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The Preparation and Characterization of Molecular Dipotassiumhexaisobutyldihydridodialuminum

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Abstract

Treatment of $^{i}Bu_2AlH$ with K affords $K_2Al_2{}^{i}Bu_6H_2$. The reactions of the latter with H_3O^+, DCl and Me_3SiCl have been studied. Spectroscopic characterization involved NMR data; ^{1}H, ^{13}C, ^{27}Al and ^{39}K, as well as a discussion of an observed low energy ν(Al–H) (non-typical) in the infrared spectrum. Finally, possible geometries for $K_2Al_2{}^{i}Bu_6H_2$ are presented.

Introduction

The potassium reductions of $^{i}Bu_2AlCl$ and $Al^{i}Bu_3$ have been described as affording catenated aluminum compounds, $Al_2{}^{i}Bu_4$ (I) [1] and $K_2Al_2{}^{i}Bu_6$ (II) [2] respectively. The chemical reactivity of I with protonic and hydridic reagents [3], as well as Lewis bases [4] has been reported. With regard to I and II, oxidation employing protonic reagents affords one mole H_2 per mole of Al–Al bonds. II is an interesting species in that it is described as soluble in benzene, hence a 'tight' ion pair was suggested. The absence of an Al–H moiety, II, was based on the absence of ν(Al–H) at *ca.* 1800 cm^{-1} [2]. The subject of this report, $K_2Al_2{}^{i}Bu_6H_2$ (III), a hydridic compound, also lacks ν(Al–H) *ca.* 1800 cm^{-1}.

The reaction of K with $^{i}Bu_2AlH$ has been reported to afford the dark brown crystalline compound, $K_2[H(^{i}Bu_2Al–Al^{i}Bu_2H]$ (IV) described as possessing an Al–Al bond [5]. The relevant analytical data, Al and K only, are consistent with the indicated stoichiometry. Furthermore, $^{i}Bu_2Al–Al^{i}Bu_2$ was indicated to react with KH to also afford IV. Separation of IV from reported reaction by-products, $KAlBu_3H$ and $KAlBu_2H_2$, was achieved by the solubility of the latter two compounds in hexane. On the other hand, these same compounds have been reported to be insoluble in aliphatic solvents [6]. These conflicting points, in addition to our continued interest in catenated aluminum organometallic compounds, prompted this investigation of the reaction between Bu_2AlH by K.

Results and Discussion

Preparation and Characterization of $K_2Al_2{}^{i}Bu_6H_2$ (III)

Treatment of K with a cyclopentane solution of $^{i}Bu_2AlH$ resulted in the formation of a dark brown solution from which golden brown microcrystalline III was isolated after filtration, and subsequent solvent removal *in vacuo.* Treatment of III with H_3O^+ is summarized by eqn. (1) with the experimental quantities indicated in parentheses.

$$K_2Al_2{}^{i}Bu_6H_2 + 4H_3O^+ \longrightarrow$$
$$2(2.0)Al(OH)_2{}^+ + 2(2.0)K^+ + 2(2.1)H_2 + 6(5.6)^{i}BuH \quad (1)$$

Two moles of H_2 were produced per mole III; the dimeric nature of III has been established via a molecular weight determination. An alternative source of H_2, rather than the Al–H moiety is the presence of reduced oxidation state Al, *i.e.* metal metal bonds. III was treated with DCl to establish the oxidation state of Al; the presence of an Al–Al bond results in the formation of D_2 whereas the Al–H moiety yields HD. Reaction of III with DCl is described by eqn. (2) with the experimental quantities indicated in parentheses.

$$K_2Al_2{}^{i}Bu_6H_2 + \text{ex. DCL} \longrightarrow$$
$$2(2.00)HD + 2(2.06)AlCl_3 + 2(2.00)KCl + 6(5.3)^{i}BuD \quad (2)$$

A slightly low yield of isobutane was observed due to the heterogenous nature of this reaction. As a consequence, black particles of nonvolatile material remained in the reaction vessel but subsequently reacted with H_3O^+,

The reaction of K with $^{i}Bu_2AlH$ is described by eqn. (3).

$$2^{i}Bu_2AlH + 3K \longrightarrow$$
$$\tfrac{1}{2}[KAl^{i}Bu_3H]_2 + Al(O) + K^{i}Bu + KH \quad (3)$$

The insoluble reaction by-product mixture was treated with H_3O^+, and produced ^iBuH and H_2 as expected, *i.e.* reaction with KH, K^iBu and Al.

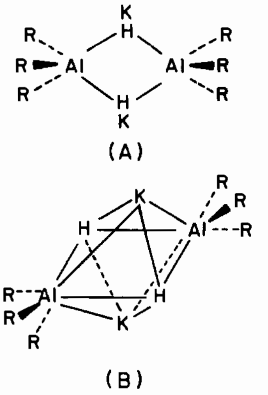
Formation of **III** most likely involves **IV** as an intermediate. In this study, excess K was employed as contrasted to the formation of **IV**. Therefore, the reactions described by eqns. (4) and (5) summarize this system.

$$2Al^iBu_2H + 2K \longrightarrow \underset{\textbf{IV}}{K_2[Al_2{}^iBu_4H_2]} \qquad (4)$$

$$K_2[Al_2Bu_4H_2] + K \longrightarrow \frac{1}{2}\underset{\textbf{III}}{[KAl^iBu_3H]_2} + KH + K^iBu + Al \qquad (5)$$

The solubility characteristics of **III** and **IV** are quite different with the former soluble in alkanes while the latter is insoluble [5].

During the characterization of reduced oxidation state organoaluminum compounds by oxidative hydrolysis, care must be exercised in concluding the presence or absence of the Al–H moiety, *i.e.* a source of H_2 in addition to reduced Al. A variety of previously characterized compounds with the Al–H moiety have routinely exhibited a strong ν(Al–H) absorption centered at *ca.* 1800 cm^{-1} [7], e.g. $Al_3B_3[N(CH_3)_2]_7H_5$ (terminal Al–H) [8], $Al_3(CH_3)_6[N(CH_3)_2]H$ (Al–H–Al bridge) [9], $Al_4(CH_3)_8[N(CH_3)_2]_2H_2$ (Al–H–Al bridge) [10]. On the other hand, Eisch has reported that mixtures of $^iBu_2AlH$ and Al^iBu_3 do not exhibit ν(Al–H) at *ca.* 1800 cm^{-1}, but rather in the region 1350–1450 cm^{-1} as subsequently established by treatment of $^iBu_2AlD$ with Al^iBu_3 [11]. A suggested explanation for the low ν(Al–H) absorption included a structure with H^- bridging three metal centers. More recently Beachley *et al.* have reported the formation of $K_2Al_2[CH_2SiMe_3]_6H_2$ (**V**) by treating $Al(CH_2SiMe_3)_3$ with KH [12]. **V** also exhibits a low energy ν(Al–H) absorption at 1560 cm^{-1}; and a geometry was suggested involving hydride interacting with three metal centers, *i.e.* a four membered ring of two Al and two H with the K interacting with the bridge Hs and positioned in the plane of the ring, *i.e.* similar to that depicted in Fig. 1A.



(A)

(B)

Fig. 1. Possible geometries for $K_2Al_2{}^i(Bu)_6H_2$.

Concerning the infrared spectrum of $K_2Al_2{}^iBu_6H_2$ (**III**) the 'diagnostic' ν(Al–H) absorption at *ca.* 1800 cm^{-1} is also absent although high energy tailing of the absorption found at 1461 cm^{-1} is present, Fig. 2. For comparison, a typical ν(Al–H) absorption, Fig. 2 (partial spectrum), is included, (Al^iBu_2H) As is discussed in the NMR section, positive spectroscopic evidence for the Al–H moiety (**III**) has been obtained in addition to the DCl reaction affording HD.

NMR Characterization of III

^1H NMR data for **III** and several related compounds are summarized in Table I. The *CH*, CH_3 and CH_2 resonances were found in the ratio 1:6.04: 1.95 respectively (calc. 1:6:2) at δ 1.90, 1.09 and –0.29, respectively. The upfield shift, $AlCH_2$, has previously been reported for K isobutyl derivatives, Table I, and is attributed to increased electron density associated with aluminum as a result of pseudo anionic character.

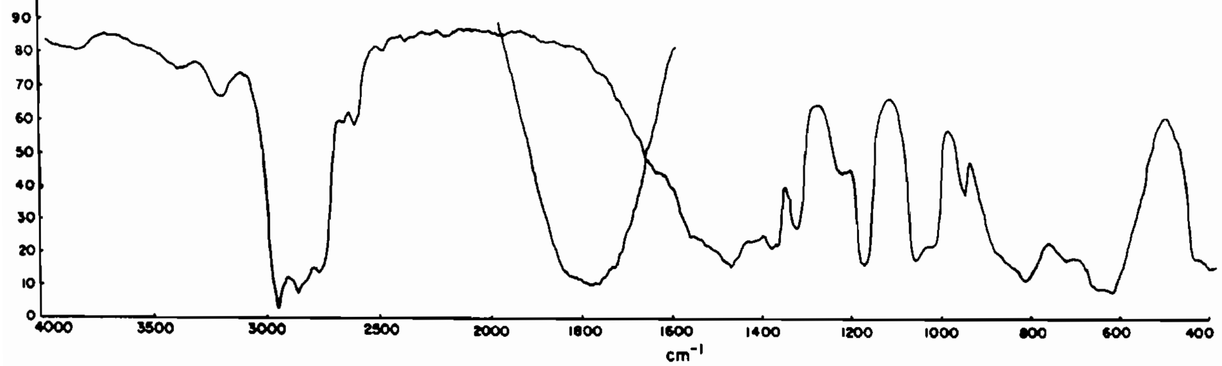


Fig. 2. Infrared spectrum of $K_2Al_2{}^iBu_6H_2$ and partial spectrum of $^iBu_2AlH$.

TABLE I. NMR Parameters Associated with Organoaluminum Compounds

Compound	CH(septet)	^1H (ppm) (J(Hz))			^{13}C(ppm)			^{27}Al(ppm) $\delta W_{1/2}$ (Hz)	^{39}K(ppm) $\delta W_{1/2}$ (Hz)
		CH_3[d]	CH_2[d]	AlH	CH_3	CH	CH_2		
$K_2Al_2{}^iBu_6H_2$[a]	1.90(6.60)	1.09(6.60)	−0.29(6.85)	2.66	29.1*	28.3*	24.8* Br	148(1953)	−22(359)
Al^iBu_3[a]	1.91(6.65)	0.98(6.65)	0.24(6.00)		28.3*	26.3*	24.0vw	268(6684)	
Al^iBu_2H[a]	1.91(6.60)	1.03(6.50)	0.41(7.00)	3.02	28.0	26.7	20.7*	173(7122)	
$K_2Al_2{}^iBu_6$[b]		1.3	−0.30		29.8	28.7	27.2		
KAl^iBu_4[b]			−0.25						
$K_2Al_2[CH_2SiMe_3]_6H_2$[c]			−0.98						
$K_2[H^iBu_3AlAlBu_3{}^iH]$[d]								135‘(460)’	

Starred items established by off resonance. [a]This work, *ca.* 10% solution in D_6 benzene. [b]Ref. 2. [c]Ref. 12. [d]Ref. 5.

Assignment of the absorption found at δ2.66, Al–H, is with reference to $^iBu_2AlH$, δ3.02, and also indicates increased shielding as compared to $^iBu_2AlH$. The ^{39}K resonance, δ−22, is consistent with a molecular formation of **III** rather than a ‘tight’ ion pair, *i.e.* shielded K with reference to aqueous KNO_3. The ^{27}Al resonance is found upfield from that of $^iBu_2AlH$, δ148 and again indicates an increase in electron density. As has recently been reported, care must be exercised regarding ^{27}Al resonances because the NMR probe signal is always found at *ca.* δ58 [13]. Finally, the ^{13}C NMR assignments were established for **III** from the related off resonance spectrum, and are typical of ^iBu aluminum derivatives.

Suggested Geometry for III

A solution molecular weight measurement in cyclopentane is consistent with the molecular dimeric formulation $K_2Al_2{}^iBu_6H_2$, while the NMR data indicate equivalent ^iBu moieties, and equivalent K and equivalent Al environments. As has been previously discussed, **III** exhibits a low energy ν(Al–H); in two other cases where this has been observed this has been attributed to hydride bridging possibly three metal centers [11, 12]. The geometry of **III** may be that suggested for analogous **V**, Fig. 1A [12]. On the other hand, **V** is colorless, whereas **III** is dark golden brown indicative of a low lying excited state. As an alternative geometry, it is suggested the two K may lie symmetrically disposed above and below the Al_2H_2 plane, Fig. 1B. Low temperature (190 K) ^1H NMR studies), toluene-d_8, indicate no agostic alkyl H interaction.

Reactivity of III

III is oxidized by H_2O and HCl to generate ^iBuH and H_2. In an effort to further evaluate the hydride reactivity of **III**, a benzene solution was treated with ethylene up to 48 °C, P(ethylene) ~300 torr. No uptake of olefin occurred. **III** was next heated, in solution, to 80 °C and no evolution of H_2, isobutane, of isobutylene took place. Both Al^iBu_3 and $Al_2{}^iBu_4$ evolve H_2 and isobutylene at 80 °C, and add ethylene to afford ethylaluminum derivatives [4].

The thermal stability of **III** with regard to elimination of isobutylene, βH migration, is likely associated with a crowded transition state. The absence of ethylene addition is attributed to hydride participating in multi metal bonding.

In order to effect hydride–halogen exchange, **III** was treated separately with Ph_3CCl and Me_3SiCl to afford Ph_3CH and Me_3SiH respectively. However, the control reactions were also carried out substituting Al^iBu_3 for **III**, and again Ph_3CH and Me_3SiH were formed.

In the case of the reaction between **III** and Me_3SiCl, the reaction residue was treated with aqueous HCl to afford isobutane, 87.5% yield based on the initial quantity of **III**, and 9.5% yield of H_2. Therefore, the hydride associated with **III** is the main source of Me_3SiH. The experimental stoichiometry associated with the reaction with Me_3SiCl, eqn. (6), indicates that the excess Me_3SiCl consumed and the excess Me_3SiH produced are a result of the reduction of Me_3SiCl by the ^iBu moiety.

$$1.0K_2Al^iBu_6H_2 + 2.34Me_3SiCl \longrightarrow 2.18Me_3SiH + \text{residue} \qquad (6)$$

Work is in progress regarding growth of crystals of **III** suitable for structure determination.

Experimental

Equipment and Techniques

Standard vacuum line procedures were employed throughout this investigation [14]. Infrared spectra were recorded with a Unicam SP 1100 spectrometer with a film of nonvolatile samples prepared by vaporization of the appropriate solvent in a N_2 atmosphere. Volatile materials were contained in a 10 cm gas cell, KBr optics. FT NMR spectra were obtained with a Bruker AM-500 spectrometer employing benzene-d_6 or toluene-d_8. Nonvolatile samples were transferred to 10 mm NMR tubes in an inert atmosphere. Solvents were distilled on to these materials, *in vacuo,* and the NMR tubes fuse sealed. ^{27}Al and ^{39}K spectra were referenced to aqueous 1 M $Al(NO_3)_3$ and 1 M KNO_3, respectively. Mass spectra were obtained with a Balzers QME 112 Quadrupole spectrometer.

Analyses

Dihydrogen was collected in a volume calibrated Toepler pump assembly and identified by combustion to H_2O over CuO at 300 °C. Aluminum and potassium were determined gravimetrically after precipitation as the 8-hydroxyquinolate [15] and tetraphenyl borate [16], respectively. Standard solutions of both elements, employing similar dilutions as unknowns, yielded 99% plus recovery of the respective cations. Isobutane quantities were determined by employing the ideal gas law. Identification was confirmed by vapor tension measurements and infrared spectroscopy.

Reagents

Diisobutylaluminum hydride, from Ethyl Corporation, was used as received and quantities were measured volumetrically in a N_2 atmosphere. Solvents utilized, cyclopentane, benzene-d_6, and toluene-d_8 were dried *in vacuo* using n-BuLi after solvent removal from the latter *in vacuo.* Solvents were then purified by fractional condensations until their respective vapor tensions agreed with the literature values. Deuterium chloride, obtained from Cambridge Isotope Laboratories, 99% D, was used as received. Prior to reactions employing DCl, the necessary portion of the vacuum line was treated with DCl, P ~600 torr. Next, fresh DCl to be used as a reactant was expanded in the same portion of the vacuum line and an aliquot was examined by gas phase IR to determine the HCl–DCl composition by integration of the appropriate relative IR absorptions. Mass spectroscopic examination of these isotope mixtures proved unsatisfactory because the apparent composition of the gas mixture changed with time in the mass spectrometer. Me_3SiCl (Aldrich) was purified by fractional condensation until its vapor tension matched the literature value.

Preparation and Purification of III

A typical synthesis of **III** involved dropwise addition of a 20% by volume (cyclopentane) solution of $^iBu_2AlH$, 56.3 mmol, to 50 ml cyclopentane containing slivers of K, 4.4 g (113 mmol). The magnetically stirred K–cyclopentane system was maintained at 0 °C for 5 h during the addition of $^iBu_2AlH$. Initial reaction is associated with development of a red color on the K surface. Next, the reaction mixture was allowed to come to room temperature and stirred for 3 days. During this time, H_2, 0.38 mmol, was evolved. The product mixture then was filtered *in vacuo* (to remove excess K, Al(O), KH and K^iBu) employing an apparatus consisting of a medium porosity glass frit fitted with glass O-ring joints and Kontes teflon stopcocks. Aliquots of **III** were transferred to 10 ml flat-bottomed bulbs which facilitated subsequent solvent vaporization *in vacuo.*

Acid Hydrolysis

Treatment of **III**, 717.2 mg (1.506 mmol), with 20% HCl afforded 8.44 mmol of ^iBuH, 3.2 mmol of H_2, while the residue solution yielded 118 mg K and 82.3 mg Al based on the isolated quantities of aluminum 8-hydroxyquinolate and potassium tetraphenyl borate. *Anal.* Calc. for **III**: Al, 11.3; ^{i}Bu, 71.8; K, 16.4; hydride, 0.42. Found: Al, 11.4; ^{i}Bu, 67.1; K, 16.5; hydride, 0.44%. Equivalent weight mg/mmol H_2: calc. 238.1; found, 224. Molecular weight: calc., 476.18; found, 418; 0.115 M in cyclopentane (isopiestic method). After hydrolysis, a small amount of organic film was observed on the H_2O surface; hence, during decomposition of **III** a secondary reaction of ^{i}Bu moieties takes place. Hydrolysis of reagent grade $^iBu_2AlH$ also results in the formation of less than stoichiometric ^iBuH, *i.e.* 1.8 BuH:H_2.

With DCl/HCl, 91.9/8.1 mol% respectively

III, 604.8 mg (1.27 mmol) was treated with DCl/HCl in the range 400–600 torr. $H_2(HD,D_2)$ and $^iBuH(D)$ were periodically removed and separated from HCl/DCl, and the latter returned to the reaction residue. After 3 days at 25 °C, the initial golden brown color of **III** was mostly white; a few black particles remained. Mass spectroscopic analysis of the dihydrogen mixture indicated 0.25 mmol H_2, 2.30 mmol HD, and 0.06 mmol D_2. Calc: mmol Al–Al = mmol $D_2/(0.92)^2$ = 0.07 or 0.05 mmol per mol **III**. Found: after solution of the reaction residue in aqueous HCl, Al, 11.7; K, 16.5%.

Infrared absorptions

III: 3200w, 2944s, 2860s, 2764s, 2600m, 1470s(br), 1380s, 1360s, 1320s, 1220m, 1170s, 1055s, 1020s, 943m, 810s(br), 715s(br), and 640s(br) cm^{-1}.

With Me₃SiCl

III, 150.6 mg (0.32 mmol), was treated with 6.11 mmol of Me_3SiCl at 0 °C followed by reaction at 25 °C for 10 h. Fractionation of the reaction mixture, –95 and –45 °C traps, resulted in the isolation of Me_3SiCl, 5.36 mmol, (stopped at –95 °C), and Me_3SiH, 0.70 mmol (thru –95 °C trap, stopped at –196 °C). Me_3SiH was identified by comparison of ν(SiH) with the literature value, 2123 cm^{-1} [15].

Hydrolysis of the reaction residue with 20% HCl produced 1.68 mmol of ^{i}BuH and 0.06 mmol of H_2. Similar treatment of $^{i}AlBu_3$ with Me_3SiCl also produced Me_3SiH.

With Ph_3SiCl

A solution of **III** in cyclopentane was treated with excess Ph_3SiCl followed by heating at 47 °C for 4 h. A ^{1}H NMR spectrum of the resulting reaction mixture indicated the formation of Ph_3SiH, ^{1}H, $\delta 5.43$. An authentic sample of Ph_3SiH exhibited a resonance at $\delta 5.49$. Similar treatment of $Al^{i}Bu_3$ in cyclopentane with Ph_3SiCl at 25 °C also produced Ph_3SiH, ^{1}H, $\delta 5.49$.

With Ethylene

III, 289 mg (0.61 mmol) in benzene, was treated with C_2H_4, 3.77 mmol (reaction pressure ~300 torr) at 48 °C for 3 h. Ethylene was quantitatively recovered.

Pyrolysis

III remained from the C_2H_4 reaction was heated in benzene for 4 h at 80 °C; no H_2, ^{i}BuH, or isobutylene were produced.

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