[CpAlN(2,6-*i*-Pr$_2$C$_6$H$_3$)]$_2$: A Dimeric Iminoalane Obtained by Alkane Elimination

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The importance of heteroatom-containing organoaluminum compounds as cocatalysts for Ziegler−Natta olefin polymerization[1] and as precursors to ceramic materials[2] and metallic thin films[3] has fueled a continuing interest in the structural properties and reactivity of this class of compounds. An ongoing, basic interest in the multiple-bonding capacity of the aluminum with heteroatoms in these systems has also provided impetus to this area of research.[4]

In the absence of steric effects that limit their ability to aggregate, alkyliminoalanes typically cluster into three-dimensional Al−N frameworks in which both the Al and N atoms are four coordinate.[5] Until the report of a trimeric iminoalane, [MeAlN(2,6-*i*-Pr$_2$C$_6$H$_3$)]$_3$, by Power and co-workers in 1988,[6] cubane-type structures with $n = 4$ were the smallest aggregates encountered for these coordinatively unsaturated iminoalanes. More recently, Roesky and co-workers reported their characterization of the first dimeric iminoalane,[7] an aggregate of four aluminum-containing fragments with an essentially planar Al$_2$N$_2$ core. Here we report the discovery of a simpler example of a dimeric iminoalane, [(η^5-C$_5$H$_5$)AlN(2,6-*i*-Pr$_2$C$_6$H$_3$)]$_2$, **2**, which also exhibits an essentially planar Al$_2$N$_2$ core. The pentahapto coordination geometry exhibited by the cyclopentadienyl ring bound to aluminum is noteworthy since it represents the first

definitive structural characterization of this type of coordination mode between an unsubstituted cyclopentadienyl ring and aluminum.

The iminoalane dimer, **2**,[8] is formed as outlined in eq 1 *via*

(1)
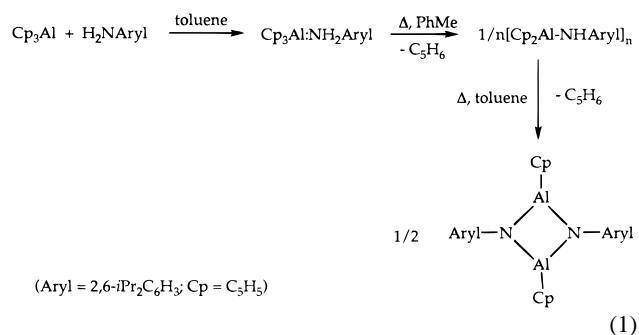
the stepwise elimination of two molecules of cyclopentadiene from Cp$_3$Al,[9] **1** (Cp = C$_5$H$_5$), upon its reaction with an equivalent amount of 2,6-diisopropylaniline. The 1:1 aluminum−amine adduct has not been obtained in pure form since it readily eliminates cyclopentadiene to form the dicyclopentadienylaluminum anilide. We have been able to isolate this compound on occasion; however, over time, even in the solid state, it further eliminates cyclopentadiene to form the iminoalane. A variable temperature ^{1}H NMR experiment indicates that the aluminum anilide intermediate is an oligomer which undergoes isomerization on the NMR time scale. On the basis of other aluminum amide systems,[10] we presume the aluminum anilide to exist as either a dimer or a trimer in solution.

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(8) The compound turns from white to brown at 220.5 °C prior to melting at 272.5 °C (uncorrected). ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.12 (d, *J* = 7 Hz, aryl-H), 6.97 (t, *J* = 7 Hz, aryl-H), 6.32 (s, C$_5$H$_5$), 3.42 (sept, *J* = 7 Hz, C*H*), 1.38 (d, *J* = 7 Hz, CH(C*H*$_3$)$_2$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 144.2, 143.7, 122.5, 119.6 (2,6-*i*-Pr$_6$H$_3$)), 107.2 (*C*$_5$H$_5$), 27.9 (*C*H(CH$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$). ^{27}Al (C$_6$D$_6$, 78.2 MHz, [Al-(H$_2$O)$_6$]$^{3+}$): δ −5. IR (KBr, Nujol): ν[cm^{-1}] = 3171 (vw), 3131 (vw), 3059 (vw), 3044 (vw), 3039 (vw), 2726 (w), 2690 (w), 1586 (sh), 1377 (s), 1367 (m), 1315 (s), 1250 (s), 1204 (sh), 1156 (vw), 1105 (m), 1049 (vw), 1040 (w), 1013 (m), 926 (m), 821 (s), 814 (s), 774 (s), 717 (s). Anal. Calcd for C$_{17}$H$_{22}$NAl: C, 76.4; H, 8.3; N, 5.2. Found: C, 76.5; H, 8.6; N, 5.2.

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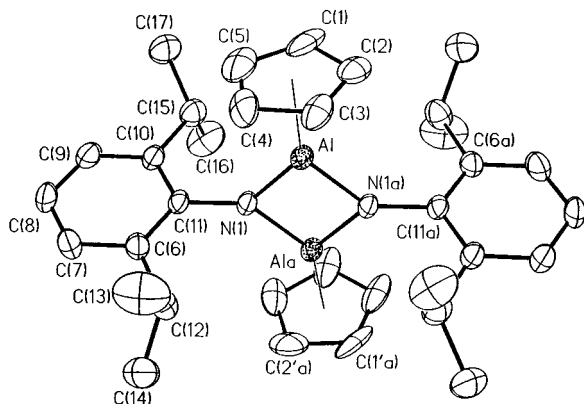
Figure 1. ORTEP drawing of molecular structure of **2** (H atoms omitted for clarity). Two benzene molecules per aluminum dimer reside in the lattice. The two equally occupied rotational orientations of the disordered Cp ring are displayed in the drawing. Selected bond distances (Å) and angles (deg): Al—N(1a) 1.796(2), Al—N(1) 1.811(3), Al—C(1) 2.27(2), Al—C(2) 2.245(12), Al—C(3) 2.220(12), Al—C(4) 2.23(2), Al—C(5) 2.26(2); N(1)—Al—N(1a) 89.18(11), Al—N(1)—Al-(a) 90.82(11).

An ORTEP drawing of the molecular structure of **2** is shown in Figure 1.[11] The molecule is centrosymmetric. Therefore, the Al_2N_2 core is flat and is nearly square, since the two unique Al—N bond lengths are very similar (1.796(2) and 1.811(3) Å), as are the Al—N—Al and N—Al—N bond angles of 90.82(11) and 89.18(11)°, respectively. By contrast, Roesky's iminoalane dimer,[7] while nearly flat, is slightly more oblong, probably due to the greater asymmetry of the complex and due to greater steric crowding from the bulky alane substituents on the core nitrogens as compared with the subsituents on the core aluminums. The Al—N distances in our iminoalane dimer are comparable to those found in Roesky's dimer and, while they are slightly longer than the Al—N distances in Power's iminoalane trimer,[6] they are within the range of Al—N bond lengths encountered in aminoalane compounds in which the aluminum centers are three coordinate.[4b] At 1.90—1.95 Å, the Al—N distances found in higher polyiminoalanes, in which the aluminum and nitrogen atoms are four-coordinate, are significantly longer.[5] Nevertheless, Power has determined that the shortening of Al—N bonds in tricoordinate aluminum amides can be attributed primarily to the ionic character of the bonds and only minimally to p—p π-bonding between the aluminum and the nitrogen. Thus, iminoalane dimers are poorer inorganic analogs of cyclobutadiene derivatives than dimeric iminoboranes, of which there are numerous examples.[12] We intend to perform *ab initio* calculations on model Al_2N_2 compounds in order to determine the degree of π overlap between the nitrogen and the aluminum in these systems and to determine the minimal energy geometry of the Al_2N_2 core in the absence of steric influences.

Solid-state[9,13] and gas-phase[14] structures of CpAl compounds determined to date have identified η^1- and η^2-coordination modes for the cyclopentadienyl rings. The X-ray crystal structure of **2** reveals yet another coordination geometry for aluminum; the pentahapto nature of the ring coordination is indicated by the narrow range of Al—Cp ring carbon distances between 2.210(12) and 2.27(2) Å. In the X-ray structure, the Cp ring is disordered in two rotational orientations in approximately equal occupancies. Both orientations are presented in the ORTEP drawing in Figure 1.

Another notable feature of the crystal structure of **2** is the perpendicular orientation of the bulky aryl groups on the aluminum atoms with respect to the Al_2N_2 core. This arrangement minimizes steric interactions between the isopropyl substituents on the aryl groups and the cyclopentadienyl rings on the aluminum atoms while eliminating any possibility of conjugation between the arene ring π-systems and the p orbitals of the Al_2N_2 core.

The title compound exhibits a very broad ($W_{1/2} \approx 3000$ Hz) ^{27}Al NMR peak (78.2 MHz, $[Al(H_2O)_6]^{3+}$ external standard) at δ −5 in C_6D_6 solvent. This is the broadest and highest field resonance we have yet observed for our cyclopentadienylaluminum compounds. The low frequency of the ^{27}Al chemical shift may be attributed to the magnetic anisotropy caused by the η^5-C_5H_5 ring. More dramatic upfield shifting of the ^{27}Al resonance to δ −114.5 has been observed by Schnöckel and co-workers for their cationic aluminum(III) metallocene, $[(\eta^5$-Cp*)$_2$Al]$^+$ (Cp* = C_5Me_5),[15] in which the aluminum atom, by bearing two pentahapto cyclopentadienyl rings, would be expected to experience even greater shielding.

It is interesting that a similar double alkyl elimination to form an iminoalane is not observed in the thermolysis of $AlMe_3$ with the bulky 2,4,6-tri-*tert*-butylanaline.[16] Rather, metalation of a *t*-Bu group occurs in preference to N—H capture. This difference highlights the greater lability of a cyclopentadienyl ring relative to a methyl substituent on aluminum.

We have begun to investigate the reactivity of the iminoalane dimer, and have found that it reacts cleanly with 1,3-di-*p*-tolylcarbodiimide to form what we suspect to be a 2 + 2 cycloaddition product. Further information on this reaction and additional studies of the reactivity of **2** will be forthcoming.

Supporting Information Available: Text giving experimental details and tables of atomic coordinates, isotropic and anisotropic thermal parameters, bond distances and angles, data collection and refinement parameters for compound **2** (11 pages). Ordering information is given on any current masthead page.

(11) Crystal data for [CpAlN(2,6-*i*-Pr$_2$C$_6$H$_3$)]$_2$: C$_{46}$H$_{56}$Al$_2$N$_2$, fw = 690.89, triclinic, $P\bar{1}$, a = 9.647 Å, b = 10.485(4) Å, c = 11.006(4) Å, α =101.86(3)°, β = 99.46(3)°, γ = 100.61(3)°, V = 1046.9(7) Å^3, Z = 1, D_x = 1.096 g cm^{-3}, T = 258 K. Of 3463 data collected (Siemens P3, Mo Kα, $2\theta_{max}$ = 48°), 3272 were independent and 3002 were observed ($2\sigma I$). $R(F)$ = 7.21%, $R_w(F^2)$ = 20.6%. All non-hydrogen atoms were anisotropically refined.
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