Hydrogen and Dihydrogen Bonding as Important Features of the Reactivity of the Bridging Hydride in Pyrazolate-Bridged Dialuminum Complexes

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Summary: Treatment of diisobutylaluminum hydride with 3,5-disubstituted pyrazoles in 2:1 stoichiometry affords the bridging hydride complexes [(μ,η¹:η¹-R₂pz)-(AliBu₂)₂(μ-H)]. A theoretical study of the reaction of [(μ,η¹:η¹-R₂pz)(AliBu₂)₂(μ-H)] with methanol predicts that the reaction proceeds by way of an intermediate containing a strong dihydrogen bond, suggesting that dihydrogen bonding is an important feature of the reactivity of organoaluminum hydrides.

Hydride transfer from aluminum is a fundamental process in diverse areas ranging from synthetic chemistry[1] to film growth of aluminum-containing materials.[2] Despite the wide use of aluminum hydrides, little is known about the mechanisms by which they react. Dihydrogen bonding, wherein a main-group-metal or transition-metal hydride forms a hydrogen bond with an acidic hydrogen compound, was recently recognized[3,4] and is being increasingly documented among the main-group-metal hydrides.[5−10] Dihydrogen bonding has been demonstrated to be an important structural element in the formation of solid-state borohydride materials and in their subsequent reactivity,[5] in the diastereoselectivity of borohydride reductions of α-hydroxy ketones,[6] and in the formation of gallium nitride from gallazane precursors.[7] The tetramethylpiperidine adduct of alane features a weak Al−H···H−N dihydrogen bond in the solid state, and it was suggested that this interaction represents a transition state for dihydrogen elimination.[8] The high melting point of the borane−ammonia adduct has been rationalized as arising from intermolecular B−H···H−N dihydrogen bonds.[9] In addition, several groups have reported molecular orbital calculations on main-group-metal complexes with dihydrogen bonds.[10] However, many questions remain regarding the importance of dihydrogen bonding in the reactivity of main-group-metal hydrides and, in particular, the widely used aluminum hydrides. Herein we describe the synthesis, reactivity, and properties of a series of pyrazolate- and hydride-bridged dialuminum complexes that are obtained upon treatment of 3,5-disubstituted pyrazoles with diisobutylaluminum hydride. The new complexes react with protic reagents and unsaturated organic compounds exclusively at the hydride. Molecular orbital calculations demonstrate that methanolysis of a model bridging hydride complex proceeds through an intermediate that contains a very strong dihydrogen bond. The results described herein help to explain why organoaluminum hydrides undergo selective reactions at the hydride[11] and imply hydrogen and dihydrogen bonding as a general feature of aluminum hydride reactivity.

Treatment of diisobutylaluminum hydride with 3,5-dimethylpyrazole, 3,5-diphenylpyrazole, or 3,5-di-*tert*-

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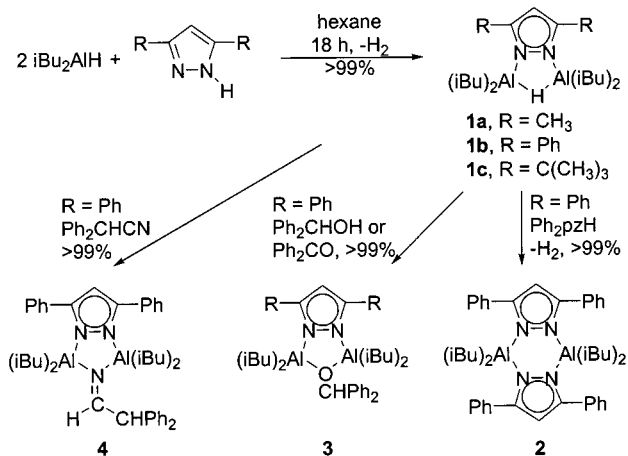(6) Galting, S. C.; Jackson, J. E. *J. Am. Chem. Soc.* **1999**, *121*, 8655.

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Scheme 1.   Synthesis and Reactions of 1a–c

Figure 1. Perspective view of **3**. Selected bond lengths (Å) and angles (deg): Al(1)−O = 1.8657(18), Al(2)−O = 1.8683(18), Al−N(1) = 1.953(2), Al(2)−N(2) = 1.918(2), Al(1)−C(29) = 1.969(3), Al(1)−C(33) = 1.972(3), Al(2)−C(37) = 1.950(4), Al(2)−C(41) = 1.978(4), O−C(16) = 1.474(3), N(1)−N(2) = 1.385(3); Al(1)−O−Al(2) = 118.69(9), Al(1)−O−C(16) = 127.52(15), Al(2)−O−C(16) = 111.99(15), Al(1)−N(1)−N(2) = 116.81(14), N(1)−Al(1)−C(29) = 109.01(11), N(1)−Al(1)−C(33) = 106.25(12), O−Al(1)−C(29) = 111.45(11), O−Al(1)−C(33) = 115.07(11), Al(2)−N(2)−N(1) = 115.47(15), N(2)−Al(2)−C(37) = 113.28(13), N(2)−Al(2)−C(41) = 105.55(14), O−Al(2)−C(37) = 108.12(13), O−Al(2)−C(41) = 110.83(14).

butylpyrazole in a 2:1 stoichiometry afforded the hydride-bridged complexes **1a–c** in quantitative yields as a colorless liquid (**1a**) or as colorless solids (**1b,c**; Scheme 1). The structures of **1a–c** were established on the basis of the spectral and analytical data.[12] The ^{1}H NMR resonances of the bridging hydride in **1a–c** appeared as singlets at δ 3.93, 4.13, and 4.05, respectively, in benzene-d_6 at ambient temperature. These resonances are shifted about 1.0 ppm downfield from the corresponding value for diisobutylaluminum hydride (δ 3.02 in benzene-d_6), which is itself trimeric in benzene.[13] The ^{1}H NMR chemical shift of the bridging hydride in **1c** was invariant (δ 4.19–4.21) between −80 and 20 °C in toluene-d_8, implying a static structure in this temperature range. The infrared spectra of **1a–c** spectra show strong broad ($w_{1/2}$ = 140−221 cm^{-1}) absorptions for the bridging hydride moieties at 1585, 1636, and 1715 cm^{-1}, respectively. For comparison, bridging hydrides of aluminum typically show strong broad absorptions between 1600 and 1800 cm^{-1}, while terminal aluminum hydrides exhibit sharper, less intense stretches between 1700 and 1820 cm^{-1}.[14]

Selected reactions of **1a,b** are outlined in Scheme 1.[12] All yields were quantitative (>99%). Treatment of **1b** with diphenylpyrazole (1 equiv) in hexane at ambient temperature led to slow hydrogen elimination over 48 h to afford the dimeric product **2**. Treatment of **1b** with diphenylmethanol (1 equiv) or benzophenone (1 equiv) afforded the diphenylmethoxide complex **3**. Treatment of **1b** with diphenylacetonitrile (1 equiv) afforded the imino complex **4**, in which hydride has been transferred to the nitrile carbon atom. The structures of **2**−**4** were established by a combination of spectral and analytical data and by X-ray crystal structure determinations for **3** and **4**.

Figure 1 shows a perspective view of **3** along with selected bond lengths and angles.[15] The molecule contains two diisobutylaluminum groups that are bonded to the nitrogen atoms of a diphenylpyrazolate ligand, with a diphenylmethoxo ligand bridging between the two aluminum atoms. The geometry about each alumi-
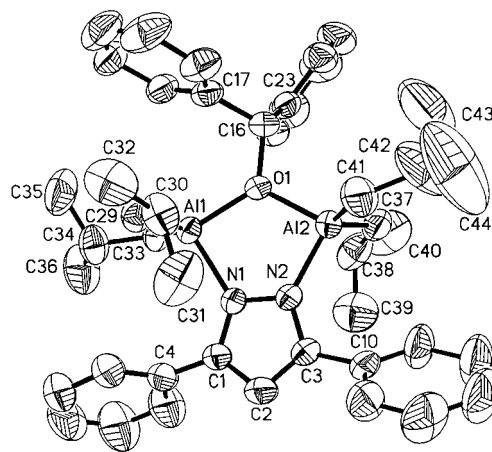
num atom is distorted tetrahedral. The sum of angles about the oxygen atom is 358.20°, indicating trigonal-planar geometry at this center. The aluminum−nitrogen bond lengths are 1.918(2) and 1.953(2) Å, which are similar to values observed in several recently reported aluminum complexes containing $\mu,\eta^1{:}\eta^1$-pyrazolato ligands.[16,17] The aluminum−oxygen bond lengths are 1.8657(18) and 1.8683(18) Å. These values are very similar to related bond lengths for μ_2-alkoxo complexes that have been recently reported (range 1.84−1.94 Å).[18]

To understand the structure, bonding, and reactivity of **1a–c**, calculations were performed at the B3LYP/6-311G(d) level of theory for the pyrazolato complex **5** and its reaction with methanol and formaldehyde.[19] The

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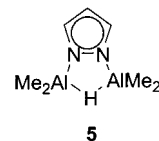
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(15) Crystal data for **3**: crystals grown from hexane at −20 °C, $C_{44}H_{58}Al_2N_2O$, triclinic, group $P\bar{1}$, a = 10.6411 Å, b = 11.6236(9) Å, c = 18.6061 Å, V = 2124.0(3) Å^3, Z = 2, T = 295(2), D_{calcd} = 1.071 g cm^{-3}, $R(F)$ = 6.63% for 9135 observed reflections (2.80 ≤ 2θ ≤ 56.58°). All non-hydrogen atoms were refined with anisotropic displacement parameters. The X-ray crystal structure of **4** will be reported in a later full paper.

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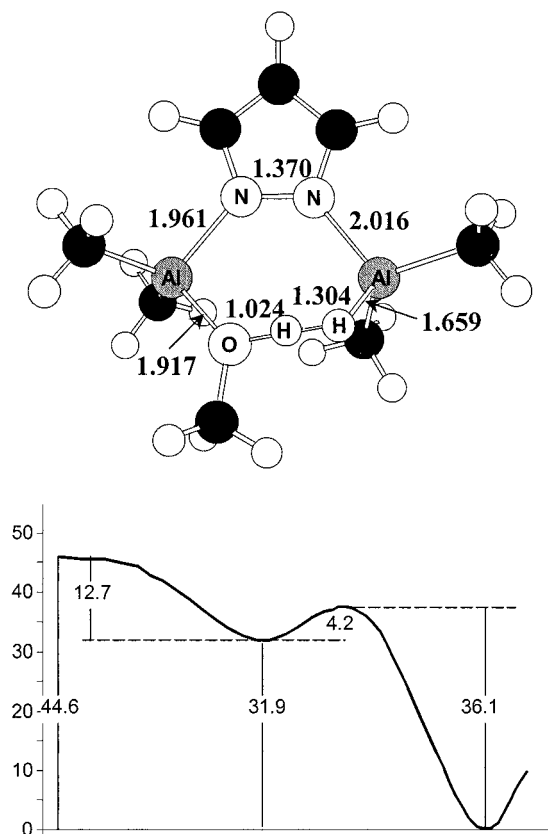
Figure 2. Dihydrogen-bridged intermediate and reaction profile for methanolysis of **5**. Energies are in kcal/mol and do not include zero point corrections.

hydrogen-bridged structure of **5** is 10 kcal/mol more stable than the corresponding conformation with a bridging methyl group and a terminal hydride. The five-membered Al_2N_2H ring of **5** is planar with aluminum–hydrogen, aluminum–nitrogen, and nitrogen–nitrogen distances of 1.725, 1.975, and 1.367 Å, respectively. Theory predicts that the reaction of **5** with methanol is barrierless and leads to a dihydrogen-bridged intermediate (Figure 2) that is 12.7 kcal/mol lower in energy. The approach to the intermediate is characterized by coordination of the methanol oxygen atom to one aluminum center, along with concomitant aluminum–hydrogen bond breakage and formation of the dihydrogen bond. A dissociative pathway, in which one aluminum–hydrogen bond is broken prior to coordination of the methanol oxygen atom to the other aluminum atom, can be ruled out due to the high calculated aluminum–hydrogen bond strength (25.8 kcal/mol). The hydrogen–hydrogen distance in the intermediate (1.304 Å) is substantially shorter than other computed and observed

dihydrogen bonds that have been previously reported (1.6–2.4 Å).[3–10] The subsequent elimination of dihydrogen to form a methoxo-bridged complex has a barrier of 4.2 kcal/mol. In the transition state for dihydrogen elimination, the hydrogen–hydrogen bond length decreases to 0.863 Å, the aluminum–oxygen bond length decreases to 1.827 Å, and the oxygen–hydrogen bond length increases to 1.432 Å. Insertion of methanol into a terminal aluminum–methyl bond to eliminate methane has a barrier of 11.8 kcal/mol. An alternate route to the methoxo-bridged complex, entailing insertion of formaldehyde into an aluminum–hydrogen bond of **5**, is also barrierless and is exothermic by 63 kcal/mol. The reaction coordinate lacks a distinct intermediate but has a plateau near −21 kcal/mol that is caused by a strong hydrogen bond-like interaction between the hydride and the positively polarized carbon atom of the formaldehyde fragment.

The results demonstrate that dihydrogen-bonded intermediates are important in protonolysis reactions of **1a**–**c** and that hydrogen-bonded-like species lie along the reaction coordinate of **1a**–**c** with unsaturated organic groups. Documentation of these interactions implies that hydrogen and dihydrogen bonding are central to reactions of aluminum hydride reagents in general. The fact that organoaluminum hydrides react exclusively at the hydride[11] is explained by barrierless access to hydrogen- and dihydrogen-bonded species, compared to the barriers associated with reaction at the carbon substituents.[20,21] Finally, diisobutylaluminum hydride is trimeric in benzene and related organoaluminum hydrides are oligomeric in noncoordinating solvents.[13] By analogy with the results presented herein, hydride transfers from organoaluminum hydrides are likely to occur through oligomeric species in which the Lewis base of the hydride acceptor species coordinates to one aluminum center and hydride transfer is effected from an adjacent aluminum-bound hydride. Alternative monomeric reaction coordinates may not enjoy the stabilization afforded by hydrogen- and dihydrogen-bonded interactions.

Supporting Information Available: Text giving synthetic procedures and analytical and spectroscopic data for **1**–**4**, tables of Cartesian coordinates for **5** and associated transition states, and X-ray crystallographic files for **3**, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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