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Heteroatom Derivatives of Cyclopentadienylaluminum: X-ray Crystal Structure of (η^5-C_5H_5)(2,6-*t*-Bu-4-Me-C_6H_2O)$_2$Al

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The cyclopentadienylaluminum aryloxide derivatives bis(cyclopentadienyl)(2,6-di-*tert*-butyl-4-methylphenoxy)-aluminum (**1**) and (η^5-cyclopentadienyl)bis(2,6-di-*tert*-butyl-4-methylphenoxy)aluminum (**2**) have been prepared via the alcoholysis of tricyclopentadienylaluminum with 2,6-di-*tert*-butyl-4-methylphenol. The X-ray crystal structure of **2** was determined. The molecule crystallizes in the monoclinic space group $C2/c$ with $a = 15.4870(6)$ Å, $b = 11.5404(5)$ Å, $c = 18.3294(7)$ Å, $\beta = 103.0990(10)°$, $Z = 4$, and $V = 3190.7(2)$ Å^3 ($R[I > 2\sigma(I)] = 0.0755$, $R_w = 0.1489$). In the solid state, the cyclopentadienyl ring is bound η^5 to the aluminum atom. Ab initio calculations on model compounds indicate that the pentahapto geometry of the cyclopentadienyl ring is due to the electron-withdrawing nature of the aryloxide ligands which allows greater π-interaction between the aluminum center and the cyclopentadienyl ligand.

Introduction

Cyclopentadienyl compounds of the main group elements exhibit a broad range of ring-coordination geometries, fluxional behaviors, and reactivities that reflect the degree of covalent versus ionic character in their bonding.[1−3] The structure and reactivity of cyclopentadienylaluminum compounds are particularly sensitive to the nature of the other ligands on the aluminum center, as well as the substitution of the cyclopentadienyl ring.[4−6] The bonding in cyclopentadienylaluminum compounds appears to be delicately balanced between the ionic bonding characteristic of alkali and alkaline earth metal cyclopentadienide compounds and the covalent bonding exhibited by cyclopentadienyl compounds of Si, Ge, Sn, and Hg. Thus, besides the monohapto, σ-type bonding typical of the latter elements, cyclopentadienylaluminum compounds exhibit η^2-, η^3-, and η^5-ring coordination geometries in the solid state. Ab initio calculations indicate that the energy differences between these geometries are very small (<2 kcal/mol).[4] This is consistent with the highly fluxional nature of these compounds in solution and our inability to “freeze out” their rearrangments on the NMR time scale.

To determine the effects of potentially π-bonding alkoxide ligands on the coordination geometry between the cyclopentadienyl ring and aluminum, we set out to prepare and structurally characterize a monomeric alkoxide analogue of Cp_2AlMe (Cp = C_5H_5), for which we have characterized an unusual bis(η^2-Cp) structure in the solid state.[7,8] Since Cp_2Al(O-*i*-Pr) is dimeric,[9,10] we needed an alkoxide derivative that would be sufficiently bulky to prevent dimer formation. The 2,6-di-*tert*-butyl-4-methylphenoxy group (BHT) has been a popular ligand for this purpose.[11−14] Described herein are our efforts to prepare and structurally characterize Cp_2Al(BHT) (**1**). Although we have been unsuccessful at determining the molecular structure of this compound, we have obtained the structure of the monocyclopentadienyl compound CpAl(BHT)$_2$ (**2**) which is obtained as a coproduct in the synthesis of Cp_2Al(BHT). The η^5-Cp coordination geometry exhibited by CpAl(BHT)$_2$ in the solid state is interesting, for it has been characterized for only one other CpAl compound, [CpAlN(2,6-*i*-$Pr_2C_6H_3$)]$_2$.[15] Ab initio calculations on model hydroxy, alkoxy, amido, and imido derivatives of cyclopentadienylaluminum offer an explanation for why both electron-withdrawing and electron-donating groups can promote η^5 Cp−Al bonding.

Experimental Section

General Procedures and Methods. All manipulations were performed using a combination of glovebox, high-vacuum, or Schlenk techniques. All solvents were distilled under nitrogen over sodium

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(1) Jutzi, P. *Adv. Organomet. Chem.* **1986**, *26*, 217−295.

(2) Jutzi, P. *Chem. Rev.* **1986**, *86*, 983−996.

(3) Jutzi, P. *J. Organomet. Chem.* **1990**, *400*, 1−17.

(4) Fisher, J. D.; Budzelaar, P. H. M.; Shapiro, P. J.; Staples, R. J.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1997**, *16*, 871−879.

(5) 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*, 1107−1109.

(6) Schonberg, P. R.; Paine, R. T.; Campana, C. F.; Duesler, E. N. *Organometallics* **1982**, *1*, 799−807.

(7) Fisher, J. D.; Wei, M.-Y.; Willett, R.; Shapiro, P. J. *Organometallics* **1994**, *13*, 3324−3329.

(8) Fisher, J. D.; Wei, M.-Y.; Willett, R.; Shapiro, P. J. *Organometallics* **1995**, *14*, 4030.

(9) Kunicki, A.; Sadowski, R.; Zachara, J. *J. Organomet. Chem.* **1996**, *508*, 249−250.

(10) Fisher, J. D.; Golden, J. T.; Shapiro, P. J.; Yap, G. P. A.; Rheingold, A. L. *Main Group Met. Chem.* **1996**, *19*, 521−530.

(11) Shreve, A. P.; Mulhaupt, R.; Fultz, W.; Calabrese, J.; Robbins, W.; Ittel, S. D. *Organometallics* **1988**, *7*, 409−416.

(12) Petrie, M. A.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 8704−8708.

(13) Healy, M. D.; Mason, M. R.; Gravelle, P. W.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1993**, 441−454.

(14) Healy, M. D.; Wierda, D. A.; Barron, A. R. *Organometallics* **1988**, *7*, 2543−2548.

(15) Fisher, J. D.; Shapiro, P. J.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1996**, *35*, 271−272.

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benzophenone ketyl (toluene, methylcyclohexane, petroleum ether). The dried solvents were stored in line-pots from which they were either vacuum-transferred from sodium benzophenone ketyl or cannulated directly. NMR solvents benzene-d_6 and chloroform-*d* 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. 2,6-Di-*tert*-butyl-4-methylphenol (Aldrich) was used as received. Cp_3Al was prepared as described previously.[7]

NMR spectra were recorded on an IBM NR-300 (300.13-MHz ^1H, 74.43-MHz ^{13}C, 78.206-MHz ^{27}Al) and an IBM NR-200 (200.13-MHz ^1H, 50.327-MHz ^{13}C, 52.148-MHz ^{27}Al). All chemical shifts are reported in parts per million and referenced to solvent (^{13}C, ^1H) or $Al(OH)_3$ (^{27}Al, external reference, δ 0 ppm). Elemental analyses were performed by Desert Analytics (Tucson, AZ).

Preparation of $Al(C_5H_5)_2(BHT)$ (1). To a solution of $AlCp_3$ (1.02 g, 4.6 mmol) in 50 mL of toluene was added 2,6-di-*tert*-butyl-4-methylphenol (1.01 g, 4.6 mmol), and the reaction mixture was heated overnight at 50 °C. All volatiles were removed in vacuo, and the remaining white, solid residue was transferred to a sublimator. Sublimation of the solid (90−100 °C, 10^{-2} Torr) afforded pure $(C_5H_5)_2(BHT)Al$ as a waxy solid. (Yield = 0.516 g, 30%; mp = 114−117 °C, uncorrected.) ^1H NMR (C_6D_6): δ 7.10 (s, 2, aryl-*H*), 6.03 (s, 10, C_5H_5), 2.29 (s, 3, aryl-CH_3), 1.47 (s, 18, aryl-$C(CH_3)_3$). ^{13}C NMR (C_6D_6): δ 152.7, 137.4, 126.1, 125.4 (aryl-*C*), 109.8 (C_5H_5), 34.1 ($C(CH_3)_3$), 30.8 ($C(CH_3)_3$), 20.4 (CH_3). ^{27}Al NMR (C_7D_8): δ −14. Anal. Calcd for $C_{25}H_{33}AlO$: C, 79.75; H, 8.83. Found: C, 78.28; H, 8.79.

Preparation of Al $(C_5H_5)(BHT)_2$ (2). To a solution of 0.52 g (2.3 mmol) of $AlCp_3$ in 25 mL of methylcyclohexane was added 2,6-di-*tert*-butyl-4-methylphenol (BHT) (1.0 g, 4.5 mmol). The reaction mixture was heated at 50 °C overnight. The solution was concentrated to ca. 10 cm^3 and cooled to −78 °C to afford $(C_5H_5)(BHT)_2Al$ as a white precipitate. (Yield = 0.40 g, 56%; mp = 162−164 °C, uncorrected.) ^1H NMR (C_6D_6): δ 7.17 (s, 4, aryl-*H*), 6.18 (s, 5, C_5H_5), 2.34 (s, 6, aryl-CH_3), 1.53 (s, 36, aryl-$C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 153.5, 138.5, 127.0, 126.0 (aryl-*C*), 110.4 (C_5H_5), 35.4 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$), 21.0 (CH_3). ^{27}Al NMR (C_6D_6): δ >0 (extremely broad and overlapping with probe signal). Anal. Calcd for $C_{35}H_{51}AlO_2$: C, 78.84; H, 9.42. Found: C, 79.28; H, 9.90.

Theoretical Calculations. All calculations were of the all-electron restricted Hartree−Fock[17a] and MP2[17b] types, using the 3-21G(*) basis set,[19−21] and were carried out using the GAMESS program[18] on IBM SP2, Silicon Graphics Challenge, and O2 workstations. All structures were fully optimized at the RHF and RMP2 levels; geometry differences between RHF and RMP2 structures were small, in agreement with earlier work.[4]

X-ray Crystallographic Procedures. Block-shaped crystals of $AlCp(BHT)_2$ were grown from a saturated toluene solution cooled at 0 °C. A suitable crystal was selected and mounted in a thin-walled, nitrogen-flushed, glass capillary. The unit-cell parameters 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 a LT-2 low-temperature apparatus operating at 193 K. Data were measured using ω scans of 0.3°/frame for 30 s, such that a hemisphere was collected. A total of 3232 independent reflections were collected. The first 50 frames were collected at the end of the data collection to monitor for decay. Cell parameters were retrieved using SMART software and refined using SAINT on all reflections. Data reduction was performed using the SAINT software which corrects for Lorentz polarization and decay. Absorption corrections were applied using XEMP supplied by Siemens in their SHEXTL-PC software.

The systematic absences in the diffraction data were uniquely consistent with $C2/c$. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in either the SHELXTL (5.1) or the SHELXTL PLUS (4.2) program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

Results and Discussion

Synthesis of $[Cp_2Al(BHT)]_x$ and $CpAl(BHT)_2$. Alcoholysis of Cp_3Al with 1 equiv of 2,6-di-*tert*-butyl-4-methylphenol produces a mixture of $[Cp_2Al(BHT)]_x$ (**1**), $CpAl(BHT)_2$ (**2**), and unreacted Cp_3Al. No $Al(BHT)_3$ was detected, although it can be formed by reacting 3 equiv of the alcohol with Cp_3Al under the same reaction conditions. $[Cp_2Al(BHT)]_x$ can be isolated cleanly from the product mixture as a waxy, white solid by sublimation (90−100 °C, 10^{-2} Torr). The ^{27}Al NMR chemical shift of −15 ppm for **1** is the highest field resonance found for any $(C_5H_5)Al$ compound to date. We attribute the low frequency of the ^{27}Al NMR signal for **1** to the shielding effects of an η^5-Cp in the compound since a comparable ^{27}Al NMR chemical shift of −5 ppm is exhibited by $[(\eta^5\text{-}C_5H_5)AlN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_2$,[15] and an extraordinarily high field signal of δ −114 was observed for Schnöckel's aluminocene cation, $[(\eta^5\text{-}C_5Me_5)_2Al]^+$,[16] which has two pentahapto-coordinated rings. Efforts to obtain suitable crystals of **1** for an X-ray structure have been unsuccessful. Furthermore, the compound decomposes over several weeks, even when stored as a solid at room temperature in a nitrogen-filled glovebox. The decomposition products have not been characterized. Compound **2** is more robust, showing only a slight gray discoloration after months of storage. We did obtain X-ray quality crystals of **2**, the molecular structure of which is described below. Compound **2** can be obtained more directly from the reaction of Cp_3Al with 2 equiv of BHT. Interestingly, its ^{27}Al NMR signal is above 0 ppm (though poorly resolved due to its overlap with the probe signal and its considerable broadness). The downfield shift of the signal relative to that of compound **2** is probably due to the deshielding effect of the additional electron-withdrawing BHT group.

Molecular Structure of $CpAl(BHT)_2$. An ORTEP drawing of the molecular structure of **2** is shown in Figure 1. Crystallographic data and selected bond lengths and angles are listed in Table 1 and Table 2, respectively. Particularly noteworthy is the η^5 geometry of the cyclopentadienyl ring. This ring coordination geometry has been found for only one other structurally characterized $(C_5H_5)Al$ compound, $[CpAlN(2,6\text{-}i\text{-}PrC_6H_3)]_2$.[15] The cyclopentadienyl ring is disordered and appears slightly slipped due to a 2-fold rotational axis that passes through the aluminum atom and the ring, though not quite through the center of the ring. Indeed, the angle between the Al−ring centroid and the mean plane of the ring is 88.4°. The structure of $CpAl(BHT)_2$ is very similar to that of $MeAl(BHT)_2$.[11] As in the structure of $MeAl(BHT)_2$, the BHT rings

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(16) Dohmeier, C.; Schnöckel, H.; Robl, C.; Schneider, U.; Ahlrichs, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1655−1657.

(17) (a) Roothan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69. (b) GAMESS MP2 implementation: Rice, J. E.; Amos, R. D.; Handy, N. C.; Lee T. J.; Schaefer, H. F. *J. Chem. Phys.* **1986**, *85*, 963. Watts, J. D.; Dupuis, M. *J. Comput. Chem.* **1988**, *9*, 158.

(18) 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.

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

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

(21) 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.

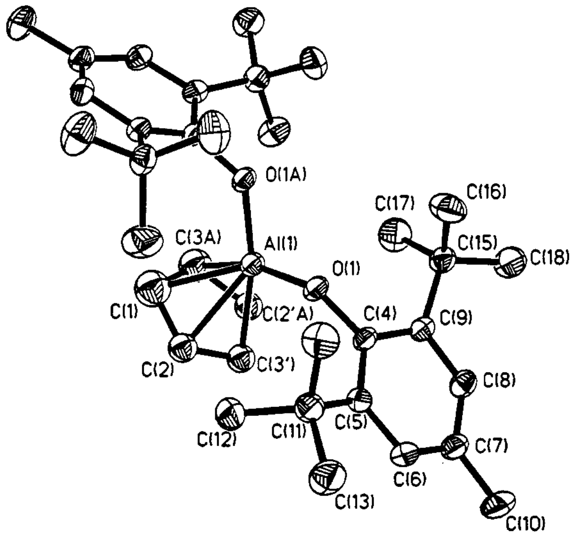

Figure 1. Molecular structure of (η^5-C_5H_5)(2,6-*t*-Bu-4-Me-C_6H_2O)$_2$-Al (**2**).Thermal ellipsoids are shown at 50% probability.

Table 1. Summary of Crystallographic Data and Structural Analysis for $AlCp(BHT)_2$ (**2**)

formula	$C_{35}H_{51}AlO_2$
fw	530.74
a, Å	15.4870(6)
b, Å	11.5404(5)
c, Å	18.3294(7)
α, deg	90
β, deg	103.0990(10)
γ, deg	90
Z	4
V, Å^3	3190.7(2)
space group	*C*2/*c*
cryst size	0.2 × 0.2 × 0.4 mm
D_{calc}, g/cm^3	1.105
μ, mm^{-1}	0.091
θ range for data collection	2.22°−27.51°
GOF on F^2	1.182
final *R* indices [$I > 2\sigma(I)$]	R^a= 0.0755, $R_w{}^b$ = 0.1489

[a] $R = \sum|F_o - F_c|/\sum|F_o|$. [b] $R_w = \{[\sum\omega(F_o - F_c)^2]/[\sum w(F_o)^2]\}^{1/2}$; $\omega = 1/[\sigma^2(F_o)^2 + (xP)^2 + (yP)^2]$, where $P = (F_o{}^2 + 2F_c{}^2)/3$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $AlCp(BHT)_2$ (**2**)

Al−O(1)	1.736(2)	Al−cnt	1.920(9)
Al−C(1)	2.274(8)	C(1)−C(2)	1.418(12)
Al−C(2)	2.259(11)	C(2)−C(3)	1.403(12)
Al−C(3)	2.246(8)	C(2′A)−C(3)	1.426(11)
Al−C(2′A)	2.238(10)	C(1)−C(3′A)	1.412(10)
Al−C(3′A)	2.278(9)		
O(1)−Al−O(1A)	101.59(13)	C(4)−O(1)−Al	134.8(2)

are almost coplanar, and the Al−Cp normal is almost perpendicular to the plane defined by the two BHT groups. At 1.736(2) Å, the Al−O bonds in **2** are significantly longer than the 1.685(2)- and 1.687(2)-Å Al−O bonds of the methyl analogue. The O−Al−O bond angle in **2** is also narrower (101.59(13)° vs 111.9(1)°). The narrower O−Al−O angle in **2** is consistent with its longer Al−O bonds and might be attributable to the greater steric bulk of the cyclopentadienyl ring relative to a methyl group.

Ab Initio Calculations. To understand the effects of heteroatom substituents on the Al−Cp interaction and to explain the occurrence of η^5-ring coordination geometries in CpAl-$(BHT)_2$ and $[CpAlN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_2$, we performed ab initio calulations at the RHF/3-21G(*) and RMP2/3-21G(*) levels on some model cyclopentadienylaluminum heteroatom derivatives.

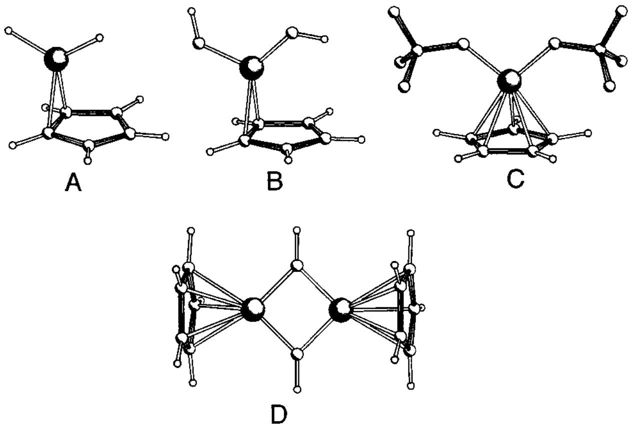

Figure 2. PLUTO drawings of calculated structures (RMP2/3-21G-(*)) for $CpAlH_2$ (A), $CpAl(OH)_2$ (B), $CpAl(OCF_3)_2$ (C), and $[CpAlNH]_2$ (D).

We started with $CpAl(OH)_2$ as the simplest model compound for our alkoxide species. This compound was found to prefer an η^2-Cp geometry. In fact, the structure calculated for CpAl-$(OH)_2$ is similar to the structure calculated earlier for $CpAlH_2$ (Figure 2). Bond distances for the two compounds are similar, and there was no obvious shift to an η^1 structure. Curiously, one of the OH bonds is aligned with the Cp ring plane, whereas the other points away from the plane; this is the *only* arrangement of the OH groups that corresponds to a local minimum. The stability of this conformation may be due to a favorable arrangement of charges (positive H closest to the negatively charged Cp ring). $CpAl(OMe)_2$ was found to prefer a similar η^2 geometry, instead of the η^5 geometry found for CpAl(BHT). Since using complete phenoxide groups would make the calculation rather large, $CpAl(OCF_3)_2$ was examined to determine the effects of a more electron-withdrawing alkoxide on the Cp−Al structure. $CpAl(OCF_3)_2$ was indeed found to prefer an η^5 structure like that of $CpAl(BHT)_2$. Furthermore, both O−C bonds are nearly parallel to the Cp, just like in the molecular structures of $MeAl(BHT)_2$ and $CpAl(BHT)_2$. From these results we conclude that *π*-donation from O to Al in CpAl-$(OR)_2$ is not strong enough to affect the Cp−Al bonding, but that the electron-withrawing character of the aryloxy groups can result in a shift toward an η^5 structure by increasing the amount of *π*-bonding in the Al−Cp interaction. Similar ligand effects on cyclopentadienyl ring geometry have been characterized in Cp*Al compounds. For example, whereas both [Cp*Al(Me)-(μ-Cl)]$_2$ and [Cp*Al(*i*-Bu)(μ-Cl)]$_2$ have η^3-bound Cp* rings,[6] [Cp*Al(Cl)(μ-Cl)]$_2$ has η^5 Cp* rings.[5] This shift toward η^5-bonding can be understood on the basis of an MO description. The aluminum atom always has one p-orbital available for Cp−Al *π*-bonding; the other is used in the formation of the two Al−X *σ*-bonds. When the Al−X bonds become more ionic (in the sense $Al^{\delta+}-X^{\delta-}$), these *σ*-bonds become more localized on the X atoms, and hence the Al *p*-orbital originally involved in the Al−X bonds *also* becomes available for Cp−Al *π*-bonding, resulting in a more covalent Al−Cp bond and a trend toward higher hapticity. In the limit of the purely ionic $CpAl^{2+}$ species, one would expect an η^5 arrangement with two strong Cp-Al *π*-bonds.

In light of the structural arguments made above for cyclopentadienylaluminum alkoxide species, the ionic character of the Al−N bonds is unlikely to be an important factor in the pentahapto Cp geometry exhibited by [CpAlN(2,6-*i*-$Pr_2C_6H_3$)]$_2$. Indeed, the calculated structure of CpAl(NH_2)$_2$ turned out to be η^2. When [CpAlNH]$_2$ was used as a simple model of the dimeric iminoalane, however, the calculated structure gave a symmetrically η^5-bound Cp ring and a nearly square Al_2N_2 core, just like the structure of [CpAlN(2,6-*i*-$Pr_2C_6H_3$)]$_2$. We believe that the explanation for the η^5-Cp geometry in the cyclopentadienyliminoalane structure is effectively the opposite of that for the structure of Cp_2Al(BHT). Because the imido substituents on each aluminum atom are strong σ- and π-donors, they stabilize polarization of the Cp−Al bond in the sense of $Al^{\delta+}$−$Cp^{\delta-}$. In this case, the substituents push the Al 3p acceptor orbital up in energy so that it is less available for Cp-Al π-bonding, and the η^5-Cp geometry arises from the ionic nature of the Al−Cp interaction. To illustrate the effects of different substituents on aluminum on the polarity of the Al−Cp bond, Table 3 lists the Mulliken charges on Cp, determined at the RHF and RMP2 levels, for some $CpAlX_2$ model compounds. Although absolute values of Mulliken charges are not very meaningful, the relative values for the charges on the Cp groups should be meaningful, and they do reflect the trend we describe.

Table 3. Mulliken Charges for CpAl Compounds (RHF/3-21G(*) and RMP2/3-21G(*))

	q(Cp)		
compound	RHF	RMP2	hapticity
CpAl(OCF_3)$_2$	−0.33	−0.25	η^5
$CpAlH_2$	−0.42	−0.32	η^2
CpAl(OH)$_2$	−0.48	−0.39	η^2
CpAl(NH_2)$_2$	−0.52	−0.43	η^2
[CpAlO]$_2$	−0.58	−0.46	η^5
[CpAlNH]$_2$	−0.64	−0.52	η^5

Thus, for aluminum we have the curious situation that, starting from an η^2 arrangement, *both increasing and decreasing* the degree of ionicity of the Cp−Al bond result in a shift to higher hapticity. One difference between the two situations is that the η^5 structure observed with electron-withdrawing X groups should have a significantly stronger Al−Cp bond. Indeed, the calculated Al−Cp distance in CpAl(OCF_3)$_2$ is only 1.87 Å compared to 1.91 Å for [CpAlNH]$_2$. That the experimental Al−Cp distances do not reflect these trends is probably due to the fact that both structures have disordered Cp rings, and both compounds are rather crowded. Overall, however, our calculations on simple model compounds appear to reproduce the trends observed in the X-ray structures of much more crowded systems, indicating that one does not need to invoke steric factors to explain the observed hapticities. Our future efforts will be directed toward expanding the database of examples of crystallographically characterized cyclopentadienylaluminum compounds in order to further test these theories.

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Supporting Information Available: An X-ray crystallographic file in CIF format for complex (η^5-C_5H_5)(2,6-*t*-Bu-4-Me-C_5H_2O)Al (**2**) is available on the Internet only. Access information is given on any current masthead page.

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