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The Preparation and Reactivity of Methylaluminum(III) Toluene-3,4-dithiolate

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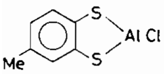
Treatment of toluene 3,4-dithiol, H_2TDT, with aluminumtrimethyl (3:2 stoichiometry) results in the quantitative formation of polymeric $Al_2(TDT)_3$ whereas a 1:1 reaction ratio affords TDTAlMe. Treatment of the latter with one equivalent of HCl results in alkylation of the aryl moiety, whereas two equivalents of HCl afford 2,7-dimethylthianthrene radical cation.

Introduction

The alkali metal reduction of i-Bu(L)AlCl derivatives (L = i-Bu, OMe, NMe_2) has been reported to afford Al_2L_4 species [1]. In the absence of electron rich or sterically bulky ligands, disproportionation was reported to take place, *i.e.*, reduction of Et_2AlCl affords $AlEt_3$ and Al metal. In an effort to prevent disproportionation and yet retain ligands susceptible to subsequent exchange, the precursor (to reduction) species,



TDTAlCl, was sought *via* reaction of TDTAlMe with HCl.

Results

Preparation and Characterization of TDTAlMe

Treatment of toluene 3,4-dithiol, H_2TDT, with aluminumtrimethyl is summarized by eqn. 1.

$$H_2TDT + AlMe_3 \rightarrow 2CH_4 + TDTAlMe \qquad (1)$$

When alkanes are employed as solvents, TDTAlMe is formed as a white crystalline precipitate insoluble in common aliphatic and aromatic solvents but reactive towards chloroalkanes. When the preparation of TDTAlMe is carried out in aromatic solvents, TDTAlMe is produced in a soluble form. However, removal of the aromatic solvent followed by replacement does not lead to subsequent solution of TDTAlMe. The infrared spectra of TDTAlMe (mull), prepared using either aliphatic or aromatic solvents, are identical.

The ^1H NMR spectrum of TDTAlMe (benzene solution) includes absorptions at 1.9 ppm (aryl Me) an −0.3 ppm (AlMe) in the expected ratio 1:1. These absorptions are two to three times as broad as those observed for the starting materials. The breadth of these signals may be attributed to the viscous nature of the solution – TDTAlMe may well be associated to varying degrees via intramolecular S–Al coordination.

The reactivity of TDTAlMe towards protonic reagents was demonstrated by quantitative evolution of CH_4, on treatment with water eqn. 2.

$$TDTAlMe + 3H_2O \rightarrow H_2TDT + Al(OH)_3 + CH_4 \qquad (2)$$

The organic product, H_2TDT, was quantitatively recovered and characterized by an exact match of its i.r. and ^1H NMR spectra with those of an authentic sample.

Attempted solution of TDTAlMe in CH_2Cl_2 and $CHCl_3$ results in decomposition as evidenced by the formation of purple colored solutions. The initial solution in CH_2Cl_2 (clear) exhibits a ^1H NMR spectrum identical to that in benzene, whereas $CHCl_3$ results in CH_4 evolution and loss of the AlMe ^1H NMR absorption. Based on mass balance Me on aluminum has been replaced by Cl. The fate of the remaining $HCCl_3$ fragment, CCl_2, is unknown – the reaction mixture was examined for the presence of C_2Cl_4, but the latter was not found.

Reaction of TDTAlMe with HCl

In an effort to prepare TDTAlCl, TDTAlMe (toluene solution) was treated with one equivalent

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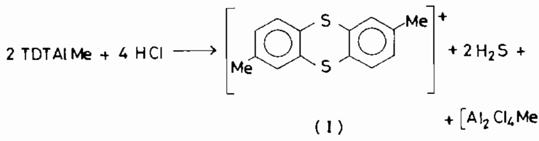
of HCl to afford the yellow complex, TDTAlMe•HCl, as summarized by eqn. 3.

$$\text{TDTAlMe} + \text{HCl} \rightarrow \text{'TDTAlMe}\cdot\text{HCl'} \qquad (3)$$

The ^1H NMR spectrum of TDTAlMe•HCl (pyridine solution) exhibits three aromatic CH_3 absorptions at 2.16, 2.24 and 2.39 ppm indicating that alkylation of the ring has taken place. This conclusion is further substantiated by the absence of the Al*Me* ^1H NMR absorption and the fact that hydrolysis of 'TDTAlMe•HCl' affords only a trace quantity of CH_4. The infrared spectra of the organic hydrolysis residue was identical to that of H_2TDT, however H_2TDT could not be recovered by applying previously successful sublimation procedures.

Treatment of TDTAlMe with two equivalents of HCl results in the formation of 2,7-dimethyl thianthrene radical cation, I, H_2S and a trace of CH_4 as ideally summarized by eqn. 4.



(4)

I was characterized by comparison of its ESR spectral features with the lit. values, g = 2.0083, a = 1.65 gauss (g = 2.008, a = 1.65 gauss) [2]. The observed 9 line hyperfine intensities have been discussed in terms of eight magnetically equivalent protons.

In order to further evaluate the carbanionic character of the AlMe moiety, associated with TDTAlMe, $AlMe_3$ was treated with H_2TDT in a 2:3 stoichiometry with the results summarized by eqn. 5.

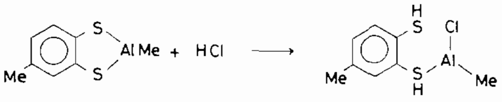
$$2AlMe_3 + 3H_2TDT \rightarrow Al_2(TDT)_3 + 6CH_4 \qquad (5)$$

The product, $Al_2(TDT)_3$, was found to be insoluble in all common solvents and is no doubt polymeric in nature.

Discussion

The ability of H_2TDT to replace all three Me moities on $AlMe_3$ has been demonstrated with the isolation of $Al_2(TDT)_3$. In order to produce cyclic TDTAlMe *vs.* bridged polymers, it is necessary to employ dilute solutions of both H_2TDT and $AlMe_3$ with the former being added to the latter.

The observed chemical reactivity of TDTAlMe towards one equivalent of HCl was unexpected in that CH_4 was not readily evolved. The fact that alkylation of the aromatic ring takes place is interpreted in terms of a Friedel Crafts reaction. The first step is viewed as protonation of S accompanied by heteronuclear S–Al bond cleavage with simultaneous nucleophilic attack by Cl^- on Al, eqn. 6.

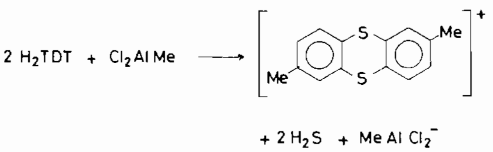


(6)

Methyl carbonium ion elimination from Al is envisioned with attack on the aryl moiety. Hydrolysis of the latter reaction mixture affords neither CH_4 nor H_2 which is consistent with the absence of AlMe and AlH moieties. The identification of the peralkylated dithiol produced on hydrolysis was not pursued.

The formation of I from reaction of TDTAlMe and two equivalent of HCl, is considered to arise from the *in situ* generated reactants H_2TDT and Me_2AlCl, eqn. 7, followed by their reaction, eqn. 8.

$$\text{TDTAlMe} + 2HCl \rightarrow H_2TDT + Cl_2AlMe \qquad (7)$$



(8)

We have demonstrated the analogous quantitative reaction, eqn. 8, employing $AlCl_3$ [3]. Furthermore, treatment of thianthrene with Lewis acids, such as $SbCl_5$, results in the formation of the radical cation as salts of $SbCl_4^-$ and $SbCl_6^-$ [4]. The observed ESR spectrum is only that of I, therefore, $MeAlCl_2^-$ is most likely polymeric in nature, *i.e.*, diamagnetic.

Experimental

Equipment

Standard vacuum line procedures were employed throughout this investigation [5]. Infrared spectra were recorded with a Perkin Elmer 457 spectrometer with samples prepared utilizing Nujol mulls. ^1H NMR spectra were recorded on a Varian A 60A or JEOL E360 spectrometer, employing TMS or the solvent as internal standards. ESR spectra were obtained with a Varian V 450-10A spectrometer and spectra reported with reference to DPPH (g = 2.0037).

Reagents

Benzene, reagent grade, Fisher Scientific Company, was dried over lithium aluminum hydride and distilled when ready to use. Pyridine, Drake Brothers, was dried over lithium aluminum hydride prior to use. Methylcyclohexane, Mallinckrodt Chemical Works, was dried over lithium aluminum hydride before use. Toluene, reagent grade, Matheson, Coleman and Bell, was dried over lithium aluminum hydride and distilled before use. Chloroform, reagent grade, Mallinckrodt Chemical Works, was dried over lithium aluminum hydride before use. Carbon tetrachloride, V.W.R. Scientific, Inc., was dried over lithium aluminum hydride and distilled when ready to use. Cyclopentane, reagent grade, Aldrich Chemical Company, was dried over lithium aluminum hydride and distilled prior to use. 3,4-Dimercaptotoluene, Aldrich Chemical Company, was sublimed at 60 °C under dynamic vacuum prior to use. A melting point of 26–27 °C was observed. Hydrogen chloride, The Matheson Company, was fractionated at −126 °C to remove water before use. Aluminumtrimethyl, Ethyl Corporation, was used as purchased.

Analytical

Aluminum was determined gravimetrically as the 8-hydroxyquinolate while chloride was titrated potentiometrically with $AgNO_3$. Sulfur interfers with this titration, therefore care must be excercised to extract all organic sulfur compounds prior to analysis. Methane was collected in a calibrated volume Toepler pump system and characterized by combustion to CO_2 and H_2O at 800 °C over CuO.

Preparation and Charactierization of TDTAlMe in Cyclopentane

In a typical reaction a freshly sublimed sample of H_2TDT (1.4122 g, 9.04 mmol) was dissolved in degassed cyclopentane, 20 ml, and slowly added to a stirred cyclopentane solution of $AlMe_3$ (0.651, 9.04 mmol), 20 ml. The $AlMe_3$ solution was maintained at −63 °C with periodic slow warming to 25 °C. Methane liberation commenced well below room temperature. After a 24 hr period at 25 °C, CH_4 was collected (17.53 mmol) and identified by its quantitative oxidation to CO_2 and H_2O. The sample was washed, *in vacuo,* with cyclopentane and toluene. *Anal.* Calc. % (Found): Al, 13.8 (13.5); H_2TDT after hydrolysis, 79.6 (78.7); CH_3, (hydrolyzable as CH_4), 7.7 (7.6).

IR data: 3010(m), 2980–2800(s), 1605(m), 1470(s), 1380(s), 1265(m), 1200(m), 1110(w), 1030(m), 1025(m), 860(m), 805(s), 700(s,br), 580(w), and 540(w) cm^{-1}. After synthesis, TDTAlMe was present as a white crystalline material (cyclopentane). This material was insoluble in diethyl ether, benzene and toluene.

The synthesis of TDTAlMe was carried out in toluene analogous to that described in cyclopentane. Aluminumtrimethyl, 0.5774 g (8.00 mmol) was treated with H_2TDT, 1.251 g (8.01 mmol) to afford 15.80 mmol CH_4 and a pale yellow brown solution, *ca.* 50 ml solution. Once the solvent was removed from this product, re-solution was not possible The infrared spectrum of the TDTAlMe produced in toluene was identical to that formed in cyclopentane.

Reactions to TDTAlMe with Chlorocarbons

Attempted solution of TDTAlMe in CH_2Cl_2 and CCl_4 results in the formation of purple solutions indicating reaction with these potential solvents. Treatment of TDTAlMe, 0.2631 g (1.34 mmol) with excess $HCCl_3$ at 25 °C affords CH_4 (1.20 mmol) over a 4 day reaction period. The remaining solvent was removed, *in vacuo*, and purified by fractional condensations and examined by i.r. spectroscopy and found to consist of only $HCCl_3$. The reaction product, 0.292 g, exhibited a weight gain of 28.9 mg. Calcd. wt. gain for replacement of Me by: 1. Cl = 27.47 mg, 2. CCl_3, 138.7 mg. The ^1H NMR spectrum of the resulting purple solution lacks the AlMe absorption at *ca.* −0.3 ppm.

Reactions of TDTAlMe with Hydrogen Chloride

A toluene solution of TDTAlMe (10.3 mmol) was treated with HCl (10.3 mmol) at 25 °C with the immediate formation of a yellow precipitate. After two weeks CH_4 (1.5 mmol) was recovered from the reaction mixture (14.6 mol percent theoretical). *IR data* on TDTAlMe•HCl: 3010(w), 2940(s), 2860(s), 1585(m), 1453(s), 1378(s), 1260(w), 1210(w), 1169(w), 1160(w), 1150(w), 1112(w), 1020(w), 865(w), 805(m), 760(w), 724(m), 678(m), 620(m), 540(m,br) and 487(m) cm^{-1}.

A sample of TDTAlMe•HCl, 0.32 g (1.38 mmol) was treated with H_2O to afford 0.35 mmol CH_4 (25.4 mol per cent theoretical). The infrared spectrum of the organic residue, extracted with toluene, was identical to that of H_2TDT. A pyridine solution of TDTAlMe•HCl exhibited four ^1H NMR absorptions in the region 2.2 to 2.4 ppm indicative of multiple alkylation of the aryl moiety (1.9 ppm in TDTAlMe and 2.3 ppm in H_2TDT).

A toluene solution TDTAlMe (2.89 mmol) was treated with HCl (5.90 mmol) to produce a dark purple solution accompanied by the evolution of H_2S (identified by i.r. spectroscopy) and CH_4 (0.42 mmol) (14.5 mol percent theoretical) during a 3 hr reaction period. Removal of all materials volatile at 25 °C, *in vacuo,* afforded a blue paramagnetic oil, g = 2.0883, a = 1.65 gauss.

Acknowledgement

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