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REACTIONS OF BIS (μ-DIPHENYLAMINO)TETRAMETHYLDIALUMINUM AND μ-DIPHENYLAMINO-μ-METHYLTETRAMETHYLDIALUMINUM WITH TRIMETHYLAMINE, DIETHYL ETHER AND DIMETHYL SULFIDE

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Summary

The reactions of $(\mu\text{-NPh}_2)_2\text{Al}_2\text{Me}_4$ and of $\mu\text{-NPh}_2\text{-}\mu\text{-MeAl}_2\text{Me}_4$ with trimethylamine, diethyl ether and dimethyl sulfide have been investigated. These studies establish that the bases cleave the nitrogen bridged system $(\mu\text{-NPh}_2)_2\text{Al}_2\text{Me}_4$ to give adducts of formula $\text{Me}_2\text{Al(NPh}_2)\cdot\text{B}$. The relative stabilities of the adducts formed appear to be in the order NMe > OEt_2 > SMe_2, with the sulfide adduct apparently dissociated even at −74°. $\mu\text{-NPh}_2\text{-}\mu\text{-MeAl}_2\text{Me}_4$ reacts with a limited supply of base to give $\text{Me}_3\text{Al}\cdot\text{B}$ and $(\mu\text{-NPh}_2)_2\text{Al}_2\text{Me}_4$, and additional base cleaves $(\mu\text{-NPh}_2)_2\text{Al}_2\text{Me}_4$ as before.

Introduction

There has been much interest in the kinetic and thermodynamic stabilities of bridged organoaluminum compounds since it was first established that these compounds often are dimeric. The alkyl-bridged species which have electron-deficient bonds have been of special interest but the systems with normal 2-electron bonds such as the halides, alkoxides and amides also have received attention. Interest in the nature of these species has been further stimulated recently by their use in the formation of a variety of polymerization catalysts, and from the studies which have established that unsymmetrically-bridged systems can exist. These studies have been reviewed in detail, both with regard to the known data on the normal 2-electron bonded systems and on the unsymmetrically bridged species which contain both normal and electron-deficient bridge bonds [1].

The early studies of Davidson and Brown [2] on bis (μ-diphenylamino)-tetramethyldialuminum, $(\mu\text{-NPh}_2)_2\text{Al}_2\text{Me}_4$, established its dimeric nature. It was stated that this product was resistant to cleavage and adduct formation with bases such as trimethylamine. More recently Kawai et al. [3] and Magnuson and Stucky [4, 5] have shown that the unsymmetrically-bridged species $\mu\text{-NPh}_2\text{-}\mu\text{-MeAl}_2\text{Me}_4$ can be prepared and is thus stable at least kinetically.

These results, and our interest in the kinetics of the bridge—terminal exchange reactions observed in organoaluminum systems led us to reinvestigate the stability of $(\mu\text{-NPh}_2)_2\text{Al}_2\text{Me}_4$ toward the Lewis bases trimethylamine, diethyl ether and dimethyl sulfide, and to investigate the reactions of these bases with $\mu\text{-NPh}_2\text{-}\mu\text{-MeAl}_2\text{Me}_4$.

Experimental

All syntheses and sample preparations were carried out on a vacuum system or in an argon-filled dry box scavenged with NaK. Dimethyl sulfide (Aldrich) trimethylamine (Matheson) and diethyl ether (Baker), as well as the solvents cyclopentane, cyclohexane and toluene (Baker reagent grade) were dried over and distilled from NaK. They were then stored on the vacuum line or in a dry box until used.

$(\mu\text{-NPh}_2)_2\text{Al}_2\text{Me}_4$ was prepared by the reaction of Me_6Al_2 and diphenylamine as described by Kawai et al. [3]. The product obtained from this reaction appeared as described and gave rise to PMR absorptions at δ 7.1 ppm (phenyl) and —0.58 ppm (methyl) in a 5/3 intensity ratio for a toluene solution. $\mu\text{-NPh}_2\text{-}\mu\text{-MeAl}_2\text{Me}_4$ was prepared by the procedure of Magnuson and Stucky [4, 5], modified in the following way: $(\mu\text{-NPh}_2)_2\text{Al}_2\text{Me}_4$ and an 8-fold excess of Me_6Al_2 were placed in a thick-walled Pyrex tube which was then sealed. This reaction mixture then was heated for a period of two weeks over a 115° oil bath. The reaction vessel was opened and the excess Me_6Al_2 was removed on the vacuum system. The solid material remaining was shown to be 94-98% $\mu\text{-NPh}_2\text{-}\mu\text{-MeAl}_2\text{Me}_4$ by examination of the low temperature PMR spectrum (toluene solvent) which showed major absorptions at δ —0.58 and 0.38 ppm in a 1/4 ratio as described by Magnuson and Stucky. A small absorption (2-6% as intense as the terminal methyl group absorption of $\mu\text{-NPh}_2\text{-}\mu\text{-MeAl}_2\text{Me}_4$) resulting from the symmetrical $(\mu\text{-NPh}_2)_2\text{Al}_2\text{Me}_4$ was also observed.

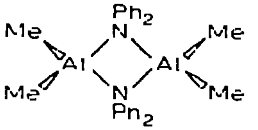
Attempts to purify the product by sublimation led to some symmetrization and loss of Me_6Al_2; thus, in our hands the sublimed product normally had a higher proportion of symmetrical compound that the unsublimed material. The extent of symmetrization appeared to be temperature-dependent, increasing with increasing temperature of the sublimation.

All NMR samples prepared for examination of the reaction of an aluminum derivative with base were made by transfer of a weighed amount of the aluminum derivative into a NMR tube in the dry box. This tube then was capped by a standard taper joint equipped with a stopcock and transferred to the vacuum system where 0.5 ml of solvent was added, followed by the desired amount of base. The quantity of each base added was determined from pressure—volume relationships and was checked by integration of the NMR spectrum of each sample.

All NMR spectra were recorded on a Varian A-60-A spectrometer equipped with variable temperature accessories. The temperatures were determined from the chemical shift separation of methanol using the calibration technique reported by Van Geet [6]. All line positions were determined relative to an internal standard of calibration using audio-frequency sideband techniques.

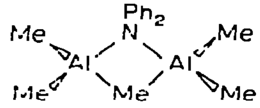
Results and discussion

The present study involves a reinvestigation of the reactions of Lewis bases, trimethylamine, diethyl ether and dimethyl sulfide with $(\mu\text{-}NPh_2)_2Al_2Me_4$ and an investigation of the reactions of these bases with $\mu\text{-}NPh_2\text{-}\mu\text{-}MeAl_2Me_4$. The first study was undertaken to determine if eqn. 1 proceeds as shown with cleavage of the bridge bonds and adduct formation, or if it in fact does not occur as



$$+\ 2\,B \rightleftharpoons 2\,Me_2Al(NPh_2)\cdot B \qquad (1)$$

originally reported [2]. The second question to be answered related to the effect addition of a Lewis base has on the symmetrization of the unsymmetrically-bridged compound as shown in eqn. 2 with the subsequent complexation of the freed Me_6Al_2 as shown in eqn. 3.

2 

$$\xrightleftharpoons{\text{base}} Me_6Al_2 + (\mu\text{-}NPh_2)_2Al_2Me_4 \qquad (2)$$

$$Me_6Al_2 + 2\,B \rightleftharpoons 2\,Me_3Al\cdot B \qquad (3)$$

To provide the data necessary to answer these questions, a series of proton NMR experiments were carried out on Me_3Al—base, $(\mu\text{-}NPh_2)_2Al_2Me_4$—base and $\mu\text{-}NPh_2\text{-}\mu\text{-}MeAl_2Me_4$—base systems. These data are collected in Table 1.

The data for the NMe_3—$(\mu\text{-}NPh_2)_2Al_2Me_4$ systems and the corresponding spectra shown in Fig. 1 clearly show that the orginal statement [2] was incorrect and that, in fact, reaction 1 proceeds with nearly complete adduct formation when the base used is trimethylamine. Examination of the data for the Et_2O—$(\mu\text{-}NPh_2)_2Al_2Me_4$ system shows similar results, while reaction of dimethyl sulfide with $(\mu\text{-}NPh_2)_2Al_2Me_4$ occurs but does not proceed to completion, and is further complicated by rapid exchange of alkyl groups and by apparent side reactions.

One may conclude from these results that cleavage of the symmetrically-bridged species $(\mu\text{-}NPh_2)_2Al_2Me_4$ occurs readily with formation of moderately stable adducts. The order of stability is thought to be $NMe_3 > OEt_2 > SMe_2$, similar to that observed for the corresponding Me_3Al adducts. An indication of this is provided in Table 2 in which the heats of formation of the $Me_3Al\cdot B$ adducts, their chemical shifts and the chemical shifts of the corresponding $Me_2Al(NPh_2)\cdot B$ adducts are shown.

Study of $\mu\text{-}NPh_2\text{-}\mu\text{-}MeAl_2Me_4$ shows first that symmetrization occurs rapidly when base is added so that reaction is complete before any observations were made. Samples of the unsymmetrically-bridged species in the absence of base were quite stable for months under similar conditions. Thus, the base certainly promotes the symmetrization. Secondly, examination of the data in

TABLE 1

PROTON CHEMICAL SHIFTS FOR A SERIES OF ALKYLALUMINUM DERIVATIVES AND THEIR LEWIS BASE ADDUCTS

Aluminum derivative	Base	Aluminum dimer/base	Chemical Shifts[a]					
			terminal methyl	bridge methyl	$Me_3Al \cdot base$	$Me_4Al(NPh_2)_2$	$Me_2(Ph_2N)Al \cdot base$	
$(\mu\text{-}NPh_2)_2Al_2Me_4$						-0.29_1		
	NMe_3	1/1.02				-0.30	-0.56_6	
	NMe_3	1/2					-0.54	
$(\mu\text{-}NPh_2)\text{-}\mu\text{-}MeAl_2Me_4$			-0.11					Exchange broadened Single line 4/1 ratio with exchange slowed allowing well-resolved lines at −10° to be observed
			-0.31	0.60				
Me_6Al_2	NMe_3	1/2			-0.66_3			
$\mu\text{-}NPh_2\text{-}\mu\text{-}MeAl_2Me_4$	NMe_3	1/1			-0.64_5	-0.33_6		
		1/2.1			-0.63_5		-0.55_7	Integrated areas 3/2
Me_6Al_2	OEt_2	1/2			-0.55_4			
$(\mu\text{-}NPh_2)_2Al_2Me_4$	OEt_2	1/1.19				-0.30_5	-0.53_1	
$(\mu\text{-}NPh_2)_2Al_2Me_4$	OEt_2	1/2.3					-0.53_7	
$(\mu\text{-}NPh_2)\text{-}\mu\text{-}MeAl_2Me_4$	OEt_2	1/1.59			-0.53_9	-0.33_8		
$(\mu\text{-}NPh_2)\text{-}\mu\text{-}MeAl_2Me_4$	OEt_2	1/2.35			-0.54_0		-0.57_3	Integrated intensity 3/2
Me_6Al_2	SMe_2	1/10			-0.53			Run at −74° with excess SMe_2 to ensure formation of Me_3AlSMe_2.
$(\mu\text{-}NPh_2)_2Al_2Me_4$	SMe_2	1/1.2	0.18[b]			-0.29_1	-0.35_9	
$(\mu\text{-}NPh_2)_2Al_2Me_4$	SMe_2	1/2.05	0.18[b]			-0.30	-0.37_0	
$(\mu\text{-}NPh_2)\text{-}\mu\text{-}MeAl_2Me_4$	SMe_2	1/1.34			-0.52	-0.30	-0.36	

[a] All chemical shifts have been reported relative to TMS = 0 and were referenced to internal cyclopentane (1.50 ppm below TMS) or to the methyl resonance in toluene (2.31 ppm below TMS). The positive values indicated are downfield from TMS. All other chemical shifts are upfield relative to this reference. All samples were 0.1 molar in toluene solvent. [b] Unidentified 3 Hz half-width.

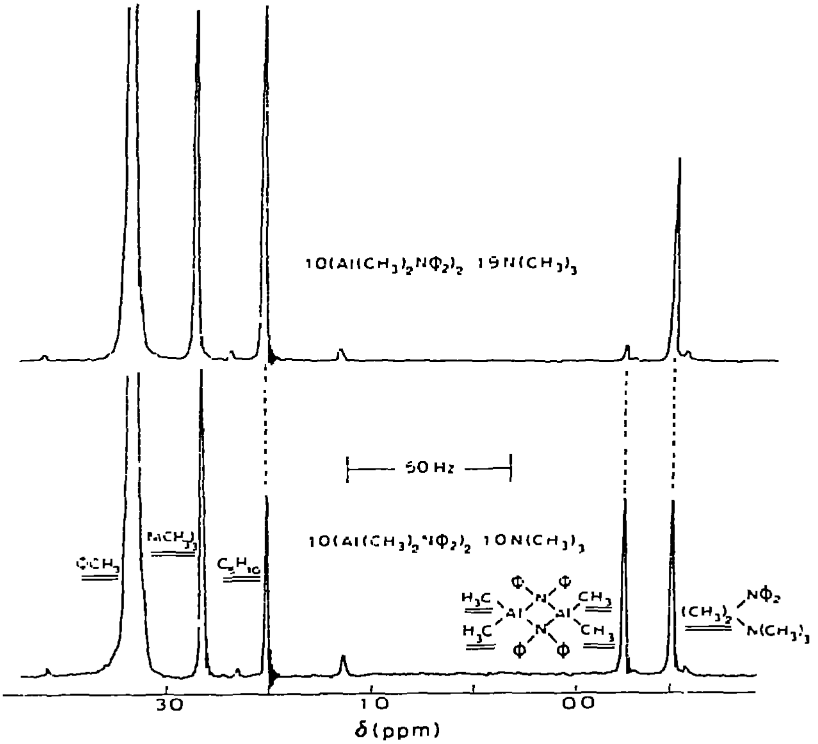


Fig. 1. The 60 MHz Proton NMR Spectra of 1.0/1.9 (upper) and 1.0/1.0 (lower) mixtures of $[AlMe_2(NPh_2)]_2$ with NMe_3 in toluene solvent.

Table 1 shows that when less than the stoichiometric amount of base is added, it is preferentially bound to the Me_3Al, leaving symmetrized $(\mu\text{-}NPh_2)_2Al_2Me_4$ in solution. If additional base is added, it then undergoes reaction with this dimer as in eqn 1.

TABLE 2

HEATS OF FORMATION AND CHEMICAL SHIFTS FOR SOME ALKYLALUMINUM LEWIS BASE ADDUCTS

Base	$Me_3Al\cdot$base [a] ΔH_f (kcal/mole)	$\delta(Me_3Al\cdot B)$ [b]	$\delta(Me_2Al(NPh_2)\cdot B)$ [b]
NMe_3	-29.96 ± 0.10	-0.66_7	-0.54_0
OEt_2	-20.21 ± 0.23	-0.55_4	-0.53_7
SMe_2	-16.69 ± 0.18	-0.54_1	-0.37_0

[a] Determined by solution calorimetry [7]. [b] Chemical shifts are relative to internal toluene solvent and have been corrected to TMS by addition of 2.31 ppm. All chemical shifts are upfield from TMS.

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