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Constrained-Geometry Aluminum Complexes with η^5;η^1-Coordination: Syntheses, Structures, and Theoretical Studies of Dicarbollylamino Aluminum(III) Complexes

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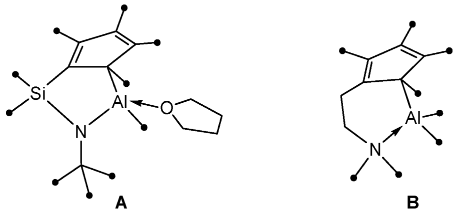
The great success of constrained-geometry catalysts in the polyolefin industry[1] has led to interest in developing main group metal anologues of these catalysts.[2] One of the reference catalysts is the titanium complex [$Me_2Si(Me_4C_5)$(*t*-BuN)]$TiCl_2$. The term "constrained geometry" is derived from the half-sandwich structure of these complexes, in which one ancillary ligand tethered to the cyclopentadienide ring functions as a σ-donor.[3a] The unique combination of η^5;η^1-coordination is believed to facilitate the incorporation of various α-olefins into growing polymer chains.[3] Among the main group metals, aluminum is of special interest because of its general utility as an alternate catalytic system for olefin polymerization.[4] Until now, however, no constrained geometry organoaluminum(III) complexes with η^5;η^1-coordination had been structurally characterized. Previously, only η^1;η^1-coordinated organoaluminum(III) complexes such as monoarmed cyclopentadienide systems containing either amido **A**[2c] or amine **B**[2b] functional ligands have been structurally characterized, as shown in Chart 1.

Aluminum appears to be particularly flexible in its coordination with a cyclopentadienyl ring, in that examples of cyclopentadienyl aluminum complexes with η^1-,[5] η^2-,[6] η^3-,[7] and η^5-[8] geometries have all been characterized.[9] However, in the case of complexes **A** and **B**, the electronic influence of the amido or amine tether should directly inhibit the formation of a π-bond between the cyclopentadienyl ring and aluminum atom, thereby only providing an η^1-type coordination geometry in the ground-state structure of the molecule.

In the search for new types of ligand systems for which η^5;η^1-coordination may be plausible, the dicarbollyl moiety has been employed as an η^5-coordinated group instead of the cyclopentadienyl (Cp) ligand. The dicarbollyl (Dcab) system is a versatile ligand that is an isolobal inorganic analogue of the Cp^- ion. To prepare constrained-geometry complexes with this dicarbollyl functionality is a challenging project since incorporation of a dicarbollyl fragment into the ligand framework will create new metal/charge combinations. The formal replacement of the monoanionic Cp^- ligand in $[CpAl(III)]^{+2}$ with the isolobal, dianionic dicarbollyl ligand $Dcab^{-2}$ to give $[(Dcab)Al(III)]^{+1}$ fragment reduces the overall charge by one unit, but leaves the gross structural and metal frontier orbital properties unchanged. Consequently, complex designs of this type can potentially be used to control secondary metal/ligand interactions; the weaker ionic character of the pendent neutral amino group enhances the metal's π-bonding interaction with the dicarbollyl ligand through η^5-coordination. Thus, it was predicted that incorporation of the dicarbollyl fragment into the ligand framework would enable construction of constrained-geometry aluminum complexes with new metal/charge combinations. Indeed, treatment of dicarbollylmethylamine **1**[10] with 1 equiv of $AlMe_3$ in toluene at 0 °C gave constrained-geometry aluminum complexes of the general formula [(η^5-$RC_2B_9H_9$)CH_2(η^1-NMe_2)]Al(Me) (R = H, **2a**; Me, **2b**) in good yield (Scheme 1).

Chart 1. Previous Examples of η^1;η^1-Bonded Aluminum(III) Complexes.



The solid-state structures of aluminum complexes **2a** and **2b** derived from single-crystal X-ray analyses revealed that they are isomorphous and isostructural (see Supporting Information). The central aluminum atom is π-bound to the [*nido*-$RC_2B_9H_9$] fragment and σ-bound to the methylamine sidearm in a constrained manner. The centroid distance from the aluminum atom is about 1.71 Å, indicating that there are strong π-bonding interactions between Al^{3+} and dicarbollide.[11] The structures of **2** reported here represent the first solid-state structural information on constrained-geometry aluminum complexes with η;$^5\eta^1$-mode coordination.

To understand the bonding interactions between the aluminum ion and dicarbollyl ligand, relativistic density functional theory (DFT) calculations using the Amsterdam density functional (ADF) code with the Becke and Perdew functional were performed on model complexes such as [(Cp)CH_2(NMe)]Al(Me) **C**, $[\{(Cp)CH_2(NMe_2)\}Al(Me)]^{+1}$ **D**, and [(Dcab)CH_2(NMe_2)]Al(Me) **2a** (Chart 2). We first concentrated on the simplest model compound, Cp-amido complex (**C**), the Lewis acid–base adduct between $AlMe^{+2}$ and $[(Cp)CH_2(NMe)]^{-2}$. We then examined the effect of adding a methyl substituent to the nitrogen atom and compensating the charge with +1 as shown in the Cp-amino complex **D**, the Lewis acid–base adduct between $AlMe^{+2}$ and $[(Cp)CH_2(NMe_2)]^{-1}$. Adding a methyl substituent to the nitrogen changes the hapticity of the Cp ring from η^3 to η^5 and the bond distance of Al–N from 1.810 to 2.091 Å. These changes occur because the two lone pairs on the amido-nitrogen atom in **C** donate electrons more efficiently than the single lone pair on the amino-nitrogen atom in **D**. This effect is partly compensated in **D** by aluminum atom's accepting more electron density from the Cp ring. In **D**, the calculated energy shows a preference for η^5;η^1-bonding, consistent with the results of the DFT calculation previously performed on the related complex, $[(\eta^5\text{-Cp})H_2Si(\eta^1\text{-NMe})\}Al]^{+1}$.[2c]

Fixing the nitrogen part in **D** and changing the Cp ring to an isolobal dicarbollyl moiety as in **2a** further increases the Al–N bond distance from 2.091 to 2.146 Å. The relative formation

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Scheme 1. Preparation of Constrained-Geometry Aluminum(III) Complexes Derived from Dicarbollylamine Ligand Showing η^5;η^1-Bonding

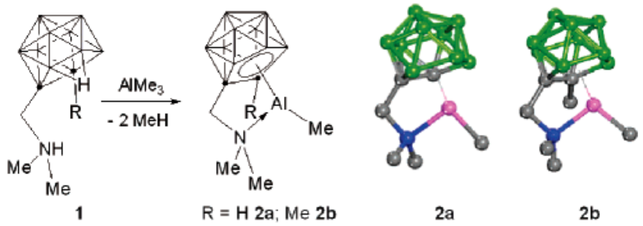
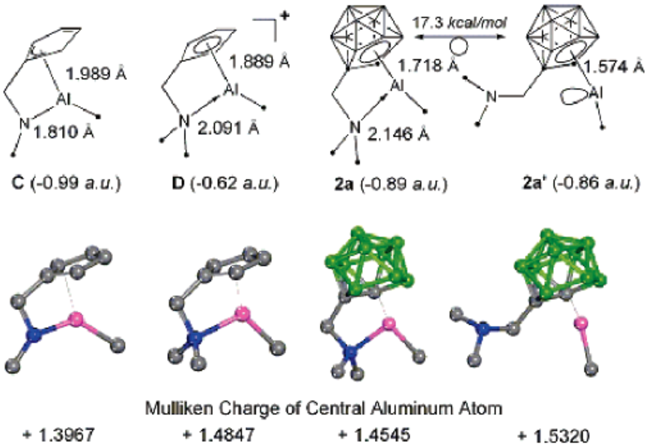


Chart 2. Optimized Structures of Constrained-Geometry Aluminum Complexes.



enthalpy of the Lewis acid−base adduct **2a** (−0.89 au) is compared with that of **C** (−0.99 au) and **D** (−0.62 au) in Chart 2. The results indicate that complex **2a** is less stable than **C**, reverting to an η^5;η^1-bonding which was authenticated in a structural study of **2**. This is consistent with the fact that the σ-bonding interaction between Al and N in **C** is stronger than that in **D** and the π-bonding interaction between Dcab and Al in **2a** is stronger than that between Cp and Al in **D**.

A strong π-type interaction between aluminum and Dcab was clearly demonstrated by the DFT calculation in which the untethered structure of **2a′** was optimized. The existence of a half-sandwich aluminum complex of **2a′** is further confirmed by a variable temperature NMR study of **2b** (see Supporting Information). Detachment of the tethered amine sidearm from the aluminum center ensures the stability of η^5-type coordination with the dicarbollyl ligand.[12] Thus, introduction of the dicarbollyl unit onto the ring stabilizes the η^5;η^1-bonding mode, which was not found for the complex [(η^1-Cp*)Me$_2$Si(η^1-N^{t}Bu)]Al(Me)(THF) **A**.[2c] We believe that both the σ-electronic contribution from the amine sidearm and the π-bonding capability of the dicarbollyl unit create an ideal bonding environment for the formation of novel constrained-geometry aluminum(III) complexes.

Herein, we report for the first time the structural characterization of the constrained-geometry aluminum(III) complexes with η^5;η^1-coordination and an explanation of the preference for the constrained geometry in dicarbollylamine ligand systems based on DFT calculations. Further studies exploring the chemistry of these unique complexes are currently under way.

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Supporting Information Available: Detailed experimental procedures including spectroscopic and crystallographic data for the structures **2a** and **2b** and listings giving optimized geometries of the crucial structures (**C**, **D**, **2a**, and **2a′**) reported (Cartesian coordinates, in Å). This material is available free of charge via the Internet at http://pubs.acs.org.

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