Inorganica Chimica Acta, 72 (1983) 187–190

The Preparation and Characterization of Dimethylaluminum γ-Picoline Dimer

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Received December 1, 1982

Reduction of dimethylchloroaluminum·γ-picoline, $(CH_3)_2ClAl{\cdot}NC_5H_4CH_3$, *with lithium affords* $[(CH_3)_2Al{\cdot}NC_5H_4CH_3]_2$. *The latter was characterized by analytical and spectroscopic means,* ^1H, ^{13}C *and* ^{27}Al *NMR, and its electronic spectrum is reported. A structure and MO bonding scheme is suggested which explains the observed diamagnetic character of the dimer as well as its extensive electronic spectrum.*

Introduction

Tetraalkyldialuminum(IV) derivatives have been reported *via* the alkali metal reduction of dialkylchloroaluminum species [1]. Bulky alkyl substituents stabilized the resulting Al–Al bond whereas CH_3 [2], C_2H_5 [3] moieties result in the disproportionation of R_4Al_2 and formation of AlR_3 and Al(0). In an effort to prepare the tetramethyl derivative, as a stabilized bis adduct, $(CH_3)_2AlCl{\cdot}\gamma$-picoline was reduced with Li. One of the reaction products $[(CH_3)_2AlNC_5H_4CH_3]_2$ is herein described.

Results and Discussion

The reaction between $[(CH_3)_2AlCl]_2$, γ-picoline and Li, in the molar ratios 1:4:2 respectively, results in an extremely complicated reaction mixture with several of the products undergoing further reaction, and decomposition, during subsequent separations. Dimethylaluminum·γ-picoline dimer, I, may be isolated from the reaction mixture as a brilliant red cyclopentane soluble species. Removal of the solvent results in the deposition of a blue oil which is only partially soluble on return of the original solvent. It was not possible to perform analytical analysis on a weighed sample of I because of these characteristics. A solution of I, an aliquot of which was examined by NMR spectroscopy, *vide infra*, was subjected to acid catalysed hydrolysis to afford CH_4 and Al(III) in the mole ratio 2:1. Subsequent ^{1}H NMR spectroscopy indicated a CH_3Al: picoline CH_3 of 2. Furthermore, I was demonstrated to be diamagnetic by ESR spectroscopy. A solution molecular weight was attempted and a value of 1.7 times the monomeric value found. Subsequent to obtaining this value, a small amount of blue oil precipitated from solution accompanied by the evolution of a trace quantity of CH_4. Hydrolysis of this molecular weight sample indicated a CH_4:Al of 1.3 consistent with decomposition of I over the experimental time period, two weeks. The acid hydrolysis of (I) is summarized by eqn. 1:

$$[(CH_3)_2AlN\bigcirc\!\!-CH_3]_2 + 6H_2O \rightarrow$$

$$4CH_4 + 2Al(OH)_3 + \text{'}NC_5H_4CH_3\text{'} \qquad (1)$$

Attempts to isolate γ-picoline, as a hydrolysis byproduct, were unsuccessful.

NMR Characterization of I

The ^{1}H NMR spectrum of I, d^6-benzene, consists of absorptions at 8.32(dblt) αH, 6.53(dblt) βH, 1.80 CCH_3, and −0.03 ppm $AlCH_3$ in the expected ratios 2:2:3:6. The assignments are consistent with those found for $(CH_3)_3Al{\cdot}N\bigcirc\!\!-CH_3$, in d^6-benzene; αH 8.17(dblt), 6.38(dblt), 1.80(C–CH_3) and −0.03(Al–CH_3) [3] ppm.

The ^{13}C NMR spectrum of I exhibits absorption at 146.58 (α), 122.19 (β), 151.8 (γ), and 20.53 (CH_3) and these assignments are also consistent with those observed for $(CH_3)_3Al{\cdot}N\bigcirc\!\!-CH_3$ in d^6-benzene, 146.51 (α), 125.82 (β), 152.15 (δ), and 20.65 $(CH_3)^3$. The CH_3–Al absorptions are not observed in either case due to the quadrupole moment of ^{27}Al, while the ^{1}H and ^{13}C NMR spectra of these two organoaluminum compounds are very similar,

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*In partial fulfillment of the Ph.D. degree, The Ohio State University, 1982.

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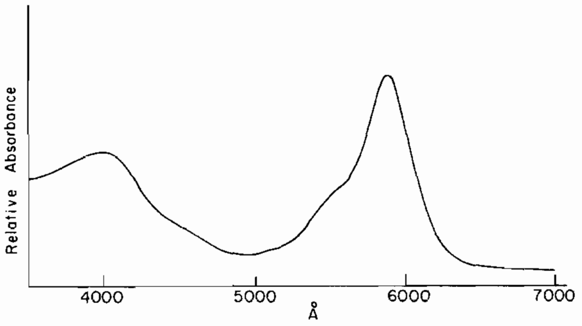

Fig. 1. Visible spectrum of I.

their respective ^{27}Al NMR and visible-$\mu\nu$ spectra are strikingly different.

The ^{27}Al NMR chemical shift of I is 44.4 ppm with an absorption width at half height of 5080 Hz, while trimethylaluminum•γ-picoline exhibits an ^{27}Al NMR chemical shift of 174.7 ppm with an absorption width at half height of 3240 Hz [3]. The very large upfield chemical shift found for I may result as a consequence of the presence of low-lying excited states that are present in I (I is highly colored) – that are absent in the trimethylaluminum•γ-picoline complex (colorless). It was reported, in a study of the ^{17}O NMR chemical shifts [4] for 'closed shell' oxy-anions of some transition metals, that a linear relationship exists between the degree of paramagnetic shielding of the oxygen nuclei and the lowest energy electronic transition observed for these anions. The ^{17}O NMR resonance appeared further downfield as the lowest energy electronic absorption appeared at longer wavelengths [4]. Also it was reported that this paramagnetic shielding need not always be negative (deshielded) [5]. A positive paramagnetic shielding was exhibited by ClF based on a comparison of its ^{19}F NMR chemical shift to that of the free ion F^- [6]. This effect was attributed to a low energy (2747 Å) $\pi^* \rightarrow \sigma^*$ transition causing shielding of the F nucleus. Positive paramagnetic shielding of the aluminum nucleus in I may explain the upfield shift of its ^{27}Al NMR absorption relative to $(CH_3)_3Al{\cdot}N\bigcirc{-}CH_3$. It should also be noted that the ^{27}Al NMR chemical shifts for triisobutylaluminum [7] and tetraisobutyldialuminum(IV) [8] (the latter contains an Al–Al bond) are 220 and 40.6 ppm with absorption widths at half height of 6000 and 5700 Hz, respectively. Similar electronic effects may be occurring for tetraisobutyldialuminum(IV) (it is also deep brown-red in color) while triisobutylaluminum is colorless.

The Electronic Spectrum of I

A solution of I in cyclopentane exhibits a brilliant red color when observed by reflected light whereas

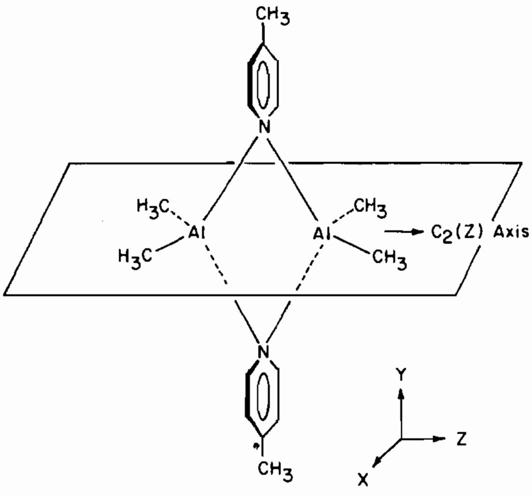

Fig. 2. Suggested structure for I.

the solution appears green by transmitted light. This is in sharp contrast to the colorless solution of $(CH_3)_3Al{\cdot}\gamma$-picoline. The ultraviolet spectrum of I exhibits a very intense absorption from 2350–2730 Å and a very weak, broad absorption at 2900 Å. γ-Picoline absorptions assigned to $\pi \rightarrow \pi^*$ transitions [9] of the K-Band appear at $\langle 2070(\log \epsilon \rangle 3.3)$Å and for the B-Band at 2440, 2510, 2550, 2620 ($\log \epsilon$ = 2.08, 3.23, 3.30, 3.20) Å in aqueous solution [10]. The B-Band appears broadened but at similar values for γ-picoline in cyclohexane [11]. The absorptions associated with I from 2350–2730 and 2900 Å may be the K and B-Band absorptions of γ-picoline that have been bathochromically shifted. The visible spectrum of I, Fig. 1, exhibits absorptions at 4137, 4505(sh), 5531(sh), and 5916 Å. The extinction coefficients of these absorptions have not been determined because of experimental difficulties, however they are believed to be quite large because very dilute solutions of I, as determined by ^1H NMR spectroscopy, are highly colored.

Suggested Structure and Bonding Associated with I

The empirical formula for I is $(CH_3)_2AlNC_5H_4CH_3$ based on analytical and ^1H NMR data. This stoichiometry, as related to a monomeric formulation, would result in a doublet state species, however, I is diamagnetic. The simplest formulation for I, consistent with initial molecular weight data, and its diamagnetic character, is a dimer, *i.e.* $[(CH_3)_2AlNC_5H_4CH_3]_2$. The geometry and bonding associated with I must be consistent with a spin paired system and explain its extremely rich electronic spectrum.

The suggested structure for I, Fig. 2, is similar to that of triphenylaluminum, $[Al(C_6H_5)_3]_2$, where the bridging phenyl plane is perpendicular to a line

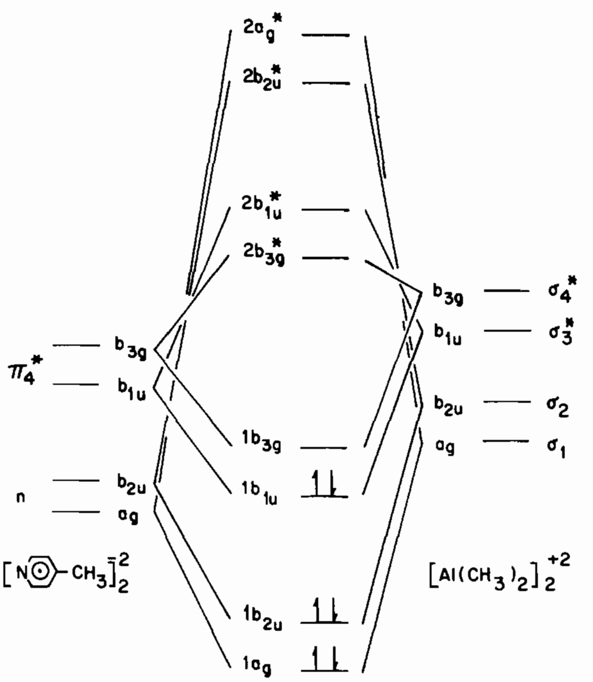

Fig. 3. Proposed qualitative molecular orbital diagram for I.

containing the two aluminum atoms [12]. The γ-picoline ring plane is perpendicular to the plane containing the four methyl groups and two aluminum atoms as well as a line containing the two aluminums, giving the dimer a symmetry of D_{2h}.

A proposed qualitative molecular orbital diagram, Fig. 3, for $[(CH_3)_2Al\cdot N\bigcirc-CH_3]_2$, was derived by combining the N(σ)-orbitals and π_4^*-molecular orbitals of two $[N\bigcirc-CH_3]^-$ and the four sp^3 group orbitals of each $Al(CH_3)_2^{+1}$ using symmetry relationships. The related orbital interaction are depicted in Fig. 4. The highest occupied molecular orbital for I is considered to be a combination of the $\pi_4^*(b_1)$ molecular orbital of two $[N\bigcirc-CH_3]^-$ and the vacant $\sigma_3(b_{1u})$ group orbital of each $Al(CH_3)_2^{+1}$, forming a molecular orbital of b_{1u} symmetry. Electronic transitions between this orbital and excited state orbitals with symmetries of a_g, b_{3g}, and b_{2g} are symmetry allowed. A larger number of electronic transitions are expected for I, and at lower energies than for $N\bigcirc-CH_3$ or $(CH_3)_3Al\cdot N\bigcirc-CH_3$. The proposed bathochromic shift of the K and B-Bands of γ-picoline, upon forming I, may be due to the suggested interaction of the π-systems of two γ-picolines using aluminum sp^3 and possibly 3d group orbitals.

As previously indicated, the ^{27}Al NMR chemical shift for I is at very high field and very near that of $Al_2(^tBu)_4$; the latter contains an Al–Al bond. Although the Al $dx^2 - y^2$, orbital combination would not be expected to result in appreciable orbital overlap, or the dyz and dxy combinations, the dz^2 orbital, a_g, may interact with the $\sigma_N(a_g)$ orbitals of δ-picoline resulting in some Al–Al bond character. On the other hand, 2 centered Al–Al bonds are oxidized by H_2O to afford H_2, and I does not afford H_2 under similar reaction conditions. It may be that I, under protonation conditions, is electronically perturbed with reduction at a ring position of γ-picoline taking place rather than the H_2 evolution.

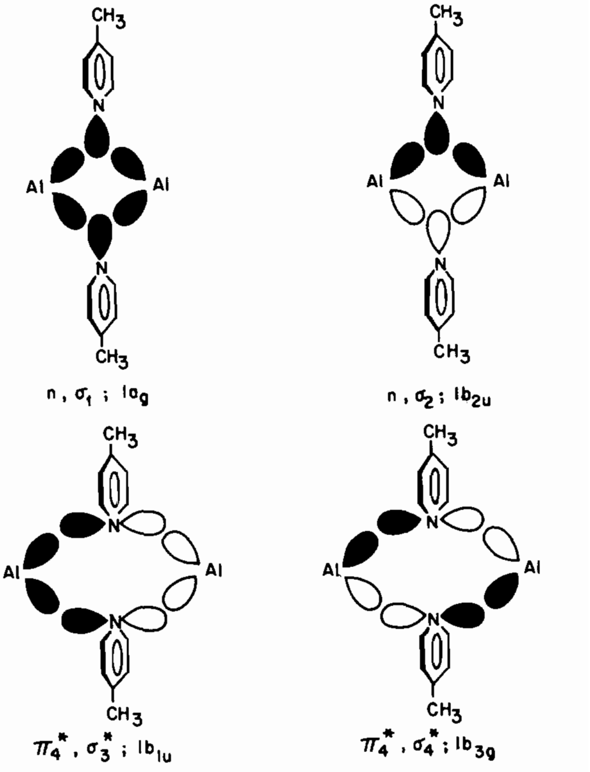

Fig. 4. Pictorial representations of bridging orbital interaction for I.

Experimental

Experimental techniques as well as equipment utilized during spectroscopic examination of materials have been previously reported [3]. ESR examination of samples were carried out with a Varian E-Line Century Series spectrometer equipped with a Varian E 102 Microwave Bridge.

Reagents

Sources and purifications of reagents not listed have been previously described [3].

Dimethylaluminumchloride

$[ClAl(CH_3)_2]_2$, was synthesized from $Al_2(CH_3)_6$ and BCl_3. In a typical reaction, 2.1 ml of BCl_3 in cyclopentane, in a tip bulb at −78 °C, was added slowly with stirring to 7.0 ml of $Al_2(CH_3)_6$ cyclopentane at −78 °C, and then warmed to room temperature. After the pressure had stabilized, the volatile compounds were removed and fractionated thru a −117 °C into a −196 °C trap and characterized by its vapor pressure [13] and infrared spectrum [14]. The material in the −117 °C trap was fractionated through −23°, −45° traps, and into a −196 °C trap. The clear colorless liquid in the −45 °C trap was refluxed over dry NaCl for 2 hours to remove any $[Cl_2AlCH_3]_2$ that was present [15] and then fractionated through a −45° into a −196° trap. The product, $[ClAl(CH_3)_2]_2$, was found in the −45 °C trap in a 87% overall yield, and characterized by its vapor pressure [16] and gas phase infrared spectrum [17]: 3010(w), 2950(s), 2895(m), 2830(vs)(shld), 1920(w), 1438(w), 1290(w), 1202(s), 958(w), 710(vs), 588(s), 340(w), and 308(w) cm^{-1}.

Synthesis and Isolation of $[(CH_3)_2Al \cdot \gamma\text{-picoline}]_2$*, I*

Dimethylaluminum chloride, $[ClAl(CH_3)_2]_2$, (1.16 ml, 6.3 mmol), was condensed into a tip bulb containing γ-picoline (2.45 ml, 27.5 mmol) at −196 °C and then the bulb was warmed slowly (cooling as necessary to prevent too vigorous a reaction) to room temperature. Diethyl ether was then condensed at −196 °C onto the white slurry, forming a solution when warmed to room temperature. Lithium (0.090 g, 13.0 mmoles) was placed into the bottom reaction bulb and the contents of the tip bulb added to the Li at room temperature with stirring. The solution immediately turned yellow, then orange within minutes, and a yellow solid formed in the orange solution after 3 hours. The reaction mixture was stirred at room temperature for 6 days and then vacuum filtered to separate a green solid from a dark yellow brown solution. All materials volatile, *in vacuo*, were removed from this solution, Et_2O and a trace of γ-picoline, identified by their respective infrared spectra. Pure γ-picoline was returned to the reaction residue and the mixture stirred for several hours at 25 °C. The volatile components were again removed with γ-picoline and Et_2O separated in −63° and −196 °C traps respectively. This procedure was continued several more times until no additional Et_2O was detected. Finally cyclopentane was added, the reaction mixture stirred, and then vacuum filtered to separate a green solid from a metallic appearing red solution, I, from which a blue oil was obtained upon removal of the solvent. Return of the solvent to the blue oil resulted in only partial solution to again afford a red solution. Acid hydrolysis of a cyclopentane solution of I afforded 0.5 mmol CH_4 while the hydrolysis residue contained 6.2 mg Al (0.23 mmol). The blue oil exhibited IR absorptions at 2890(nujol), 1608(m), 1430(nujol), 1375(nujol), 1285(w), 1214(w)(shld), 1165(m), 1060(w), 1025(w)(shld), 1007(m), 680(s), 540(w), and 490(w) cm^{-1}.

An isopiestic molecular weight determination, in benzene, was attempted, but decomposed before equilibrium was attained. The sample from the molecular weight determination was hydrolyzed and found to evolve 1.30 mmol CH_4 per 1.0 mmol of aluminum. Data obtained prior to equilibrium, but before extensive decomposition of (I) had occurred, indicated a molecular weight of 1.7 times its monomeric weight.

Acknowledgement

Support of this work by the Chemistry Department of The Ohio State University is appreciated. NMR spectra were obtained at The Ohio State University Campus Chemical Instrument Center with the assistance of Dr. C. Cottrell.

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