the polymeric structure of $[\{1,3\text{-}(SiMe_3)_2C_5H_3\}_2Yb]_\infty$,[26] i.e., a close contact is present between the metal and a methyl group of a neighboring metallocene unit at 2.872(7) Å (the radii of seven-coordinate Yb^{2+} and Ba^{2+} differ by 0.30 Å[17]). The europium derivative $[\{1,3\text{-}(SiMe_3)_2C_5H_3\}_2Eu]_\infty$ displays the same type of intermolecular metal···methyl contact at 3.091(6) Å;[26] the difference in Eu^{2+} and Ba^{2+} radii is 0.18 Å, so that the contact distances in the europium and barium structures are equivalent.[17]

The trimethylsilyl group with the bridging interaction in **3** (Si6) is displaced from the cyclopentadienyl ring plane by 0.33 Å (equivalent to 10.3°), which is only slightly more than the maximum displacements observed in **1** and **2**; the next largest displacement in **3** is at 0.26 Å (= 8.1°), involving Si3. The closest intramolecular methyl···methyl′ contact is found between the eclipsed trimethylsilyl groups containing Si2 and Si6 at 3.66 Å (C14···C28).

Relative Orientations of Tris(trimethylsilyl) Rings

The presence of three trimethylsilyl groups on a Cp^{3Si} ring allow for six distinct possible relative orientations of the two rings in a metallocene (with three eclipsed C_5 rings and three staggered rings).[27] Among those possibilities, three different orientations are observed in the $(Cp^{3Si})_2Ae$ series. The magnesium[16] and calcium complexes both adopt the same eclipsed configuration [Figure 5(a)] with twist angles of 1° [for Mg(a)], 5° [for Mg(b)] and 8° [for Ca (**1**)] (Table 1). The analogous germanium complex adopts the same arrangement of silyl groups in the solid state,[27] as does the ferrocene derivative $(Cp^{3Si})_2Fe$.[28] Calculations with $(Cp^{3Si})_2Ge$ demonstrated that this conformation lies in a steric energy minimum.[27] The two rings in $(Cp^{3i})_2Ca$ also adopt the same relative orientation;[21] this seems to be a favored arrangement for 1,2,4-substituted rings in complexes with metal radii ≤ 1.0 Å. The orientation probably reflects a balance between steric repulsions and van der Waals attractive forces in these complexes; with larger metals and greater separation of the rings, steric repulsions between substituents are less energetically costly, and more eclipsing of substituents is possible.

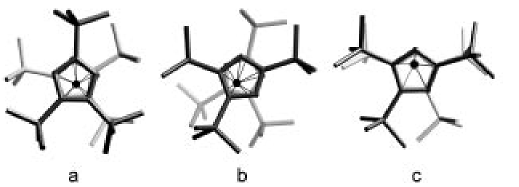

Figure 5. Orientation of the tris(trimethylsilyl)cyclopentadienyl rings in $(Cp^{3Si})_2Ae$ [Ae = Mg, Ca (**1**): (a); Sr (**2**): (b); Ba (**3**): (c)]

The rings in **2** crystallize in a staggered conformation [Figure 5(b)] with a twist angle of 18° between them (Table 1). In contrast, **3** adopts an orientation with two sets of eclipsed trimethylsilyl substituents [Figure 5(c)]; the cyclopentadienyl rings are in correspondingly close alignment (twist angle of 2°). The bending of the metallocene occurs so that the staggered substituents are on the "closed" side of the metallocene. The interaction of the barium metal center with the bridging methyl group takes place from the "open" side.

Degree of Bending in Cp'_2Ae Complexes

Despite the controversy that still surrounds the issue, the bending observed in many base-free main-group and lanthanide metallocenes is probably most readily understood through the use of various polarization models of bonding, although the participation of low-lying d-orbitals has also been proposed.[3,29−31] The amount of possible bending is limited by steric repulsions between the substituent groups, and therefore the bending angle changes not only with the metal radius and polarizability, but also with the bulk of the cyclopentadienyl ligands. Consequently, before the bending observed in metallocenes with differently substituted Cp′ rings can be compared in a meaningful way, possible ring orientations, the existence of coordination oligomers, and distortions from crystal packing all need to be taken into account.

The complexes reported here illustrate the difficulties involved in establishing such metal/bending correlations. For example, the bending angles (ring centroid−metal−ring centroid) of the four known $(Cp^{3Si})_2Ae$ compounds decrease as the metal radii increase from Mg to Sr [i.e., 171.1°, 166.7°, and 159.4° for $(Cp^{3Si})_2Mg$, $(Cp^{3Si})_2Ca$ and $(Cp^{3Si})_2Sr$, respectively] but then increase slightly for barium (162.2°). The break in the trend reflects the change from the mononuclear structures to the dimeric geometry of the barium compound, whose ring bending angle is evidently influenced by the bridging methyl group.

Comparisons of bending angles using metallocenes with only a single type of metal suffer from similar anomalies, although the difficulties may not always be apparent in small sets of compounds. For instance, the bending angles of calcocenes open from $Cp^*{}_2Ca$ (147.0°) to $(Cp^{4i})_2Ca$ (162.3°) to $(Cp^{3Si})_2Ca$ (166.7°). The order is repeated with barocenes [i.e., $Cp^*{}_2Ba$ (131°) < $(Cp^{4i})_2Ba$ (154°) < $(Cp^{3Si})_2Ba$ (162.2°)], even though $Cp^*{}_2Ba$ exists as a coordination polymer and $(Cp^{3Si})_2Ba$ is a coordination dimer in the solid state. Based on the progression in bending angles, there might be a temptation to conclude that the Cp^{3Si} ring is effectively more bulky than Cp^{4i}. However, the structure of bis(1,2,4-triisopropylcyclopentadienyl)calcium, (Cp^{3i})$_2$Ca, despite having two fewer isopropyl groups than (Cp^{4i})$_2$Ca, has a wider bending angle (169.7°) than either (Cp^{4i})$_2$Ca or (Cp^{3Si})$_2$Ca.[32] This counterexample demonstrates that the approach to linearity in the solid state is not solely a function of the number and size of ring substituents, but that packing effects may be involved as well. Great care is needed when proposing the existence of quantitative relationships between steric bulk and bending angles in such conformationally flexible molecules.

The Case of Bulky Beryllocenes

Almost all crystallographically characterized magnesocenes, including Cp$_2$Mg,[33] [(tBu)C$_5$H$_4$]$_2$Mg,[34] [(PhCH$_3$CH)C$_5$H$_4$]$_2$Mg,[35] and (Me$_4$C$_5$H)$_2$Mg[36] have parallel rings. The slight tilting of the rings observed in (Cp^{3Si})$_2$Mg (7.8°) has been ascribed to the large amount of steric encumbrance around the Mg^{2+} center generated by the two Cp^{3Si} rings.[16] The steric pressure on a beryllocene with Cp^{3Si} rings might be even greater, and could conceivably destabilize the complex through the operation of "steric oversaturation."[37] Although we were not successful in isolating a beryllocene containing two Cp^{3Si} rings, combination DFT/semiempirical (ONIOM) calculations were performed on several possible conformations of (Cp^{3Si})$_2$Be, including η^1/η^1, η^1/η^5, and η^5/η^5, to try to establish the steric feasibility of such a structure.

The η^1/η^1 geometry shown in Figure 6(a) was used as a starting geometry in optimization. The unsubstituted position on the rings was chosen as the site of ligation, both to minimize steric interactions between the rings and from the fact that in (η^5-C$_5$Me$_4$H)(η^1-C$_5$Me$_4$H)Be,[20] the beryllium atom is attached to the unsubstituted carbon atom in the η^1-bonded ring. Nevertheless, during optimization one ring rotated relative to the other, and the structure collapsed to an η^1/η^5 geometry [Figure 6(b)]. The beryllium atom is now attached to a carbon atom bearing a trimethylsilyl group; the Be−C(η^1) distance is 1.781 Å (cf. 1.827 Å in Cp$_2$Be[38]),

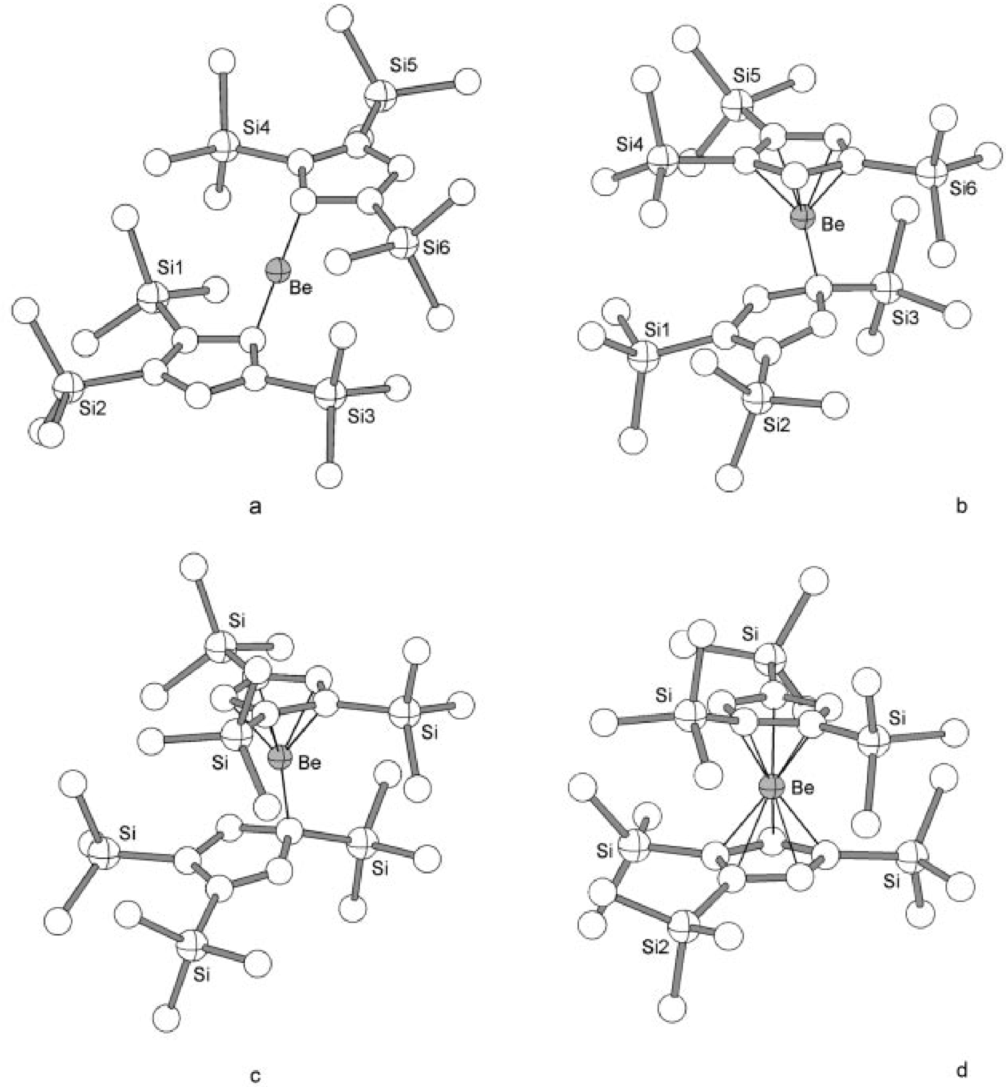

Figure 6. ONIOM-optimized geometries (H atoms omitted) for (Cp^{3Si})$_2$Be

and Si3 is bent out of the C_5 plane by 1.03 Å (32.8°). Such a rearrangement can be rationalized on electronic grounds, as silicon atoms help stabilize negative charges on adjacent atoms; the bending distortion also serves to increase the negative charge on the carbon atom.[39] The Be−C(η^5) bonds are in the narrow range from 1.901 to 1.934 Å, and average 1.923 Å, nearly matching the average Be−C(η^5-Cp) bond length in the parent molecule (1.93 Å[38]). The structure is a local minimum on the potential energy surface (PES) (no imaginary frequencies), but a similar η^1/η^5 structure can be obtained that is formally related to the first by a ring rotation [Figure 6(c)]. The latter geometry is also a minimum on the PES, and has nearly identical geometric parameters [Be−C(η^1) = 1.780 Å; Be−C(η^5) = 1.921 Å (av)]. Structure (b) in Figure 6 is 1.9 kcal mol^{-1} higher in enthalpy ($\Delta H°$) than structure (c) a difference that is not meaningful at this level of theory. The height of the energy barrier that might separate the two forms, however, is not known.

The stability of an η^5/η^5 configuration was evaluated by starting from an eclipsed conformation similar to that in Figure 5(a). The sandwich geometry was retained during optimization [Figure 6(d)]; a frequency calculation indicated that it was a local minimum ($N_{\mathrm{imag}} = 0$). The angle between the ring planes is 6.9°, and the metallocene is somewhat slipped, with Be−C bonds ranging from 2.04 to 2.14 Å; the latter distance is slightly longer than the maximum distance observed in Cp^*_2Be (2.11 Å), which is already long compared to the Be−C bond length in the parent molecule.[38] Even so, there are no intermolecular methyl···methyl′ contacts closer than 3.64 Å; the closest analogous contact in Cp^*_2Be is at 3.63 Å. The η^5/η^5 structure is 3.3 kcal mol^{-1} higher in enthalpy ($\Delta H°$) than structure (c) in Figure 6; the height of the energy barrier that separates the η^1/η^5 and η^5/η^5 forms is not known. In any case, the failure of the reactions designed to produce $(Cp^{3Si})_2Be$ (like the initial attempts to form Cp^*_2Be[40,41]) is probably best ascribed to kinetic difficulties, rather than to fundamental steric limitations on the geometry of the beryllocene.

Conclusion

The 1,2,4-tris(trimethylsilyl)cyclopentadienyl ligand has now been incorporated into unsolvated metallocenes containing metals from magnesium to barium. A balance between steric repulsions and van der Waals attractive forces evidently directs the relative ring orientations. A configuration with a single eclipsed substituent seems to be a favored arrangement in complexes with smaller metals ($r \leq 1.0$ Å); the larger metals adopt arrangements that may be influenced more by intermolecular interactions. With the exception of $(Cp^{3Si})_2Mg$, whose rings are non-parallel owing to high steric pressure within the complex, the other metallocenes are all bent less than their Cp, Cp* or Cp^{4i} counterparts, although the trends are not uniform for all combinations of metals and cyclopentadienyl rings. In addition, three trimethylsilyl substituents do not block access to the metal center as completely as do four isopropyl groups; **3** forms a coordination dimer, for example, whereas $(Cp^{4i})_2Ba$ remains rigorously monomeric. Hence the bending angle of a metallocene, although reflecting the steric bulk of the cyclopentadienyl rings, is not a completely reliable indicator of the shielding of the metal center.

Experimental Section

General Remarks: All manipulations were performed with the rigorous exclusion of air and moisture using high vacuum, Schlenk, or drybox techniques. Anhydrous calcium, strontium or barium iodide (Strem Chemicals or Cerac, 95%) were heated under vacuum (150 °C, 10^{-6} Torr) to remove residual amounts of free iodine. K[1,2,4-$(SiMe_3)_3C_5H_2$] was prepared as described previously.[15] Solvents for reactions were distilled under nitrogen from sodium or potassium benzophenone ketyl. NMR solvents were vacuum-distilled from Na/K (22:78) alloy and stored over molecular sieves (4 Å). Proton (^{1}H) and carbon (^{13}C) NMR spectra were obtained with a Bruker NR-300 spectrometer at 300 and 75.5 MHz, respectively, and were referenced to the residual resonances of C_6D_6 (δ = 7.15 and 128.0 ppm) or [D_8]THF (δ = 3.58 and 67.4 ppm). Infrared data were measured with KBr pellets as described previously.[18] Elemental analyses were performed by Desert Analytical Laboratory, Tucson, AZ; the low carbon value found for **1** reflects a not uncommon problem with highly air-sensitive organo(alkaline-earth) compounds.[42]

Synthesis of [1,2,4-$(SiMe_3)_3C_5H_2]_2$Ca (1): CaI_2 (0.145 g, 0.49 mmol) and K[1,2,4-$(SiMe_3)_3C_5H_2$] (0.291 g, 0.91 mmol) were added to a flask under nitrogen at room temperature. Diethyl ether (45 mL) was added to the flask, and the reaction mixture was stirred overnight, concentrated to dryness under vacuum, and the residue extracted with hexanes. The extract was filtered, and the filtrate concentrated to an oil that crystallized upon standing, yielding **1** as air-sensitive, colorless crystals (0.100 g, 37%). This material sublimed at 125−140 °C and 10^{-5} Torr to give a white powder (0.093 g, 34%), m.p. 164 °C. $C_{28}H_{58}CaSi_6$ (603.36): calcd. C 55.74, H 9.69; Ca, 6.64; found C 54.41, H 10.20; Ca, 6.70. ^{1}H NMR (C_6D_6, 20 °C): δ = 6.96 (s, 2 H, ring-C*H*), 0.38 [s, 27 H, Si(C*H*$_3$)$_3$] ppm. ^{1}H NMR ([D_8]THF, 20 °C): δ = 6.76 (s, 2 H, ring-C*H*), 0.28 [s, 18 H, Si(C*H*$_3$)$_3$], 0.17 [s, 9 H, Si(C*H*$_3$)$_3$] ppm. ^{13}C NMR (75.5 MHz, C_6D_6, 20 °C): δ = 133.1 (2C, ring-*C*H), 131.7 [ring-*C*Si(CH$_3$)$_3$], 126.5 [ring-*C*Si(CH$_3$)$_3$], 2.0 [Si(*C*H$_3$)$_3$], 1.1 [Si(*C*H$_3$)$_3$]. Selected IR bands (KBr): $\tilde{\nu}$ = 2956 (s), 2904 (m), 1633 (m), 1556 (m), 1250 (vs), 1116 (w), 1016 (m), 977 (m), 833(vs), 526 (w) cm^{-1}. Crystals for X-ray structural analysis were grown by slow concentration of a saturated hexanes solution of **1** at room temperature.

Synthesis of [1,2,4-$(SiMe_3)_3C_5H_2]_2$Sr (2): SrI_2 (0.100 g, 0.29 mmol) and K[1,2,4-$(SiMe_3)_3C_5H_2$] (0.176 g, 0.54 mmol) were added to a flask under nitrogen at room temperature. Diethyl ether (55 mL) was added to the flask, and the reaction mixture was stirred overnight, concentrated to dryness, and the residue extracted with hexanes. The extract was filtered, and the filtrate concentrated to an oil that crystallized upon standing, yielding **2** as air-sensitive, colorless crystals (0.125 g, 71%). Analytically pure material was obtained by sublimation at 140−165 °C and 10^{-6} Torr to give a white crystalline solid (71 mg, 40%), m.p. 94−96 °C. $C_{28}H_{58}Si_6Sr$ (650.90): calcd. C 51.67, H 8.98; found C 51.93, H 9.20. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ = 6.89 (s, 2 H, ring-C*H*), 0.37 [s, 9 H, Si(C*H*$_3$)$_3$], 0.34 [s, 18 H, Si(CH_3)$_3$] ppm. ^{1}H NMR ([D$_8$]THF, 20 °C): δ = 6.69 (s, 2 H, ring-C*H*), 0.27 [s, 18 H, Si(CH_3)$_3$], 0.17 [s, 9 H, Si(CH_3)$_3$] ppm. ^{13}C NMR (75.5 MHz, C_6D_6, 20 °C): δ = 132.4 (2C, ring-*C*H), 130.0 (ring-*C*Si(CH$_3$)$_3$], 125.5 (ring-*C*Si(CH$_3$)$_3$], 1.9 [Si(*C*H$_3$)$_3$], 1.1 [Si(*C*H$_3$)$_3$]. Selected IR bands (KBr): ṽ = 2957 (vs, br), 1247 (vs, sh), 1091 (ms), 1005 (ms), 850 (vs, br), 751 (s) cm^{-1}. Crystals for X-ray structural analysis were grown by slow concentrated of a saturated hexanes solution of **2** at room temperature.

Synthesis of [1,2,4-(SiMe$_3$)$_3$C$_5$H$_2$]$_2$Ba (3): BaI_2 (0.455 g, 1.2 mmol) and K[1,2,4-(SiMe$_3$)$_3$C$_5$H$_2$] (0.794 g, 2.5 mmol) were added to a flask under nitrogen at room temperature. Diethyl ether (65 mL) was added to the flask, and the reaction mixture was stirred overnight, concentrated to dryness, and the residue extracted with hexanes. The extract was filtered, and the filtrate concentrated to dryness to yield a beige powder (0.42 g, 50%). The crude product was sublimed at 140 °C and 10^{-7} Torr to give air-sensitive, colorless crystals of **3** (0.206 g, 24%), m.p. 139−140 °C. $C_{28}H_{58}BaSi_6$ (700.61): calcd. C 48.00, H 8.34; found C 47.97, H 8.40. ^{1}H NMR (C_6D_6, 20 °C): δ = 6.78 (s, 2 H, ring-C*H*), 0.35 [s, 18 H, Si(CH_3)$_3$], 0.33 [s, 9 H, Si(CH_3)$_3$] ppm. ^{1}H NMR ([D$_8$]THF, 20 °C): δ = 6.60 (s, 2 H, ring-C*H*), 0.25 [s, 18 H, Si(CH_3)$_3$], 0.17 [s, 9 H, Si(CH_3)$_3$] ppm. ^{13}C NMR (75.5 MHz, C_6D_6, 20 °C): δ = 133.1 (2 C, ring-*C*H), 130.5 (ring-*C*Si(CH$_3$)$_3$], 125.4 (ring-*C*Si(CH$_3$)$_3$], 2.0 [Si(*C*H$_3$)$_3$], 0.9 [Si(*C*H$_3$)$_3$]. Selected IR bands (KBr): ṽ = 2955 (s), 2897 (m), 1436 (w), 1250 (s), 1092 (m), 1005 (m), 978 (m), 830 (vs), 752 (m), 689 (w), 629 (w) cm^{-1}. Crystals for X-ray structural analysis were obtained from the sublimation of **3**.

Attempted Syntheses of [1,2,4-(SiMe$_3$)$_3$C$_5$H$_2$]$_2$Be: $BeCl_2$ (0.031 g, 0.39 mmol) and K[1,2,4-(SiMe$_3$)$_3$C$_5$H$_2$] (0.252 g, 0.79 mmol) were added to a flask under nitrogen at room temperature. Diethyl ether (20 mL) was added to the flask, and the reaction mixture was stirred at room temperature for 3 d, concentrated to dryness under vacuum, and the residue extracted with hexanes. ^{1}H NMR analysis of the extract indicated that only starting materials were present. The reaction was repeated in a 1:1 diethyl ether/toluene mixture, which was refluxed under nitrogen for 3 days. A black residue was left at the completion of the reaction, and no metallocene was isolated on workup of the reaction mixture.

X-ray Crystallographic Studies: The crystal structure measurement and refinement data for **1**−**3** are given in Table 2. Measurements on **1** and **2** were performed with a Rigaku AFC6S diffractometer at Vanderbilt University with graphite-monochromated Cu-K_α radiation (λ = 1.54178 Å). A crystal of each compound was sealed in a glass capillary tube. Selected crystal and data collection parameters for the present study are given in Table 2. The space groups were determined from reflection conditions and intensity statistics. Data collection was performed using continuous ω-2θ scans with stationary backgrounds (peak/background counting time = 2:1). The structures were solved by direct methods and Fourier techniques with TEXSAN software. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in calculated positions based on packing considerations and *d*(C−H) = 0.95 Å. The positions were fixed for the final cycles of refinement. Measurements on **3** were performed on a Siemens SMART system at the X-ray Crystallography Laboratory at the University of Minnesota. A crystal of **3** was attached to a glass fiber, and mounted for data collection at 173(2) K. Data collection and structure solution were conducted at the X-ray Crystallography Laboratory at the University of Minnesota. All calculations were performed using the SHELXTL V5.0 suite of programs. A successful direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Several full-matrix least-squares/difference Fourier cycles were performed that located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic dis-

Table 2. Crystal data and summary of X-ray data collection

	1	**2**	**3**
Empirical formula	$C_{28}H_{58}CaSi_6$	$C_{28}H_{58}Si_6Sr$	$C_{28}H_{58}BaSi_6$
Molecular mass [g·mol^{-1}]	603.36	650.90	700.62
Color of crystal	colorless	colorless	colorless
Cryst dimension [mm]	0.68 × 0.35 × 0.30	0.80 × 0.45 × 0.38	0.25 × 0.15 × 0.06
Space group	$P2_1/n$	$C2/c$	$C2/c$
Temperature [K]	293	293	173(2)
a [Å]	12.928(2)	20.616(3)	20.3972(5)
b [Å]	18.463(2)	20.304(3)	11.1368(2)
c [Å]	17.049(2)	9.697(3)	33.9370(8)
β [°]	95.09(1)	105.79(2)	97.552(1)
V [Å^3]	4053(2)	3906(2)	7642.2 (3)
Z	4	4	8
D(calcd.) [g/cm^3]	0.989	1.107	1.218
Radiation type	Cu-K_α	Cu-K_α	Mo-K_α
Abs. coeff [cm^{-1}]	31.65	38.3	12.42
Scan speed [°/min]	8.0	4.0	
Scan width	0.94 + 0.30 tan θ	1.73 + 0.30 tan θ	
F(000)	1329	1392	2928
Limits of data collection [°]	6 ≤ 2θ ≤ 120	6 ≤ 2θ ≤ 120	1.21 ≤ θ ≤ 25.03
Total reflections	6559	3093	22 399
Unique reflections	6250	2999	6736
No. with $I > n\sigma(I)$	2698 (n = 3)	2164 (n = 3)	4849 (n = 2)
R_1 indices [$I > n\sigma(I)$]	0.053 (n = 3; F)	0.040 (n = 3; F)	0.052 (n = 2; F^2)
wR_2 indices [$I > n\sigma(I)$]	0.062 (F)	0.044 (F)	0.117 (F^2)
Goodness of fit	1.87 (F)	1.69 (F)	1.015 (F^2)
Max/min peak (final diff. map) [e/Å^3]	0.19/−0.35	0.48/−0.32	1.4/−0.81

placement parameters. SAME restraints were applied to the disordered Si(4)/C(20)/C(21)/C(22) group, which was found to be occupied in a 0.53:0.47 ratio. CCDC-210464 (**1**), -210465 (**2**) and -210466 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Computational Details: Calculations on $(Cp^{3Si})_2Be$ were performed using the Gaussian 03 W suite of programs.[43] A full geometry optimization using even the relatively modest 6-31G(d,p) basis set would have involved a computationally expensive set of 839 basis functions. An ONIOM calculation[44] was performed instead, using the 6-31G(d,p) basis set on Be, the ten carbon atoms of the cyclopentadienyl rings, and the directly attached atoms (hydrogen or silicon). The semi-empirical PM3 method was used for the 18 methyl groups. The B3PW91 functional, which incorporates Becke's three-parameter exchange functional[45] with the 1991 gradient-corrected correlation functional of Perdew and Wang,[46] was used; this hybrid functional has previously been shown to provide realistic geometries for organometallic species.[47,48] Frequency calculations were used to establish that all optimized geometries were local minima ($N_{\mathrm{imag}} = 0$).

Acknowledgments

Acknowledgment is made to the National Science Foundation for support.

[1] W. J. Evans, L. A. Hughes, T. P. Hanusa, R. J. Doedens, *Organometallics* **1986**, *5*, 1285−1291.
[2] R. A. Williams, T. P. Hanusa, J. C. Huffman, *Organometallics* **1990**, *9*, 1128−1134.
[3] T. P. Hanusa, *Organometallics* **2002**, *21*, 2559−2571.
[4] P. Jutzi, N. Burford, *Chem. Rev.* **1999**, *99*, 969−990.
[5] M. Kaupp, *Angew. Chem. Int. Ed.* **2001**, *40*, 3535−3565.
[6] M. Kaupp, P. v. R. Schleyer, M. Dolg, H. Stoll, *J. Am. Chem. Soc.* **1992**, *114*, 8202−8208.
[7] T. K. Hollis, J. K. Burdett, B. Bosnich, *Organometallics* **1993**, *12*, 3385−3386.
[8] D. J. Burkey, T. P. Hanusa, *Comments, Inorg. Chem.* **1995**, *17*, 41−77.
[9] R. A. Andersen, J. M. Boncella, C. J. Burns, R. Blom, A. Haaland, H. V. Volden, *J. Organomet. Chem.* **1986**, *312*, C49−C52.
[10] R. A. Andersen, R. Blom, C. J. Burns, H. V. Volden, *J. Chem. Soc., Chem. Commun.* **1987**, 768−769.
[11] T. V. Timofeeva, J.-H. Lii, N. L. Allinger, *J. Am. Chem. Soc.* **1995**, *117*, 7452−7459.
[12] P. Jutzi, W. Leffers, S. Pohl, W. Saak, *Chem. Ber.* **1989**, *122*, 1449−1456.
[13] P. Jutzi, R. Sauer, *J. Organomet. Chem.* **1973**, *50*, C29−C30.
[14] M. J. Harvey, T. P. Hanusa, M. Pink, *J. Chem. Soc., Dalton Trans.* **2001**, 1128−1130.
[15] M. J. Harvey, T. P. Hanusa, *Organometallics* **2000**, *19*, 1556−1566.
[16] C. P. Morley, P. Jutzi, C. Krüger, J. M. Wallis, *Organometallics* **1987**, *6*, 1084−1090.
[17] R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751−767.
[18] R. A. Williams, K. F. Tesh, T. P. Hanusa, *J. Am. Chem. Soc.* **1991**, *113*, 4843−4851.
[19] H. Sitzmann, T. Dezember, M. Ruck, *Angew. Chem. Int. Ed.* **1998**, *37*, 3114−3115.
[20] M. Del Mar Conejo, R. Fernandez, E. Gutierrez-Puebla, A. Monge, C. Ruiz, E. Carmona, *Angew. Chem. Int. Ed.* **2000**, *39*, 1949−1951.
[21] D. J. Burkey, T. P. Hanusa, J. C. Huffman, *Adv. Mater. Opt. Electron.* **1994**, *4*, 1−8.
[22] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, New York, **1960**.
[23] M. Visseaux, D. Barbier-Baudry, O. Blacque, A. Hafid, P. Richard, F. Weber, *New J. Chem.* **2000**, *24*, 939−942.
[24] H. Sitzmann, T. Dezember, O. Schmitt, F. Weber, G. Wolmershauser, M. Ruck, *Z. Anorg. Allg. Chem.* **2000**, *626*, 2241−2244.
[25] D. J. Burkey, T. P. Hanusa, *Acta Crystallogr., Sect. C* **1996**, *52*, 2452−2454.
[26] P. B. Hitchcock, J. A. K. Howard, M. F. Lappert, S. Prashar, *J. Organomet. Chem.* **1992**, *437*, 177−189.
[27] P. Jutzi, E. Schlueter, M. B. Hursthouse, A. M. Arif, R. L. Short, *J. Organomet. Chem.* **1986**, *299*, 285−295.
[28] J. Okuda, E. Herdtweck, *Chem. Ber.* **1988**, *121*, 1899−1905.
[29] I. Bytheway, P. L. A. Popelier, R. J. Gillespie, *Can. J. Chem.* **1996**, *74*, 1059−1071.
[30] V. N. Sapunov, K. Kirchner, R. Schmid, *J. Organomet. Chem.* **2001**, *214*, 143−185.
[31] V. M. Rayon, G. Frenking, *Chem. Eur. J.* **2002**, *8*, 4693−4707.
[32] D. J. Burkey, R. A. Williams, T. P. Hanusa, *Organometallics* **1993**, *12*, 1331−1337.
[33] W. Bünder, E. Weiss, *J. Organomet. Chem.* **1975**, *92*, 1−6.
[34] M. G. Gardiner, C. L. Raston, C. H. L. Kennard, *Organometallics* **1991**, *10*, 3680−3686.
[35] M. Westerhausen, N. Makropoulos, B. Wieneke, K. Karaghiosoff, H. Noeth, H. Schwenk-Kircher, J. Knizek, T. Seifert, *Eur. J. Inorg. Chem.* **1998**, 965−971.
[36] H. Schumann, J. Gottfriedsen, M. Glanz, S. Dechert, J. Demtschuk, *J. Organomet. Chem.* **2001**, *617−618*, 588−600.
[37] T. P. Hanusa, *Chem. Rev.* **1993**, *93*, 1023−1036.
[38] K. W. Nugent, J. K. Beattie, T. W. Hambley, M. R. Snow, *Aust. J. Chem.* **1984**, *37*, 1601−1606.
[39] S. Harder, M. Lutz, A. W. G. Straub, *Organometallics* **1997**, *16*, 107−113.
[40] C. J. Burns, R. A. Andersen, *J. Organomet. Chem.* **1987**, *325*, 31−37.
[41] S. J. Pratten, M. K. Cooper, M. J. Aroney, *J. Organomet. Chem.* **1990**, *381*, 147−153.
[42] H. Sitzmann, F. Weber, M. D. Walter, G. Wolmershaeuser, *Organometallics* **2003**, *22*, 1931−1936.
[43] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 2003*, Revision B.01, Gaussian, Inc., Pittsburgh PA, **2003**.
[44] S. Dapprich, I. Komaromi, K. S. Byun, K. Morokuma, M. J. Frisch, *J. Molec. Struct. THEOCHEM* **1999**, *462*, 1−21.
[45] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648−5652.
[46] J. P. Perdew, Y. Wang, *Phys. Rev. B* **1992**, *45*, 13244−13249.
[47] T. Ziegler, *Chem. Rev.* **1991**, *91*, 651−667.
[48] J. D. Smith, T. P. Hanusa, *Organometallics* **2001**, *20*, 3056−3062.

Received May 13, 2003