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The preparation and characterization of tetraneopentyl tetraaluminum(4)

Eugene P. Schram* and **Narasimhan Sudha**

Evans Chemical Laboratory, The Ohio State University, 140 West 18th Avenue, Columbus, OH 43210 (U.S.A.)

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Abstract

The synthesis of bis(neopentyl)aluminum chloride and subsequent reduction with potassium affords tetraneopentyl tetraaluminum(4). Analytical characterization of the latter is described and spectroscopic results are discussed. Reaction mechanisms are suggested for the reduction of bis(isobutyl) and bis(neopentyl)aluminum chloride as well as possible subsequent decomposition pathways.

Introduction

Our previous studies involving low oxidation state organoaluminum compounds ($<3+$) have utilized the isobutyl moiety, ^{i}Bu. These investigations have included development of the chemistry associated with $Al_2{}^iBu_4$ (**I**) [1, 2], and the syntheses of $KAl_2{}^iBu_3$ (**II**) and $K_3Al_5{}^iBu_{10}$ (**III**) [3]. With regard to **I**, a single metal metal bond is present whereas **II** and **III** may involve anionic metal clusters. Recently the synthesis and crystal structure of tetrakis[bis(trimethylsilyl)methyl] dialuminum(4), $[(Me_3Si)_2CH]_4Al_2$ (**IV**), has been reported which contains a single AlAl bond [4].

Compounds **I** and **III** undergo decomposition in solution as a result of disproportionation. In an effort to continue the development of low oxidation state aluminum chemistry, we have carried out the reduction of bis(neopentyl)aluminum chloride, $[Me_3CCH_2]_2AlCl$ (**V**), and now report the formation and characterization of tetraneopentyl tetraaluminum(4), $[Me_3CCH_2Al]_4$ (**VI**).

Results and discussion

The precursor to **VI**, **V** results from a series of reactions starting with the preparation of Me_3CCH_2Li (NeoLi), eqn. (1).

$$NeoCl + 2Li \longrightarrow NeoLi + LiCl \qquad (1)$$

Next $AlCl_3$ is treated with a 10% excess of NeoLi ideally summarized by eqn. (2).

$$AlCl_3 + 3NeoLi \longrightarrow (Neo)_3Al + 3LiCl \qquad (2)$$

The final reaction involves the stoichiometry controlled moiety exchange, eqn. (3).

$$2(Neo)_3Al + AlCl_3 \longrightarrow 3(Neo)_2AlCl \qquad (3)$$

This series of reactions has been employed for the synthesis of $(Neo)_2AlBr$ [5]. When one attempts to prepare R_2AlCl compounds directly, eqn. (4),

$$2RLi + AlCl_3 \longrightarrow R_2AlCl + 2LiCl \qquad (4)$$

reaction mixtures usually result which are association complexes between R_2AlCl and $RAlCl_2$ [6]. It is surprising that it was possible to prepare $[(Me_3Si)_2CH]_2AlCl$, in diethylether, according to the reaction represented by eqn. (4) [4].

Characterization of $(Neo)_2AlCl$ (V) and $(Neo)_3Al$ (VII)

VII was purified by vacuum distillation. The ^{1}H NMR and IR spectra agreed with the literature values [5]. **V** was purified by sublimation, *in vacuo*, and analytically characterized by neopentane evolution resulting from acid hydrolysis, eqn. (5) (with the experimental quantities indicated (in brackets).

$$1(1.0)(Neo)_2AlCl + 2H^+ \longrightarrow 2(2.0)NeoH + Al^{3+} + Cl^- \qquad (5)$$

Spectroscopic data associated with **V** are summarized in 'Experimental'.

Preparation and characterization of tetraneopentyl tetraaluminum(4) (VI)

The reduction of **V** by K affords **VI** as a non-volatile brown solid, eqn. (6).

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*Author to whom correspondence should be addressed.

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$$2(\mathrm{Neo})_2\mathrm{AlCl} + 2\mathrm{K} \longrightarrow \tfrac{1}{4}[\mathrm{AlNeo}]_4 + \mathrm{Al(Neo)}_3 + 2\mathrm{KCl} \quad (6)$$

Acid hydrolysis of **VI** is summarized by eqn. (7) (with the experimental quantities indicated in brackets).

$$1(1.0)[\mathrm{AlNeo}]_4 + 12\mathrm{H}^+ \longrightarrow 4(3.9)\mathrm{NeoH} + 4(4.1)\mathrm{H}_2 + 4(4.0)\mathrm{Al}^{3+} \quad (7)$$

The molecular weight of **VI** was determined in solution, and indicates a tetramer of AlNeo, i.e. $[\mathrm{AlNeo}]_4$. Subsequent hydrolysis and analysis of the molecular weight sample resulted in the molar ratios, $\mathrm{NeoH{:}H_2{:}Al^{3+}}$ of 0.96:1.00:1.03, respectively. Because the evolution of H_2, during the hydrolysis of **VI**, could result from either oxidation of Al or protonation of the Al–H moiety, it is necessary to establish the absence of the latter. The infrared spectrum of **VI** clearly indicates the absence of a strong broad absorption, νAlH, in the $1800\ \mathrm{cm}^{-1}$ region as well as multi metal centered hydrogen bridge bonding in the range 1350–$1450\ \mathrm{cm}^{-1}$ [7]. Furthermore, no ^{1}H NMR absorption for Al–H is found in the range 2.5–3.4 ppm [5, 7]. Finally, treatment of **VI** with D_2O produces D_2 whereas if the Al–H moiety was present HD would be evolved.

Suggested geometry for VI

The oxidative hydrolysis of 1 mol of **VI** produces 4 mol of H_2 and the required 8 mol of electrons are most likely associated with bonding orbitals. Two possible geometries for **VI** are a four membered Al ring, and a tetrahedral Al core with *exo* neopentyl moieties σ bonded to Al. The four membered ring would involve three coordinate Al, hence one would expect Al to exhibit Lewis acid character. Treatment of **VI** with Et_2O affords a brown solution from which Et_2O can be quantitatively removed *in vacuo* at 25 °C. Based on the lack of stable adduct formation, between **VI** and Et_2O, the four membered ring geometry would appear less likely. The infrared spectrum of **VI** exhibits a strong, broad absorption, 950–$500\ \mathrm{cm}^{-1}$ center at *c.* $750\ \mathrm{cm}^{-1}$, which may be associated with a cage absorption; this strong broad absorption is absent in **VII**, see Fig. 1. **VI** is isoelectronic with B_4Cl_4 (T_d), and the latter exhibits a strong broad IR absorption in the gas phase, centered at $1010\ \mathrm{cm}^{-1}$, which has been suggested to be associated with a cage absorption [8]. Subsequently this absorption was assigned to B–B and B–Cl stretch, degenerate [9].

If one assumes a T_d geometry for **VI**, 4 Al with *exo* σ Al–C bonds, the C sp^3 and Al s orbitals transform at A_1, and T_2, while the Al p orbitals transform as A_1, E, T_1 and $2T_2$. The suggested ground state electron configuration is $(A_1)^2(T_2)^6$. Consistent with this bonding model is the fact that the ^{1}H NMR δ CH_2 of the neopentyl moiety **VI** is shifted downfield from **VII** by 0.30 ppm, i.e. delocalization of carbon electron density to the suggested Al cluster.

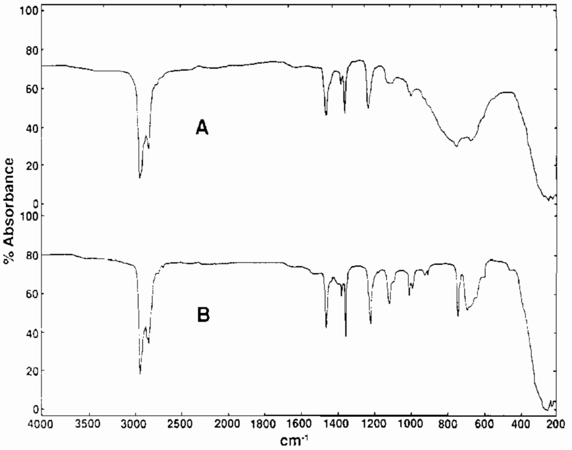

Fig. 1. IR spectra of tetraneopentyl tetraaluminum(4) (A) and trisneopentyl aluminum (B).

Formation and solution decomposition of $Al_2{}^iBu_4$ and '$Al_2(Neo)_4$'

Reduction of $^iBu_2AlCl$

The slow addition of an alkane solution of $^iBu_2AlCl$ to K (−15 °C) results in the formation of $Al_2{}^iBu_4$ [3, 10]. K is present in excess except for the last aliquot addition of $^iBu_2AlCl$. $Al_2{}^iBu_4$ is stable in solution for several days at 25 °C but after this period of time decomposition is obvious because finely divided Al(0) is deposited, and Al^iBu_3 is produced, as ideally represented by eqn. (8) [1].

$$3\mathrm{Al}_2\mathrm{Bu}_4 \longrightarrow 2\mathrm{Al}(0) + 4\mathrm{Al}^i\mathrm{Bu}_3 \quad (8)$$

When a hexane solution of $^iBu_2AlCl$ is rapidly added to K (15 min), followed by a 24 h reaction period at −15 °C, all the K is consumed and a red–brown solution color develops which is typical of $Al_2{}^iBu_4$. However, the resulting non-volatile product is not $Al_2{}^iBu_4$ based on the ^{1}H NMR spectrum which consists of six doublets and two septets. The chemical shifts of these absorptions are not those of $Al_2{}^iBu_4$ [11]. In separate studies we have observed Al^iBu_3 to react with K to afford complex reaction mixtures which are also red–brown in color. Others have reported this latter reaction system affords $[2K^+][Al_2{}^iBu_6]^{2-}$ which was claimed to contain an Al–Al bond [12].

Regarding the reaction mechanism associated with the formation of $Al_2{}^iBu_4$, it is suggested that $[Al^iBu_2]^1$ is generated (slow addition of

$^{i}Bu_2AlCl$), i.e. excess K is present, eqn. (9), followed by this intermediate functioning as a nucleophile toward $^{i}Bu_2AlCl$, eqn. (10).

$$^{i}Bu_2AlCl + 2K \longrightarrow [^{i}Bu_2Al]^{1-} + 2K^+ + Cl^- \qquad (9)$$

$$[^{i}Bu_2Al]^{1-} + {^{i}Bu_2AlCl} \longrightarrow Al_2{^{i}Bu_4} + Cl^- \qquad (10)$$

Reduction of V

The addition of a hexane solution of **V** to K does not result in appreciable reaction below 24 °C based on the absence of the red–brown solution color of the product. After removal of KCl, **VI** and **VII** were separated and isolated in high yield. Concerning the formation of **VI**, it is suggested that the reaction intermediate, $[Al_2(Neo)_4]$, is produced, eqn. (11), followed by disproportionation to produce **VI** and **VII**, eqn. (12).

$$2(Neo)_2AlCl + 2K \longrightarrow [Al_2(Neo)_4] \qquad (11)$$

$$[Al_2(Neo)_4] \longrightarrow \tfrac{1}{4}[AlNeo]_4 + Al(Neo)_3 \qquad (12)$$

The difference between the disproportionation of $Al_2{^{i}Bu_4}$, eqn. (8), and that of 'Al_2Neo_4', eqn. (12), is the former affords Al(0) whereas the latter results in the formation of **VI**, eqn. (12). We suggest the different paths for disproportionation for $Al_2{^{i}Bu_4}$ and 'Al_2Neo_4' may be associated with the fact that $Al_2{^{i}Bu_4}$ has been demonstrated to eliminate isobutylene and subsequently adds ethylene to afford the $Al-CH_2CH_2CH_2CH_3$ moiety [1]. From this reactivity pattern one may infer the formation of an Al–H intermediate. While these reactions took place at 80 °C, a low concentration of the Al–H moiety may be produced in solutions of $Al_2{^{i}Bu_4}$ at 25 °C. A possible reaction decomposition sequence for $Al_2{^{i}Bu_4}$ is summarized by eqns. (13) and (14), and is under investigation.

$$^{i}Bu_2Al-Al^{i}Bu_2 \rightleftarrows {^{i}Bu_2Al}-Al(^{i}Bu)(H) + (CH_3)_2C{=}CH_2 \qquad (13)$$

$$^{i}Bu_2Al-Al(^{i}Bu)(H) \longrightarrow Al^{i}Bu_3 + Al(0) + \tfrac{1}{2}H_2 \qquad (14)$$

We are currently developing the derivative chemistry of **VI** as well as attempting crystal growth for a subsequent X-ray structure determination. Thus far only golden colored microcrystalline material has been observed in saturated toluene solutions.

Experimental

Equipment and techniques

Standard vacuum line procedures were employed throughout this investigation [13]. Filtrations were carried out *in vacuo* employing a medium porosity glass frit assembly equipped with O ring joints and teflon stop cocks. IR spectra were recorded with a Perkin-Elmer 283B spectrophotometer, from a film of non-volatile sample 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 250 at 250.13 MHz spectrometer employing benzene-d_6 and pentane-d_{12}. Mass spectra H_2, HD and D_2 were obtained with a Balzers QME 112 quadrupole spectrometer. Molecular weight measurements were obtained by the isopiestic method using cyclopentane as the solvent and sublimed azobenzene as the standard.

Analysis

Hydrolyses were carried out *in vacuo* with 20% HCl. Dihydrogen was collected in a volume calibrated Toepler pump assembly and identified by combustion to H_2O over CuO at 300 °C. Aluminum was determined gravimetrically after precipitation as the 8-hydroxyquinolate [14]. The analytical procedure for potassium involves precipitation as $KB(C_6H_5)_4$ [15]. Neopentane quantities were determined by employing the ideal gas law. Identification was confirmed by vapor tension measurements and IR spectroscopy.

Reagents

Cyclopentane and hexane were distilled from $LiAlH_4$. Cyclopentane was further purified by fractional condensation until its vapor tension agreed with the literature value. Methyl lithium, neopentyl chloride, $AlCl_3$, benzene-d_6, D_2O (99.8% D) and K, Aldrich Chemical Co., were used as received.

Synthesis of neopentyllithium

A mixture of neopentyl chloride, 25 g (234 mmol) and 6.3 g (excess) of Li wire containing 1% Na in *c.* 300 ml of hexane was stirred and refluxed under argon for one week. The LiCl and excess Li were removed by filtration *in vacuo*. The neopentyllithium was isolated from the filtrate as a white crystalline solid. Yield: 13.47 g (74%). ^1H NMR (benzene-d_6): δ 1.12 (s, 9H, Me); −0.70 (S, 2H, CH_2); lit. [16]: δ 1.13 (s, 9H, Me); −0.67 (s, 2H, CH_2).

Synthesis of $Al(CH_2CMe_3)_3$ (VII)

$LiCH_2CMe_3$, 6.84 g (87 mmol), dissolved in 190 ml of hexane, was added over a period of 1 h to a suspension of $AlCl_3$, 3.86 g (29 mmol) in 60 ml of hexane at 0 °C. The resulting mixture was refluxed under argon for 36 h. Hexane was removed *in vacuo*, and the product, $Al(CH_2CMe_3)_3$, purified by vacuum distillation to yield 5.93 g (85%

based on $AlCl_3$). $Al(CH_2CMe_3)_3$: colorless liquid, b.p. 42–44 °C (dynamic vacuum). ^1H NMR (benzene-d_6): δ 1.04 (s, 9H, Me); 0.53 (s, 2H, CH_2); lit. [5]: δ 1.11 (s, 9H, Me); 0.56 (s, 2H, CH_2). IR (neat liquid, cm^{-1}): 2950(s), 2860(s), 1465(s), 1382(s), 1360(s), 1223(s), 1120(s), 1010(s), 990(m), 925(m), 908(m), 748(s), 695(m), 675(sh), 650(sh), and 465(m).

Synthesis of $Al(CH_2CMe_3)_2Cl$ (V)

VII, 1.783 g (7.4 mmol) and $AlCl_3$, 0.494 g (3.7 mmol), each in 25 ml of hexane, were heated in an evacuated flask in an oil bath maintained between 60 and 70 °C for 18 h. The hexane was removed *in vacuo* and the product **V** was purified by sublimation at 75–80 °C *in vacuo* to yield 2.062 g (91% based on $AlCl_3$) of white crystalline solid. **V**: m.p. 47–50 °C. After hydrolysis found: 1.46 mmol CMe_4/0.735 mmol **V**; calc. 1.47 mmol CMe_4/0.735 mmol **V**. ^1H NMR (benzene-d_6): δ 1.12 (s, 9H, Me); 0.68 (s, 2H, CH_2). IR (Nujol mull cm^{-1}): 2952(s), 2854(s), 1464(s), 1376(s), 1362(s), 1230(s), 1130(s), 1095(m), 1010(m), 995(m), 930(m), 910(w), 760(s), 740(m), 670(s, br), 465(sh), 450(m).

Synthesis and reactivity of VI

The synthesis of **VI** was carried out six times. In a typical reaction **V**, 2.063 g (10.07 mmol), dissolved in *c.* 30 ml hexane, was added in *c.* 2 ml aliquots to a stirred hexane (40 ml) K, 0.395 g (10.1 mmol) (small pieces) mixture. The addition took place over 3 h at *c.* 25 °C, followed by stirring for *c.* 60 h or until all the K was consumed. Next the reaction mixture was filtered *in vacuo* to remove KCl, and the solution transferred to a flat bottom flask containing a teflon coated magnetic spin bar. Hexane and **VII** were removed at 25 °C, 10^{-5} torr, and **VII** separated from hexane by condensation of the former at 0 °C. The brown solid **VI** was repeatedly dissolved in hexane and residual **VII** removed as previously described. Due to the high reactivity of **VII** it is difficult to quantitatively isolate this material, however about 1 ml (*c.* 4 mmol) was obtained, while the weight of the filtered product **VI** was *c.* 400 mg for a *c.* 80% yield. Residual **VI** was not completely dissolved away from the KCl. Analytical samples are best purified as above but utilizing **VI** in the 20–30 mg range to facilitate removal of **VII**. *Anal.* Calc. for **VI**: Al, 27.5; neopentyl, 72.5. Found: Al, 27.9; neopentyl, 72.1%. Treatment of the hydrolysis solution with $NaB(C_6H_5)_4$ did not afford $KB(C_6H_5)_4$ [15]; we previously employed this analytical procedure for K with excellent results [3]. Equivalent weight (mg/mmol H_2 on hydrolysis): calc., 98.1; found, 95.7. The molecular weight was determined by the isopiestic method in cyclopentane utilizing sublimed azobenzene as the standard. Calc. for $(AlNeo)_4$, 392.3; found, 369.6 (0.0188 M solution). Hydrolysis of the molecular weight sample produced neopentane, 0.26 mmol; dihydrogen, 0.27 mmol; and Al^{3+}, 0.28 mmol. Treatment of **VI** with D_2O produced D_2, 89% abundance as was determined by mass spectroscopy. **VI**, IR (evaporated hexane film): 2942(s), 2900(sh), 2852(m), 1462(m), 1440(sh), 1395(sh), 1380(w), 1359(m), 1230(m), 1126(w), 1095(w), 1005(sh), 992(w), 950–500(s) with maximum absorptions at 750 and 650. ^1H NMR, −80 °C, (pentane-d_{12}): δ 1.06 (t, 9H, Me, $J_{HH} \sim$ 1 Hz); δ 0.83 (multiplet, 2H, CH_2 $J_{HH} \sim 1$ Hz). Similar proton coupling has been observed for $[(CH_3)_3CCH_2]_2Mg$ [17]. Thermolysis of **VI** generates neopentane at 59 °C *in vacuo*. **VI**, 60 mg (0.15 mmol) was treated with Et_2O, 5.81 mmol, at 25 °C for 10 h. The Et_2O was removed from the red–brown solution and quantitatively recovered. **VI** is very soluble in alkanes and TMS, less soluble in Et_2O, and least soluble in benzene.

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