

## Evidence of the Facile Hydride and Enolate Addition to the Imine Bond of an Aluminum–Salophen Complex

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The isolation of complexes **2** and **3**, unambiguously characterized by single-crystal X-ray diffraction, demonstrates that nucleophilic additions to the aluminum-coordinated imino bond of salophen complex **1** can be achieved under very mild conditions.

In the last decades, particular attention has been paid to the synthesis and study of metal complexes of diimino tetradentate Schiff bases, such as salen and salophen ligands.<sup>1</sup> This is due to several reasons: one of the most important is the role played by a number of these derivatives in biological processes<sup>2</sup> as well as in many catalytic chemical transformations.<sup>3</sup> Among the metals that form stable complexes with salen and salophen ligands, aluminum occupies a central role in the development of new catalysts<sup>4</sup> because the cationic nature of such complexes makes them feasible candidates in activating and catalyzing reactions in which a very strong Lewis acid is required.

In the course of our studies on the chemistry of salophen complexes<sup>5</sup> and on their use as building blocks for solid-state supramolecular architectures in the presence of bidentate

ligands, we isolated two new dimeric aluminum complexes, **2** and **3**. Crystals of **2** were obtained by slow evaporation from a solution of **1** and excess of 4,4'-bipyridine in a 2:1 mixture of methanol and acetonitrile, whereas crystals of **3** were obtained by slow evaporation from a solution of **1** and an excess of DABCO (1,4-diazabicyclo[2.2.2]octane) in a 2:1 mixture of methanol and acetone. Their X-ray single-crystal analyses<sup>6</sup> revealed dimeric complexes **2** and **3** with an Al<sub>2</sub>(OR)<sub>2</sub> (R = H or CH<sub>3</sub>) bridging unit. One of these OR bridging groups can be lost to afford cationic species observed by mass spectroscopy as the predominant peak.<sup>7</sup> In both complexes, one of the iminic bonds in each salophen unit is transformed into a single bond with sp<sup>3</sup>-hybridized nitrogen and carbon atoms (Scheme 1).

The molecular structures and relevant geometrical parameters of the centrosymmetrical aluminum complexes **2** and **3** are reported in Figure 1. The structure of the Al<sub>2</sub>O<sub>2</sub> moiety in these mixed imine–amine complexes strictly reminds us

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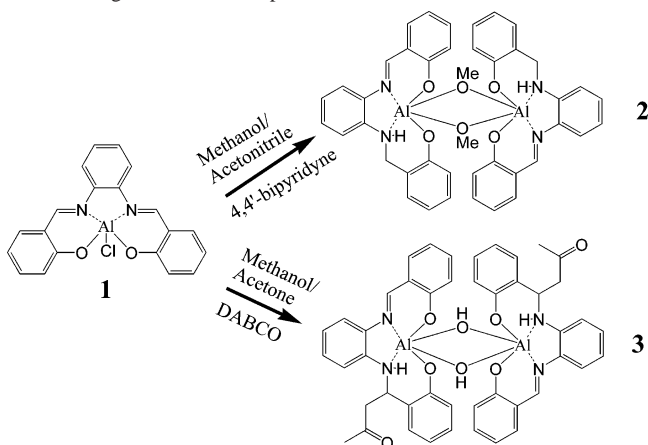
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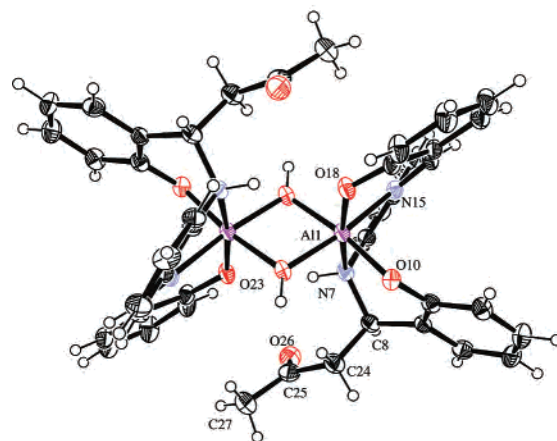
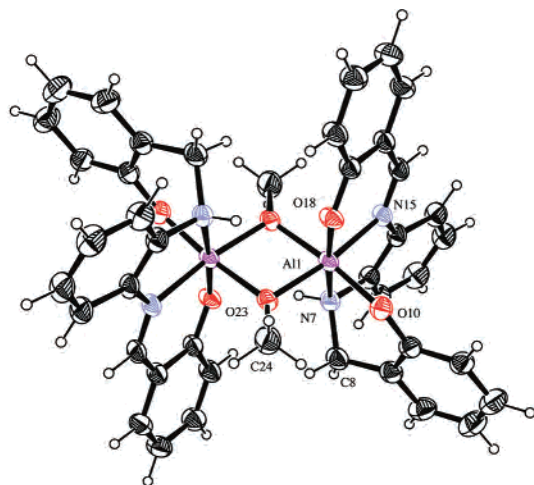
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- (6) Crystal data of **2**: C<sub>42</sub>H<sub>38</sub>Al<sub>2</sub>N<sub>4</sub>O<sub>6</sub>·2CH<sub>3</sub>OH, fw = 812.810, Huber CS four-circle diffractometer, Mo K $\alpha$  radiation, a full data set with 2 $\theta$  = 50°, monoclinic, P2<sub>1</sub>/n, a = 10.686(1) Å, b = 15.044(2) Å, c = 12.505(2) Å,  $\beta$  = 91.70(2)°, V = 2009.5 (4) Å<sup>3</sup>, Z = 2, 2542 reflections [I > 2 $\sigma$ (I)], 265 parameters, R1 = 0.0581 [for I > 2 $\sigma$ (I)], wR2 = 0.1772, GOF (on F<sup>2</sup>) = 1.132. Crystal data of **3**: C<sub>24</sub>H<sub>22</sub>AlN<sub>2</sub>O<sub>5</sub>, fw = 445.42, Bruker-Nonius Kappa APEX II diffractometer, Mo K $\alpha$  radiation, a full data set with 2 $\theta$  = 50°, triclinic, P1, a = 9.1356(5) Å, b = 11.4023(8) Å, c = 11.6400(8) Å,  $\alpha$  = 86.139(3)°,  $\beta$  = 69.337(3)°,  $\gamma$  = 78.056(3)°, V = 1109.9 (1) Å<sup>3</sup>, Z = 2, 2542 reflections [I > 2 $\sigma$ (I)], 298 parameters, R1 = 0.0753 [for I > 2 $\sigma$ (I)], wR2 = 0.1631, GOF (on F<sup>2</sup>) = 1.063. The structures were solved by direct methods and refined using SHELX programs (Sheldrick, G. M. SHELXTL 6; Bruker AXS Inc.: Madison, WI, 2001). All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed into their calculated positions and refined on riding atoms with U = 1.3U<sub>C</sub> and 1.5U<sub>O</sub>.
- (7) ESI-MS for **2**: m/z 717.34 (calcd for [2 – OCH<sub>3</sub>]<sup>+</sup>, m/z 717.22). ESI-MS for **3**: m/z 815.29 (calcd for [3 – OH]<sup>+</sup>, m/z 815.26).

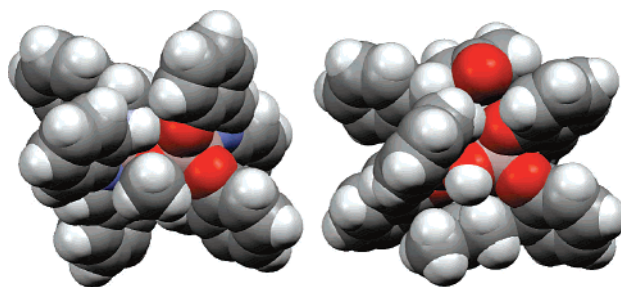
**Scheme 1.** Complexation Experiments and Chemical Structures of the Resulting Aluminum Complexes

of the related dimeric bis(iminic)<sup>8</sup> and bis(aminic)<sup>9</sup> aluminum complexes previously described by Atwood et al. The octahedral coordination and the Al<sub>2</sub>O<sub>2</sub> four-membered ring are only slightly modulated by the different bridging units, i.e., -OCH<sub>3</sub> and -OH in **2** and **3**, respectively (Figure 1). Obviously, the main change in the structure of the salophen unit comes from the coexistence of the aminic and iminic bond. The torsion angles -5.05° and -9.38° for the iminic bond (N15-C16-C18-O18) in **2** and **3**, respectively, are equal to the corresponding ones in the dimeric aluminum-salen complex described by Atwood et al.,<sup>8</sup> whereas the angles 43.14° and 41.04° (N7-C8-C10-O10) for **2** and **3**, respectively, are equal to those for the corresponding dimeric ethylenediaminealuminum complex.<sup>9</sup> The mixed imine-amine ligand twists from the regular butterfly conformation<sup>10</sup> of the salophen ligand to a V-shaped conformation. The only other example present in the literature is the one reported by Atwood et al. for a dimeric aluminum phosphinate complex, in which the corresponding torsion angles are 4.97° and 38.33°.<sup>11</sup> Similarly, the coordination to the aluminum occurs from the convex part of the V-shaped ligand, viz., >Al<, where ">" represents the ligand. Such a convex salophen coordination has also been observed in a dimeric zirconium-bis(salophen) complex.<sup>11b</sup> The hydrogen atoms on the newly formed sp<sup>3</sup> atoms (N7 and C8) in **2** have enough space and do not effect the relative orientation of the outermost phenyl groups, whereas the large -CH<sub>2</sub>COCH<sub>3</sub> groups in **3** press the phenyl groups closer to each other, resulting in a more compact structure (Figure 2). The sterical crowding around the new sp<sup>3</sup> atoms is relaxed by the V shape of the ligands so that abnormal torsion angles around N7 and C8 are avoided.

Clearly, the nucleophilic attack of one of the imine bonds of the aluminum-salophen complex **1** is responsible for the



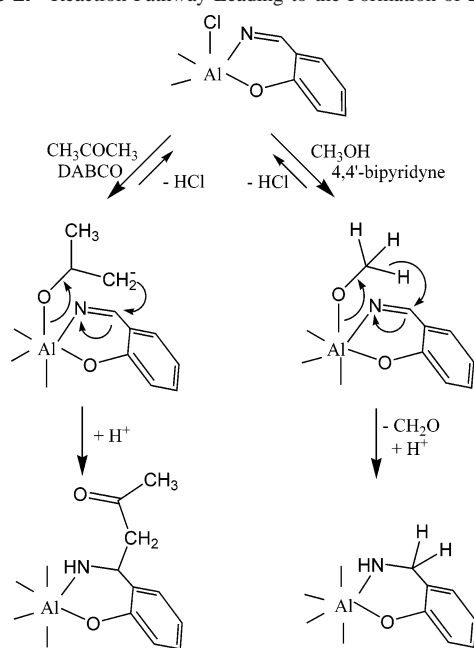
**Figure 1.** Plot of the complexes **2** (top) and **3** (bottom) with thermal displacement factors (at 30 and 40% probability levels for **2** and **3**, respectively) with labels on selected atoms. The geometrical data (Å and deg) for **2**, **3**, respectively, are as follows: Al1-O10 1.837(3), 1.827(3); Al1-O18 1.833(3), 1.848(3); Al1-O23 1.863(2), 1.849(3); Al1-O23\* 1.923(3), 1.879(3); Al1-N15 2.008(3), 2.015(4); Al1-N7 2.082(3), 2.124(4); O10-Al1-O23 97.4(1), 95.7(2); O10-Al1-N15 93.4(1), 94.3(2); O23\*-Al1-N15 91.6(1), 92.1(2); O23-Al1-O23\* 77.3(1), 77.4(2); O10-Al1-O23\* 173.8(1), 171.7(2); O23-Al1-N15 167.9(1), 168.5(2); O18-Al1-N7 173.6(1), 170.1(1).



**Figure 2.** Corey-Pauling-Koltun plots for **2** and **3** (aluminum atoms are magenta, nitrogen atoms are blue, and oxygen atoms are red).

formation of compounds **2** and **3**, and the mild conditions involved suggest a remarkable activation of this bond through its coordination to the aluminum center. Nevertheless, the formation of the two structurally different addition products requires different rationales that take into account the conditions in which they were obtained and the nature of the nucleophiles. In the case of **2**, a mechanism involving a

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**Scheme 2.** Reaction Pathway Leading to the Formation of **2** and **3**

Meerwein–Ponndorf–Verley-type reduction<sup>12</sup> can be envisaged (Scheme 2), as was already proposed for the formation of similar osmium and titanium complexes.<sup>13</sup> In coordinating media such as methanol, **1** releases chloride and coordinates two solvent molecules in the apical positions, assuming an octahedral geometry.<sup>8</sup> The increasingly acidic coordinated methanol easily deprotonates in the presence of weak bases, 4,4'-bipyridine in this case, and intramolecular hydride transfer from the coordinated alkoxide occurs, with the consequent formation of formaldehyde. The proximity between the coordinated alkoxides and the imine bond, evidenced by previously reported X-ray structures of methanol-coordinated aluminum complexes, strongly supports this hypothesis.<sup>8,14</sup> In addition, the slow evaporation conditions in which the complexes were obtained, leading to highly concentrated solutions, may suggest also an intermolecular pathway in which the hydride comes from a second methanol–aluminum–salophen complex. It is worth mentioning that similar dimeric “half” Schiff base complexes

with iron and nickel have been obtained in completely different conditions by dioxygen oxidation of the fully reduced metal–salen complexes.<sup>9,11a</sup>

It is likely that the addition of acetone to one of the imine carbons of the salophen ligand, leading to the isolation of product **3**, proceeds via a different mechanism. As in the previous case, coordination of acetone to aluminum increases its acidity and deprotonation of the methyl group can be easily achieved by DABCO, whereupon the intramolecular enolate attack of the imine bond and the subsequent protonation of nitrogen, carried out by methanol or by the protonated base, lead to the formation of **3**. To the best of our knowledge, the only example present in the literature concerning solvent nucleophilic addition to the imine bond of an aluminum–salophen complex is that reported by Atwood et al.<sup>11</sup> In such an example, the addition of tetrahydrofuran was claimed to be a direct consequence of the presence of phosphinic acid. Our findings demonstrate that such kinds of reactions can occur also under milder conditions, without the use of strong acids. It must also be mentioned that an alternative mechanism, similar to that previously discussed, implying the attack of methoxide on the imine bond, may operate to give a labile intermediate, an aminal, in equilibrium with the reagents. In this case, acetone addition, which is irreversible under given conditions, should shift the equilibrium toward the formation of complex **3**.

Detailed mechanistic studies on these aspects are currently in progress, especially to better evaluate the role of the base, without which no reaction occurs.

In conclusion, here we reported that in the aluminum–salophen complex **1** the reactivity of the imine bond is remarkably enhanced through coordination to the metal, and this makes nucleophilic additions easy even under mild conditions, as is demonstrated by the isolation of derivatives **2** and **3**. Moreover, the results of this work can offer prospects for developing convenient synthetic routes to new, nonsymmetric aluminum–salophen complexes that may have interesting applications in catalysis.

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**Supporting Information Available:** X-ray crystal data in CIF format (CCDC numbers are 641999 for **1** and 642000 for **2** and are available upon request from the Cambridge Crystallographic Data Centre at [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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