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The syntheses, structures, bonding, and reactivity of cyclopentadienylaluminum(III) derivatives

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Contents

Abstract

Cyclopentadienylaluminum compounds have been a curiosity due to the ring-slipped structures they exhibit and due to their highly fluxional nature, which has prevented the freezing out of discrete solution structures on the NMR time scale. Lately, increased attention toward these compounds in the form of molecular structure determinations, theoretical calculations, and ^{27}Al-NMR spectroscopic measurements is providing a clearer picture of the bonding between the aluminum and its cyclopentadienyl ring(s). A variety of ring coordination geometries (η^1, η^2, η^3, η^5) have been identified in molecular structures of

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these compounds, and although theoretical calculations reveal very small energy differences between different haptotropes, consistent with their highly fluxional behavior in solution, there is close agreement between the calculated ground state geometries for the compounds and the geometries they exhibit in the solid state and in solution. Theory and experiment reveal a delicate balance of covalent π-interactions and ionic interactions between the aluminum and its cyclopentadienyl ring. Although the balance is easily tipped by steric effects, some structural trends are emerging. The solution ^{27}Al-NMR chemical shifts of cyclopentadienylaluminum compounds are surprisingly diagnostic of their geometries, exhibiting a strong correlation with coordination numbers that take into account the hapticity of the cyclopentadienyl ring.

Keywords: Cyclopentadienylaluminum compounds; Dihapto coordination geometry; Bonding

1. Introduction

Since Drew and Haaland proposed an unusual dihapto coordination geometry for the cyclopentadienyl ring of $CpAlMe_2$ ($Cp = C_5H_5$) to explain the gas phase electron diffraction pattern for the molecule 25 years ago [1], the structure and bonding in cyclopentadienylaluminum compounds has been regarded with some curiosity by main group chemists; however, it is only recently that these compounds have received extensive enough attention to reveal some interesting trends which shed light on the nature of the interaction between the cyclopentadienyl rings and the aluminum. The elegant work of Schnöckel et al. in isolating cyclopentadienyl derivatives of aluminum in the rare +1 oxidation state has contributed to a renewed interest in these species, and readers are directed to other articles for more details on those compounds [2,3]. This article will focus primarily on the properties of cyclopentadienyl compounds of aluminum in the +3 formal oxidation state.

2. Syntheses, structures and reactivities

2.1. The unusual molecular structure of $Al(\eta^2\text{-}C_5H_5)_2Me$ (**1**)

It was the eyebrow-raising bis-dihapto geometry of the cyclopentadienyl rings in the molecular structure of Cp_2AlMe (**1**) [4,5] (Fig. 1) which instigated much of the chemistry that has emerged from our own labs at the University of Idaho. As mentioned above, a dihapto ring-coordination geometry was invoked much earlier as one of the best models for the gas phase electron diffraction pattern for $CpAlMe_2$ and was determined to be the most stable geometry in CNDO/2 [1] and ab initio SCF-MO [6] calculations on this molecule. In the solid state, however, this molecule adopts a polymeric structure with a ···Cp–Al–Cp–Al··· backbone exhibiting η^1 coordination by the aluminum atoms at 1,3-positions on opposite sides of each ring [7]. Thus, the X-ray crystal structure of **1** was the first solid-state structural identification of a η^2 mode of Cp coordination by aluminum to, not one, but both of its cyclopentadienyl rings.

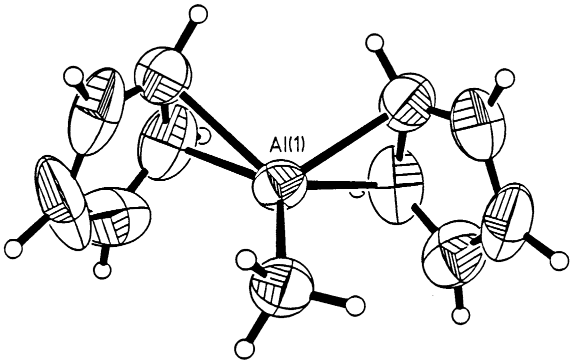

Fig. 1. Molecular structure of Cp$_2$AlMe. Reprinted with permission from Ref. [4]. Copyright 1994 The American Chemical Society.

Despite its low symmetry in the solid state, **1** undergoes a very facile rearrangement in solution which exchanges the environments among the cyclopentadienyl ring hydrogens and among the carbons. This rearrangement is so rapid that only a single resonance is observed in the ^{1}H- and ^{13}C-NMR spectra of a toluene-d_8 solution of the compound cooled at -90°C in a 7 T magnetic field. Similar fluxional behavior had been documented earlier for CpAlMe$_2$ and other cyclopentadienylaluminum alkyl compounds [8,9]. Besides undergoing internal rearrangement, Cp$_2$AlMe was found to undergo ligand redistribution quite readily to form Cp$_3$Al (**2**) and CpAlMe$_2$, behavior that had also been documented for CpAlMe$_2$ [10]. In fact, it was through this ligand redistribution that the Lewis base adducts of **2** were originally prepared [4]. Cp$_3$Al(C≡N-*t*-Bu) precipitates selectively from a mixture of *tert*-butyl isocyanide and **1** in petroleum ether solution. An X-ray crystal structure determination revealed that this compound possesses C_3 symmetry in the solid state (Fig. 2), the three η^1-Cp rings related by a 3-fold rotational axis passing through the aluminum isocyanide bond. Even with an isocyanide molecule occupying the formally empty p orbital of the Cp$_3$Al, the motion of the aluminum atom about its cyclopentadienyl rings could not be frozen out on the NMR time scale to reveal the mechanism by which Cp hydrogens and carbons were being equivalenced.

2.2. Syntheses, structures and reactivity of homoleptic cyclopentadienylaluminum compounds

The first reported preparations of Cp$_3$Al involved the reaction of elemental aluminum with either cyclopentadienyl IIB compounds [11] or dicyclopentadienylmercury [12]. Cp$_3$Al can also be made by reacting AlCl$_3$ with 1.5 equivalents of Cp$_2$Mg. Other homoleptic cyclopentadienylaluminum compounds, namely (C$_5$MeH$_4$)$_3$Al (**3**), (1,2,4-C$_5$Me$_3$H$_2$)$_3$Al (**4**), and (C$_5$Me$_4$H)$_3$Al (**5**), have been prepared in the same fashion using the appropriate magnesocene reagents [13]. The molecular structures of compounds **2**, **4** and **5** are shown in Figs. 3–5, respectively. In the crystal of **2** there are two unique Cp$_3$Al molecules in the unit cell. In one

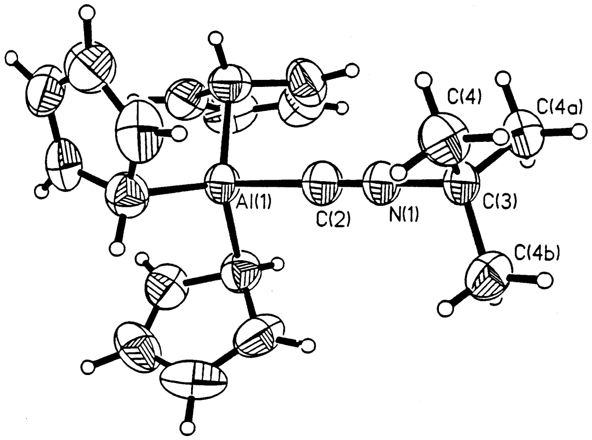

Fig. 2. Molecular structure of $Cp_3Al(CN\text{-}t\text{-}Bu)$. Reprinted with permission from Ref. [4]. Copyright 1994 The American Chemical Society.

molecule, all of the Cp rings approach an η^2 coordination geometry. In the other molecule, two Cp rings are effectively η^2, and the third is η^1. A quite different structure is observed for compound **4**, with one of the trimethylcyclopentadienyl rings coordinated in an η^5 fashion while the remaining two rings are each coordinated η^1. Increasing ligand sterics by adding a fourth methyl group to the cyclopentadienyl ring in **4** results in a structure in which all the rings are nearly η^1, with one ring adopting a perpendicular orientation to its Al–C vector as if to approach an η^3 geometry.

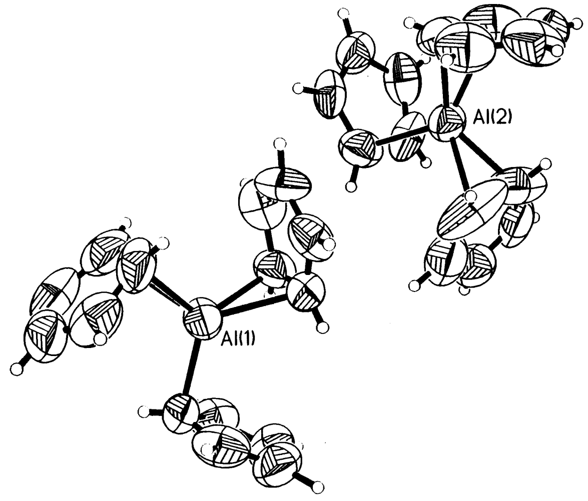

Fig. 3. Molecular structure of Cp_3Al (two independent molecules). Reprinted with permission from Ref. [13]. Copyright 1997 The American Chemical Society.

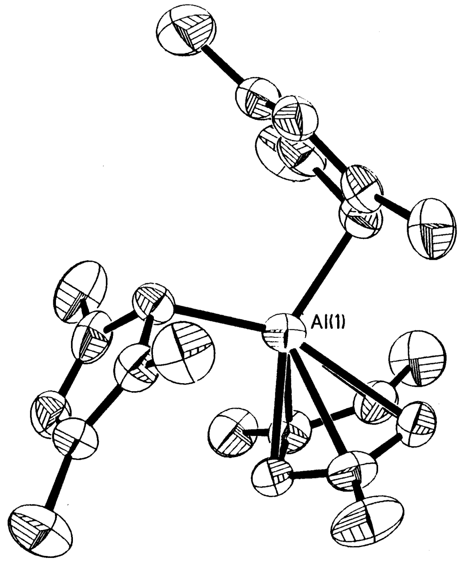

Fig. 4. Molecular structure of $(1,2,4\text{-}Me_3C_5H_2)_3Al$. Reprinted with permission from Ref. [13]. Copyright 1997 The American Chemical Society.

It is apparent from these structures that the mode of coordination of the cyclopentadienyl ring to aluminum is very flexible, with a very shallow energy profile, such that the aluminum is able to migrate freely about the ring. Hence, the molecules are highly fluxional in solution, exhibiting very simple, signal-averaged ^1H- and ^{13}C-NMR spectra that cannot be frozen out under experimentally accessible conditions. A preliminary examination of the reactivity of these homoleptic cyclopentadienylaluminum compounds indicates that increasing the sterics of the cyclopentadienyl rings leads to increased reactivity with respect to small molecule insertion. Whereas **2** merely coordinates unsaturated Lewis bases such as $C\equiv N$-*t*-Bu and $N\equiv C$-*t*-Bu, undergoing no further reaction, even at elevated temperatures, **5** actually inserts two molecules of $C\equiv N$-*t*-Bu into one of its cyclopentadienyl rings to form the heterometallacycle $(\eta^1\text{-}C_5Me_4H)_2\overline{Al\{C(=N^tBu)-C(=N}^t\text{-}Bu)(C_5Me_4H)\}$ [14]. Examination of the reaction of compound **4** with $C\equiv N$-*t*-Bu by ^1H-NMR spectroscopy indicated that a similar double insertion of *t*-butyl isocyanide had occurred. The reactions between **5** and other small unsaturated molecules such as $C\equiv NMe$, $C\equiv N$(mesityl), $N\equiv C$-*t*-Bu, CS_2, CO_2, and SO_2 were not clean; thus, the nature of the reaction products were not determined, although insertion probably occurs in these instances as well [15].

2.3. Structures of pentamethylcyclopentadienylaluminum compounds

Efforts to include Cp_3^*Al ($Cp^* = C_5Me_5$) in this series of homoleptic cyclopentadienylaluminum compounds have been unsuccessful to date, presumably for steric reasons. Cp^*_2Mg transfers only one Cp* ring to $AlCl_3$ to form $[Cp^*AlCl_2]_2$ [16], which was prepared previously by Roesky et al. by the reaction of $C_5Me_5SiMe_3$ with $AlCl_3$ [17]. Whereas the reaction of three equivalents of KCp* with $GaCl_3$ affords $GaCp^*_3$ [18], a similar reaction between three equivalents of either NaCp* or KCp* and $AlCl_3$ affords $[Cp^*_2AlCl]_x$ (**6**) and an equivalent of unreacted MCp* (M = Na, K). Compound **6** is only moderately stable in the solid state. Isolated as a white, microcrystalline solid, it turns violet over days at room temperature under a nitrogen atmosphere. The molecularity of this compound has not yet been determined. A single crystal grown from a pentane/methylene chloride solution of the compound afforded the structure of Schnöckel's ion pair $[Cp^*_2Al][Cp^*AlCl_3]$ [19]. Evidence for the ionization of **6** to form the decamethylaluminocenium cation has been found in the ^1H- and ^{27}Al-NMR spectra of the compound in benzene-d_6, $CDCl_3$, and CD_2Cl_2 solutions. As expected, the degree of ionization increases with increasing solvent polarity [20].

Cp^*_2AlMe (**7**) is prepared in the same manner as **6** by reacting two equivalents of NaCp* with $AlMeCl_2$. An X-ray crystal structure of **7** revealed it to be monomeric with a bis-η^2 ring coordination geometry similar that of the parent compound, **1** [20].

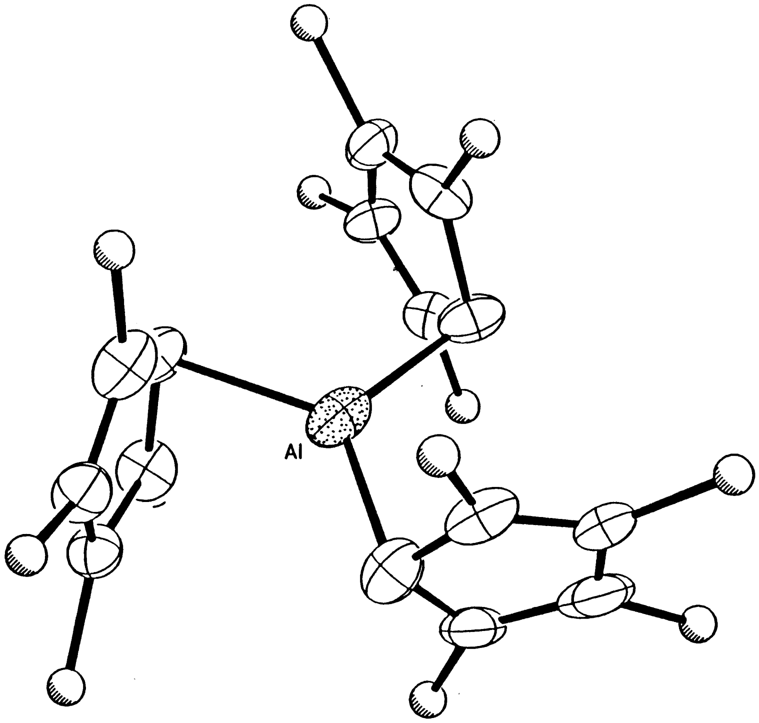

Fig. 5. Molecular structure of $(1,2,3,4\text{-}Me_4C_5H)_3Al$. Reprinted with permission from Ref. [13]. Copyright 1997 The American Chemical Society.

The first reported pentamethylcyclopentadienylaluminum compounds were prepared by Paine et al. [21,22]. Reaction of $[AlR_2Cl]_2$ ($R = CH_3$, C_2H_5, i-C_4H_9) with either Cp*MgCl or LiCp* afforded $[Cp^*Al(\mu\text{-}Cl)R]_2$. X-ray crystal structures of two of these dimers revealed η^3 coordination between the Cp* rings and the aluminum atoms. When two alkyl groups beside the Cp* ring are present on aluminum, as in the monomeric Cp^*AlR_2 (R = Me, Et, i-Bu) compounds, a trihapto geometry is believed to exist between the Cp* ring and aluminum based on the ^{27}Al-NMR chemical shifts of these compounds [49]. On the other hand, when two chlorine ligands are present beside the Cp* in the dimeric compound $[Cp^*AlCl_2]_2$, η^5-coordination of the Cp* ligands is observed [17]. The chelated compounds (η^1: η^1-$C_5Me_4CH_2CH_2NMe_2$)$AlMe_2$ and ($\eta^{2/3}$:η^1-$C_5Me_4CH_2CH_2NMe_2$)$AlCl_2$ [23], in relation to the above-mentioned Cp*Al compounds, may be regarded as Cp*Al compounds with a coordinated amine, exemplifying the effect of the Lewis base in causing the cyclopentadienyl ring to slip to a lower hapticity.

2.4. Syntheses, structure and reactivity of aluminocenium compounds

The decamethylaluminocenium cation was first prepared and structurally characterized by Schnöckel et al. [19]. It was formed in a disproportionation reaction involving the Al(I) cluster $[(Cp^*Al)_4]$. An X-ray crystal structure of $[Cp^*_2Al][Cp^*AlCl_3]$ revealed the expected parallel ring sandwich geometry for the cation, with the η^5-Cp* rings in a staggered orientation. The anion contained an η^1-bound Cp*.

More direct synthetic routes to the decamethylaluminocenium cation using the Al(III) compounds **6** and **7** have now been developed [20]. Bochmann et al. made use of the methanide ion abstraction chemistry of $B(C_6F_5)_3$ to generate $[Cp_2Al]^+[MeB(C_6F_5)_3]^-$ from Cp_2AlMe [24]. This aluminocenum species is an effective initiator at ca. −50 to −70°C for the cationic polymerization of isobutene and the copolymerization isobutene with isoprene. Following Bochmann's example, we treated **7** with $B(C_6F_5)_3$ to form $[Cp^*_2Al][B(C_6F_5)_3Me]$ (**8**), which is more thermally stable in solution than its Cp analog. The ^{27}Al-NMR spectral data for **8** in $CDCl_3$ indicated that the methanide ion had been transferred completely to the boron center [20]. In contrast to its Cp analog, $[AlCp^*_2]^+$ is effective at initiating the cationic polymerization of substrates such as isobutene, isoprene, and styrene at room temperature but exhibits poor activity at −78°C. Following the example of Rhodes et al. for the synthesis of $[SnCp^*]^+[B(C_6F_5)_4]$ [25], the pentamethylaluminocenium cation has also been prepared by reacting $[Cp^*_2AlCl]_x$ with either $LiB(C_6F_5)_4$ or $NaB(C_6F_5)_4$ [20]. While more stable than the parent aluminocenium cation, $[Cp^*_2Al]^+$ does undergo a slow decomposition in $CDCl_3$ and CD_2Cl_2 solutions at room temperature, generating free Cp*H in the process. The nature of the aluminum-containing decomposition products has not yet been determined.

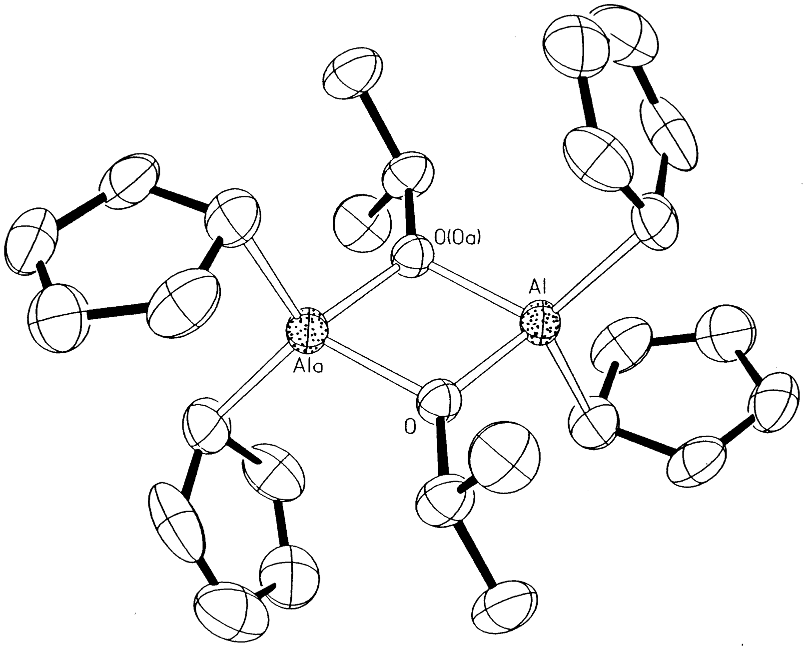

Fig. 6. Molecular structure of $[Cp_2Al(O^iPr)]_2$. Reprinted with permission from Ref. [28]. Copyright 1996 Freund Publishing.

2.5. Syntheses and structures of cyclopentadienylaluminum (III) heteroatom derivatives

The electronic influence of heteroatom substituents, vis a vis alkyl groups, should have a direct effect on the aluminum atom's ability to π-bond with its cyclopentadienyl ring(s), thereby providing a measure of the importance of π-bonding in determining the preferred ring coordination geometry in the ground state structure of the molecule. Therefore, the syntheses of dicyclopentadienylaluminum alkoxide and amide derivatives were undertaken in order to compare their molecular structures with that of compound **1**. The synthesis of $AlCp_2(O\text{-}i\text{-}Pr)$, **9**, from the reaction of NaCp with $AlCl_2(O\text{-}i\text{-}Pr)$ was first reported in a patent in 1965 [26]. In 1996, the molecular structure of the compound was reported by Kunicki et al. [27]. As can be seen in Fig. 6, **9** is dimeric, with bridging isopropoxide ligands between the aluminum atoms and η^1 Cp rings. A dimeric structure with bridging isopropoxide ligands and η^1 cyclopentadienyl rings was also exhibited by $[(C_5Me_4H)AlCl(\mu\text{-}O\text{-}i\text{-}Pr)]_2$, which is formed along with $(C_5Me_4H)MgCl$ in the reaction of $(C_5Me_4H)_2Mg$ with $AlCl_2(O\text{-}i\text{-}Pr)$ [28].

In order to discourage dimerization of the dicyclopentadienyl aluminum alkoxide, incorporation of a bulky alkoxide substituent was pursued. Alcoholysis of $AlCp_3$ with 2,6-di-*tert*-butyl-4-methylphenol (BHT-H) is non-specific, affording a mixture of $[AlCp_2BHT]_x$ (**10**) and $AlCp(BHT)_2$, (**11**), which are separable by a combination of sublimation and crystallization techniques [30]. Efforts to obtain X-ray quality crystals of **10** have been unsuccessful. The compound is unstable and decomposes when stored in the solid state under N_2. The nature of the decomposition has not yet been established, although an X-ray quality crystal of $[AlCp(\mu\text{-}O)BHT]_2$ (**12**) was obtained from a benzene solution of **10** that had been stored over days in an evacuated, air-tight vessel (Fig. 7) [15]. Further investigation is necessary to determine whether **12** resulted from an intermolecular decomposition of **10** with itself or from the presence of adventitious water or oxygen in the vessel. The geometry of the cyclopentadienyl rings in **12** is consistent with the structure predicted by ab initio calculations (RHF/3-21G(*)) [29] on the doubly oxo-bridged $[CpAlO]_2$ and is the same ring coordination geometry exhibited in the molecular structure of **11** (Fig. 8).

Ab initio calculations [30] indicate that the η^5 geometry of the Cp ring in compound **11** is favored by an *increase* in π-bonding between the aluminum and the cyclopentadienyl ring, made possible by the ionic nature of the Al–O bonds (cf. $CpAl(OCF_3)_2$). A similar η^5 arrangement of Cp rings is encountered for quite opposite reasons in the structure of $[CpAlN(2,6\text{-}i\text{-}Pr_2C_6H_3]_2$ (**13**) (Fig. 9), which forms in the reaction of Cp_3Al with 2,6-diisopropylaniline via the originally targeted dicyclopentadienylaluminum anilide intermediate [31]. Ab initio calculations on the model compound $[CpAlNH]_2$ also predict pentahapto Cp rings, in this case due to the greater ionic character of the Al–Cp bond as a result of the strong π- and σ-donating properties of the imino groups which stabilize polarization of the Cp–Al bond in the sense $Al^{\delta+}\text{–}Cp^{\delta-}$ and destabilize the Al 3*p* acceptor orbital so much that it is less available for Cp–Al π bonding. By contrast, an η^2 structure is predicted for $CpAl(NH_2)_2$ since the NH_2 group is only a weak π-donor and a moderate σ-acceptor [30].

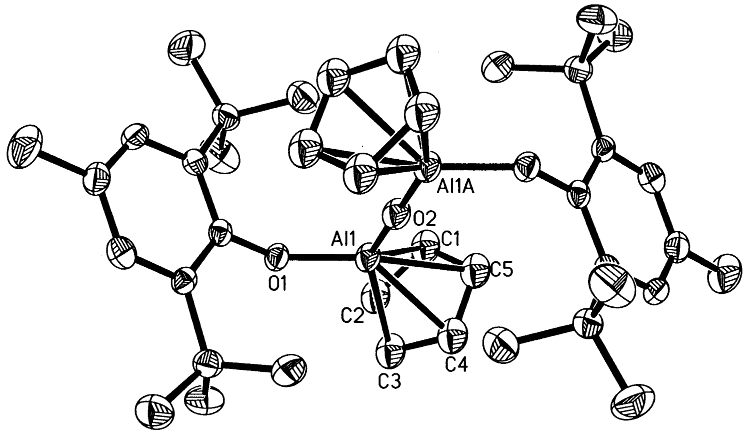

Fig. 7. Molecular structure of $[CpAl(BHT)]_2(\mu\text{-}O)$. Thermal ellipsoids are shown at 50% probability. Cyclopentadienyl rings are disordered between the two orientations shown. Selected bond lengths and angles: Al(1)–O(1) 1.724(2) Å, Al(1)–O(2) 1.6766(8) Å, Al-centroid Å, O(2)–Al(1)–O(1) 111.17(7)°.

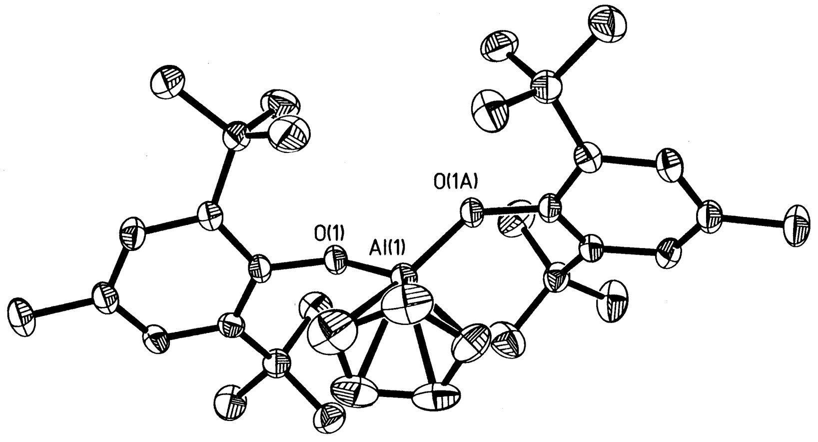

Fig. 8. Molecular structure of $CpAl(BHT)_2$. Reprinted with permission from Ref. [30]. Copyright 1998 The American Chemical Society.

The solid state structures that have been encountered for bulky imide and amide derivatives of Cp*Al seem to contradict the arguments made in the preceding paragraph, but in these cases steric interactions between the Cp* ring and other bulky groups on the aluminum could override electronic preferences. The iminoalane cluster reported by Schulz et al. in 1994 [32] displays an η^1 arrangement for the Cp*–Al unit within the Al_2N_2 heterocycle, perhaps as a consequence of steric crowding from the other Cp* and $(SiMe_3)_2N-$ groups nearby. The molecular structure of the Cp*Al–diazabutadiene complex, $[\eta^5\text{-}C_5Me_5)\text{-}AlN(Mes)CH{=}CHN(Mes)]$, recently reported by Cowly [33], like compounds **11** and **13**, exhibits a coplanar arrangement of arene rings parallel to the plane of an η^5 cyclopentadienyl ring.

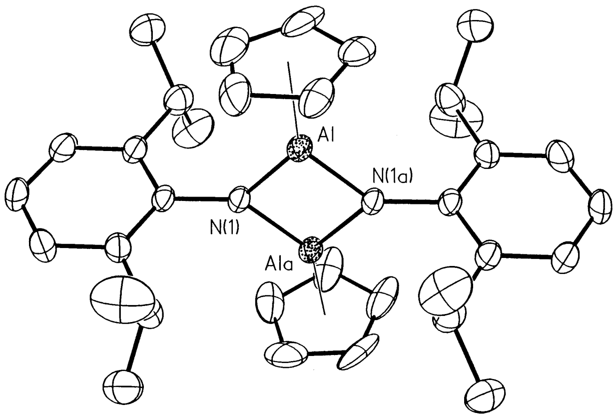

Fig. 9. Molecular structure of $[CpAlN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_2$. Reprinted with permission from Ref. [31]. Copyright 1996 The American Chemical Society.

3. Using theory to explain bonding and predict structures

3.1. Theoretical calculations on model cyclopentadienylaluminum compounds

The variety of cyclopentadienyl ring geometries displayed in the X-ray crystal structures of cyclopentadienylaluminum compounds and the highly fluxional nature of the compounds in solution are manifestations of a very shallow potential energy surface for ring slippage and a delicate balance between covalent and ionic forces in the bonding of the aluminum with its cyclopentadienyl ring(s). This is far from being a recent revelation since in 1975 Gropen and Haaland reported using ab initio SCF-MO methods to calculate an energy barrier of 2.36 kcal mol^{-1} for the internal rotation of the cyclopentadienyl ring in $H_2Al(C_5H_5)$ via an $\eta^2 \rightarrow \eta^3 \rightarrow \eta^2$ pathway [6]. Anh et al. used extended Hückel calculations to compute the energies for the transit of various organic and organometallic groups across a cyclopentadienyl ring [34]. Consistent with the experimental findings for $Me_2Al(C_5H_5)$ and the theoretical findings for $H_2Al(C_5H_5)$, isolobal CH_2^{2+} was found to prefer an in-plane orientation relative to the ring with an η^2 geometry being the most stable. In this case, however, the least stable η^5 geometry was found to be 4.5 eV (1.0×10^2 kcal mol^{-1}) higher in energy. More recently, Peter Budzelaar performed Hartree–Fock type calculations at the RHF/3-21G(*), RHF/6-31G(*), and MP2/6-31G* levels on a variety of cyclopentadienylaluminum compounds including Cp_2AlH_2, Cp_2AlMe_2, and Cp^*AlMe_2 [13]. These calculations revealed that similar transits of AlH_2 and $AlMe_2$ across a cyclopentadienyl ring are essentially unrestricted with energy differences within 5 kcal mol^{-1} between the different haptotropes and within 1–2 kcal mol^{-1} between the η^2 and η^5 geometries (Fig. 10).

Since the potential energy surface for ring slippage is so shallow for cyclopentadienylaluminum compounds, the structures adopted in the solid state could be influenced easily by crystal packing forces. Nevertheless, with the exception of $CpAlMe_2$, there has been considerable agreement between the observed solid state structures and calculated ground state structures. In the absence of steric effects, monomeric monocyclopentadienylaluminum compounds appear to prefer an η^2 ring coordination geometry if the other substituents on the aluminum are not particularly strong σ and π electron donors or are not strongly electron withdrawing (e.g. $CpAlH_2$, $CpAl(OH)_2$, $CpAl(OMe)_2$). This can perhaps be attributed to the weak interaction between the formally vacant Al 3p orbital with the e_1 π orbital of the Cp ring originally identified by Gropen and Haaland [6]. In the other cases, a shift toward higher hapticities is encountered either because of stronger π-interactions between the aluminum and the Cp ring or greater charge separation between the aluminum and the Cp ring, leading to a more symmetric, ionic interaction [30]. Of the other main group elements, beryllium [35–38] and zinc [39–44] appear to be most similar to aluminum in their bonding with cyclopentadienyl rings, exhibiting extremely low, experimentally inaccessible barriers to ring migration as well as a range of hapticities in the solid state. This is consistent with the diagonal relationship between these elements in the periodic table and the precarious balance of ionic and covalent bonding characteristics expected from their position at the

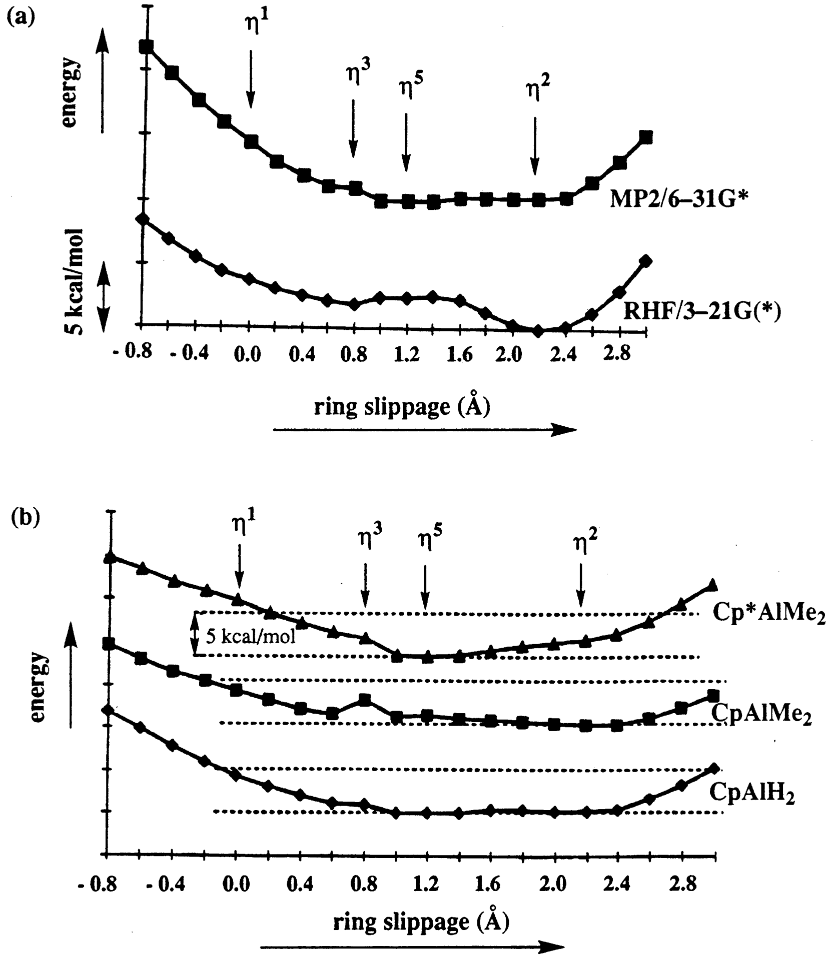

Fig. 10. (a) Energy profile for ring slippage in $CpAlH_2$ at RHF/3-21G(*) and MP2/6-31G*. (b) Energy profiles for ring slippage of $CpAlH_2$, $CpAlMe_2$, and Cp^*AlMe_2 at MP2/6-31G* (estimated from RHF/3-21G(*) calculations). The ring slippage coordinate is arbitrarily set at 0.0 Å for an η^1 geometry. Reprinted with permission from Ref. [13]. Copyright 1997 The American Chemical Society.

boundary between the more ionicly bonding alkali and alkaline earth metals and the more covalently bonding *p*-block elements.

3.2. Relating ^{27}Al-NMR chemical shifts to the structures of cyclopentadienylaluminum compounds

The strong correlation between ^{27}Al-NMR chemical shift and the coordination number of the organoaluminum compounds [45–48] has been used by Benn et al. to propose $(\eta^3\text{-Cp})Al(\eta^1\text{-Cp})_2$ as a five-coordinate structure for tricyclopentadienylaluminum consistent with its ^{27}Al-NMR chemical shift of 88 ppm [48]. Using these same guidelines, Scherer and Kruck proposed η^3 geometries for their Cp^*AlR_2 compounds (R = Me, Et, *i*-Bu) due to ^{27}Al-NMR signals of 71.6–72.7 ppm and η^2 geometries for monomeric cyclopentadienylaluminum compounds with unsubstituted or monosubstituted Cp rings due to ^{27}Al signals in the region of 150 ppm [49]. The solution ^{27}Al-NMR chemical shifts of various cyclopentadienylaluminum compounds are listed in Table 1. To the extent that the solution structures of the compounds may be inferred from their crystal structures, there indeed appears to be merit in this system of basing ring geometry assignments on ^{27}Al-NMR chemical shifts.

The combination of ring geometries exhibited by the two unique molecules in the crystal structure of $AlCp_3$ may be regarded as consistent with the five-coordinate

Table 1
^{27}Al-NMR chemical shifts of various cyclopentadienylaluminum(III) compounds

Compound	$\delta(^{27}Al)^a$	Coordination number^b	Ref.
$(\eta^2\text{-}Cp)_2AlMe$	72.7	5 (5)	[4]
Cp_2AlEt	52	5	[5]
$(\eta^{1-2}{:}\eta^2{:}\eta^2\text{-}Cp_3)Al$	88	5(5–6)	[48]
$(\eta^1\text{-}Cp)_3Al(C{\equiv}N\text{-}t\text{-}Bu)$	118	4(4)	[5]
$Cp_3Al(N{\equiv}C\text{-}t\text{-}Bu)$	110	4	[5]
$(MeCp)_3Al$	83	5	[13]
$(1,2,4\text{-}Me_3C_5H_2)_3Al$	65	5(7)	[13]
$(1,2,3,4\text{-}Me_4C_5H)_3Al$	64	3(5)	[13]
$(\eta^1\text{-}C_5Me_4H)_2\overline{Al\{C({=}NtBu)C({=}N}{}^tBu)(C_5Me_4H)$	150	4(4)	[14]
$[Cp_2Al(O\text{-}i\text{-}Pr)]_2$	103	4(4)	[28]
$[(1,2,3,4\text{-}Me_4C_5H)(O\text{-}i\text{-}Pr)ClAl]_2$	85	5(4)	[28]
$[(\eta^5\text{-}Cp)AlN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_2$	78	5(7)	[31]
$(\eta^5\text{-}Cp)Al(BHT)_2$	>0	5–6	[30]
$Cp_2Al(BHT)$	-14	7	[30]
Cp^*AlMe_2	71.6	5	[49]
Cp^*AlEt_2	72.2	5	[49]
$Cp^*Al(i\text{-}Bu)_2$	72.7	5	[49]
$(t\text{-}BuC_5H_4)Al(i\text{-}Bu)_2$	147.1	4	[49]
$CpAlMe_2$	149.8	4	[49]
$(MeCp)AlMe_2$	152.6	4	[49]
$CpAlEt_2$	145.5	4	[49]
$(MeCp)AlEt_2$	142.4	4	[49]
$Cp^*\overline{AlN(Mes)CH{=}CHN}(Mes)$	45	7	[33]
$(\eta^1{:}\eta^1\text{-}C_5Me_4CH_2CH_2NMe_2)AlMe_2$	152.9	4	[23]
$(\eta^1{:}\eta^{2/3}\text{-}C_5Me_4CH_2CH_2NMe_2)AlMe_2$	65.4	5	[23]
$(\eta^5\text{-}Cp^*)_2Al^+$	-114.5	(10)	[19]
Cp_2Al^+	-126.4	–	[24]

[a] Chemical shifts are referenced to an $[Al(H_2O)_6]^{3+}$ external standard (δ 0) and were obtained in non-coordinating solvents to which the chemical shifts are essentially insensitive (i.e. $CDCl_3$, C_6D_6, d_8-toluene).

[b] Coordination number indicated by ^{27}Al chemical shift (coordination number exhibited in X-ray crystal structure).

geometry predicted by the ^{27}Al chemical shift for the compound. Coordination of an isocyanide molecule to the aluminum shifts the ring geometries to η^1 and the coordination number to four, resulting in a higher frequency $\delta(^{27}\mathrm{Al})$ of 118 [5]. The $\delta(^{27}\mathrm{Al})$ of 64 for $\mathrm{Al(C_5Me_4H)_3}$ [13] reflects a five-coordinate geometry, indicating perhaps that in solution the compound adopts the $\{\eta^3, \eta^1, \eta^1\}$ combination of ring geometries that it appears to be approaching in the solid state. A strong correlation between $\delta(^{27}\mathrm{Al})$ and structure is observed for $(\eta^1{:}\eta^1\text{-}\mathrm{C_5Me_4CH_2CH_2NMe_2)AlMe_2}$ and $(\eta^1{:}\eta^{2/3}\text{-}\mathrm{C_5Me_4CH_2CH_2NMe_2)AlMe_2}$, which exhibit ^{27}Al chemical shifts of δ 152.9 ppm (4-coordinate) and 65.4 ppm (5-coordinate), respectively. Given the highly fluxional nature of cyclopentadienylaluminum compounds, the apparent sensitivity of their ^{27}Al-NMR chemical shifts to the ground state coordination geometry of the cyclopentadienyl ring is surprising. Nevertheless, ^{27}Al-NMR is clearly a useful tool for determining the structures of these species in solution. The $\delta(^{27}\mathrm{Al})$ of 85 for $[(1,2,3,4\text{-}\mathrm{Me_4C_5H)(O}\text{-}i\text{-}\mathrm{Pr)ClAl]_2}$ is lower than expected from the four-coordinate geometry of the aluminum exhibited in the solid state. It may indicate a dissociation of the dimers in solution to 5-coordinate monomers with η^3 cyclopentadienyl rings. In order to explore this possibility, we plan to re-examine this system and determine its molecularity in solution.

The ^{27}Al chemical shifts for the η^5-cyclopentadienylaluminum compounds which have been characterized to date are generally higher field of what one would expect based on the effective coordination number of the aluminum and are very sensitive to the nature of the other substituents on the aluminum. Whereas the seven-coordinate compound **4** exhibits chemical shift of δ 65, Cowly's seven-coordinate CpAl-diazabutadiene complex exhibits an ^{27}Al-NMR peak at δ 45, and the structurally similar, dimeric iminoalane **13** exhibits a much higher field resonance at δ -5. The ^{27}Al-NMR resonance for $\mathrm{CpAl(BHT)_2}$ (**11**) is difficult to distinguish from the NMR probe signal but appears as a shoulder on the high field side of the probe signal which occurs at ca. δ 60. Although the molecular structure of $\mathrm{Cp_2Al(BHT)}$ (**10**) has not yet been determined, its high field ^{27}Al chemical shift of -13 ppm indicates that at least one of its cyclopentadienyl rings is η^5.

The aluminocenium cations $\mathrm{Cp_2Al^+}$ and $\mathrm{Cp^*_2Al^+}$ have the highest field ^{27}Al-NMR chemical shifts yet observed for normal-valent organoaluminum compounds [19,24]. Exceptionally high field shifts have been observed for other nuclei sandwiched by one or two cyclopentadienyl rings and is at least partly attributable to ring current phenomena [50].

Ab initio calculations of ^{27}Al-NMR chemical shifts have been useful for explaining the wide range of chemical shifts exhibited by Al(I) compounds and, in particular, for relating the ^{27}Al chemical shifts of Cp*Al(I) and CpAl(I) compounds to their electronic structures [3,51]. Similar calculations on cyclopentadienylaluminum(III) compounds may offer insight into the wide range of ^{27}Al-NMR chemical shifts exhibited by η^5 systems in addition to providing theoretical support for the use of ^{27}Al-NMR chemical shifts to deduce ring coordination geometries.

4. Summary and outlook

A clearer picture of the bonding in cyclopentadienylaluminum compounds is developing through a combination of molecular structure determinations, theoretical calculations, and NMR spectroscopic measurements. Structures with η^1, η^2, η^3, and η^5 cyclopentadienyl ring coordination geometries have been characterized crystallographically. Ab initio calculations reveal a relatively flat potential over the whole range of η^1-η^5 structures, such that migration of the aluminum about the cyclopentadienyl ring is essentially unrestricted, and distinct structures cannot be frozen out in solution on the NMR time scale. The ground state geometries between the aluminum and its cyclopentadienyl ring(s) depend on a delicate balance between ionicity, π-bonding, and steric repulsion. For simple CpAl compounds, an η^2-geometry is preferred in the absence of Lewis base adducts or π-bonding substituents which reduce the Cp–Al π-bonding. Increasing ionicity between the aluminum and its non-cyclopentadienyl substituents results in a stronger, more covalent Cp–Al bond, thereby shifting the structures to higher hapticities. A similar trend is observed among Cp*Al compounds. Interestingly, with very strong σ and π donor ligands, the Cp–Al interaction becomes more ionic, in which case an η^5 geometry is again preferred.

Given the shallowness of the potential-energy surfaces for ring slippage in cyclopentadienylaluminum compounds, the structures exhibited in the solid state could deviate from the solution phase ground state geometries as a result of packing forces within the crystal. Fortunately, the ^{27}Al-NMR chemical shifts of the compounds appear to be sensitive to ring hapticity in terms of their contribution to the coordination number of the aluminum, thus providing an additional experimental method for determining the ground state geometries of the compounds. The wide range of ^{27}Al chemical shifts exhibited by five-coordinate η^5 compounds is curious and could be a reflection of the relative contributions of π-bonding and ionic bonding to the η^5-Cp–Al interaction. Additional structural and chemical shift data along with further theoretical examination of model compounds should answer this question. On the horizon is a cogent relationship between the nature of the bonding between the aluminum and its cyclopentadienyl ring(s), the ring coordination geometries, and the ^{27}Al-NMR chemical shifts of cyclopentadienylaluminum(III) compounds.

So far there has been little investigation into the reactivity of cyclopentadienylaluminum(III) compounds. The small molecule insertion and cationic initiation of olefin polymerization demonstrated with these compounds to date recommends their further exploration as Lewis acid promoters for organic transformations such as Diels–Alder reactions, reactions involving the reduction or coupling of ketones and aldehydes [52–54], and other nucleophile–electrophile reactions [55], as catalysts for cationic and anionic olefin polymerizations and ring-opening polymerizations [56–59], and as catalysts for the insertion polymerization of olefins [60]. The amenability of the cyclopentadienyl ligand toward synthetic modifications which change the electronic and steric properties of the ligand is an attractive feature which might be exploited in these applications.

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