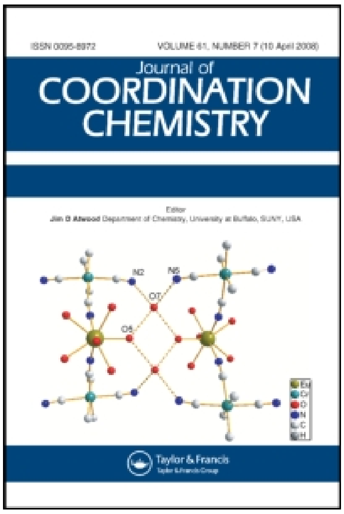

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Sterically Crowded Aryloxide Compounds of Aluminum: Complexes with Diethyl Ether and Tetrahydrofuran

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NOTE

STERICALLY CROWDED ARYLOXIDE COMPOUNDS OF ALUMINUM: COMPLEXES WITH DIETHYL ETHER AND TETRAHYDROFURAN

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The Et_2O and THF Lewis acid-base adducts of $AlR(BHT)_2$ and $AlR_2(BHT)$ [R = Me, Et; BHT-H = 2,6-di-*tert*-butyl-4-methylphenol], have been prepared and characterized by elemental analyses, ^1H and ^{13}C NMR spectroscopy.

Keywords: Aluminum, aryloxides, adducts, synthesis

INTRODUCTION

The reaction of trimethylaluminum or triethylaluminum with one equivalent of phenol was first demonstrated, by Mole,[1] to yield bridging phenoxide compounds, (*1*).

$$AlR_3 + PhOH \xrightarrow[R\,=\,Me,\,Et]{} \tfrac{1}{2}[R_2Al(\mu\text{-}OPh)]_2 + RH \qquad (1)$$

Analogous reactions with the sterically hindered 2,6-di-*tert*-butyl-4-methylphenol (BHT-H, from the trivial name butylated hydroxytoluene) result not in the formation of the mono-aryloxide compounds, $AlR_2(BHT)$, but the bis-aryloxides, $AlR(BHT)_2$.[2,3]

A recent NMR study[3] of the species present in solutions of $AlMe_x(BHT)_{3-x}$ showed that the equimolar mixture of $AlMe_3$ and BHT-H results not in the mono-aryloxide but two concurrent disproportionations, (*2*) and (*3*). In the case of $AlEt_3$ a single equilibrium exists, (*4*).

$$Al_2Me_5(BHT) \rightleftharpoons \tfrac{1}{2}Al_2Me_6 + AlMe_2(BHT) \qquad (2)$$

$$3AlMe_2(BHT) \rightleftharpoons Al_2Me_5(BHT) + AlMe(BHT)_2 \qquad (3)$$

$$2AlEt_2(BHT) \rightleftharpoons \tfrac{1}{2}Al_2Et_6 + AlEt(BHT)_2 \qquad (4)$$

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The mono-aryloxide compounds may be trapped, however, by the addition of a Lewis base, (*5*).[4]

$$\text{“AlR}_2\text{(BHT)”} + \text{L} \longrightarrow \text{AlR}_2\text{(BHT)(L)} \qquad (5)$$
$$\text{L} = \text{PMe}_3\text{, py, 3,5-Me}_2\text{py}$$

We have become interested in the reactivity of ketones, aldehydes and esters with monomeric aluminum compounds.[5] It would be desirable therefore to have available discrete monomeric aluminum aryloxides. We have therefore investigated the preparation of stable Lewis acid-base complexes of $AlR_2(BHT)$ that are readily synthesized and isolated but which dissociate in solution and allow reactivity at the metal center to occur.

We report here the synthesis and characterization of the diethyl ether (Et_2O) and tetrahydrofuran (THF) adducts of $AlR(BHT)_2$ and $AlR_2(BHT)$ (R = Me, Et).

EXPERIMENTAL

Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY. Melting points were determined in sealed capillaries and are uncorrected. NMR spectra, in C_6D_6, were recorded on Bruker AM-250 (^1H) and Bruker AM-500 (^{13}C) spectrometers [δ in ppm relative to external $SiMe_4$]. All manipulations were carried out under nitrogen. Solvents were dried, distilled, and degassed prior to use.

$AlMe_3$ (2.0 M solution in hexane) and $AlEt_3$ (1.0 M solution in hexane) were used as supplied (Aldrich). BHT-H (Aldrich) was sublimed prior to use. The syntheses of AlMe $(BHT)_2$ and $AlEt(BHT)_2$ were carried out according to literature methods.[2,3,4]

Selected ^1H and ^{13}C NMR data are given in Tables I and II respectively. Melting point and analytical data are given in Table III. Full ^1H and ^{13}C NMR and IR data are available as supplementary material (see below).

TABLE I
Selected ^1H NMR data (ppm) for the new aluminum compounds.

	^1H			
Compound	Al-C*H*	Al-C-C*H*	O-C*H*	O-C-C*H*
(1) $AlMe(BHT)_2(OEt_2)$	−0.04 (s)		3.76 (q)	0.67) (t)
			J(H-H) = 7.5 Hz	
(2) $AlMe(BHT)_2(THF)$	−0.06 (s)		3.69 (m)	1.02 (m)
(3) $AlEt(BHT)_2(OEt_2)$	0.54 (q)	1.25 (t)	3.65 (q)	0.75 (t)
	J(H-H) = 7.5 Hz		*J*(H-H) = 7.5 Hz	
(4) $AlEt(BHT)_2(THF)$	0.56 (q)	1.36 (t)	3.75 (m)	1.00 (m)
	J(H-H) = 7.5 Hz			
(5) $AlMe_2(BHT)(OEt_2)$	−0.32 (s)		3.46 (q)	0.67 (t)
			J(H-H) = 7.5 Hz	
(6) $AlMe_2(BHT)(THF)$	−0.33 (s)		3.47 (m)	0.99 (m)
(7) $AlEt_2(BHT)(OEt_2)$	0.35 (q)	1.31 (t)	3.57 (q)	0.79 (t)
	J(H-H) = 7.5 Hz		*J*(H-H) = 7.5 Hz	
(8) $AlEt_2(BHT)(THF)$	0.30 (q)	1.21 (t)	3.57 (m)	1.14 (m)
	J(H-H) = 7.5 Hz			

TABLE II
Selected ^{13}C-{^1H} NMR data (ppm) for the new aluminum compounds.

	^{13}C-{^1H}			
Compound	Al-*C*H	Al-C-*C*H	O-*C*H	O-C-*C*H
(1) $AlMe(BHT)_2(OEt_2)$	−3.49		65.54	11.80
(2) $AlMe(BHT)_2(THF)$	−3.78		72.51	24.75
(3) $AlEt(BHT)_2(OEt_2)$	4.01	9.64	65.48	12.55
(4) $AlEt(BHT)_2(THF)$	4.68	10.25	73.24	24.38
(5) $AlMe_2(BHT)(OEt_2)$	−5.35		66.06	12.83
(6) $AlMe_2(BHT)(THF)$	−6.44		70.93	24.55
(7) $AlEt_2(BHT)(OEt_2)$	2.98	9.77	66.60	12.93
(8) $AlEt_2(BHT)(THF)$	2.57	9.97	71.43	25.02

TABLE III
Analytical data* for the new aluminum compounds.

Compound	m.p. (°C)	C%	H%
(1) $AlMe(BHT)_2(OEt_2)$	158–159	75.38 (75.76)	10.73 (10.71)
(2) $AlMe(BHT)_2(THF)$	178–180	75.94 (76.04)	9.95 (10.39)
(3) $AlEt(BHT)_2(OEt_2)$	120–121	75.23 (76.01)	10.35 (10.80)
(4) $AlEt(BHT)_2(THF)$	150–154	75.30 (76.28)	10.38 (10.49)
(5) $AlMe_2(BHT)(OEt_2)$	101–103	70.66 (71.95)	10.13 (11.22)
(6) $AlMe_2(BHT)(THF)$	115–118	72.00 (72.37)	10.10 (10.70)
(7) $AlEt_2(BHT)(OEt_2)$	75–77	73.09 (72.97)	10.93 (11.45)
(8) $AlEt_2(BHT)(THF)$	110–112	73.71 (73.36)	11.06 (10.97)

* Calculated values in parentheses.

$AlMe(BHT)_2(OEt_2)$ (1)

To a pentane (20 cm^3) solution of $AlMe(BHT)_2$ (0.96 g, 2.00 mmol) was added Et_2O (excess). The resulting solution was stirred for 1 h and the solvent removed under vacuum. The remaining white solid was washed with pentane (2 × 5 cm^3) and dried under vacuum. Yield: 1.03 g, 93%.
Compounds **2**, **3** and **4** were prepared in an analogous manner to **1**.

$AlMe_2(BHT)(OEt_2)$ (5)

To a pentane (40 cm^3) solution of BHT-H (2.00 g, 9.09 mmol) was added $AlMe_3$ (4.55 cm^3, 9.10 mmol). The resulting mixture was stirred for 1 h, and then Et_2O (excess) added *via* syringe. The volume was then reduced to *ca* 15 cm^3 under vacuum, and the solution cooled (−20°C) to give white crystals. Yield: 3.06 g, 96%. Compounds **6**, **7** and **8** were prepared in an analogous manner to **5**.

RESULTS AND DISCUSSION

Interaction of $AlMe_3$ with 2 equivalents of BHT-H in pentane allows the isolation of $AlMe(BHT)_2$.[2,3,4] Addition of Et_2O or THF to pentane solutions of $AlMe(BHT)_2$ results in the formation of the Lewis acid-base adducts $AlMe(BHT)_2L$ [L = Et_2O (**1**), THF (**2**)], which may be recrystallized from hydrocarbon solvents. The ^1H and ^{13}C NMR signals for the aluminum methyl ligands of **1** and **2** are downfield of those found for $AlMe(BHT)_2$.[3,4] This downfield shift is consistent with an increase in *p* character in the Al–C bond in going from planar sp^2 to a tetrahedral sp^3 aluminum centre.[6] The ethyl compounds $AlEt(BHT)_2(OEt_2)$ (**3**) and $AlEt(BHT)_2(THF)$ (**4**) are prepared in an analogous manner to the methyl derivatives.

Addition of Et_2O to an equimolar mixture of $AlMe_3$ and BHT-H at room temperature, results in the isolation of a single product, $AlMe_2(BHT)(OEt_2)$ (**5**), as a white crystalline solid. The mono-aryloxide compounds $AlMe_2(BHT)(THF)$ (**6**), $AlEt_2(BHT)(OEt_2)$ (**7**) and $AlEt_2(BHT)(THF)$ (**8**) are all prepared by the same route.

We have previously shown[6] that for complexes of the type Me_3AlPR_3 the aluminum-methyl ^{13}C resonance shifts downfield with increasing phosphine steric bulk, and with increased donor ability. Steric effects, however, were found to be the major contribution. A similar trend is observed for compounds **1**, **2** and **5**, **6**. In each case the Et_2O adduct's Al–Me resonance is downfield as compared to those in the analogous THF adducts. This difference is consistent with the greater steric bulk of the Et_2O ligand with respect to THF.

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SUPPLEMENTARY MATERIAL AVAILABLE

Full ^1H and ^{13}C NMR, and IR spectroscopic data for compounds **1**–**8** (5 pages) are available from the authors upon request.

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