

Regarding the Structures and Fluxionality of Tricyclopentadienylaluminum Compounds

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Received November 29, 1996[⊗]

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**), (MeC₅H₄)₃Al (**2**), (1,2,4-Me₃C₅H₂)₃Al (**3**), (1,2,3,4-Me₄C₅H)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 { η^2 , $\eta^{1.5}$, $\eta^{1.5}$ } combination of ring geometries and the other with an { η^2 , $\eta^{1.5}$, η^1 } combination of ring-coordination geometries. In the crystal structure of compound **3**, one cyclopentadienyl ring is coordinated η^5 to the aluminum while the other two rings are η^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 °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 (η^1 , η^2 , η^3 , η^5).

Introduction

The cyclopentadienyl ligand is probably best known for its pentahapto-coordination geometry with transition metals. In the absence of accessible d orbitals, π -type interactions are weaker, and deviation from η^5 -geometry by “ring slippage” is often observed. These “ring-slipped” (η^1 , η^2 , η^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 σ -bonded (η^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 η^1 but $\eta^{1.5}$, η^2 , or η^3 , 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 elec-

tron diffraction data on CpAlMe₂ (Cp = C₅H₅) 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 $\eta^1 \leftrightarrow \eta^5$ haptotropic shifts, to compete with the traditional fluxional behavior of σ -cyclopentadienyl compounds. X-ray crystal structures of the homoleptic cyclopentadienylaluminum compounds Cp₃Al, (1,2,4-Me₃C₅H₂)₃Al, and (1,2,3,4-Me₄C₅H)₃Al 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 tetramethylcyclopentadienyl rings in (1,2,3,4-Me₄C₅H)₃Al exhibit a monohapto-coordination geometry, higher ring hapticities are seen for Cp₃Al, and in the structure of (1,2,4-Me₃C₅H₂)₃Al, we have characterized, for the first time, η^1 and η^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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⊗ Abstract published in *Advance ACS Abstracts*, February 1, 1997.

(1) Jutzi, P. *Adv. Organomet. Chem.* **1986**, *26*, 217.

(2) Jutzi, P. *J. Organomet. Chem.* **1990**, *400*, 1.

(3) Jutzi, P. *Pure Appl. Chem.* **1990**, *62*, 1035.

(4) Jutzi, P. *Chem. Rev.* **1986**, *86*, 983.

(5) Bennett, M. J., Jr.; Cotton, F. A.; Davison, A.; Faller, J. W.; Lippard, S. J.; Morehouse, S. M. *J. Am. Chem. Soc.* **1966**, *88*, 4371.

(6) Cotton, F. A. *J. Am. Chem. Soc.* **1967**, *89*, 6136.

(7) Cotton, F. A. *Acc. Chem. Res.* **1968**, *1*, 257.

(8) Cotton, F. A.; Hunter, D. L.; Jamerson, J. D. *Inorg. Chem. Acta* **1975**, *15*, 245.

(9) Drew, D. A.; Haaland, A. *Acta Chem. Scand.* **1973**, *27*, 3735.

(10) Gropen, T.; Haaland, A. *J. Organomet. Chem.* **1975**, *92*, 157.

(11) Trong Anh, N.; Elian, M.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 110.

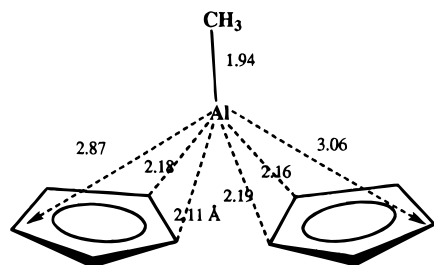


Figure 1. Molecular structure of $(\eta^2\text{-C}_5\text{H}_5)_2\text{AlMe}$ with selected distances between atoms (Å).

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 $\text{Cp}_2\text{AlMe}^{12}$ (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 Cp_2AlMe offered the first solid-state characterization of an η^2 -coordinated cyclopentadienyl ring on aluminum.

A similar η^2 -Cp coordination geometry was invoked as the best model for the gas-phase electron diffraction pattern for CpAlMe_2 .⁹ CNDO/2 and *ab initio* calculations performed by Gropen and Haaland on CpAlMe_2 and CpAlH_2 ,¹⁰ respectively, and extended Hückel calculations performed by Hoffmann and co-workers on isoelectronic CpCH^{2+} ¹¹ predict an η^2 -Cp to be the preferred ground-state geometry in these species; however, a geometry with an η^1 -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 $\eta^1 \leftrightarrow \eta^5$ haptotropic shift, might be involved, 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, Cp_3Al .

Results and Discussion

Synthesis, Molecular Structure, and Solution NMR Properties of Cp_3Al (1). Earlier we reported a

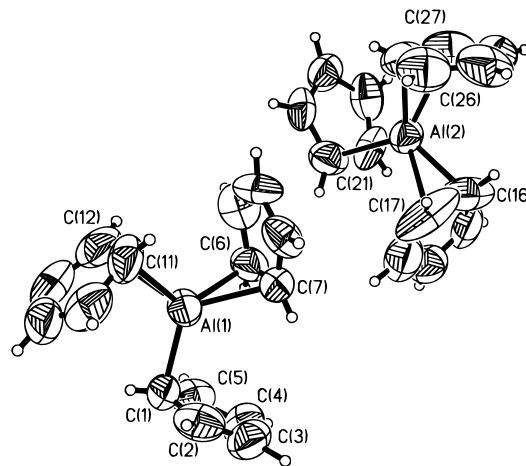
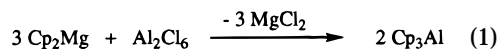


Figure 2. ORTEP drawing of the two independent molecules in the structure of Cp_3Al (1). Thermal ellipsoids are shown at the 50% probability level.

new, convenient synthetic route to Cp_3Al 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 Cp_3Al 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 Cp_3Al 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 η^2 -geometries. In one molecule, two rings are coordinated in more of an $\eta^{1.5}$ 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 2.32(2) and 2.304(10) Å, respectively. The third ring approaches more of an η^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 $\text{Cp}_3\text{-Al}$ structure exhibits more of an $\{\eta^2, \eta^{1.5}, \eta^1\}$ combination of ring geometries about the aluminum atom. The Al-nearest carbon distances in the η^2 ring are 2.106(7) and 2.161(7) Å. The $\eta^{1.5}$ ring exhibits Al-nearest carbon distances of 2.047(7) and 2.324(9) Å. Although the third ring may be regarded as η^1 , 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

(12) Fisher, J. D.; Wei, M.-Y.; Willett, R.; Shapiro, P. J. *Organometallics* **1994**, *13*, 3324.

Table 1. Crystallographic Data for Cp₃Al (1), (Me₃C₅H₂)₃Al (3), and (Me₄C₅H)₃Al (4)

	Cp ₃ Al (1)	(Me ₃ C ₅ H ₂) ₃ Al (3)	(Me ₄ C ₅ H) ₃ Al (4)
cryst syst	monoclinic	orthorhombic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 1
<i>a</i> (Å)	13.5042(8)	8.734(1)	9.301(5)
<i>b</i> (Å)	10.9653(7)	15.506(2)	10.363(6)
<i>c</i> (Å)	17.3152(7)	15.891(2)	14.810(8)
α (deg)	90	90	99.59(3)
β (deg)	96.914(2)	90	99.95(3)
γ (deg)	90	90	114.30(3)
<i>V</i> (Å ³)	2545.3(2)	2152.1(5)	1235.7(8)
<i>Z</i>	8	4	2
<i>T</i> (K)	299	233	298
λ (Å)	0.701 73 (Mo Kα)	0.701 73 (Mo Kα)	0.701 73 (Mo Kα)
ρ _{calcd} (g/cm ³)	1.160	1.076	1.054
μ (mm ⁻¹)	0.129	0.098	0.092
transm factors (max, min)	0.903, 0.606	0.993, 0.866	none
<i>R</i> (<i>F</i>) ^a	0.0959 (<i>F</i> > 2σ(<i>F</i>))	0.0474 (<i>F</i> > 2σ(<i>F</i>))	0.1298 (<i>F</i> > 4σ(<i>F</i>))
w <i>R</i> (<i>F</i> _o ²) ^b	0.1604	0.1018	0.1437

^a *R* = Σ|*F*_o - *F*_c|/Σ|*F*_o|. ^b w*R* = {[Σw(*F*_o - *F*_c)²]/[Σw(*F*_o)²]}^{1/2}; w = 1/σ²(*F*_o)² + (*xP*)² + (*yP*)², where *P* = (*F*_o² + 2*F*_c²)/3.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1

Al(1)–C(1)	2.016(7)	Al(1)–C(11)	2.047(7)
Al(1)–C(7)	2.106(7)	Al(1)–C(6)	2.161(7)
Al(1)–C(12)	2.324(9)	C(1)–C(2)	1.41(1)
C(1)–C(5)	1.43(1)	C(2)–C(3)	1.34(1)
C(3)–C(4)	1.35(1)	C(4)–C(5)	1.36(1)
C(6)–C(10)	1.37(1)	C(6)–C(7)	1.41(1)
C(7)–C(8)	1.382(9)	C(8)–C(9)	1.35(1)
C(9)–C(10)	1.35(1)	C(11)–C(15)	1.40(1)
C(11)–C(12)	1.40(1)	C(12)–C(13)	1.33(1)
C(13)–C(14)	1.33(1)	C(14)–C(15)	1.36(1)
Al(2)–C(16)	2.05(1)	Al(2)–C(22)	2.092(7)
Al(2)–C(26)	2.093(9)	Al(2)–C(21)	2.192(7)
Al(2)–C(27)	2.30(1)	Al(2)–C(17)	2.32(2)
C(16)–C(17)	1.34(2)	C(16)–C(20)	1.36(1)
C(17)–C(18)	1.33(2)	C(18)–C(19)	1.35(1)
C(19)–C(20)	1.33(1)	C(21)–C(25)	1.377(9)
C(21)–C(22)	1.40(1)	C(22)–C(23)	1.38(1)
C(23)–C(24)	1.37(1)	C(24)–C(25)	1.33(1)
C(26)–C(30)	1.38(1)	C(26)–C(27)	1.38(1)
C(27)–C(28)	1.36(1)	C(28)–C(29)	1.34(2)
C(29)–C(30)	1.37(1)		
C(5)–C(1)–Al(1)	104.5(5)	C(15)–C(11)–Al(1)	102.3(6)
C(10)–C(6)–Al(1)	103.3(5)	C(20)–C(16)–Al(2)	104.2(6)
C(13)–C(12)–Al(1)	105.3(6)	C(18)–C(17)–Al(2)	107.1(9)
C(2)–C(1)–Al(1)	94.7(5)	C(25)–C(21)–Al(2)	99.7(5)
C(8)–C(7)–Al(1)	103.2(5)	C(28)–C(27)–Al(2)	107.8(7)
C(5)–C(1)–Al(1)	104.5(5)	C(23)–C(22)–Al(2)	100.4(6)
C(10)–C(6)–Al(1)	103.3(5)	C(30)–C(26)–Al(2)	106.1(6)
C(13)–C(12)–Al(1)	105.3(6)		

of (η¹-Cp)₃Al(CN-*t*-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 3 × η¹ (i.e. {η¹, η¹, η¹}) Cp coordination geometry in the solid state. The geometrical parameters, Ga–αC 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 attribut-

able to the slightly smaller covalent radius and higher electronegativity of the gallium. Indium, 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 η⁵-coordination geometry with two of its four coordinated cyclopentadienyl rings.

Like its heavier group 13 congeners, **1** is highly fluxional. An averaged signal for the rings is observed at δ 6.1 in 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 η^{1.5} and η²-Cp 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 1,2-shifts as a viable mechanism for this averaging. The tetracoordinate aluminum compound Cp₃Al(CN-*t*-Bu)¹² is, likewise, highly fluxional and exhibits averaged ¹H and ¹³C NMR spectra in toluene-*d*₈ 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 118.¹² This downfield shifting of ²⁷Al NMR resonances for the tetracoordinate cyclopentadienylaluminum compounds relative to tricoordinate 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 {η³, η¹, η¹} combination of ring geometries.^{16,17} 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

(13) Beachley, O. T., Jr.; Getman, T. D.; Kirss, R. U.; Hallock, R. B.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1985**, *4*, 751.

(14) Einstein, F. W. B.; Gilbert, M. M.; Tuck, D. G. *Inorg. Chem.* **1972**, *11*, 2832.

(15) Atwood, J. L.; Smith, K. D. *J. Am. Chem. Soc.* **1973**, *95*, 1488.

(16) Benn, R.; Janssen, E.; Lehmkuhl, H.; Rufinska, A. *J. Organomet. Chem.* **1987**, *333*, 155.

(17) Scherer, M.; Kruck, T. *J. Organomet. Chem.* **1996**, *513*, 135.

may be too simplistic for cyclopentadienylaluminum complexes, in which the degree of electron delocalization in the rings should have a 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 cyclopentadienylaluminum compounds.^{21,22} We attribute the anomalous trend in chemical shifts observed here to the greater electron delocalization in the cyclopentadienyl rings of three-coordinate cyclopentadienylaluminum compounds. This delocalization is apparent in the carbon-carbon bond lengths of the Cp rings in the crystal structures of Cp_2AlMe and Cp_3Al . By contrast, more localized, diene type bonding is reflected in the bond lengths of the cyclopentadienyl rings in the crystal structure of $\text{Cp}_3\text{Al}(\text{CN}-t\text{-Bu})$, in which the aluminum is clearly four-coordinate, tetrahedral.

Methyl-substituted tricyclopentadienylaluminum 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 $(\text{MeC}_5\text{H}_4)_3\text{Al}$ (**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 ^1H NMR spectrum was observed for a toluene- d_8 solution of **2** down to -90°C in a 300 MHz magnetic field. In this case, the averaged spectrum consists of a single resonance at δ 2.2 due to the methyl group and an AA'BB' pattern at δ 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 γ 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 $(1,2,4\text{-C}_5\text{Me}_3\text{H}_2)_3\text{Al}$ (**3**) in order to study its dynamic behavior in solution by ^1H and ^{13}C NMR spectroscopy.

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

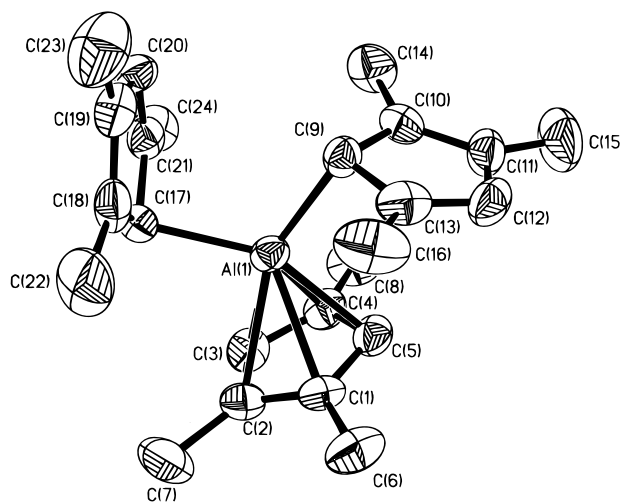


Figure 3. ORTEP drawing of the molecular structure of $(1,2,4\text{-C}_5\text{Me}_3\text{H}_2)_3\text{Al}$ (**3**). Thermal ellipsoids are shown at the 50% probability level.

as our ring-transfer reagent. Despite the presence of three methyl substituents on the cyclopentadienyl rings, aluminum migration in this compound was again too rapid to show any perceptible broadening of the averaged ^1H and ^{13}C NMR spectra down to -110°C in a 300 MHz magnetic field. The averaged ^1H NMR spectrum in 50:50 $\text{CD}_2\text{Cl}_2/\text{Freon-11}$ consists of two peaks in a 2:1 ratio at δ 1.87 and 1.92, respectively, assigned to the methyl groups and a single peak at δ 4.72 due to the cyclopentadienyl ring protons. The corresponding ^{13}C spectrum exhibits peaks at δ 12.7 and 15.1 from the methyl groups and δ 99.5, 115.0, and 119.5 from the cyclopentadienyl ring carbons. The ^{27}Al NMR chemical shift for **3**, at δ 65, is shifted upfield of that for **1**, probably due to the more electron-donating nature of the trimethylcyclopentadienyl rings.

An X-ray structure of the compound offers a possible explanation for why the compound is still too fluxional to overcome the fast-exchange limit at low temperature in the ^1H and ^{13}C NMR solution spectra. The ORTEP drawing of the molecule is shown in Figure 3. A new combination of ring-coordination modes on the aluminum is now observed in which one of the rings is η^5 and the other two are η^1 to the aluminum. A similar combination of η^1 and η^5 rings has been characterized in beryllocene²³ and in some zirconocene structures.²⁴⁻²⁶ Selected bond lengths and angles for the structure are listed in Table 3. The η^5 ring is slightly tilted, with carbon atoms C(1), C(4), and C(5) canted toward the aluminum atom. The reason for this tilting is not immediately obvious; however, tilting of the η^5 ring has been characterized in the zirconocene complexes $[(\text{C}_3\text{H}_7)_4\text{-C}_5\text{H}_1_2\text{Zn}]^{25}$ and $(\text{C}_5\text{Me}_4\text{Ph})_2\text{Zn}^{24}$ and may perhaps be attributable to steric strain since tilting of the η^5 ring was not observed in the solid-state structure of beryllocene.²³ Presumably due to the presence of two different η^1 cyclopentadienyl rings on the aluminum, the crystallographic structure of **3** does not suffer from a

(18) Benn, R.; Rufinska, A.; Lehmkuhl, H.; Janssen, E.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 779.

(19) Benn, R.; Rufinska, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 861.

(20) Benn, R.; Janssen, E.; Lehmkuhl, H.; Rufinska, A.; Angermund, K.; Betz, P.; Goddard, R.; Krüger, C. *J. Organomet. Chem.* **1991**, *411*, 37.

(21) Fisher, J. D.; Shapiro, P. J.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1996**, *35*, 271.

(22) Dohmeier, C.; Schnöckel, H.; Robl, C.; Schneider, U.; Ahlrichs, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1655.

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

(24) Fischer, B.; Wijkens, P.; Boersma, J.; Kotten, G. v.; Smeets, W. J. J.; Budzelaar, P. H. M. *J. Organomet. Chem.* **1989**, *376*, 223.

(25) Burkey, D. J.; Hanusa, T. P. *J. Organomet. Chem.* **1996**, *512*, 165.

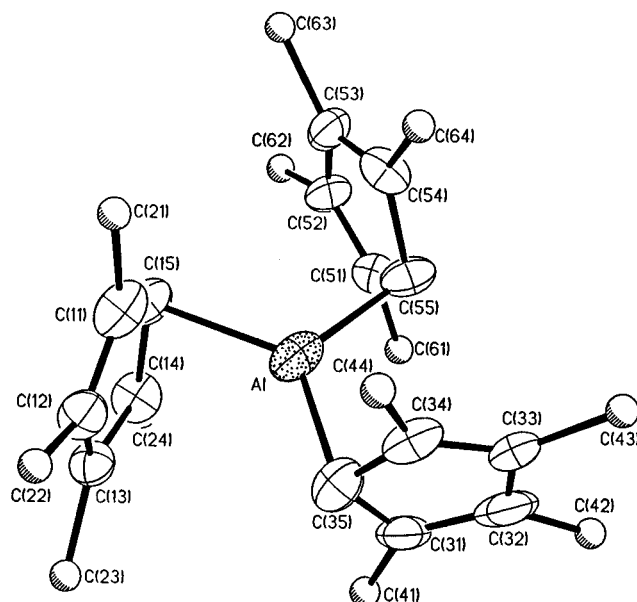
(26) Blom, R.; Boersma, J.; Budzelaar, P. H. M.; Fischer, B.; Haaland, A.; Volden, H. V.; Weidlein, J. *Acta Chem. Scand.* **1986**, *40*, 113.

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

Al(1)–C(17)	2.042(3)	Al(1)–C(1)	2.257(3)
Al(1)–C(5)	2.179(3)	Al(1)–C(3)	2.406(3)
Al(1)–C(4)	2.265(3)	C(1)–C(2)	1.406(5)
Al(1)–C(2)	2.409(3)	C(4)–C(5)	1.416(5)
C(1)–C(5)	1.427(5)	C(9)–C(13)	1.455(5)
C(2)–C(3)	1.403(5)	C(10)–C(11)	1.357(5)
C(3)–C(4)	1.417(5)	C(11)–C(12)	1.441(6)
C(9)–C(10)	1.464(4)	C(12)–C(13)	1.345(5)
C(11)–C(15)	1.507(6)	C(17)–C(18)	1.448(5)
C(17)–C(21)	1.481(5)	C(18)–C(19)	1.369(5)
C(21)–C(24)	1.492(5)	C(19)–C(20)	1.425(5)
Al(1)–C(9)	2.055(3)	C(20)–C(21)	1.354(5)
C(17)–Al(1)–C(9)	109.2(2)	C(10)–C(9)–Al(1)	105.3(2)
C(13)–C(9)–Al(1)	106.9(2)	C(18)–C(17)–Al(1)	103.8(2)
C(21)–C(17)–Al(1)	98.6(2)		

disordering of the rings with respect to their hapticity toward metal, a problem which was encountered with the structures of beryllocene and some of the zirconocene complexes. Thus, the pattern of C–C bond lengths in each of the cyclopentadienyl rings may be evaluated reliably. Whereas, the η^5 ring in **3** is still aromatic, exhibiting C–C bond lengths in the range of 1.405(3)–1.427(5) Å, the η^1 rings exhibit more localized, diene type structures. As in other structurally characterized cyclopentadienylaluminum compounds having mono-hapto-ring coordination,^{12,27} the aluminum resides at the allylic carbon of each of the η^1 rings. The arrangement of the rings on aluminum in the solid state suggests that an alternate fluxional mechanism may dominate the NMR signal averaging observed for **3**, one which involves each of the cyclopentadienyl rings rocking between η^1 and η^5 coordination to the aluminum. *Ab initio* calculations on model cyclopentadienylaluminum compounds (*vide infra*) indeed indicate that $\eta^1 \leftrightarrow \eta^5$ haptotropic shifts are as facile as 1,2-migrations in these systems. Molecular dynamics calculations performed by Blöchl and co-workers likewise indicate the contribution of very rapid 1,2 migrations and $\eta^1 \leftrightarrow \eta^5$ rearrangements to the fluxional mechanism of beryllocene.^{28,29} This similarity in the fluxional dynamics of cyclopentadienylaluminum and cyclopentadienylberyllium compounds is consistent with the diagonal relationship between aluminum and beryllium in the periodic table.

Molecular Structure of (C₅Me₄H)₃Al (4). 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 homo-leptic cyclopentadienylaluminum compounds described herein. As can be seen from the ORTEP drawing in Figure 4, each of the cyclopentadienyl rings coordinate the aluminum in an η^1 -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

**Figure 4.** ORTEP drawing of the molecular structure of (C₅Me₄H)₃Al (**4**). Thermal ellipsoids are shown at the 30% probability level.**Table 4. Selected Bond Lengths (Å) and Angles (deg) for 4**

Al–C(35)	1.99(1)	Al–C(55)	2.01(2)
Al–C(15)	2.09(1)	Al–C(14)	2.48(2)
Al–C(11)	2.53(2)	C(32)–C(33)	1.31(2)
C(11)–C(15)	1.48(2)	C(33)–C(34)	1.40(2)
C(12)–C(13)	1.33(2)	C(34)–C(35)	1.40(2)
C(13)–C(14)	1.44(2)	C(52)–C(53)	1.27(2)
C(11)–C(12)	1.43(2)	C(51)–C(55)	1.43(2)
C(14)–C(15)	1.44(2)	C(53)–C(54)	1.45(2)
C(31)–C(35)	1.57(2)	C(51)–C(52)	1.35(2)
C(31)–C(32)	1.42(2)	C(54)–C(55)	1.52(2)
C(35)–Al–C(55)	116.1(6)	C(35)–Al–C(15)	126.5(6)
C(55)–Al–C(15)	117.4(6)	C(34)–C(35)–Al	102(1)
C(14)–C(15)–Al	88(1)	C(11)–C(15)–Al	88.5(8)
C(54)–C(55)–Al	95.6(8)	C(31)–C(35)–Al	98.0(8)
C(51)–C(55)–Al	102(1)		

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 η^3 coordination like that exhibited in the solid-state structures of [Cp*Al(R)Cl]₂ [Cp* = C₅Me₅; R = CH₃, C₂H₅, *i*-C₄H₉] characterized by Paine and co-workers^{30,31} or as a σ -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*-butyl isocyanide.²⁷

The ¹H NMR spectrum of the compound in toluene-*d*₈ exhibits two resonances for the ring methyls which remain unchanged down to –90 °C. In this case, the spectrum of a rigid species would be indistinguishable from the averaged spectrum of a fluxional species;

(27) Shapiro, P. J.; Vij, A.; Yap, G. P. A.; Rheingold, A. L. *Polyhedron* **1995**, *14*, 203.

(28) Margl, P.; Schwarz, K.; Blöchl, P. E. *J. Chem. Phys.* **1995**, *103*, 683.

(29) Margl, P.; Schwarz, K.; Blöchl, P. *J. Am. Chem. Soc.* **1994**, *116*, 11177.

(30) Schonberg, P. R.; Paine, R. T.; Campana, C. F. *J. Am. Chem. Soc.* **1979**, *101*, 7725.

(31) Schonberg, P. R.; Paine, R. T.; Campana, C. F.; Duesler, E. N. *Organometallics* **1982**, *1*, 799.

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 $(\eta^1\text{-C}_5\text{Me}_4\text{H})_2\text{Al}\{\text{C}(=\text{N-}t\text{-Bu})\text{C}(=\text{N-}t\text{-Bu})(\text{C}_5\text{Me}_4\text{H})\}$ was originally assigned incorrectly²⁷ 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 $\text{Cp}^*_3\text{-Al}$ by reacting decamethylmagnesium with aluminum chloride. Instead, only one Cp^* ring can be transferred to the aluminum in this manner to produce $(\text{Cp}^*\text{AlCl}_2)_2$, which has been characterized previously.³² We have encountered a similar problem with sterics in our preparation of $[(\text{C}_5\text{Me}_4\text{H})(\text{Cl})\text{Al}(\mu\text{-O-}i\text{-Pr})_2]_2$,³³ instead of the corresponding dicyclopentadienylaluminum compound, from the reaction of $(\text{C}_5\text{Me}_4\text{H})_2\text{Mg}$ 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^*_3Al should be preparable since gallium has been shown to support three Cp^* rings in Cp^*_3Ga , which was prepared by reacting NaCp^* with GaCl_3 .³⁴ 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 between AlCl_3 and 3 equiv of Cp^*Na , from which we cleanly obtain a white, crystalline solid which we presently formulate as Cp^*_3Al .³⁵ 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 ^1H 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 Com-

(32) Koch, H.-J.; Schulz, S.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G.; Heine, A.; Herbst-Irmer, R.; Stalke, D.; Sheldrick, G. M. *Chem. Ber.* **1992**, *125*, 1107.

(33) Fisher, J. D.; Golden, J. T.; Shapiro, P. J.; Yap, G. P. A.; Rheingold, A. L. *Main Group Met. Chem.* **1996**, *19*.

(34) Schumann, H.; Nickel, S.; Weimann, R. *J. Organomet. Chem.* **1994**, *468*, 43.

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

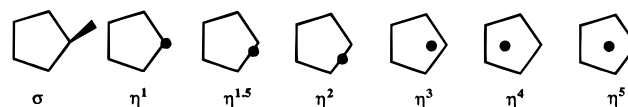


Figure 5. Cp–Al bonding arrangements.

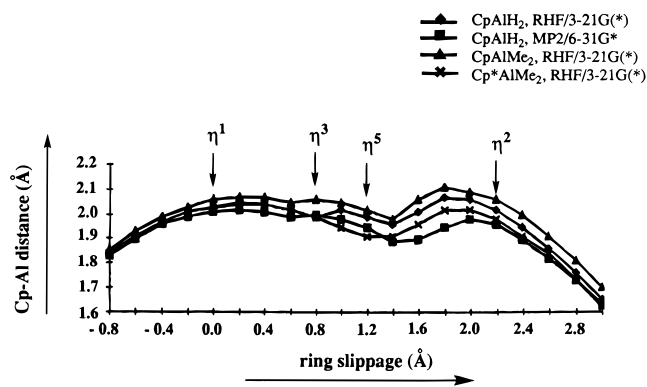


Figure 6. Perpendicular Cp–Al ring distance in CpAlH_2 , CpAlMe_2 , and Cp^*AlMe_2 as a function of ring slippage. The ring slippage coordinate is arbitrarily set at 0.0 Å for η^1 geometry.

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 η^1 and σ interactions or between η^4 and η^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 η^1 – η^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 σ , but in the η^1 – η^5 range the cyclopentadienyl ring remains a nearly symmetrical pentagon. It is clear that a description in terms of traditional valence structures for η^3 (A) or η^2 (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.

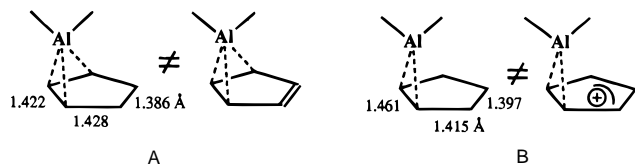


Figure 7. Comparison of calculated structures of η^3 - and η^2 -CpAlMe₂ (B) with valence bond representations.

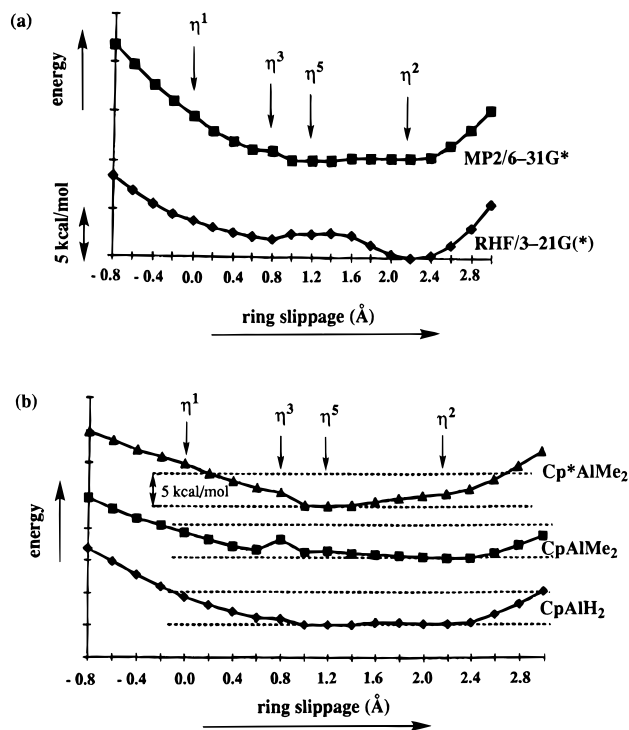


Figure 8. (a) Energy profile for ring slippage in CpAlH₂ at RHF/3-21G* and MP2/6-31G*. (b) Energy profiles for ring slippage of CpAlH₂, CpAlMe₂, and Cp*AlMe₂ at MP2/6-31G* (estimated). The ring slippage coordinate is arbitrarily set at 0.0 Å for an η^1 geometry.

The potential energy surface for ring slippage is very flat, allowing for essentially free movement of the AlH₂ 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 η^5 structure somewhat relative to the η^2 and η^3 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^{36–38} must therefore be caused by 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

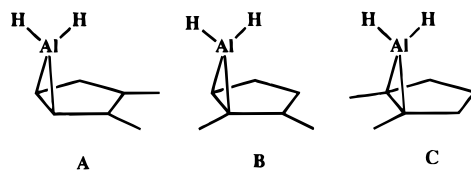


Figure 9. Possible η^2 isomers of (1,2-Me₂C₅H₃)AlH₂.

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 η^5 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.³⁹ 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 η^2 or η^3 geometry, with an η^5 geometry much higher in energy. On the basis of electron counting alone, an η^1 geometry should also be less favorable, although it should be stabilized relative to η^2 and η^3 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 η^1 – η^5 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.^{28,29} Cyclopentadienylzinc compounds, likewise, have been found to exhibit this so-called *peripheral* type of bonding involving a delicate balance of covalent and ionic interactions.²⁵

Effect of Ring-Methyl Groups on Geometry. Introduction of methyl substituents on the ring destabilizes η^2 and η^3 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 η^3 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 × η^1 geometry exhibited in the solid

(36) Amlöf, J.; Faegri, K.; Schilling, B. E. R. *Chem. Phys. Lett.* **1984**, *106*, 266.

(37) Dobbs, K. D.; Hehre, W. J. *J. Comput. Chem.* **1987**, *8*, 861.

(38) Lüthi, H. P.; Ammeter, J. H.; Almlöf, J.; Faegri, K., Jr. *J. Chem. Phys.* **1982**, *77*, 2002.

(39) For example, in the η^2 structure the barrier for AlH₂ rotation is 13 kcal/mol at RHF/3-21G*(*).

(40) GAMESS-UK is a package of *ab initio* programs written by M. F. Guest, J. H. van Lenthe, J. Kendrick, K. Schöffel, P. Sherwood, and R. J. Harrison, with contributions from D. Amos, R. J. Niessen, V. R. Saunders, and A. J. Stone. The package is derived from the original GAMESS due to M. Dupuis, D. Spangler, and J. Wendoloski, NRCC Software Manual: Guest, M. F.; Fantucci, P.; Harrison, R. J.; Kendrick, J.; van Lenthe, J. H.; Schöffel, K.; Sherwood, P. *GAMESS-UK User's Guide and Reference Manual 1*, Revision C.0; Computing for Science (CFS) Ltd.: Daresbury, U.K., 1993.

state by compound **4**, and it would also be consistent with the $\{2 \times \eta^1, \eta^5\}$ geometry exhibited by compound **3**. In Cp^*AlMe_2 , the calculated potential-energy curve begins to show some preference for η^5 -bonding, which avoids both steric repulsion and charge concentration. However, the energy differences are still rather small, such that crystal packing forces or the steric and electronic effects of the other ligands on the Al atom could easily be large enough to overcome this intrinsic preference.

Comparison of Calculated and Observed Geometries for Di- and Tricyclopentadienylaluminum Compounds. The following is a brief comparison between the the calculated and the crystallographically-determined geometries of Cp_2AlH , Cp_2AlMe , and Cp_3Al . A more detailed listing of parameters for the optimized structures of Cp_2AlH , Cp_2AlMe , and Cp_3Al is provided in the Supporting Information.

The two Cp_2Al compounds prefer η^2/η^1 (at 3-21G^(*)) or $2 \times \eta^{1.5}$ (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 $2 \times \eta^2$ geometry crystallographically characterized for Cp_2AlMe . The calculated metal–ring distances (2.061 and 2.064 Å) show reasonable agreement with the observed distances (2.014 and 2.027 Å).

Cp_3Al 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 values (1.97–2.02 Å) and the same propeller-type arrangement of the rings was found.

Final Comments

Whereas the bonding between a cyclopentadienyl ring and a transition metal may be regarded as largely covalent by virtue of the involvement of the metal d-orbitals in π -interactions with the ring, the bonding between cyclopentadienyl rings and main group metals and metalloids generally involves both ionic and covalent contributions.¹ The balance between the ionic and covalent contributions to bonding between the main group element and the ring depends on the spatial extent of the metal orbitals, the s/p energy difference for the element, and the electronegativity difference between the elements and carbon. At one extreme are the elements B, Si, and Hg, which exhibit a strong preference for covalent σ -bonding by virtue of their relatively high electronegativities. At the other extreme are the electropositive alkali and alkaline earth metals, which generally exhibit more ionic, η^5 -bonding. The remaining p-block metals run the gamut between the two extremes. As a consequence, they are chameleon-like, adopting a variety of structures which are highly sensitive to the sterics and electronics of the ring system and the remaining coordination environment of the element. The crystallographically-characterized tricyclopentadienylaluminum compounds described herein are illustrative of this chameleon-like behavior, exhibiting dramatic changes in their solid-state geometries upon introduction of a Lewis base adduct and introduc-

tion of methyl substituents onto the cyclopentadienyl rings.

Theoretical calculations reveal that there is a shallow potential energy surface connecting the different ring hapticities for aluminum which makes the balance between different geometries very delicate. Although the precise details differ somewhat depending on basis set and correlation treatment, regardless of the theoretical level, the energies of the η^2 to η^5 structures are within 1–2 kcal/mole, indicating that movement of the aluminum over the ring plane is essentially unrestricted. In fact, the ease with which aluminum is apparently able to slip about its cyclopentadienyl ring makes the question of preferred fluxional mechanism effectively moot. Clearly, there would be no hope of freezing out this motion for observation by solution NMR techniques and the magnitude of crystal packing forces is likely to override any effects due to innate geometrical preferences in energy barrier measurements made by solid-state NMR. Nevertheless, we are examining these complexes by variable-temperature, ¹³C CPMAS NMR in order to determine if the different geometries can be distinguished spectroscopically. We will also continue to examine the effects of attaching different ligands to aluminum and introducing substituents on the cyclopentadienyl rings on the solid-state geometries of cyclopentadienylaluminum compounds.

The variation in reactivity exhibited by these cyclopentadienylaluminum compounds is also noteworthy. The small-molecule insertion chemistry of $(\text{Me}_4\text{C}_5\text{H})_3\text{Al}$ contrasts remarkably with the behavior of the parent compound, Cp_3Al , 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 CaH_2 (petroleum ether). The solvents were then stored in line-pots from which they were vacuum transferred from sodium benzophenone ketyl. NMR solvents: benzene-*d*₆, toluene-*d*₆, CDCl_3 , and CD_2Cl_2 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.^{41,42} 1,1'-Dimethylmagnesocene and bis(1,2,4-trimethylcyclopentadienyl)magnesium were prepared in the same manner from the corresponding methyl-substituted cyclopentadienes. Tris(1,2,3,4-tetramethylcyclopentadienyl)aluminum was prepared as described previously.²⁷

NMR spectra were recorded on an IBM NR-300 (300.1 MHz ¹H, 75.4 MHz ¹³C, 78.2 MHz ²⁷Al) and an IBM NR-200 (200.1 MHz ¹H, 50.3 MHz ¹³C, 52.1 MHz ²⁷Al). All chemical shifts are reported in ppm and referenced to solvent (¹³C, ¹H) or

(41) Eisch, J. J.; Sanchez, R. *J. Organomet. Chem.* **1985**, *296*, C27.

(42) Duff, A. W.; Hitchcock, P. B.; Lappert, M. F.; Taylor, R. G.; Segal, J. A. *J. Organomet. Chem.* **1985**, *293*, 271.

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 type⁴³ and were carried out using the GAMESS program⁴⁰ on an SP2 workstation. All structures were optimized at the RHF/3-21G(*)^{44–46} level, and a number were reoptimized at RHF/6-31G*;^{47–49} CpAlH₂ was also studied at MP2/6-31G*.⁵⁰ All structures mentioned in the text were fully optimized as minima or saddle points. Ring slippage paths for CpAlH₂, CpAlMe₂, and Cp*AlMe₂ were calculated by sliding the projection of the Al atom on the ring plane along the bisector of a CCC angle. This means that only two degrees of freedom were fixed for each point. The slippage path for CpAlH₂ was calculated at the RHF/3-21 G(*) and the MP2/6-31G* levels. Paths for CpAlMe₂ and Cp*AlMe₂ were only calculated at the RHF/3-21G(*) level; the CpAlH₂ MP2/6-31G*-RHF/3-21G(*) difference was then added as a correction.

Procedures. **Cp₃Al (1).** Toluene (75 mL) was added to the combined solids of Cp₂Mg (5.2 g, 34 mmol) and AlCl₃ (3.0 g, 22 mmol), and the reaction mixture was stirred at 40 °C overnight (approximately 12 h). The reaction mixture was filtered to remove the MgCl₂, which was washed repeatedly with toluene to remove the soluble reaction product. The toluene from the combined filtrates was removed *in vacuo* to afford a yellow oil which was redissolved in 50 mL of petroleum ether. **1** precipitated as a white solid from the petroleum ether solution as it was cooled at –78 °C. Yield: 3.0 g, 61%. ¹H NMR (CDCl₃): δ 5.9 (s, C₅H₅). ¹³C NMR (CDCl₃): δ 112.0 (C₅H₅). ²⁷Al NMR (C₆D₆): δ 81. Anal. Calcd for C₁₅H₁₅Al: C, 81.0; H, 6.8. Found: C, 81.0; H, 6.6.

(C₅H₄Me)₃Al (2). Compound **2** was prepared in the same manner as described above for **1**, except that (C₅H₄Me)₂Mg (2.83 g, 21.2 mmol) was combined with AlCl₃ (2.83 g, 21.2 mmol). The product was isolated as a yellow oil. Yield: 2.40 g, 42.8%. ¹H NMR (C₆D₆): δ 5.5, 5.9 (m, C₅H₄CH₃), 2.1 (s, C₅H₄CH₃). ¹³C NMR (C₆D₆): δ 113.6, 102.6 (C₅H₄CH₃), 15.2 (C₅H₄CH₃). ²⁷Al NMR (C₆D₆): δ 83. A satisfactory elemental analysis on this compound could not be obtained due to difficulties with purifying the oil. Cyclopentadienylaluminum compounds fall apart readily upon analysis by mass spectrometry; thus, the parent ion was not detected, although (C₅H₄Me)₂Al⁺ was observed. Its exact mass was measured as 185.0932 au (theoretical: 185.0911). MS(EI): *m/z* 214 ((C₅H₄Me)₂Al⁺ + C₂H₅, 14.0), 185 ((C₅H₄Me)₂Al⁺, 100), 158 ((C₅H₄Me)₂Al⁺ – CH₃ – C, 37.6), 143 ((C₅H₄Me)Al⁺ + C₂H₅ + H, 34.4), 128 ((C₅H₄Me)Al⁺ + CH₃ + H, 34.4), 107 ((C₅H₄Me)Al⁺ + H, 31.2).

(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)₂Mg (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 30 mL of petroleum ether and cooling the solution at –60 °C afforded **3** as a white, microcrystalline solid. Yield: 1.36 g, 57%. ¹H NMR (C₆D₆): δ 4.96 (s, 2, C₅-(CH₃)₃H₂), 2.09 (s, 3, C₅-(CH₃)₃H₂), 2.00 (s, 6, C₅-(CH₃)₃H₂). ¹³C NMR (CDCl₃): δ 128.5, 128.2, 99.8 (C₅-(CH₃)₃H₂), 15.3, 12.9 (C₅-(CH₃)₃H₂). ²⁷Al NMR (C₇D₈): δ 65. Anal. Calcd for C₂₄H₃₃Al: C, 82.7; H, 9.5. Found: C, 82.8; H, 9.3.

Crystal Structure Determinations of Cp₃Al (1) and

(43) Roothan, C. C. *J. Rev. Mod. Phys.* **1951**, *23*, 69.

(44) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

(45) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797.

(46) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(47) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *66*, 217.

(48) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(49) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(50) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(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 3531 independent reflections were collected for the crystal of **1** and 2717 independent reflections for the crystal of **3**. The first 50 frames were recollected at the end of data collection to monitor 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 XEMP, which is supplied by Siemens in their SHEXTL-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 *F*², SHELXL-93 (Sheldrick, G. M., 1993), incorporated in SHELXTL-PC V5.03 (Siemens, 1995).

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 synthesis, and refined by full-matrix least-square procedures on *F*². All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions.

Crystal Structure Determination of (1,2,3,4-Me₄C₅H)₃Al (4). A colorless, block-shaped crystal of **4**, grown from a saturated toluene solution that was cooled at –60 °C, was mounted in a thin-walled, nitrogen-flushed, glass capillary. The unit cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($2\theta \leq 25^\circ$).

No evidence of symmetry higher than triclinic was observed in either the photographic or diffraction data. *E*-statistics suggested the centrosymmetric space group option, *P* $\bar{1}$, which yielded chemically reasonable and computationally stable results of refinement. The structure was solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. No absorption corrections were required because of <10% variation in the integrated intensities of the γ -scans. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXTL (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 Cp₂AlH, Cp₂AlMe, and Cp₃Al (20 pages). Ordering information is given on any current masthead page.

OM9610049