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Regarding the Structures and Fluxionality of Tricyclopentadienylaluminum Compounds

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X-ray crystallographic studies, low-temperature 1H and 13C NMR studies, and 27Al NMR studies of a series of homoleptic tricyclopentadienylaluminum compounds ([C5H5]3Al (1), (MeCyH9)3Al (2), (1,2,4-Me3CyH9)3Al (3), (1,2,3,4-Me4CyH10)3Al (4)] are reported along with ab initio calculations on model cyclopentadienylaluminum compounds. The ring-coordination geometries exhibited by the tricyclopentadienylaluminum compounds in the solid state vary with the number of methyl substituents on the cyclopentadienyl rings. The X-ray crystal structure of compound 1 revealed two unique molecules in the unit cell, one with an \( \eta^1, \eta^2, \eta^3 \) combination of ring geometries and the other with an \( \eta^2, \eta^1, \eta^5 \) combination of ring-coordination geometries. In the crystal structure of compound 3, one cyclopentadienyl ring is coordinated \( \eta^2 \) to the aluminum while the other two rings are \( \eta^1 \). Compound 4 exhibits monohapto coordination of all three tetramethyl-substituted cyclopentadienyl rings in the solid state. These compounds are highly fluxional in solution and exhibit averaged 1H and 13C NMR spectra in the fast-exchange limit at temperatures as low as \(-110^\circ C\). This behavior is explained by the ab initio calculations on model cyclopentadienylaluminum compounds which reveal almost negligible (1–2 kcal/mol) energy differences between different ring hapticities (\( \eta^1, \eta^2, \eta^3, \eta^5 \)).

Introduction

The cyclopentadienyl ligand is probably best known for its pentahapto-coordination geometry with transition metals. In the absence of accessible d orbitals, \( \pi \)-type interactions are weaker, and deviation from \( \eta^4 \)-geometry by “ring slippage” is often observed. These “ring-slipped” (\( \eta^1, \eta^2, \eta^3 \)) structures are more commonly observed among the cyclopentadienyl—main-group-metal compounds.1–3 Along with these ring-slipped geometries, cyclopentadienyl compounds of the main-group elements exhibit varying degrees of fluxionality. Two different sigmatropic processes have been identified experimentally for \( \sigma \)-bonded (\( \eta^1 \)) species, a 1,2-hydrogen shift and a 1,2-shift of the main-group element.4 Detailed mechanistic information on these systems has been obtained, where possible, with the help of variable-temperature NMR techniques.

In the case of aluminum, rearrangements are too fast at accessible temperatures to be monitored by NMR. Moreover, equilibrium structures are frequently not \( \eta^1 \) but \( \eta^{1.5}, \eta^2, \) or \( \eta^6 \) which complicates the discussion of “the sigmatropic process”. Nevertheless, it has generally been assumed, by extrapolation from experimentally characterizable systems, that a similar “ring-whizzing”5–8 mechanism is responsible for the dynamic behavior observed in the \( 1H \) and \( 13C \) NMR spectra of cyclopentadienylaluminum compounds. Gas-phase electron diffraction data on \( \text{CpAlMe}_2 \) (Cp = \( \text{C}_5\text{H}_5 \)) and theoretical calculations at the semi-empirical and extended Hückel levels support a ring-whizzing mechanism.9–11 Here we report new physical and theoretical evidence that suggests that the energy surface for cyclopentadienylaluminum compounds is shallow enough to allow other rearrangements, such as \( \eta^1 \leftrightarrow \eta^6 \) haptotropic shifts, to compete with the traditional fluxional behavior of \( \sigma \)-cyclopentadienyl compounds. X-ray crystal structures of the homoleptic cyclopentadienylaluminum compounds \( \text{Cp}_2\text{Al}, (1,2,4-\text{Me}_3\text{CyH}_9)_3\text{Al}, \) and \( (1,2,3,4-\text{Me}_4\text{CyH}_{10})_3\text{Al} \) reveal a dramatic effect of methyl substitution of the rings on their preferred mode of coordination to the aluminum atom in the solid state. Whereas all three tetramethycyclopentadienyl rings in \( (1,2,4-\text{Me}_3\text{CyH}_9)_3\text{Al} \) exhibit a monohapto-coordination geometry, higher ring hapticities are seen for \( \text{Cp}_2\text{Al} \), and in the structure of \( (1,2,3,4-\text{Me}_4\text{CyH}_{10})_3\text{Al} \) we have characterized, for the first time, \( \eta^2 \) and \( \eta^5 \) ring geometries in the same molecule (vide infra). Ab initio calculations on model compounds reveal that the different ring hapticities are so close in energy that subtle changes in the ring substitution or in the electronic and steric demands of the other ligands on the aluminum can easily tip the balance with respect to the preferred


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ground-state geometries of the molecules as well as, perhaps, the lowest energy pathway for ring fluctuation.

Background

The unusual bis-dihapto Cp-coordination geometry which we characterized for CpAlMe12 (Figure 1) stimulated our interest in the molecular structures and fluxional behavior of cyclopentadienylaluminum compounds. In addition to representing the first structural characterization of a dicyclopentadienylaluminum compound, this X-ray crystal structure of CpAlMe offers the first solid-state characterization of an ?/2-coordinated cyclopentadienyl ring on aluminum.

A similar y ?2-Cp coordination geometry was invoked as the best model for the gas-phase electron diffraction pattern for CpAlMe9. CNDO/2 and ab initio calculations performed by Groepen and Haaland on CpAlMe9 and CpAlH5,10 respectively, and extended Hückel calculations performed by Hoffmann and co-workers on iso electronic CpCH2+ predict an ? ?2-Cp to be the preferred ground-state geometry in these species; however, a geometry with an ? ?/2-Cp is less than 5 kcal/mol higher in energy. Thus, a mechanism involving the circumambulatory migration of the aluminum about the cyclopentadienyl ring through a series of 1,2-shifts is entirely consistent with the highly fluxional nature of these compounds as evidenced by the averaged 1H and 13C NMR spectra of the compounds in solution at temperatures as low as −110 °C at 7 T (1H NMR: 300 MHz) (vide infra).

In order to identify the mechanism for rearrangement experimentally and to determine if alternate pathways, such as an ?/2, ?;L5, ?/2-shifts is possible, we included methyl substituents on the cyclopentadienyl rings of the aluminum in the hope of slowing down the dynamics to the extent of “freezing out” ring motion on the NMR time scale. As described below, our efforts to slow the fluxionality of these molecules in solution were unsuccessful. Nevertheless, our structural characterizations of these compounds reveal an extraordinary flexibility in the manner in which aluminum coordinates its cyclopentadienyl ligands and a very delicate dependence of the cyclopentadienyl ligand geometry on the sterics and electronics of the complex. We begin with a description of the synthesis, molecular structure, and solution properties of the simplest homoleptic cyclopentadienylaluminum compound, CpaAl.

Results and Discussion

Synthesis, Molecular Structure, and Solution NMR Properties of CpaAl (1). Earlier we reported a


new, convenient synthetic route to CpaAl by reacting magnesocene and trichloroaluminum in a 1.5:1 ratio in a hydrocarbon solvent with gentle warming (equation 1).12 Our initial preparations of CpaAl by this method afforded the material as a light yellow oil. We have since found that we can isolate this material as a crystalline, low-melting solid (mp = 46 °C, uncorrected) by using rigorously clean starting materials and carefully crystallizing the compound from a petroleum ether solution in order to eliminate minor impurities from the product that prevent it from crystallizing. Single crystals of 1 were obtained in this manner for an X-ray structure determination. There are two unique CpaAl molecules in the unit cell of the crystal, both of which are shown in the ORTEP drawing in Figure 2. Selected bond distances and angles for both structures are listed in Table 2. In the absence of a Lewis base, the cyclopentadienyl rings are able to approach y ?2-geometries. In one molecule, two rings are coordinated in more of an y/2,1.6 fashion to the aluminum, with one carbon on each ring closely bound to the aluminum at distances of 2.049(11) and 2.093(9) Å and the second carbon 0.2–0.3 Å slightly more distant at 2.232(2) and 2.304(10) Å, respectively. The third ring approaches more of an y ?2-geometry with Al-nearest carbon distances of 2.092(7) and 2.192(7) Å. All of the other carbons of the three rings are more distant from aluminum than the nearest carbons by 0.4 Å or more. The canting of each of the rings toward one carbon is also reflected in the angles between the Al–C vectors and the ring plane, these angles being more acute for the more closely coordinated carbon. The roughly equivalent C–C bond lengths in the rings, ranging from 1.325(11) to 1.397(10) Å, reflect a retention of aromaticity in the rings. The second CpaAl structure exhibits more of an (y/2, y/2, y/2) combination of ring geometries about the aluminum atom. The Al-nearest carbon distances in the y/2 ring are 2.106(7) and 2.161(7) Å. The y/2, y/2 ring exhibits Al-nearest carbon distances of 2.047(7) and 2.324(9) Å. Although the third ring may be regarded as y/2, the Al–C(1) bond distance of 2.016(7) Å being shorter than all the other Al–C distances in the ring by >0.5 Å, the pattern of C–C bond lengths in the ring is not consistent with the localized, diene structure exhibited by the cyclopentadienyl rings.
Tricyclopentadienylaluminum Compounds

Table 1. Crystallographic Data for Cp3Al (1), (Me5C5H5)3Al (3), and (Me6C6H6)3Al (4)

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<th>Space Group</th>
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<th>b (Å)</th>
<th>c (Å)</th>
<th>α (deg)</th>
<th>β (deg)</th>
<th>γ (deg)</th>
<th>V (Å³)</th>
<th>Z</th>
<th>T (K)</th>
<th>ρcal (g/cm³)</th>
<th>μ (mm⁻¹)</th>
<th>R{Fy}(F0)²</th>
<th>wR{Fy}(F0)²</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8</td>
<td>299</td>
<td>0.701 73 (Mo Kα)</td>
<td>0.129</td>
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<td>0.1604</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>233</td>
<td>0.701 73 (Mo Kα)</td>
<td>0.098</td>
<td>0.093, 0.866</td>
<td>0.1298</td>
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<td>P1</td>
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Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1

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<th>Bond Lengths (Å)</th>
<th>Angles (deg)</th>
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<td>Al(1)—C(2)</td>
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<tr>
<td>Al(1)—C(3)</td>
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<td>Al(2)—C(27)</td>
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<td>Al(2)—C(26)</td>
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<tr>
<td>Al(2)—C(27)</td>
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<tr>
<td>Al(2)—C(28)</td>
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<td></td>
</tr>
<tr>
<td>Al(2)—C(29)</td>
<td>2.30(1)</td>
<td></td>
</tr>
</tbody>
</table>

Like its heavier group 13 congeners, 1 is highly fluxional. An averaged signal for the rings is observed at δ 6.1in the 1H NMR spectrum and δ 114 in the 13C NMR spectrum for a 50:50 CD2Cl2/Freon-11 solution sample of the compound. These signals show no noticeable broadening down to -100 °C at 7 T. The combination of 1H and 13C ring coordination exhibited by the two Cp3Al molecules in the X-ray structure suggests a simultaneous “whizzing” of the three rings about the aluminum via a series of 2,12-shifts as a viable mechanism for this averaging. The tetracoordinate aluminum compound Cp3Al(CN-i-Bu)12 is, likewise, highly fluxional and exhibits averaged 1H and 13C NMR spectra in toluene-d8 with no noticeable broadening down to -100 °C, the temperature at which the compound begins to precipitate from solution. Interestingly, the 27Al chemical shift of δ 81 (relative to an Al(OH)3 external standard) for 1 is at a higher field than that of the four-coordinate Cp3Al(CN-t-Bu) which has a chemical shift of δ 118. This downfield shifting of 27Al NMR resonances for the tetracoordinate cyclopentadienylaluminum compounds relative to tetracoordinate aluminum runs counter to the trend typically observed for organoaluminum and aluminum alkoxide compounds. The relatively high-field 27Al chemical shift for Cp3Al has previously been considered to be diagnostic of a tetrahedral aluminum center with an (η¹, η¹, η¹) combination of ring geometries. While a clear relationship between coordination number and 27Al NMR chemical shift does indeed appear to exist for more classical structures in which the coordination number is unequivocal,16,18-20 we suspect that such an interpretation of the slightly smaller covalent radius and higher electronegativity of the gallium, in Cp3In, displays its larger size by adopting a coordination number of 4 through the formation of a polymeric structure in which the indium atoms are linked together by bridging, η¹-coordinated cyclopentadienyl rings. The nonbridging cyclopentadienyl rings are η¹-coordinated to the indium as well. Cp3Sc also exhibits a polymeric structure in which one ring bridges two scandium atoms by η¹ coordination to each one. Unlike the main group metals, the scandium is able to use its 3d orbitals to adopt an η¹-coordination geometry with two of its four coordinated cyclopentadienyl rings.

of (η¹-Cp)3Al(CN-i-Bu). Rather, C(1)—C(2), at 1.414(10) Å, and C(1)—C(5), at 1.428(10) Å, are longer than the three remaining C—C bonds in the ring with distances in the range 1.338(10)–1.356(10) Å.

These molecular structures for Cp3Al are considerably different from the molecular structures characterized for the related homoleptic tricyclopentadienyl group 13 compounds Cp3Ga13 and Cp3In14 and the d-block relative, Cp3Sc.15 Cp3Ga exhibits a ζ by η¹ (i.e. (η¹, η¹, η¹), η¹) Cp coordination geometry in the solid state. The geometrical parameters, Ga—O distances, and ring C—C distances are comparable to that of the unique η¹-Cp—Al interaction characterized in our structure. The uniform η¹-coordination between the gallium and its cyclopentadienyl rings, as compared with the higher hapticities exhibited by aluminum, is perhaps attributable to the slightly smaller covalent radius and higher electronegativity of the gallium, in Cp3In, displays its larger size by adopting a coordination number of 4 through the formation of a polymeric structure in which the indium atoms are linked together by bridging, η¹-coordinated cyclopentadienyl rings. The nonbridging cyclopentadienyl rings are η¹-coordinated to the indium as well. Cp3Sc also exhibits a polymeric structure in which one ring bridges two scandium atoms by η¹ coordination to each one. Unlike the main group metals, the scandium is able to use its 3d orbitals to adopt an η¹-coordination geometry with two of its four coordinated cyclopentadienyl rings.

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may be too simplistic for cyclopentadienylnitrogen complexes, in which the degree of electron delocalization in the rings should have an effect on the magnetic field experienced by the aluminum. The aromaticity of the cyclopentadienyl ring has been shown to cause considerable anisotropic upfield shifting of the $^{27}$Al NMR signals in other cyclopentadienyl aluminum compounds.$^{23,24}$ We attribute the anomalous trend in chemical shifts observed here to the greater electron delocalization in the cyclopentadienyl rings of three-coordinate cyclopentadienylnitrogen complexes. This delocalization is apparent in the carbon–carbon bond lengths of the Cp rings in the crystal structures of CpAlMe and CpaAl. By contrast, more localized, diene type bonding is reflected in the bond lengths of the cyclopentadienyl rings in the crystal structure of CpaAl(CN-t-Bu), in which the aluminum is clearly four-coordinate, tetrahedral.

Methyl-substituted tricyclopentadienylnitrogen compounds were prepared in an effort to slow down the motion of the rings on the aluminum in order to possibly "freeze out" the ground-state structure on the NMR time scale and identify the mechanism of the averaging along with an activation barrier for the process. By placing methyl groups on the rings, we hoped to sterically impede the traversal of the aluminum about the cyclopentadienyl ring. With this goal in mind, we first prepared (Me$_5$C$_5$H$_3$)$_2$Al(2), in the same manner as 1, by reacting 1.5 equiv of 1,1-dimethylmagnesocene with trichloroaluminum. The compound was isolated as a light yellow oil. Its noncrystalline nature is possibly due to the presence of minor CpAl impurities in the product which are carried over from the small CpH contamination in the methylcyclopentadiene. As with the parent compound, an averaged $^1$H NMR spectrum was observed for a toluene-$d_6$ solution of 2 down to $-90 \, ^\circ$C in a 300 MHz magnetic field. In this case, the averaged spectrum consists of a single resonance at $\delta 2.2$ due to the methyl group and an AA$^1$BB$^2$ pattern at $\delta 5.5$, 5.9 for the protons on the cyclopentadienyl ring. This result is not surprising since the aluminum need only migrate back and forth between the two unsubstituted ring carbons $\gamma$ to the methyl-substituted carbon (carbons 3 and 4) in order to achieve this averaging effect without ever having to traverse the methyl-substituted ring carbon. Three methyl substituents in the 1, 2, and 4 positions of the cyclopentadienyl ring are necessary if the aluminum is to be required to migrate over a methyl-substituted ring carbon to achieve this averaging via a 1,2-element shift mechanism. We therefore prepared (1,2,4-C$_5$Me$_5$H$_3$)$_2$Al (3) in order to study its dynamic behavior in solution by $^1$H and $^{13}$C NMR spectroscopy.

**Synthesis, Molecular Structure, and Solution NMR Properties of (1,2,4-C$_5$Me$_5$H$_3$)$_2$Al (3).** Tris-(1,2,4-trimethylcyclopentadienylnitrogen)aluminum (3) was prepared in the same manner as the other tricyclopentadienylnitrogen compounds by using (1,2,4-C$_5$Me$_5$H$_3$)$_2$Mg

![Figure 3. ORTEP drawing of the molecular structure of (1,2,4-C$_5$Me$_5$H$_3$)$_2$Al (3). Thermal ellipsoids are shown at the 50% probability level.](image-url)
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Tricyclopentadienylaluminum Compounds

The preparation of 4 along with its unique insertion chemistry with t-butyl isocyanide was reported earlier.\(^{(27)}\) Since that report, the X-ray crystal structure of the compound has been determined. A discussion of the overall molecular geometry is worthwhile for purposes of comparison with the structures of the other homoleptic cyclopentadienylaluminum compounds described herein. As can be seen from the ORTEP drawing in Figure 4, each of the cyclopentadienyl rings coordinate aluminum in an \(\eta^5\)-fashion. Presumably the additional sterics due to tetramethyl substitution of the cyclopentadienyl rings favor an \(3 \times \eta^1\) geometry over the \(2 \times \eta^1, \eta^5\) geometry exhibited by compound 3. Selected bond lengths and angles are listed in Table 4. Given the poor refinement of the structure due to the weakly diffracting nature of the crystal, the bond lengths are of limited value for interpreting the nature of the bonding in the molecule. In this respect, bond angles are more reliable for they are more sensitive to changes in orbital hybridizations. Therefore, it is noteworthy that the C(11)-C(15) ring plane forms an 87.0° angle with the Al-C(15) vector as compared to the other rings, for which the corresponding angles to the aluminum are 104.1 and 103.1°. Whereas C(11) and C(14) are more distant by ca. 0.3-0.4 Å, the narrower angle might be viewed either as an approach toward \(\eta^4\) coordination that exhibited in the solid-state structures of [Cp*Al(R)Cp\(_2\)] \(^{(30)}\) or as a \(\sigma\)-type interaction between an unhybridized \(p\) orbital on C(15) and Al. In any case, the greater steric bulk of the rings leads to greater ring slippage in addition to conferring a greater reactivity to the complex, which, unlike Cp3Al, inserts tert-butyli isocyanide.\(^{(27)}\)

The \(^1\)H NMR spectrum of the compound in toluene-\(d_8\) exhibits two resonances for the ring methyls which remain unchanged down to \(-90^\circ\) C. In this case, the spectrum of a rigid species would be indistinguishable from the averaged spectrum of a fluxional species.\(^{(27)}\)

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for 3

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<td>C(20)-C(21)</td>
<td>1.354(5)</td>
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Table 4. Selected Bond Lengths (Å) and Angles (deg) for 4

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<th>Bond</th>
<th>Length (Å)</th>
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<td>C(34)-C(35)</td>
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<tr>
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Figure 4. ORTEP drawing of the molecular structure of \((C_5Me_5H)_3Al\) (4). Thermal ellipsoids are shown at the 30% probability level.
however, in all likelihood, compound 4 is highly fluxional like the others. The $^{27}$Al chemical shift for 4 of δ 64 is consistent with the chemical shifts exhibited by the other tricyclopentadienylaluminum compounds. The $^{27}$Al chemical shift for (η$_1^\text{-}C_5\text{Me}_5\text{H}_5)$Al(C(=N-t-Bu)C-
(N-t-Bu)(C_5\text{Me}_5\text{H}_5)) was originally assigned incorrectly$^{27}$ and is actually δ 150. Again, we find that the three-coordinate aluminum atom resonates at a higher field than the four-coordinate aluminum atom.

Interestingly, we have been unable to prepare Cp*Al by reacting decamethylmagnesocene with aluminum chloride. Instead, only one Cp* ring can be transferred to the aluminum in this manner to produce (Cp*AlCl)$_2$, which has been characterized previously.$^{32}$ We have encountered a similar problem with steric in our preparation of [(C_5\text{Me}_5\text{H}_5)(Cl)(μ-O-Pr)]$_2$ instead of the corresponding dicyclopentadienylaluminum compound, from the reaction of (C_5\text{Me}_5\text{H}_5)Mg and dichloroaluminum isopropoxide. It appears that the strong alkoxide and chloride bridges in these compounds interfere with further replacement of the chloride ligands by the bulkier cyclopentadienyl ligands. From steric considerations alone, Cp*Al should be separable since gallium has been shown to support three Cp* rings in Cp*Ga, which was prepared by reacting NaCp* with GaCl$_3$. In order to explore the possibility that a greater thermodynamic driving force for the cyclopentadienyl ligand for chloride ligand metathesis is necessary to overcome the stability of the bridged aluminum species, we have recently carried out the reaction of AlCl$_3$ and 3 equiv of Cp*Na, from which we cleanly obtain a white, crystalline solid which we presently formulate as Cp*Al.$^{36}$ Further characterization of this material is in progress.

**Theoretical Calculations.** Since we found the balance between different ring hapticities to be so delicate for cyclopentadienylaluminum compounds, and since we were unable to assess the nature of the ring motion in these compounds by examining their solution $^1$H and $^{13}$C NMR spectra at low temperatures, theoretical calculations at the ab initio level (RHF/3-21G(*), RHF/6-31G*, and MP2/6-31G*) were undertaken on model compounds in order to determine the energy profiles of these compounds with respect to ring hapticity and to assess the nature of the metal—ring bonding in these compounds.

In this study, we first concentrated on the simplest model compound, CpAlH$_2$. We then looked at the effect of adding alkyl substituents to the cyclopentadienyl ring and replacing the hydride ligands with alkyl groups. The structures of some di- and tricyclopentadienylaluminum compounds were examined as well. By comparing the results of these calculations with experimental data acquired by ourselves and others, we have developed a general picture of the bonding between cyclopentadienyl ligands and aluminum.

**Calculated Structures and Potential Energy Surface for Ring Slippage in Various Model Compounds.**

(35) P.J.S., University of Idaho, unpublished results.

**Figure 5.** Cp—Al bonding arrangements.

<table>
<thead>
<tr>
<th>CpAlH$_2$, RHF/3-21G(*)</th>
<th>GaAlH$_4$, MP2/3-21G*</th>
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<tr>
<td>CpAlMe$_2$, RHF/3-21G(*)</td>
<td>Cp<em>AlMe$_2$, RHF/3-21G(</em>)</td>
</tr>
</tbody>
</table>

**Figure 6.** Perpendicular Cp—Al ring distance in CpAlH$_2$, CpAlMe$_2$, and Cp*AlMe$_2$ as a function of ring slippage. The ring slippage coordinate is arbitrarily set at 0.0 Å for $\eta^3$ geometry.

**pounds.** Assigning hapticities to cyclopentadienylaluminum compounds can be somewhat dubious. Classically, ligand hapticity has referred to the number of atoms of the ligand directly bound to the metal. With “slipped” cyclopentadienyl ligands, this definition becomes problematic since bonding to each of the carbons of the ring becomes a matter of degree as opposed to an absolute distinction between coordinated vs noncoordinated atoms. For the purposes of this report it is most convenient to use the perpendicular projection of the aluminum atom onto the ring plane. Figure 5 illustrates several possible types of metal—ring bonding using such a projection. While we will not attempt to distinguish between $\eta^1$ and $\sigma$ interactions or between $\eta^1$ and $\eta^5$ geometries, the classification of the compounds within the remaining categories is obvious.

Ring slippage paths for CpAlH$_2$, CpAlMe$_2$, and Cp*AlMe$_2$ were calculated by sliding the projection of the Al atom on the ring plane along the bisector of a CCC angle in a manner similar to that used by Hoffmann and co-workers to calculate the transits of different main-group and transition metal fragments across a cyclopentadienyl ring.$^{11}$ This means that only two degrees of freedom were fixed for each point. The slippage path for CpAlH$_2$ was calculated at the RHF/3-21G(*) and MP2/6-31G*$^*$ levels. Paths for CpAlMe$_2$ and Cp*AlMe$_2$ were only calculated at the RHF/3-21G(*) level, and the MP2/6-31G*—RHF/3-21G(*) energy difference for CpAlH$_2$ was then added as a correction.

During movement of the AlH$_2$ moiety over the ring, the perpendicular metal—ring distance does not vary much, remaining between 1.89 and 2.02 Å over the whole range of $\eta^1$—$\eta^5$ structures. Figure 6 shows this variation as a function of ring slippage and also contains the corresponding values for CpAlMe$_2$ and Cp*AlMe$_2$. The ring geometry also remains fairly constant during slippage. Some localization occurs when the bonding becomes truly $\sigma$, but in the $\eta^1$—$\eta^5$ range the cyclopentadienyl ring remains a nearly symmetrical pentagon. It is clear that a description in terms of traditional valence structures for $\eta^3$ (A) or $\eta^5$ (B) is inappropriate (Figure 7).

Calculated potential energy surfaces for the transit of the AlH$_2$ moiety over the ring are shown in Figure 6.
Figure 8. (a) Energy profile for ring slippage in CpAIH₂ at RHF/3-21G(*) and MP2/6-31G*. (b) Energy profiles for ring slippage of CpAlH₂, CpAlMe₂, and Cp*AlMe₂ at MP2/6-31G* (estimated). The ring slippage coordinate is arbitrarily set at 0.0 Å for an r² geometry.

The potential energy surface for ring slippage is very flat, allowing for essentially free movement of the AIH₂ moiety over the ring. The effects of both basis set improvement (3-21G(*) to 6-31G*) and correlation correction (RHF to MP2) on the energy profile were small. Correlation corrections stabilized the r² structure somewhat relative to the r² and r² structures. Comparison of the energy curves in Figure 8 shows that the range of easily accessible structures is similar at the two levels of theory. This is an important conclusion, for it implies that describing a cyclopentadienyl group does not require very sophisticated theoretical methods, even when one has to consider ring-slippage phenomena. The well-known difficulties of an RHF description for compounds such as ferrocene and correlation effects of the metal d-electrons rather than a deficiency in the description of the cyclopentadienyl ligand.

The potential-energy surfaces for ring slippage in CpAlMe₂ and Cp*AlMe₂ are compared with that of CpAlH₂ in Figure 8. The potential-energy profiles of the dimethylaluminum derivatives are, likewise, very shallow and indicate that there is little chance of freezing out ring motion by low-temperature, solution NMR methods.

This leaves us with the question of how to describe the metal–ring bonding. Even though a purely ionic model would have a rather flat deformation potential and a constant ring geometry like that obtained in the calculations described above, truly ionic cyclopentadienides such as the alkali metal salts invariably prefer r² structures. Furthermore, the AlH₂ moiety has a very pronounced rotational preference (in which the AlH₂ plane bisects the ring) for each position above the cyclopentadienyl ring. Such an orientational preference would not be expected for an ionic cyclopentadienyl–Al interaction.

On the other hand, a purely covalent description would result in a definite hapticity preference as determined by a simple electron-counting rule (the 8-electron rule, comparable to the 18-electron rule in transition metal chemistry). In the present case, this would imply a definite preference for an r² or r² geometry, with an r² geometry much higher in energy. On the basis of electron counting alone, an r¹ geometry should also be less favorable, although it should be stabilized relative to r² and r² by the large s/p energy difference for aluminum.

Apparently the ionic and covalent interactions between a cyclopentadienyl ring and aluminum are very delicately balanced, resulting in a flat potential over the whole range of r²–r² structures. A similar flexibility in the bonding profile has been experimentally and theoretically determined for beryllocene, there being at most an 11 kJ mol⁻¹ difference in energy between the various possible haptotropes. Cyclopentadienylzinc compounds, likewise, have been found to exhibit this so-called peripheral type of bonding involving a delicate balance of covalent and ionic interactions.

Effect of Ring-Methyl Groups on Geometry.

Introduction of methyl substituents on the ring destabilizes r² and r² structures which have the Al atom near a methyl group. Thus, for (1,2-Me₂C₅H₃)AlH₂ at 3-21G*(−), isomer B (Figure 9) is 2 kcal/mol less stable than A, and C is not even a local minimum, reverting to an r² structure (with the Al atom away from the methyl groups) without a barrier. This must be partly a steric effect since the methyl groups bend back farther from the ring plane than the hydrogens to reduce steric repulsion with the adjacent aluminum fragment. The electronic factor would be due to the electron-donating methyl groups destabilizing the concentration of negative charge in the region occupied by the Al atom. This would explain the 3 × r² geometry exhibited in the solid.

begins to show some preference for the element, and the electronegativity difference is expected to be facile in this system. While there is some discrepancy between the combination of ring hapticities in the calculated structure and the two molecular geometries characterized in the crystal structure of the compound, the calculated metal—ring distances (2.014 and 2.027 Å) show reasonable agreement with the observed values (2.014 and 2.027 Å).

The two Cp₂Al compounds prefer \( \eta^3/\eta^1 \) (at RHF/3-21G*) or \( \eta^2/\eta^1 \) (at RHF/6-31G*) structures; barriers for haptotropic shifts were not determined but are expected to be very small. These calculated geometries are in fairly close agreement with the \( 2 \times 2 \eta^2 \) geometry crystallographically characterized for Cp₂AlMe. The calculated metal—ring distances (2.061 and 2.064 Å) show reasonable agreement with the observed distances (2.014 and 2.027 Å).

Cp₂Al prefers an \( \{\eta^2, 2 \times \eta^1\} \) structure at both RHF/3-21G(*) and RHF/6-32G* levels. Again, ring slippage is expected to be facile in this system. While there is some discrepancy between the combination of ring hapticities in the calculated structure and the two molecular geometries characterized in the crystal structure of the compound, the calculated metal—ring distances (1.91—2.03 Å) show reasonable agreement with the observed distances (2.014 and 2.027 Å).

The variation in reactivity exhibited by these cyclopentadienylaluminum compounds is also noteworthy. The small-molecule insertion chemistry of \( \text{MeCpHA} \) contrasts remarkably with the behavior of the parent compound, Cp₂Al, which forms only adducts with these molecules, and undoubtedly arises from the steric strain in the molecule produced by the bulky tetramethylcyclopentadienyl rings. This aspect of cyclopentadienylaluminum chemistry in particular merits further exploration since it could lead to novel applications of these compounds to organic synthesis and catalysis, two areas in which organoaluminum compounds have been found to be especially useful.

**Experimental Section**

**General Considerations.** All manipulations were performed using a combination of glovebox, high-vacuum, or Schlenk techniques. Solvents were distilled under nitrogen over sodium benzophenone ketyl (toluene) or CaH₂ (petroleum ether). The solvents were then stored in line-pots from which they were vacuum transferred from sodium benzophenone ketyl (toluene) or CaH₂ (petroleum ether). Benzene-de, toluene-d₅, CDCl₃, and CD₂Cl₂ were dried over activated 4 Å molecular sieves. Argon was purified by passage over oxy tower BASF catalyst (Aldrich) and 4 Å molecular sieves. Aluminum trichloride (Aldrich) was sublimed prior to use. Freon 11 (Aldrich) was used as received. Dicyclopentadiene and methylcyclopentadiene dimer were cracked under nitrogen and stored at –70 °C prior to use. Magnesocene was prepared as described in the literature.\(^{42}\) \(^{1,12}\) 1,1’-Dimethylmagnesocene and bis(1,2,4-trimethylcyclopentadienyl)magnesium were prepared in the same manner from the corresponding methyl-substituted cyclopentadienes. Tris(1,2,3-tetramethylcyclopentadienyl)aluminum was prepared as described previously.\(^{27}\)

NMR spectra were recorded on an IBM NR-300 (300.1 MHz \( ^1\text{H} \), 75.4 MHz \( ^13\text{C} \), 78.2 MHz \( ^27\text{Al} \)) and an IBM NR-200 (200.1 MHz \( ^1\text{H} \), 50.8 MHz \( ^13\text{C} \), 52.1 MHz \( ^27\text{Al} \)). All chemical shifts are reported in ppm and referenced to solvent \( ^1\text{HCl} \) or \( ^3\text{HCl} \) (41) Eisch, J. J.; Sanchez, R. C. Organometallics, Vol. 16, No. 5, 1997, 878.

Al(OH)₃ (27Al, external reference, δ 0 ppm). Elemental analyses were determined by Desert Analytics (Tucson, AZ). Mass spectrometry data was acquired at Washington State University’s mass spectrometry facilities.

Theoretical Methods. All calculations were of the all-electron closed-shell restricted Hartree–Fock type and were carried out using the GAMESS program on an SP2 workstation. All structures were optimized at the RHF/3-21G(*) and the MP2/6-31G* levels. Paths for CpAlMe₂ were calculated at the RHF/3-21G(*) level, and CpAlMe₂ was studied at MP2/6-31G*. All structures mentioned in the text were fully optimized as minima or saddle points. Ring slippage paths for CpAlH₂, CpAlMe₂, and Cp₂AlMe₂ were calculated by sliding the projection of the Al atom on the ring plane along the bisector of a CCC angle. This methodology was only used to generate data for comparison with other similar cases.

NMR (CDCl₃): δ 5.9 (s, C₅-H), 13C NMR (CDCl₃): δ 112.0 (C₅-H). Anal. Calcd for C₅H₅Al₂: C, 81.0; H, 6.6. Found: C, 81.0; H, 6.6. (C₅H₅)AlMe (2). Compound 2 was prepared in the same manner as described above for 1, except that (C₅H₅)AlMe₂ (2.83 g, 21.2 mmol) was combined with Alda (2.83 g, 21.2 mmol). The product was isolated as a yellow oil. Yield: 2.40 g, 42.8%. 1H NMR (CDCl₃): δ 5.5, 5.9 (m, C₅H₅), 2.1 (s, CH₃). Anal. Calcd for C₅H₅AlMe: C, 82.7; H, 9.3. Found: C, 82.8; H, 9.3. (1,2,4-Me₃C₅H₂)₃Al (3). Compound 3 was prepared in the same manner as described for 1. The reaction of (1,2,4-Me₃C₅H₂)₃AlMe (2.42 g, 10.2 mmol) and AlCl₃ (0.91 g, 6.8 mmol) afforded 2 as a pale orange oil after removal of the toluene. Dissolution of the oil in 50 mL of petroleum ether and cooling the solution at −60 °C afforded a white, microcrystalline solid. Yield: 1.89 g, 57%. 1H NMR (CDCl₃): δ 4.28 (s, 2, CH₃). 13C NMR (CDCl₃): δ 128.5, 129.3, 129.9 (C₅(CH₃)₃). 27Al NMR (CDCl₃): δ 65. Anal. Calcd for C₅H₅Al: C, 82.7; H, 9.3. Found: C, 82.8; H, 9.3.

Crystal Structure Determinations of Cp₃Al (1) and (1,2,4-Me₃C₅H₂)₃Al (3). Long, yellow, needle-shaped crystals of 1 were grown from a petroleum ether solution cooled at −78 °C. Block-shaped crystals of 3 were grown from a toluene solution cooled at −78 °C. Suitable crystals were selected and mounted in thin-walled, nitrogen-flushed, glass capillaries. The unit-cell parameters for each compound were obtained by the least-squares refinement of 120 reflections.

Data were collected using a Siemens SMART CCD (charge-coupled device) based diffractometer equipped with an LT-2 low-temperature apparatus operating at 273 K. Data were measured using ω scans of 0.3° per frame for 30 s, such that a hemisphere was collected. A total of 3561 independent reflections were collected for the crystal of 1 and 2717 independent reflections for the crystal of 3. The first 50 frames were rechecked to determine the data collection efficiency for decay. Cell parameters were determined using SMART software (V. 4.043, Siemens Analytical Instruments Division, Madison, WI, 1995) and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software (V. 4.035, Siemens, 1995), which corrects for Lp and decay. Absorption corrections were applied using XEPI, which is supplied by Siemens in their SHEXL-PC software. The structures were solved by the direct method using the SHELX-90 program (Sheldrick, G. M. University of Göttingen, Germany, 1986) and refined by least-squares methods on F². The structures were solved by the direct method using the SHELX-90 program (Sheldrick, G. M. University of Göttingen, Germany, 1986) and refined by least-squares methods on F². All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions.

The systematic absences in the diffraction data were uniquely consistent for the assigned space groups. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-square procedures on F². All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHEXL-XL (5.3) program library.

Acknowledgment. We are grateful to the National Science Foundation for supporting this work through Grant No. CHE-9320407. The establishment of the Single-Crystal X-ray Diffraction Laboratory at the University of Idaho was supported by the NSF-Idaho EPSCoR Program, the National Science Foundation, and the M. J. Murdock Charitable Trust of Vancouver, WA. We also thank Dr. Gary Knerr of the University of Idaho for his assistance in acquiring NMR data.

Supporting Information Available: Details of the structure determinations, including listings of atomic coordinates, thermal parameters, and bond distances and angles, and a table providing structural details for RHF/3-21G(*) and RHF/6-31G(*) optimized structures of Cp₃AlH, Cp₃AlMe, and Cp₃Al (20 pages). Ordering information is given on any current masthead page.