

Lewis Acidity Expressed in Neutral Electron-Rich Aluminum(III) Complexes: An Example of Ligand-Defined Catalysis

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Received July 5, 2000

Distorting the ground-state coordination geometry of certain silicon,¹ transition metal,² and main group metal³ complexes leads to metal–ligand complexes that expand their typical coordination numbers in generating Lewis acid–base complexes. Lewis acidic organometallic species exhibiting this type of behavior have recently been implicated as operative intermediates in carbonyl additions, cycloadditions, and conjugate addition reactions.⁴ However, little information regarding the origin of the reactivity expressed by these putative hypercoordinate metal complexes relative to their coordinatively unsaturated analogues currently exists. Investigations described herein of the tetracoordinate Al(III)–triamine complex **1** responsible for catalysis in ketene–aldehyde cycloadditions reveal definitive evidence that a neutral, pentacoordinate Lewis acid–base adduct derived from **1** is the catalytically active species (Figure 1). Evaluating Lewis acidic behavior of related Al(III) complexes as a function of metal electronics, ligand structure, and coordination geometry provides evidence of a unique form of ligand-defined catalysis in which coordinative distortion overcomes inherently unfavorable metal electronics to afford catalytically active, hypercoordinate Al(III) Lewis acids.

A series of optically active Al(III) complexes have recently been reported as Lewis acid catalysts for asymmetric ketene–aldehyde cycloaddition reactions.⁵ On the basis of accepted criteria for Lewis acidity, the neutral tetracoordinate, electron-rich Al(III)–alkyl complexes **1** and **2** seemed to be poor candidates for Lewis acidic catalysts.⁶ To understand the potent catalytic activity expressed by **1**, an X-ray diffraction structure of the Al(III)-based cyclocondensation catalyst was obtained. The X-ray structure indicates **1** to be a four-coordinate complex adopting a trigonal monopyramidal (tmp) geometry with the methyl and triflamide ligands defining the equatorial plane of the bipyramidal

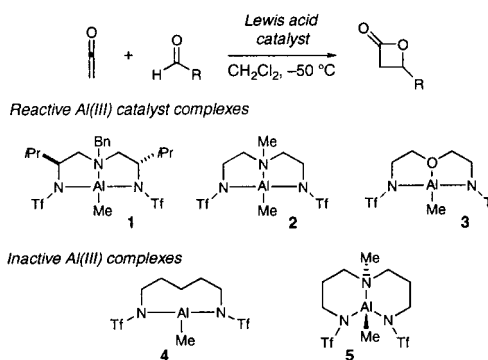


Figure 1. Lewis acid catalysts for ketene–aldehyde cycloadditions.

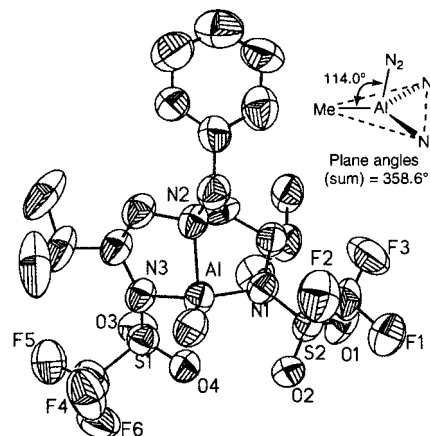


Figure 2. X-ray structure of Al(III)–triamine complex **1**.

structure [$\sum(\text{plane angles}) = 358.6^\circ$] (Figure 2). This crystal structure data suggested that the distorted trigonal monopyramidal coordination geometry defined in **1** by the tridentate ligand was responsible for the observed Lewis acidity by providing a vacant $d_{z^2} p$ orbital disposed ideally to accept a fifth ligand.

X-ray crystal structure analysis in conjunction with $^1\text{H}/^{13}\text{C}$ NMR investigations of Lewis acid–base association expressed by **1** provided definitive evidence for a neutral, five-coordinate Lewis acid–base complex acting as the catalytically active species in the AAC reactions. A toluene solution of **1** containing dimethylformamide (DMF) as a representative carbonyl Lewis base deposited colorless crystals of the **1**·DMF complex (Figure 3). As expected, Lewis base coordination occurs at the vacant “apical” coordination site on the tmp Al ion to deliver the five-coordinate Lewis acid–base complex, with dimethylformamide coordination imparting minimal perturbation to the Al ion’s trigonal plane relative to the free catalyst [$\sum_{\text{angles}}(\mathbf{1}) = 358.6^\circ$; $\sum_{\text{angles}}(\mathbf{1}\cdot\text{DMF}) = 357.8^\circ$].

To probe the dynamics of Lewis acid–base association promoted by the Al[triamine] catalyst, the binding of DMF to **1** was examined by ^1H NMR.⁷ The spectra obtained from titrating **1** with progressive amounts of DMF [0.10 equiv (0.012 M) to 2.0 equiv (0.24 M)] in CD_2Cl_2 are presented in Figure 4. Only the Lewis acid–base complex and the parent catalyst complex are observed during the titration experiment; no time-averaging of resonances that would accompany dynamic Lewis acid–base association is observed. Only in the presence of excess DMF was the unbound Lewis base observed. Therefore, despite the electron-rich nature of the highly coordinated Al–alkyl complex **1**, carbonyl binding is strongly favored even at ambient temperatures

(7) The Al–alkyl complex **1** was verified by ^1H NMR as the catalyst resting state during these cyclocondensation reactions. See ref 5.

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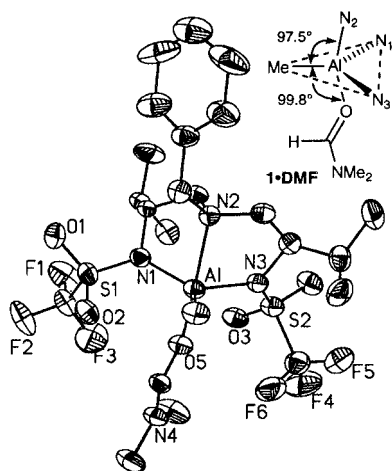


Figure 3. X-ray crystal of **1**-dimethylformamide complex.

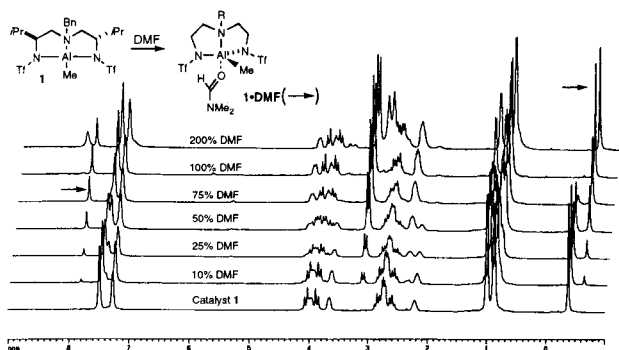


Figure 4. Titration of **1** with dimethylformamide (^1H NMR).

and dissociation of the Lewis acid–base complex is slow on the NMR time scale.⁸

To validate our hypothesis relating distorted metal coordination geometry and the Lewis acidity expressed by **1**, the Al(III) complexes **2–5** were prepared to probe structural requirements for Lewis acidic behavior in structurally and electronically related Al(III) complexes. The catalyzed cycloaddition of ketene and hydrocinnamaldehyde was selected as a test reaction for evaluating the kinetic profiles of the putative Al(III) catalyst complexes **1–5** (Figure 1).⁹ The tetracoordinate complexes **2** and **3**, direct structural analogues of **1**, are effective reaction catalysts (10 mol %), providing $\geq 95\%$ conversion in 1.8–7.5 h.¹⁰ Complex **4** lacking a Lewis basic residue in the ligand backbone and, thus, the coordinative distortion present in **1–3** is inactive as a reaction catalyst despite being coordinatively unsaturated.¹¹ This observation suggests that despite the more highly coordinated nature of **1–3**, ligand-defined geometric distortion enhances Lewis acidity relative to the coordinatively unsaturated analogue.

The Lewis acidity of Al(III)[triamine] complex **5**,¹² identical in coordination number and ligand electronics to **1** and differing only in chelate size, provided further evidence of the relationship between metal coordination geometry and catalyst activity. Geometry optimization of complex **5**¹³ indicated that the expanded chelate size of the propylene triamine-derived ligand conferred

(8) Addition of excess aldehyde to the **1**·DMF complex (CD_2Cl_2 , 23 °C) results in no exchange of the bound DMF indicating that carbonyl coordination to **1** is irreversible under these conditions.

(9) Ketene was generated in situ from acetyl bromide and Hünig's base using the reaction conditions described in ref 5.

(10) Reaction times to 95% conversion: 450 (**1**), 410 (**2**), and 110 (**3**) min. Rate constants (k) calculated for initial stages of reaction (pseudo-first-order kinetics during $t = 0–60$ min): $k(\mathbf{1}) = 1.2 \times 10^{-4}$, $k(\mathbf{3}) = 3.4 \times 10^{-4}$.

(11) Using 10 mol % **4**, the acetyl bromide–hydrocinnamaldehyde test reaction proceeds to $\sim 20\%$ conversion over 8 h but does not turn over.

(12) The trans relationship existing between the methyl ligand and the *N*-methyl substituent in **5** is assumed based on the absence of an nOe between the corresponding resonances in the ^1H NMR.

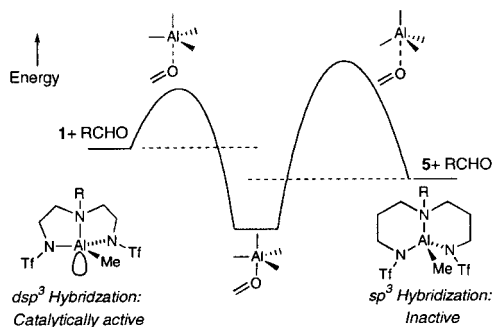


Figure 5. Ligand-defined Lewis acidity in Al(III) complexes.

sufficient conformational mobility to allow the Al(III) ion to adopt a low-energy, tetrahedral coordination geometry.¹⁴ The Al(III) complex **5** did not form a Lewis acid–base adduct with DMF even in the presence of excess Lewis base and is completely inactive as a cycloaddition catalyst.

The radical departure in the reactivity of **5** relative to the cyclocondensation catalyst **1** despite similar electronics and coordination numbers provides compelling evidence of the ligand-defined Lewis acidity available to **1**. The dsp^3 Al ion hybridization in **1** provides a low-lying metal-centered LUMO, thus disposing the Al(III) center ideally to accommodate a fifth ligand and complete the tnp coordination geometry achieved in the Lewis acid–base complex (Figure 5). Conversely, the electron-rich, highly coordinated complex **5**, lacking any ligand-imposed coordinative distortion, exhibits minimal Lewis acidic character. These results suggest that the distorted coordination geometry present in **1** functions to dramatically attenuate the energetic barrier associated with reorganizing the ground-state geometry (tetrahedral) of related four-coordinate Al(III) complexes required to access pentacoordinate species.¹⁵ This ligand-defined catalysis can be interpreted as arising from a combination of ground-state destabilization of the distorted metal complex and a stabilization of the transition state leading to Lewis acid–base association for the preorganized tnp catalysts relative to analogous tetrahedral complexes. The ligand, therefore, acts primarily to define a catalytically active coordination geometry rather than assisting in defining electronic properties within the metal complex necessary for catalysis.¹⁶

It is anticipated that exploiting ligand-defined metal geometries to influence catalyst electrophilicity and reactivity will provide new avenues for developing unique Lewis acid catalysts.

Acknowledgment. The National Science Foundation (CHE-9875735) and the Merck Research Laboratories are gratefully acknowledged for support of this work.

Supporting Information Available: Experimental procedures and X-ray coordinates (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) Geometry optimization was performed using the Spartan molecular dynamics package utilizing the PM3 parameters. This parameter set provided a close match between the X-ray structure of **1** and the geometry optimized structure obtained using Spartan. Thus, this parameter set was considered to provide the most representative geometry of Al(III) complex **5**.

(14) Efforts to obtain an X-ray structure of **5** were unsuccessful.

(15) Reacting complex **5** with excess DMF, even at elevated temperatures, failed to elicit formation of a Lewis acid–base adduct. This observation is indicative of the large energetic barrier that would accompany accessing a pentacoordinate complex derived from **5**.

(16) Ligand-induced stabilization of the reaction intermediate involved in olefin dihydroxylation by OsO_4 -amine complexes plays a crucial role in the ligand acceleration characteristic of these reactions. For leading references to extensive research on this topic, see: (a) Pidun, U.; Boehme, C.; Frenking, G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1917. (b) Torrent, M.; Deng, L.; Duran, M.; Sola, M.; Ziegler, T. *Organometallics* **1997**, *16*, 13. (c) Norrby, P.-O.; Rasmussen, T.; Haller, J.; Strassner, T.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 10188.