Reactivity of Tetraisobutyldialuminum toward Water, Hydrogen Chloride, Toluene-3,4-dithiol, Pentacarbonylmanganese Hydride, and Diborane

Mark A. Miller and Eugene P. Schram*

Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210

Received November 16, 1984

The relative reactivities of Al-Al and Al-C bonds, $Al_2(i\text{-}Bu)_4$, have been examined employing the protonic reagents H_3O^+, HCl(g), toluene-3,4-dithiol, and $HMn(CO)_5$. Excess H_2O, pH 1, results in 100% cleavage of both Al-Al and Al-C bonds, whereas the Al-Al bond exhibits greater reactivity toward HCl(g). In a similar manner the -SH moiety also reacts more readily with the metal-metal bond. In contrast the weak acid $HMn(CO)_5$ is unreactive toward $Al_2(i\text{-}Bu)_4$. The latter also reacts with a hydride source, B_2H_6, to afford an insoluble material with the empirical stoichiometry AlB_2H_4. On the basis of deuterolysis data, the molecular formulation $Al_2(BH_2)_4$ is suggested with extensive intermolecular hydrogen bonding.

Introduction

While the chemistry of catenated boron compounds is quite well developed,[1] e.g., B_2X_4 where X is specific combinations of F, Cl, Br, I, OCH_3, $N(CH_3)_2$, CH_3,[2] and *t*-Bu,[2] catenated aluminum chemistry is largely unexplored. The first reported example of the latter, $Al_3(CH_3)_3[N(CH_3)_2]_2$, I, was demonstrated to contain two Al-Al two-electron two-centered bonds by oxidative hydrolysis. I was prepared by treatment of $B_2(NMe_2)_4$ with $AlMe_3$ and is a red oil which was subsequently demonstrated to be an isomer mixture by ^{13}C NMR spectroscopy.[3] The second example of catenated aluminum arose from the K reduction of RYAlX to afford RYAlAlRY where X is Cl, R is isobutyl, and Y is isobutyl, dimethyl, or isobutoxy.[4] Again, oxidative hydrolysis demonstrated the presence of an Al-Al bond. Although a molecular weight was not reported, we have found this species to be monomeric in cyclopentane.

The less complex nature of $Al_2(i\text{-}Bu)_4$, II, as compared to I, results in II being the preferred species with regard to development of the chemistry of the Al-Al bond. We report herein the reactivity of II toward H_3O^+, HCl, toluene-3,4-dithiol, manganese pentacarbonyl hydride, and B_2H_6.

Results and Discussion

Protonic Reactants. The oxidative hydrolysis of II employing water is described by eq 1, with H_2 evolution

$$Al_2(i\text{-}Bu)_4 + 6H_2O \rightarrow 2Al(OH)_3 + H_2 + 4i\text{-}BuH \quad (1)$$

resulting from reduction of H_2O by Al(II) to afford Al(III). As indicated, both Al-Al and Al-C bonds are completely cleaved. In an effort to evaluate the relative reactivity of Al-Al and Al-C bonds toward protonic sources, II was treated with HCl(g) employing the stoichiometries indicated by eq 2. While 74% of the Al-Al bonds were

$$Al_2(i\text{-}Bu)_4 + 2.2HCl \rightarrow 0.74H_2 + 0.74i\text{-}BuH \quad (2)$$

cleaved, only 18% of the available *i*-Bu moieties reacted to yield isobutane. The colorless nonvolatile reaction residue was separated from metallic Al (8.3% of originally available as II) and subsequent treatment with H_2O to afford the remaining 82% of *i*-Bu moieties as *i*-BuH. During this latter reaction no additional H_2 was evolved; hence all the Al present was in the 3+ oxidation state. In a separate experiment, the ^1H NMR spectrum of the nonvolatile filtrate, after reaction with HCl, was obtained which exhibited pairs of doublets centered at 0.49, (CH_3), 0.71 (CH_3) ppm and 1.09 (CH_2), 1.26 (CH_2) ppm with the former of each group ca. 5 times more intense than the latter—these absorptions are assigned to $(i\text{-}Bu)_2AlCl$ and $i\text{-}BuAlCl_2$, respectively. Because of the complex nature of this mixture, direct comparison of the chemical shifts to the pure materials is not valid; however, the Δ values, (CH_2) ppm - (CH_3) ppm, are in good agreement with the values we observed: $i\text{-}Bu_2AlCl$, 1.16 and 0.57 ppm (Δ = 0.59), and the most intense doublets, 0.49 and 1.09 ppm (Δ = 0.60). With regard to the filtrate, no molecular material containing AlAl bonds is present on the basis of the absence of H_2 during hydrolysis; hence the reaction of II with HCl, 1:2 reaction ratio, is ideally described by eq 3 and 4 with the small excess HCl present (overall 1:2.2 $Al_2(i\text{-}Bu)_2$:HCl) affording $i\text{-}BuAlCl_2$ (eq 5). The small

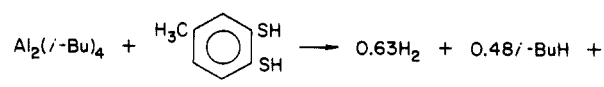
$$Al_2(i\text{-}Bu)_4 + HCl \rightarrow (i\text{-}Bu)_2AlH + ClAl(i\text{-}Bu)_2 \quad (3)$$

$$(i\text{-}Bu)_2AlH + HCl \rightarrow (i\text{-}Bu)_2AlCl + H_2 \quad (4)$$

$$(i\text{-}Bu)_2AlCl + HCl \rightarrow i\text{-}BuAlCl_2 + i\text{-}BuH \quad (5)$$

amount of Al(0) isolated, after HCl treatment, may be associated with either disproportionation of initial II (this is typical behavior for solutions of II) or disproportionation of reaction intermediates in the presence of HCl. In any event the reactivity of the Al-Al bond, toward cleavage by HCl, predominates, and no derivatives such as $Al_2i\text{-}Bu_{4-x}Cl_x$ were isolated. With regard to disproportionation of dialuminum derivatives, one may envisage an intramolecular 1 - 2 ligand shift to afford Al(3+) and Al(1+) species with the latter ultimately affording Al(0). Indeed, when Et(MeO)AlCl is reduced with K, aluminum metal is produced.[4]

In an effort to prevent a 1 - 2 ligand shift, by chelation of Al, II was treated with toluene-3,4-dithiol (III) with the observed stoichiometries of volatile reaction products indicated (eq 6). Rather than selective Al-C bond cleavage,



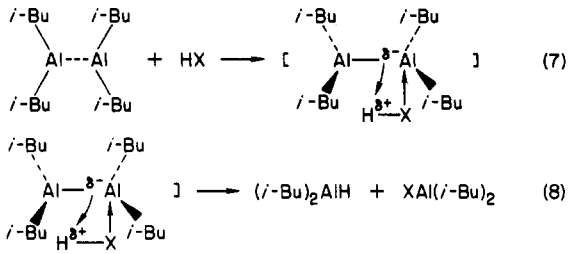
nonvolatile material (6)

87% of III reacted (0 °C/8 h) to cleave 63% of the metal-metal bonds and 12% of the Al-C bonds, again indicating the greater reactivity of the Al-Al than Al-C bond toward protic reagents.

(1) For a review see: R. J. Brotherton, Progress in Boron Chemistry, Vol. 1, H. Steinberg and A. L. McCloskey, Eds.; The MacMillan Co., New York, 1964, pp 1-77.
(2) W. Biffar, H. Noth, and H. Pommerening, *Angew. Chem., Int. Ed. Engl.*, **56**, 19 (1980).
(3) M. Jackson, unpublished work.
(4) H. Hoberg and S. Krause, *Angew. Chem.*, 88, 760 (1976).

0276-7333/85/2304-1362$01.50/0

With regard to a possible reaction mechanism, associated with Al–Al bond cleavage, a model involving nucleophilic attack at aluminum (eq 7 and 8) is attractive where X is OH, Cl, or $S(HS)C_7H_6$. In an effort to explore this pos-



tulate, $Al_2(i\text{-}Bu)_4$ was treated with $HMn(CO)_5$, 1:2 molar ratio, respectively. After 1 h at 25 °C a 2.25% yield of H_2 was noted and ca. 0.2% yield of available *i*-Bu moieties as *i*-BuH. After 6 days at 25 °C a 12% yield of H_2 and 2.6% yield of *i*-BuH were realized. In addition $Mn_2(CO)_{10}$, trace quantity was recovered from the reaction mixture along with $HMn(CO)_5$. Therefore the H_2 evolution, associated with the reaction between II and $HMn(CO)_5$, most likely arises from decomposition of the latter. In order to eliminate the possibility that II reacted with the potential nucleophile $Mn_2(CO)_{10}$, these two reagents were allowed to react, 1:1 mole ratio, for 2 weeks at ca. 25 °C; $Mn_2(CO)_{10}$ was quantitatively recovered while II partially decomposed as evidenced by the presence of Al(0) in the reaction vessel. It is difficult to judge whether or not the decomposition was accelerated by the presence of $Mn_2(CO)_{10}$.

With Diborane. In an effort to effect alkyl–hydrogen exchange,[5] II was treated with excess B_2H_6. A rather surprising reaction took place in that only a relatively small amount of H_2 was evolved—an expected side reaction if the anticipated dialuminum hydride derivative was unstable. Furthermore, only a trace of isobutane was obtained. Alkylation of diborane takes place on the basis of the fact that a volatile boron species was obtained which exhibited infrared absorptions characteristic of the *i*-Bu moiety by comparison to isobutane; e.g., multiplet 2860–2890 cm^{-1} (m) and 2950 cm^{-1} (s). In addition, the BH_2 moiety is indicated by the doublet absorptions at 2577 (m) and 2481 (m) cm^{-1}, i.e., ν_{BH}(sym) and ν_{BH}(antisym). Hence this volatile byproduct is tentatively characterized as 1,1-diisobutyldiborane rather than isobutyldiborane or 1,2-diisobutyldiborane because the former would be expected to exhibit three ν(BH) absorptions and the latter only one. With regard to the monoalkylated derivatives, it is possible to have coincident absorptions—suffice is to say alkyldiborane(s) are produced.

The interesting product, which precipitates from cyclopentane solution during reaction, was separated from soluble reaction byproducts by repeated vacuum filtrations to afford a material with the appearance of anthracite coal. This species exhibits the stoichiometry AlB_2H_4.

Characterizations of AlB_2H_4 (IV). Analytical characterization of IV indicates a 1:2 Al:B stoichiometry while hydrolysis (D_3O^+) is consistent with a hydride:M–M ratio of 1.5 where M is Al and/or boron (the oxidative hydrolysis of M–M affords D_2, whereas the MH moiety produces HD). Thirteen millimoles of H_2 (isotopic mixture) are produced per 2 mequiv Al, with this oxidation hydrolysis described by eq 9. This formulation of III (eq 9), involves

$$(H_2B)_2Al\text{–}Al(BH_2)_2 + 18D_2O \rightarrow 2Al(OD)_3 + 4B(OD)_3 + 8HD + 5D_2 \quad (9)$$

a combination of five M–M and eight M–H bonds for an MH–M–M value of 1.6 (experiment 1.5), thus preserving the Al–Al bond during reaction between II and B_2H_6.

The infrared spectrum of IV is quite simple and consistent with IV representing the monomer unit of a H-bridged polymer. Absorptions are found at 2460 (m), 2400 (m), 2120 (m), 1155 (m), 765 (w), and 485 (m) cm^{-1}. The absorptions at 2460 and 2400 cm^{-1} are assigned to terminal ν_{BH_2}(sym) and ν_{BH_2}(antisym)[6] while the bands at 2250 and 2110 cm^{-1} are associated with B–H–Al bridging. The absence of a strong-broad absorption in the 1800 cm^{-1} region is consistent with the absence of Al–H moieties.[7] IV is insoluble in cyclopentane, benzene, and toluene but dissolves with reaction in THF and diethyl ether; hence a solution molecular weight measurement has not as yet been possible. The insolubility and infrared absorption at 2250 and 2110 cm^{-1} are consistent with a polymeric formulation for IV with B–H–Al intermolecular bridging. IV is quite thermally stable, in vacuo, with H_2 evolution commencing at ~170 °C. A search for a suitable solvent for IV continues in an effort to obtain molecular weight and NMR spectroscopic data.

Experimental Section

Equipment and Techniques. Standard vacuum line procedures were employed throughout this investigation.[8] Infrared spectra were recorded with a Perkin-Elmer 457 spectrometer with nonvolatile samples prepared utilizing Nujol and Fluorolube mulls and KBr plates. Volatile samples were contained in a 10-cm gas cell. ^1H NMR spectra were recorded with a JEOL E360 spectrometer employing the solvent as an internal reference. ^{27}Al spectra were recorded with Varian HA-100 (32.1-MHz) spectrometer and referenced to $Al^{3+}(H_2O)_6$. The composition of isotopic dihydrogen mixtures was determined with an AEI MS10 spectrometer. The isotopic purity of D_2O was determined by treatment with BCl_3 and measuring the relative amounts of HCl and DCl produced by IR spectroscopy. Quantities of H_2 were determined by collection in a calibrated Toepler pump system.

Analysis. After oxidative hydrolysis, boron was determined by the standard manitol–NaOH titration[9] while aluminum was precipitated as the 8-hydroxyquinolate.[10]

Reagents. Tetraisobutyldialuminum, $Al_2(i\text{-}Bu)_4$ (II), was prepared by the literature method.[4] Acid hydrolysis of II, 137.5 mg (0.49 mmol), affords 0.48 mol of H_2 (calculated 0.49 mmol), and 1.97 mmol of *i*-BuH (calculated 1.96 mmol), while an isopiestic molecular weight determination in cyclopentane (0.019 M) indicates a monomeric species, calculated 282 and found 270. The ^1H NMR spectrum of II consists of a doublet centered at 0.21 ppm, a septet centered at 2.11 ppm, and a doublet centered at 1.16 ppm in the ratio 2:1:6, respectively [$AlCH_2CH(CH_3)_2$], while the ^{27}Al NMR spectrum consists of a singlet at 40.6 ppm, $W_{1/2}$ = 5700 Hz. The infrared spectrum of II does not exhibit any absorptions between 2500 and 1600 cm^{-1}; $\nu_{Al\text{–}H}$ (~1800 cm^{-1}) is typically broad, 200–300 cm^{-1}, and strong;[7] hence the absence of Al–H moieties is assured. **HCl**, the Matheson Co., was passed through a −126 °C trap prior to use. **(*i*-Bu)AlCl**, Texas Alkyls, Inc., was used as received. **$Mn_2(CO)_{10}$**, Aldrich Chemical Co., was sublimed at 50 °C, in vacuo, prior to use. **$HMn(CO)_5$** was prepared by the literature method.[11] Toluene-3,4-dithiol, Aldrich Chemical Co., was sublimed at 60 °C, in vacuo, prior to use. **B_2H_6**, Callery Chemical Co., was passed through a −126 °C trap prior to use, 194 torr at −112 °C. Solvents were dried by stirring over

(5) H. I. Schlesinger, A. E. Finholt, and A. C. Bond, Jr., *J. Am. Chem. Soc.*, 69, 1199 (1947).

(6) W. C. Price, R. Fraser, T. Robinson, and H. C. Longust-Higgins, *Discuss. Faraday Soc.*, 9, 131 (1950).

(7) J. D. Glore, R. E. Hall, and E. P. Schram, *Inorg. Chem.*, 11, 550 (1972).

(8) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, 1969.

(9) I. M. Kolthoff, E. B. Sandell, E. J. Meehan, and S. Bruckenstein, "Quantitative Chemical Analysis", 4th ed., MacMillan, New York, 1971, p 787.

(10) Reference 9, p 600.

(11) W. F. Egell and W. M. Riser, Jr., *J. Am. Chem. Soc.*, 83, 5451 (1966).

$LiAlH_4$ and purified by vacuum fractionation until their vapor tensions match those of the pure materials. **D_2O**, A Teledyne Co., was used as received.

Reactions of $Al_2(i\text{-}Bu)_4$ (II). With HCl. II, 0.532 g (0.54 mmol), was dissolved in 10 mL of cyclopentane, the solution frozen at −196 °C, and HCl, 1.18 mmol, condensed into the reaction bulb. After 2 h at 25 °C, H_2, 0.40 mmol, and *i*-BuH, 0.38 mmol, were produced. The colorless reaction mixture was vacuum filtered through a glass frit and the filtrate treated with excess H_2O to produce *i*-BuH, 1.60 mmol—no additional H_2 was evolved. In a separate experiment the filtrate, nonvolatile, was examined by ^1H NMR and IR spectroscopy. The infrared spectrum lacked an absorption in the 1800 cm^{-1} region consistent with the absence of the AlH moiety.[7] Furthermore, it is virtually identical with that of $(i\text{-}Bu)_3Al$ with the addition of two absorptions at 498 and 473 cm^{-1} assigned to ν_{AlCl_2} by comparison to the spectrum of $EtAlCl_2$, 502 and 486 cm^{-1}.[12]

With Toluene-3,4-dithiol. II, 0.293 g (1.04 mmol), dissolved in 10 mL of cyclopentane, was treated with toluene-3,4-dithiol, III, 0.1558 g (0.998 mmol), dissolved in 10 mL of cyclopentane at 0 °C for 8 h to produce H_2, 0.63 mmol, and *i*-BuH, 0.48 mmol. The reaction solution remained dark red-brown, and a brown precipitate was present. The latter was insoluble in Et_2O and THF. An infrared spectrum of this material lacked an absorption in the 1800 cm^{-1} range (ν_{AlH}) but exhibited absorption at ~2530 cm^{-1} (ν_{SH}) found at 2533 and 2529 cm^{-1} in III. A ^1H NMR spectrum indicated the presence of the Al–*i*-Bu moiety with doublets centered at 0.42 (CH_2) and 1.26 ppm (CH_3) and singlets at 3.52 and 3.60 ppm (SH), found at 3.5 and 3.8 ppm in III. Integration of the doublet absorption centered at 0.42 ppm and the two singlets at 3.60 and 3.52 ppm indicated a sixfold greater concentration of *i*-Bu than SH moieties.

With Pentacarbonylmanganese Hydride and Dimanganese Decacarbonyl. II, 0.3760 g (1.33 mmol), was dissolved in benzene, and the mixture was frozen at −78 °C, treated with $HMn(CO)_5$, 0.5358 g (2.73 mmol), and allowed to warm to 25 °C with stirring for 1 h to afford 0.03 mmol of H_2 and ~0.01 mmol of *i*-BuH. The reactants were recombined and stirred at 25 °C for 6 days. Volatile materials were separated by fractional condensation to afford 0.13 mmol of H_2 (0.16 mmol total) and isobutane, 0.19 mmol, which was identified by comparison of its IR spectrum with an authentic sample. In addition $HMn(CO)_5$ and a trace of $Mn_2(CO)_{10}$ were recovered. A ^1H NMR spectrum of the benzene-soluble portion of the reation residue, red-brown in color, exhibited doublets centered at 0.32 and 1.29 ppm (*i*-Bu) and a singlet at −7.54 ppm ($HMn(CO)_5$) indicating an approximate $[HMn(CO)_5]$:[*i*-Bu] ratio of 1:2, respectively.

II, 0.3276 g (1.16 mmol), dissolved in cyclopentane, was added to a cyclopentane solution of $Mn_2(CO)_{10}$, 0.2274 g (1.16 mmol), and the mixture stirred for 3 weeks at 25 °C. No volatile product were evolved, and $Mn_2(CO)_5$, 0.2201 g, was recovered from the reaction mixture.

With Diborane. In a typical reaction II was dissolved in cyclopentane and subsequently treated with excess B_2H_6, total pressure ~700 torr, 1–2 days, and from 25 to 40 °C. B_2H_6 was added to the stirred reaction mixture until excess B_2H_6 was recovered. The observed reaction stoichiometries were as follows: II, 0.1321 g (0.47 mmol), B_2H_6, 2.10 mmol, $II/B_2H_6 = 4.5$; II, 0.0886 g (0.31 mmol), B_2H_6, 1.36 mmol, $II/B_2H_6 = 4.3$; II, 0.2102 g (0.74 mmol), B_2H_6, 3.28 mmol, $II/B_2H_6 = 4.4$. A volatile isobutylborane derivative was condensed in a −63 °C trap, $P = 4.5$ torr at 0 °C, which exhibited infrared absorptions at 2577 and 2481 cm^{-1} (BH_2), 1159 and 1114 cm^{-1} assigned to ν_{BC_2}.[13]

During reaction between II and B_2H_6, the color of the initial solution, red-brown, was discharded and a black material, AlB_2H_4, IV, precipitated from solution. IV was repeatedly washed with cyclopentane and benzene, in vacuo, and collected on a glass frit. Removal of the solvents from the filtrate afforded a colorless nonvolatile liquid, at 25 °C, which was not further investigated. IV was treated with $D_3O^+Cl^-$ (78% D) to afford 1.38 mmol of dihydrogen (26% H_2, 54% HD, and 20% D_2). [M–H]/[M–M] bond calculation where M is B and/or Al:

$$[MH] \xrightarrow{D_3O^+} 0.78HD + 0.22HH$$

$$[M\text{–}M] \xrightarrow{D_3O^+} 0.78MD \xrightarrow{D_3O^+} (0.78)^2D_2 + (0.22)(0.78)HD$$

$$[M\text{–}M] \xrightarrow{D_3O^+} 0.22MH \xrightarrow{D_3O^+} (0.22)(0.78)HD + (0.22)^2H_2$$

$$[MH]/[MM] = 1.5$$

The hydrolysis residue contained 0.215 mmol of Al and 0.427 mmol of B, B/Al = 1.99: mg of Al found/mmol of H_2 (isotope mixture), 4.20; mg of B found/mmol of H_2 (mixture), 3.34. Calcd for $Al_2B_4H_8$ (five M–M bonds): 4.15 and 3.32, respectively. M–H/M–M calcd for $Al_2B_4H_8$: 1.6. Found: 1.5.

Acknowledgment. Support of this work by The Ohio State University is appreciated.

Registry No. I, 96666-23-8; II, 60253-71-6; III, 496-74-2; $B_2(NMe_2)_4$, 1630-79-1; $AlMe_3$, 75-24-1; HCl, 7647-01-0; $HMn(CO)_5$, 16972-33-1; $Mn_2(CO)_{10}$, 10170-69-1; B_2H_6, 19287-45-7; 1,1-diisobutyldiborane, 84495-27-2.

(12) E. Maslowski, Jr., "Vibrational Spectra of Organometallic Compounds", Wiley, New York, 1977, p 40.

(13) W. J. Lehmann, C. O. Wilson, and I. Shapiro, *J. Chem. Phys.*, 28, 777 (1958).