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The Preparation and Characterization of the Dianion, 1,1′-Bis(trimethylaluminyl)-1,1′,4,4′-Tetrahydro-4,4′-Dimethylbipyriate

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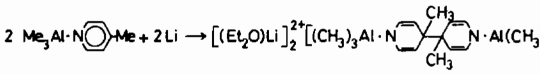
Reduction of trimethylaluminum·γ-picoline, $(CH_3)_3Al\cdot NC_5H_4CH_3$, with two equivalents of Li affords $[LiO(C_2H_5)_2]_2^{2+}[(CH_3)_3AlNC_5H_4CH_3]_2^{2-}$. NMR spectroscopic characterization of the latter is consistent with coupling at the γ positions, while visible spectroscopy is interpreted to indicate $Al_{d\pi} \leftarrow N_{p\pi}$ bonding.

Introduction

As part of an ongoing investigation directed towards the reduction of organoaluminum (III) compounds, trimethylaluminum·γ-picoline was treated with Li. Chemical and spectroscopic characterization of the resulting coupled anionic product are reported.

Results and Discussion

Trimethylaluminum·γ-picoline, $Me_3Al\cdot NC_5H_4$-CH_3, was treated with Li, in diethylether solution; the resulting chemical reaction is described by eqn. 1.



(1)

The indicated product, (I), is analytically pure and when subjected to acid catalyzed hydrolysis affords acceptable quantities of methane and Al(III), (found) eqn. 2,

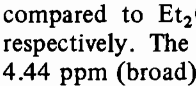
$$6H_2O + [Et_2O\cdot Li]_2^{2+}[(CH_3)_6Al_2N_2C_{12}H_{16}]^{2-} \longrightarrow 6CH_4 + 2Li^{1+} + 2Al(OH)_3 + 2Et_2O + \text{‘}[N_2C_{12}H_{16}]^{2-}\text{’} \quad (5.6) \quad (2.0) \qquad (2)$$

The nature of the organic residue was not investigated, *i.e.* ‘$[N_2C_{12}H_{16}]^{2-}$.’ The quantity of Et_2O present in I was confirmed by integration of the appropriate ^1H NMR absorptions, CH_3Al (–0.64 ppm) and $(CH_3CH_2)_2O$ quartet (3.32 ppm) found in the expected ratio, 2.25.

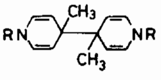
Unsuccessful attempts were made to isolate the 1,1′-4,4′-tetrahydro-4,4′-dimethylbipyridine moiety, as one of its reportedly stable N-carboethoxy [1] or N-methyl [2] derivatives, by treating (I) with ethyl chloroformate and ethyl chloroformate in conjunction with urea dissolved in methanol, and a solution of methyl iodide in methanol, respectively. It appears that the 1,1′,4,4′-tetrahydro-4,4′-dimethylbipyridine moiety is unstable when the Al–N bond of (I) is cleaved, producing methylpiperidines and methylpyridines based on ^1H NMR data.

NMR Spectroscopy

The ^1H NMR spectrum of (I), in benzene, consists of absorptions at 6.56 (doublet, αH), 4.44 (broad, βH), 3.32 (quartet, $(CH_3CH_2)_2O$), 0.99 (distorted triplet $(CH_3CH_2)_2O$ and ring CH_3), and –0.64 ppm (CH_3Al) in the expected ratios 2:4:9:9 respectively. The distorted triplet is a result of overlapping signals from CH_3C ring and the CH_3 of diethyl ether as was shown by treating I with $OP[N(CH_3)_2]_3$ to quantitatively displace the ether (the ether was subsequently removed). The resulting solution exhibited a singlet absorption at 1.01 ppm and was assigned to CH_3–C ring by analogy to



found at 1.07 ppm [2]. The presence of the latter absorption as a singlet is consistent with the absence of hydrogen at the 4-position, *i.e.* a product coupled at the 4-position is found. The ether ^1H NMR absorptions, associated with I, are also consistent with complexation to Li^+, 3.32 (CH_2) and 0.89 ppm (CH_3) as compared to Et_2O in benzene, 2.65 and 0.50 ppm respectively. The absorptions at 6.56 (doublet) and 4.44 ppm (broad) are assigned to the α and β hydrogens of the 1,1′, 4,4′-tetrahydro-4,4′-dimethylbipyridine moiety based on their appearance, in compounds of the type



at 6.47, 4.99 ppm for $R = Si(CH_3)_3$ [3] and 5.78, 4.29 ppm for $R = CH_3$ [2]. The –0.64 ppm absorp-

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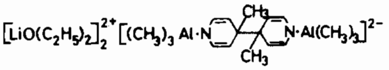
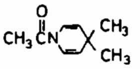
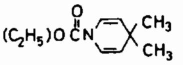
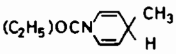
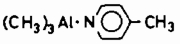
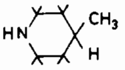
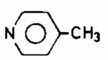
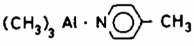
TABLE I. ^{13}C NMR Chemical Shifts of Heterocyclic Ring Systems.

Compound	α-C	β-C	γ-C	CH$_3$(Ring)
	134.43	100.39	42.52	27.40
 [4]	121.0 118.9	117.9 117.3	29.1	32.1
 [5]	120.3	115.9	30.8	32.5
 [1]	121.99	111.52	27.46	24.50
 [6]	127.9	91.7	30.8	33.0
	146.51	125.82	152.15	20.65
 [7]	46.9	35.8	31.5	22.7
 [8]	149.8	125.0	147.4	21.4

tion is assigned to the methyl groups on aluminum, found at –0.08 and –0.32 ppm in trimethylaluminum·γ-picoline and trimethylaluminum·diethyl ether, respectively. The upfield shift experienced by the methyl groups in (I) is attributed to the increased electron density on the aluminum as a result of the anionic nature of this species.

A ^{13}C NMR spectrum of (I) exhibits absorptions at 134.43 (α-C) 100.39 (β-C), 43.53 (γ-C), 27.40 (CH$_3$ ring), and –8.57 ppm (CH$_3$) with these assignments based on the related data presented in Table I.

The absorption at –8.57 ppm is assigned to the methyl groups on aluminum based on their appearance at –7.94 ppm in



The ^{27}Al NMR absorption for (I) appears at 154.2 ppm, upfield from that of trimethylaluminum·γ-picoline (174.7 ppm), which is consistent with a higher electron density on aluminum as expected from its aluminate character. Caution must be exercised when comparing ^{27}Al NMR chemical shift data of various organoaluminum adducts for it is reported [9] that their values depend on the nature of the donor atom rather than the strength of the complex.

Infrared Spectroscopy

The infrared spectrum of (I) exhibits absorptions for diethyl ether [10] at 1387 (δ_s C–CH$_3$), 1055 (ν_{as}CO), 904 (ν_sCO), and 779 (β C–CH$_3$) cm^{-1} and methyl groups on aluminum at 1173 (δ_s Al–CH$_3$) [11] and 685 (νAlC) [10] cm^{-1}. Absorptions for the 1,1′,4,4′-tetrahydro-4,4′-dimethylbipyridyl moiety appear at 1639 and 1630 (νC=C), 1553 (νC=C), 1286 (δ = C–H) [12] and 1018 (ν_sNC$_2$) [13, 14] cm^{-1}; these absorptions are absent in the infrared spectra of $(CH_3)_3Al{\cdot}NC_5H_4CH_3$ and $(CH_3)_3Al{\cdot}O(C_2H_5)_2$, and their appearance in I is at values typical for alkenes.

Ultraviolet-Visible Spectroscopy

The ultraviolet spectrum of (I), Fig. 1, exhibits two sets of absorptions in the ranges 2406–2775 and

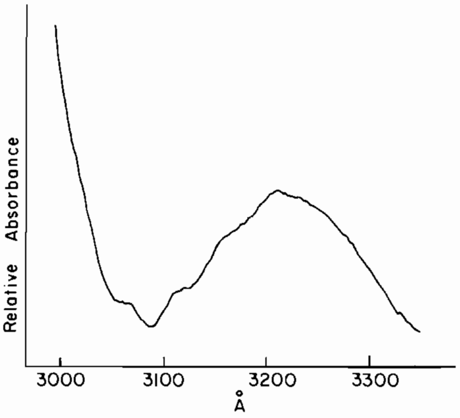


Fig. 1. Ultraviolet spectrum of I.

3037–3231 Å which may correspond to the 2310 ($\epsilon = 7500$) and 2700 ($\epsilon = 3200$) Å absorptions of 1,4,4-trimethyl-1,4-dihydropyridine [15, 16]. These absorptions are consistent with a bathochromic shift occurring upon replacement of the methyl group bound to nitrogen by a $Al(CH_3)_3$ moiety. It was reported that bathochromic shift occurred upon replacement of the H bound to the nitrogen of 1,4-dihydropyridine (2780 Å, $\epsilon = 2500$) by a $Si(CH_3)_3$ moiety (2880 Å, $\epsilon = 1390$) [17]. Red shifts are observed upon conversion of 1,4-dihydropyridines to their corresponding anions, for example, a shift from 2340 to 4290 Å occurred in the case of 3,5-dicyano-4-methyl-1,4-dihydropyridine [18]. Based on the small value of the red shift in (I), the negative charge appears to reside mainly on the aluminum. The bathochromic shift that (I) exhibits is believed not to be due to conjugation [19] of the two ring's unsaturated systems because of the similarity (*i.e.* no red shift) of reported spectral data for 1,1′,4,4′-tetrahydro-4,4′-dimethylbipyridines [2] and 1,4-dihydro-4,4-dimethylpyridines [15].

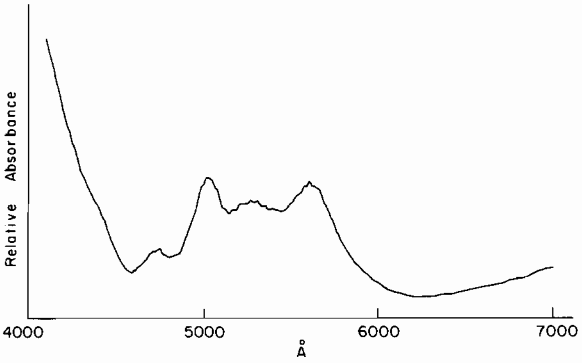
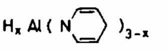
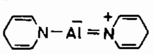


Fig. 2. Visible spectrum of I.

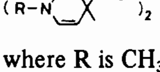
The visible spectrum of (I), Fig. 2, exhibits a very strong absorption at 4000 Å that extends off scale and four less intense absorptions at 4798, 5108, 5307, and 5683 Å. The deep red color of I is believed to be attributed to $Al_{d\pi} \leftarrow N_{p\pi}$ bonding enhanced as a result of the anionic character of I. This conclusion is based on the fact that aluminum dihydropyridyl compounds,



where X = 0, 1 and 2, range in color from red to yellow as a result of



bond character [20, 21]. Furthermore, N-(diethylaluminyl)-piperidine is colorless [22, 23], as are the molecular analogues



where R is CH_3 [2] and $(CH_3)_3Si$ [3].

Experimental

Apparatus

Chemical reactions were carried out in a standard vacuum line employing techniques and analytical procedures previously described [24]. Manipulation under an inert atmosphere, argon or nitrogen, were carried out in a modified Kuwanee dry box fitted with a purification train consisting of a 4A Linde Molecular series, Ridox and CX670 activated charcoal. Filtrations were effected employing a medium porosity glass frit while the apparatus was assembled utilizing O-ring seals.

Spectroscopic Equipment

Infrared spectra were obtained on a Perkin-Elmer model 457 grating spectrometer in the range 4000 to 400 cm^{-1}. A 10 cm cell fitted with polished KBr discs was used to obtain gas phase spectra of volatile compounds. Non-volatile solids were mulled, in the dry box, using dried Nujol and KBr plates. The spectra of liquid samples were obtained neat and all spectra were calibrated either by the 1376 cm^{-1} absorption of Nujol or the 1601 cm^{-1} of polystyrene. ^1H NMR spectra were obtained utilizing a Varian HA-100 spectrometer while ^{13}C and ^{27}Al spectra were obtained with a Brucker WP-80 and Brucker MH 300 spectrometers, respectively. The spectra were calibrated using the solvent as an internal reference with the chemical shifts being reported in ppm with respect to the standard reference for that particular nucleus. The standard reference is taken as 0.00 ppm with positive chemical shift values downfield from it. Standards were tetramethylsilane for ^1H and ^{13}C NMR, and the aluminum (III) hexaaquo cation, in an aqueous acidic solution, for ^{27}Al NMR. Electronic spectra were obtained on a Carey Model 14 Recording Spectrophotometer, Applied Physics Corporation, in the visible (3000–7000 Å) and ultraviolet (1950–3500 Å) regions on compounds dissolved in either diethyl ether or cyclopentane. Solution concentrations were varied so as to obtain maximum absorption heights and/or best definition of absorptions.

Reagents

Benzene, C_6H_6, Anal. Reagent, Mallinckrodt Inc., was dried over $LiAlH_4$ and distilled prior to use. Benzene-d^6, 99.5 atom % D, C_6D_6, RCK Sharp & Dohme Canada Limited, was dried over $LiAlH_4$ and stored in vacuo. Its ^1H NMR spectrum showed little if any H/D exchange had taken place. Diethyl Ether, anhydrous, Anal. Reagent, $O(C_2H_5)_2$, Mallinckrodt Inc., was dried over $LiAlH_4$ or Na/benzophenone and distilled prior to use. Cyclopentane, C_5H_{10}, Aldrich Chemical Company Inc., was dried over $LiAlH_4$ or Na/benzophenone and distilled prior to use. Lithium, rod, Li, Ventron, was used as received and only exposed to an inert argon atmosphere. γ-Picoline, NC_5H_7, Eastman Kodak Company, was dried over CaH_2, distilled, and stored in vacuo. Trimethylaluminum, $Al_2(CH_3)_6$, Ethyl Corporation or Texas Alkyls Inc., was used as received.

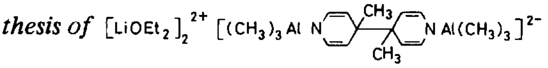
Trimethylaluminum·Diethyl Ether, $(CH_3)_3Al \cdot O(C_2H_5)_2$

It was synthesized by condensing into a reaction bulb 0.51 ml (2.6 mmol) of $Al_2(CH_3)_6$ and 0.55 ml (5.3 mmol) of diethyl ether and slowly warming to room temperature. The colorless liquid exhibited a ^1H NMR spectrum in benzene, with absorptions at 3.47(qt), 0.88(t), and –0.32 ppm in a ratio of 1.0, 1.5, 2.2. Its infrared spectrum matched that reported in the literature [25].

Trimethylaluminum·γ-Picoline, $(CH_3)_3Al \cdot NC_5H_4CH_3$

It was synthesized by condensing 0.75 ml (3.9 mmol) of $Al_2(CH_3)_6$ and 0.73 ml (7.5 mmol) of γ-picoline into a reaction bulb and slowly warming to room temperature. Characterization of the white product included its melting point of 74.4–75.8 °C and ^1H NMR spectrum, in benzene, with absorptions at 8.17 (dblt), 6.38 (dblt), 1.72, and 0.08 ppm in a ratio of 1.0 (CCH_3): 3.1 ($AlCH_3$) for the latter two absorptions. Its infrared spectrum consisted of absorptions at: 2970–2840 (Nujol), 2720 vw, 2488 vw, 1943 vw, 1848 vw, 1677 vw, 1625 s (νC=N(ring) [26, 27]), 1598 vw (shld), 1557 vw (νC=C [26], νC=C (ring) [27]), 1502 vw (νC=C [26], νC=C (ring) [27]), 1463 (Nujol), 1378 Nujol), 1310 vw, 1226 m (δ_{ip}CH [27]), 1205 w (X-Sensitive [27]), 1173 s (δ_s(Al)CH_3 [28]), 1063 m (δ_{ip}CH [27]), 1030 s (Ring Breathing [26, 27]), 974 vw (δ_{op}CH), 809 s (X-Sensitive [27]), 718 w (shld) (δ_{op}Ring [27]), 697 vs (brd) (νAlC [25]), 610 m (shld) (νAlC [25]), 567 w (X-Sensitive [27]), 526 w (ν_sAlC [25]), 495 m (δ_{op}CH [27]) and 267 w cm^{-1}. The ^{13}C NMR spectrum in d^6-benzene, exhibited absorptions at 152.15, 146.51, 125.82, 20.65, and –7.94 ppm), while the ^{27}Al NMR spectrum exhibited an absorption at 174.7 ppm with a peak width at half height of 3240 Hz.

Synthesis of



I

Trimethylaluminum, $Al_2(CH_3)_6$, (2.0 ml, 10.4 mmol) was condensed into a tip bulb containing γ-picoline (2.0 ml, 20.8 mmol) and allowed to warm slowly to room temperature. Diethyl ether was condensed onto trimethylaluminum·γ-picoline and this solution added at room temperature with stirring to 0.14 g (20.2 mmol) of lithium. The solution color changed to yellow, then orange, and finally dark red as the reaction progressed. After six days, the red solution was vacuum filtered to remove a small amount of unreacted lithium. A viscous red oil, (I), was obtained from the red solution upon removal of the diethyl ether. Acid hydrolysis of (I) 1.1873 g, produced 13.59 mmol of CH_4. The hydrostat contained 4.85 mmol of aluminum and the presence of lithium was confirmed by the observed carmine color during a platinum wire flame test [29] on (I). *Anal.* Calcd. for (I): 10.96% Al, 18.31% hydrolyzable CH_3. Found 11.01, 18.36% respectively.

Acknowledgement

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