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Sterically crowded aryloxide compounds of aluminum

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ABSTRACT

The chemistry of aluminum compounds containing sterically demanding aryloxide ligands is presented. In particular, those of compounds derived from 2,6-di-tert-butyl-4-methylphenol (BHT-H, from the trivial name butylated hydroxytoluene). The synthesis and structure of three-coordinate monomeric derivatives, and their ligand exchange reactions, are discussed in comparison to the more typical four-coordinate oligomeric aluminum alkoxide and aryloxide compounds. The reactions of the sterically crowded aryloxide compounds is divided into four general classes: oxidation and hydrolysis, the formation of Lewis acid-base complexes, the reaction with organic carbonyls, and the reaction with main group halides. Alane-aryloxide compounds are discussed separately, as are the 1,3-diphenyltriazenide derivatives. Finally, a discussion of the Al–O bonding interactions in four-coordinate aluminum aryloxides is presented, giving spectroscopic and theoretical evidence for and against various postulates to explain the presence of short Al–O distances and large Al–O–C angles.

A. INTRODUCTION

The chemistry of aluminum has been exhaustively studied due to the commercial applications of the metal and its alloys, and the diversity of reactivity displayed by its compounds. Aluminum metal is used in the building, transportation and packaging industries, and is also widely used in electrical power lines [1]. Aluminum compounds have found many uses, for example, the halides as Lewis acid catalysts [2], the hydrides as reducing agents in organic synthesis [3], the alkyl derivatives as co-catalysts or precursors to co-catalysts in Ziegler–Natta polymerization [4] or as alkyl transfer reagents [5], the alkoxides and aryloxides as precursors in sol-gel processes [6], or as additives to increase lubrication properties and thermal characteristics of oils [7].

Aluminum alkyls are often cited as representative examples of main group organometallic compounds. Despite their status as relative latecomers among industrial main group organometallics (the use of the trialkyls only became widespread after Ziegler's report of the "direct synthesis" in 1949) [8], aluminum alkyls have become more important and their derivatives more abundant than the older organolithium or organomagnesium compounds [9]. As is typical of main group organometallic compounds, organoaluminum compounds have highly reactive metal–carbon bonds, often spontaneously inflaming in air. The high Lewis acidity of these species is readily seen from their propensity to form oligomeric complexes and to coordinate strongly to Lewis bases [1]. The chemistry of non Lewis base adducts of aluminum is dominated by dimeric species. Trimeric, tetrameric and higher oligomeric structures are also known. As a consequence, the chemistry of aluminum is dominated by structures in which the aluminum is either four- or six-coordinate. Examples of five-fold coordination have increased over the past few years [10]. The small number of three-coordinate aluminum species may be attributed to the very high steric barriers that must be in place in order to make dimerization unfavorable.

With the exception of $Al[N(SiMe_3)_2]_3$ [11] (1969), all examples of condensed phase three-coordinate aluminum species have been published recently (1986–1992), and are indicative of progress in the synthesis of low coordination number species of all metals. Notable advances have been made over the past two decades, usually as a result of the use of sterically demanding, bulky ligands [12]. Although not exclusively, these ligands have been used to stabilize otherwise inaccessible coordination numbers usually by the inhibition of oligomerization. Specifically, the bulky aryloxide derived from 2,6-di-tert-butyl-4-methylphenol (see Fig. 1; BHT-H from the trivial name butylated hydroxytoluene) has been used to isolate transition metal and main group compounds [13–18]. Pasynkiewicz's reports on the synthesis of $AlMe(BHT)_2$ [2,19] and the ESR of the oxidation product [10], were published in the late 1970s, however, the structure of this compound, confirming it to be monomeric with a three-coordinate aluminum center was not published until 10 years later, by Ittel and co-workers [21]. In the interim, BHT derivatives of aluminum were already being used as industrial co-catalysts [22] and in organic synthesis.

The isolation of monomeric three-coordinate aryloxide aluminum compounds, $AlR_x(BHT)_{3-x}$ ($x = 0,1,2$), presents a unique opportunity to undertake fundamental studies of the structure, bonding and reactivity of aluminum without the complications synonymous with oligomerization, i.e., possible differences in reactivity between bridging and terminal ligands. It is the goal of this review to present a detailed compilation of the results obtained both in our laboratories and by other workers.

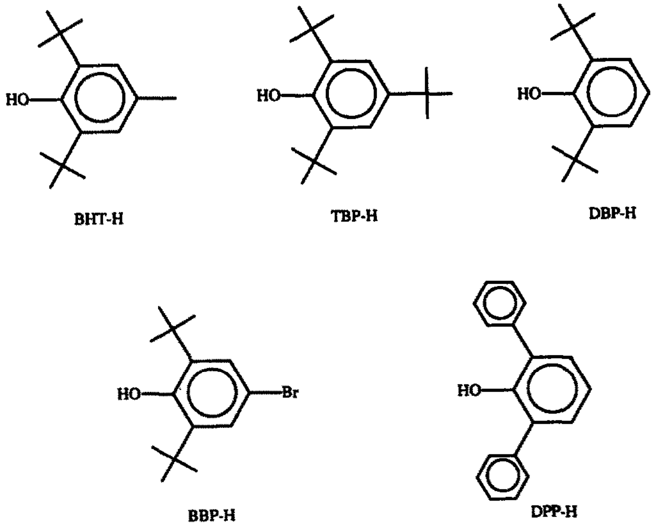


Fig. 1. Sterically hindered phenols; abbreviations are as used herein.

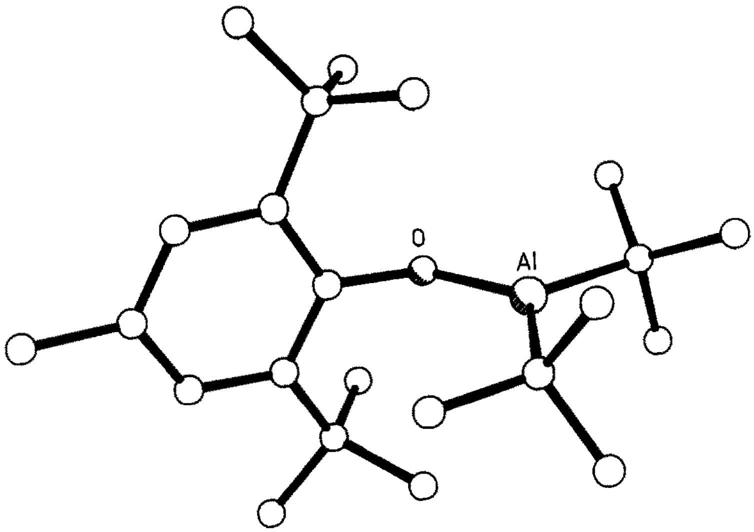


Fig. 2. The molecular structure of Al(^{t}Bu)$_2$(BHT).

B. SYNTHESIS OF THREE-COORDINATE ARYLOXIDE DERIVATIVES

(i) Mono-aryloxide compounds

The reaction of AlMe$_3$ with one equivalent of BHT-H does not yield the mono-aryloxide complex but instead the bis-aryloxide, AlMe(BHT)$_2$ [19]. A similar effect is observed for the ethyl derivatives [21]. This result has been explained in terms of ligand exchange reactions (see Section C) [21]. The mono-aryloxide may be isolated in the case of the methyl by the reaction of BHT-H with a fourfold excess of AlMe$_3$ [23], however, redissolution of the product results in ligand redistribution and the isolation of AlMe(BHT)$_2$. Given that the ligand exchange process occurs via the formation of dimeric complexes [21], it is reasonable to expect that stable monomeric monoaryloxides should be isolable if sterically more demanding alkyl groups are employed; this is indeed observed. The reaction of BHT-H with Al(^{i}Bu)$_3$ [24] and Al(^{t}Bu)$_3$ [25] in a 1:1 molar ratio yields the mono-aryloxides Al(^{i}Bu)$_2$(BHT) and Al(^{t}Bu)$_2$(BHT) respectively (eqn. (1)).

$$AlR_3 + BHT\text{-}H \rightarrow AlR_2(BHT) + RH, \qquad R = {}^{i}Bu, {}^{t}Bu \qquad (1)$$

Both compounds are monomeric in the gas phase and solution, and while the iso-butyl derivative is a liquid [24], Al(^{t}Bu)$_2$(BHT) [25] and its 2,4,6-tris-tert-butylphenoxide (TBP, see Fig. 1) analogue [25] are crystalline solids allowing for crystallographic confirmation of their solid state structure.

The molecular structure of Al(^{t}Bu)$_2$(BHT) is shown in Fig. 2; selected bond lengths and angles are given along with those for Al(^{t}Bu)$_2$(TBP) in Table 1. The aluminum centers in both Al(^{t}Bu)$_2$(BHT) and Al(^{t}Bu)$_2$(TBP) are in a distorted trigonal-planar geometry; the two O–Al–C angles are asymmetric and differ by about 13°. In both structures, the Al centers have essentially planar coordination, and there is a somewhat close approach to the Al (ca. 1.94–2.34 Å) of one of the aryloxide *ortho*-tert-butyl hydrogens. The minor deviation of the geometry at aluminum from planarity is such that the aluminum is always displaced towards the closest hydrogen. In addition, there is an inverse correlation between the Al···H distance and the amount of asymmetry in the O–Al–C angles. These data are suggestive of an agostic $C–H \rightharpoonup Al$ interaction between the aryloxide tert-butyl groups and the aluminum. Such agostic $C–H \rightharpoonup M$ interactions have been suggested in other Group 13 compounds [26].

(ii) Bis-aryloxide compounds

As noted above, the reaction of AlMe$_3$ with one equivalent of BHT-H yields, upon reaction work-up, the bis-aryloxide, AlMe(BHT)$_2$ [19]. The same product is also formed by the reaction of AlMe$_3$ with two equivalents of BHT-H, and by similar reactions other alkyl derivatives may also be prepared (eqn. (2)) [19,21,23]

$$AlR_3 + 2BHT–H \rightarrow AlR(BHT)_2 + 2RH, \qquad R = Me, Et, {}^iBu \tag{2}$$

TABLE 1

Selected bond lengths (Å) and angles (°) for three-coordinate aryloxide compounds of aluminum

Compound	Al–O	Al–C	O–Al–O	O–Al–C	Al–O–C
Al(^{t}Bu)$_2$(BHT)[a]	1.710(2)	1.976(3)		110.7(1)	129.4(1)
Al(^{t}Bu)$_2$(IBP)[a,b]	1.709	1.987 1.995		110.6 123.4	135.2
AlMe(BHT)$_2$[c]	1.687(2) 1.685(2)	1.927(3)	111.9(1)	123.9(1) 123.6(1)	140.5(2) 146.8(2)
Al(^{i}Bu)(DBP)$_2$[d]	1.682(1) 1.702(1)	1.952(2)	110.1(1)	120.1(1) 129.8(1)	157.3(1) 134.7(1)
Al(BHT)$_3$[e]	1.657(6) 1.640(5) 1.647(7)		119.1(3) 120.9(3) 119.9(3)		175.0(6) 177.6(5) 179.0(3)

[a] M.A. Petrie, M.M. Olmstead and P.P. Power, J. Am. Chem. Soc. 113 (1991) 8704.
[b] Average values of the six crystallographically independent molecules in the asymmetric unit.
[c] A.P. Shreve, R. Mulhaupt, W. Fultz, J. Calabrese, W. Robbins and S.D. Ittel, Organometallics, 7 (1988) 409.
[d] R. Benn, E. Janssen, H. Lehmkuhl, A. Rufinska, K. Angermund, P. Betz, R. Goddard and C. Krüger, J. Organomet. Chem., 411 (1991) 37.
[e] M.D. Healy and A.R. Barron, Angew. Chem. Int. Ed. Engl., 31 (1992) 921.

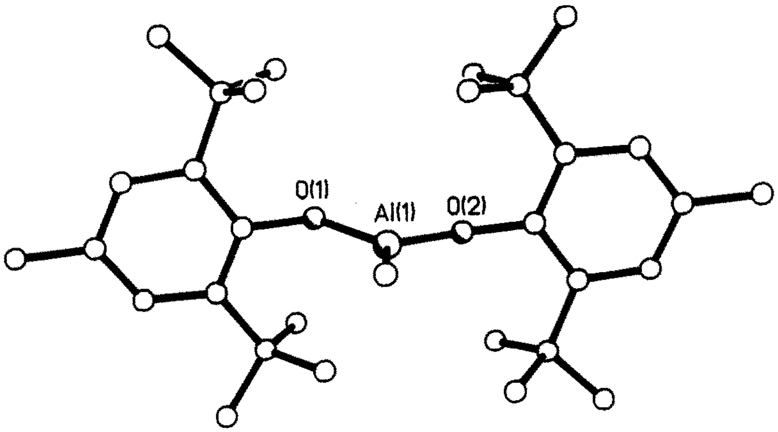


Fig. 3. The molecular structure of AlMe(BHT)$_2$.

Yamamoto and co-workers have demonstrated the application in organic synthesis (see Section F) of the TBP and 4-bromo-2,6-di-tert-butylphenoxide (BBP, see Fig. 1) compounds while Benn et al. [27] have reported the synthesis of the 2,6-di-tert-butyl phenoxide (DBP, see Fig. 1) derivative of the iso-butyl compound. All the bis-aryloxide compounds isolated are monomeric in solution, the gas phase and the solid (as determined for AlMe(BHT)$_2$ [21] and Al(^{i}Bu)(DBP)$_2$ [27] by X-ray crystallography.

The molecular structure of AlMe(BHT)$_2$ is shown in Fig. 3; selected bond lengths and angles for both AlMe(BHT)$_2$ and Al(^{i}Bu)(DBP)$_2$ are given in Table 1. In both cases, the aluminum atom is trigonal planar (Σ X–Al–Y = 360°). As with Al(^{t}Bu)$_2$(BHT) [25], there is a slight distortion of the aluminum out of the CO$_2$ plane in AlMe(BHT)$_2$ towards one of the hydrogen atoms of one of the *ortho*-tert-butyl groups of one of the BHT ligands (Al–H = 1.95 Å), suggesting the possibility of a weak C–H$\rightarrow$Al interaction.

It is interesting to note that in both AlMe(BHT)$_2$ and Al(^{i}Bu)(DBP)$_2$, the molecules adopt structures in which the two phenoxide rings are almost coplanar and perpendicular to the plane defined by the AlO$_2$ fragment (see Fig. 4). This is unexpected on steric grounds, but does allow the AlO$_2$ fragment to be isolobal to the allyl anion. The two

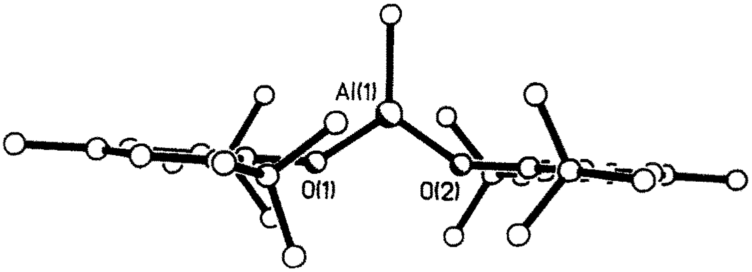


Fig. 4. Alternative view of AlMe(BHT)$_2$ showing the unusual coplanarity of the two BHT groups.

bulky aryloxide groups should force the interligand angle between them to be large, but this is not observed. The O–Al–O bond angles (average = 111°) are much smaller than the O–Al–C angles (average = 124°).

A number of three-coordinate non-alkyl bis-aryloxide derivatives have been reported, although none have been crystallographically characterized. Mehrotra reported, in a review article [18], the synthesis of the mixed alkoxide/aryloxide complex $Al(O^iPr)(BHT)_2$ (eqn. (3)) which, based on solution molecular weight measurement, was proposed to be monomeric.

$$Al(O^iPr)_3 + 2BHT\text{-}H \rightarrow Al(O^iPr)(BHT)_2 \qquad (3)$$

The amido/aryloxide compound $Al(BHT)_2(NHAr')$ ($Ar = 2,4,6\text{-}Cl_3C_6H_2$) was prepared (eqn. (4)) and characterized to be monomeric based upon ^{27}Al NMR spectroscopy and mass spectroscopy [29].

$$AlH(BHT)_2(OEt_2) + H_2NAr' \xrightarrow[-Et_2O]{} Al(BHT)_2(NHAr') + H_2 \qquad (4)$$

(iii) Tris-aryloxide compounds

Attempts to prepare a three-coordinate homoleptic aluminum aryloxide have been consistently unsuccessful, including resorting to such extreme reaction conditions as thermolysis of $AlEt_3$ in neat BHT-H [21]. In each case, only the bis-aryloxide compounds, e.g., $AlR(BHT)_2$, could be isolated. These results suggested that perhaps steric constraints preclude the formation of the tris-aryloxide complex. However, the tris-BHT derivative has been successfully prepared from the interaction of $AlH(BHT)_2(OEt_2)$ with a further equivalent of BHT-H in refluxing toluene (eqn. (5)) [30].

$$AlH(BHT)_2(OEt_2) + BHT\text{-}H \xrightarrow[-Et_2O]{\text{toluene, } \Delta} Al(BHT)_3 + H_2 \qquad (5)$$

The ^{27}Al NMR spectrum of $Al(BHT)_3$ shows a single resonance ($\delta = 3.2$) [29,30]. Although this ^{27}Al NMR signal is in a region normally associated with six-coordinate aluminum centers [31], it follows the general trend observed for monomeric three-coordinate aryloxide derivatives, i.e., mono-aryloxide compounds have resonances around 190 ppm, while those for the bis-aryloxides are found at ca. 100 ppm [27]. The three coordinate geometry about aluminum has been confirmed by an X-ray crystal structure analysis [29,30] (Fig. 5); selected bond lengths and angles are given in Table 1.

The coordination around aluminum in $Al(BHT)_3$ is trigonal planar [Σ O–Al–O = 359.9(3)°] with the aromatic rings forming a propeller-like arrangement around the aluminum, canted ca. 56° from the AlO_3 plane. The average Al–O distance and Al–O–C angle are 1.648(7) Å and 177.2(5)°, respectively. The former represents the shortest Al–O bond to be reported.

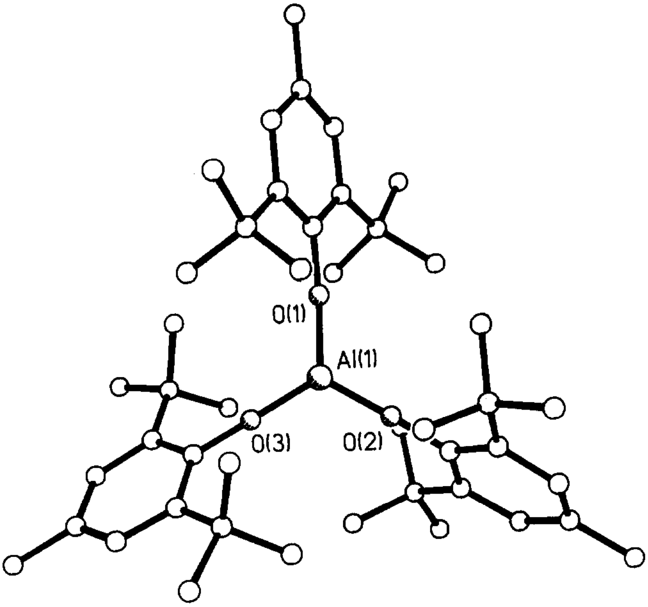


Fig. 5. The molecular structure of $Al(BHT)_3$.

C. LIGAND EXCHANGE

As was noted above, the reaction of $AlMe_3$ with 1 equiv. of BHT-H does not yield the mono-aryloxide, but $AlMe(BHT)_2$ [19]. It was originally suggested that this was due to the disproportionation of $AlMe_2(BHT)$ as shown in eqn. (6), and removal of the volatile Al_2Me_6 occurred in vacuo [19].

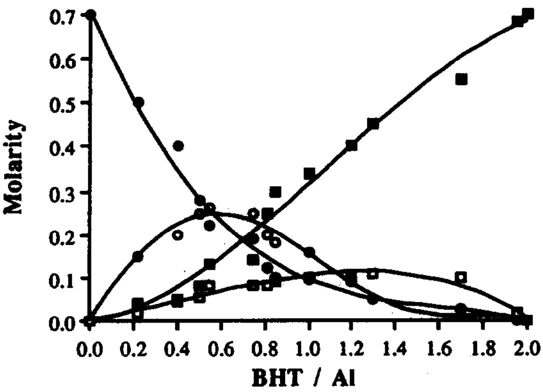


Fig. 6. Composition of the $AlMe_x(BHT)_{3-x}$ system as a function of the BHT to aluminum ratio; Al_2Me_6 (●), $Al_2Me_5(BHT)$ (○), $AlMe_2(BHT)$ (□) and $AlMe(BHT)_2$ (■).

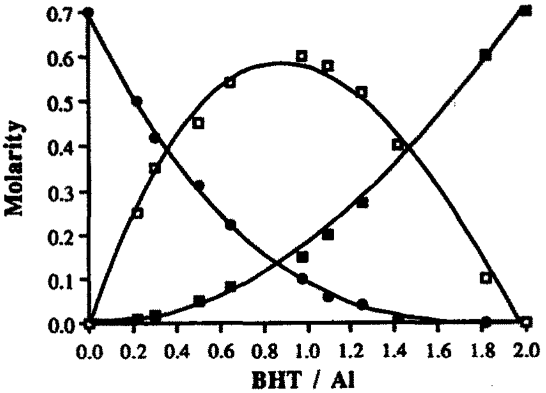


Fig. 7. Composition of the $AlEt_x(BHT)_{3-x}$ system as a function of the BHT to aluminum ratio; $AlEt_3$ (●), $AlEt_2(BHT)$ (□) and $AlEt(BHT)_2$ (■).

$$2AlMe_2(BHT) \rightleftharpoons \tfrac{1}{2}Al_2Me_6 + AlMe(BHT)_2 \qquad (6)$$

In fact the reaction is more complex. Based upon a variable temperature ^1H NMR study Ittel et al. [21] proposed the presence of two concurrent disproportionation reactions (eqns. (6) and (7)), with equilibrium constants at –80°C of 55.5 $M^{-1/2}$ and 0.143 $M^{1/2}$, respectively. The speciation present in solution at various Al/:BHT ratios is shown in Fig. 6.

$$3AlMe_2(BHT) \overset{K_{eq}}{\rightleftharpoons} Al_2Me_5(BHT) + AlMe(BHT)_2 \qquad (7)$$

$$Al_2Me_5(BHT) \overset{K_{eq}}{\rightleftharpoons} \tfrac{1}{2}Al_2Me_6 + AlMe_2(BHT) \qquad (8)$$

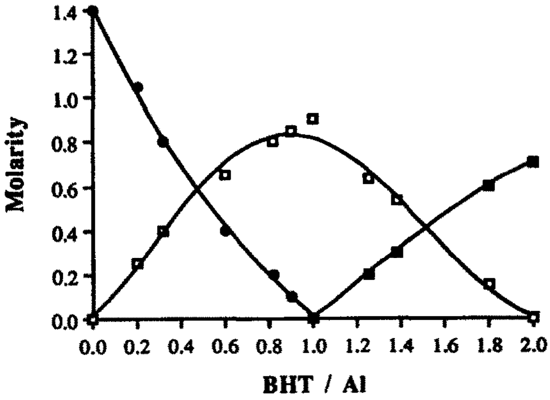


Fig. 8. Composition of the $Al(^iBu)_x(BHT)_{3-x}$ system as a function of the BHT to aluminum ratio; $Al(^iBu)_3$ (●), $Al(^iBu)_2(BHT)$ (□) and $Al(^iBu)(BHT)_2$ (■).

As indicated by Fig. 7, the reaction of BHT-H with $AlEt_3$ is somewhat simpler than that observed for $AlMe_3$ and BHT-H. The initial species formed is $AlEt_2(BHT)$, however at a very early stage of BHT-H addition, $AlEt(BHT)_2$ is also observed. The system exists as a single equilibrium (eqn. (9)) with an equilibrium constant of 0.137 $M^{-1/2}$ at −80°C [21].

$$2AlEt_2(BHT) \overset{K_{eq}}{\rightleftharpoons} \tfrac{1}{2}Al_2Et_6 + AlEt(BHT)_2 \qquad (9)$$

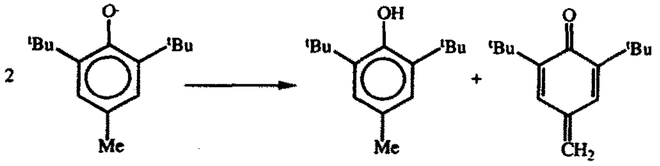
The reaction between $Al(^iBu)_3$ with BHT-H shows the simplest behavior; monomeric $Al(^iBu)_3$ reacts completely with BHT-H to give $Al(^iBu)_2(BHT)$ [21,24]. As a second equivalent of BHT-H is added, the initial product, $Al(^iBu)_2(BHT)$, is consumed and $Al(^iBu)(BHT)_2$ is formed [21]. This behavior is depicted in Fig. 8, and supports the observed isolable nature of $Al(^iBu)_2(BHT)$. It should be noted, however, that at 110°C and 10^{-4} Torr, the mono-aryloxide disproportionates to $Al(^iBu)_3$ and $Al(^iBu)(BHT)_2$ [24]. Under these conditions the trialkyl is removed as a vapor, driving the reaction to completion.

D. OXIDATION AND HYDROLYSIS

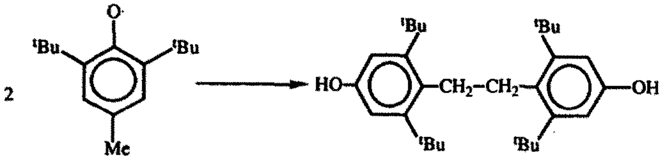
While the Lewis acid-base complexes $AlR_x(BHT)_{3-x}L$ ($x = 0,1,2$) are moderately air stable [23], decomposition occurring primarily due to hydrolysis, the three-coordinate compounds are all very sensitive to oxygen and/or water. Even small amounts of air cause rapid darkening and lead to the formation of BHT-H as the major isolable product. Pasynkiewicz et al. [20] observed that during oxidation of $AlR(BHT)_2$ (R = Me, ^iBu) gaseous products are evolved. Oxidation of $AlMe(BHT)_2$ gave methane and iso-butylene, while with $Al(^iBu)(BHT)_2$ only iso-butylene and iso-butane are evolved. This observation precludes the formation of a free alkyl radical, R, which has been suggested to be prevalent in the propagation steps of the oxidation of organoaluminum compounds [32]. Furthermore, the lack of methanol or iso-butanol formed upon hydrolysis after oxidation indicated that the formation of Al–O–R bonds does not take place during oxidation.

From ESR and IR spectroscopic studies, it was determined that the oxidation reaction of monomeric $AlR(BHT)_2$ proceeds according to eqn. (10) with the resulting BHT radical reacting further according to eqns. (11) and (12) [20].

$$AlR(BHT)_2 \xrightarrow{O_2} [BHT] + \text{radical containing Al and BHT} \qquad (10)$$



(11)



(12)

The hydrolysis of $AlR_x(BHT)_{3-x}$ does not allow for the isolation of any other products than BHT-H. By contrast, the addition of 1 equiv. of water to the $AlH(BHT)_2(OEt_2)$ results in the qualitative formation of the dimeric hydroxide complex $[Al(OH)(BHT)_2]_2$ (eqn. (13)) [29].

$$AlH(BHT)_2(OEt_2) + H_2O \xrightarrow[-Et_2O]{} \tfrac{1}{2}[Al(OH)(BHT)_2]_2 + H_2 \qquad (13)$$

E. LEWIS ACID-BASE COMPLEXES

(i) Mono-aryloxide complexes

While NMR studies (see Section C) have shown that an equimolar mixture of AlR_3 ($R = Me$, Et) and BHT-H results not in the mono-aryloxide but a complex equilibrium mixture of species [21], the mono-aryloxide compounds may be trapped by the addition of a Lewis base (eqn. (14)) [23].

$$AlR_3 + BHT\text{-}H \xrightarrow{-RH} \text{“}AlR_2(BHT)\text{”} \xrightarrow{L} AlR_2(BHT)(L) \qquad (14)$$

$R = Me, Et; L = \text{Lewis base}$

When the Lewis base is a phosphine, Et_2O or THF, the mono-aryloxide is the only product observed, however, when nitrogen donor Lewis bases such as pyridine are employed, $AlR_3(L)$ and $AlR(BHT)_2(L)$ are formed as minor co-products [33]. This mixture of products and their approximate ratios is consistent with the proposal of four species in solution at equilibrium, i.e., $AlMe(BHT)_2$, $AlMe_2(BHT)$, $Al_2Me_5(BHT)$, and Al_2Me_6 (see eqns. (7) and (8)) [21]. The formation of a mixture with pyridine versus PMe_3 is indicative of the decreased basicity and increased steric bulk of PMe_3 as compared to pyridine [23,33]. Thus, while PMe_3 reacts preferentially with the least sterically hindered monomeric species, $AlMe_2(BHT)$, pyridine will additionally cleave aryloxide or alkyl bridged dimers.

The mono-aryloxide complexes are readily obtained for all Lewis bases by the use of the diethylether complex [34] provided, of course, that they can displace the ether (eqn. (15)) [35]. Complexes of organic carbonyls are discussed in Section F.

$$AlR_2(BHT)(OEt_2) + L \xrightarrow[-Et_2O]{} AlR_2(BHT)(L) \qquad (15)$$

L = THF, PMe_3, MeCN, py, 4-Mepy, 3,5-Me_2py, 2,6-Me_2py, py$\cdot$O, NH_3, H_2N^nBu, H_2N^tBu, $HNEt_2$, HN^iBu_2

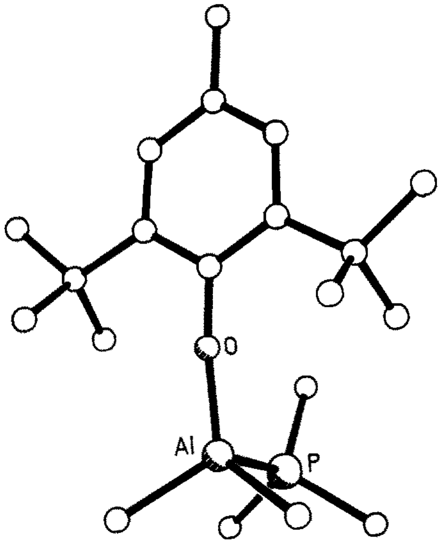


Fig. 9. The molecular structure of $AlMe_2(BHT)(PMe_3)$.

Several mono-aryloxide Lewis base complexes have been crystallographically characterized; representative examples are given in Figs. 9 and 10 [23,33,35]. In all cases, the geometry around aluminum is distorted tetrahedral, with the angles associated with the Lewis base being the most acute. The Al–C bonds [1.960(5)–1.978(2) Å] are within the range found for aluminum-alkyls (1.90–2.01Å) [36]. The Al–L distances are also within the ranges for non-aryloxides compounds of aluminum. In all the compounds, the Al–O distances (1.71–1.74 Å) are longer than those reported for three-coordinate

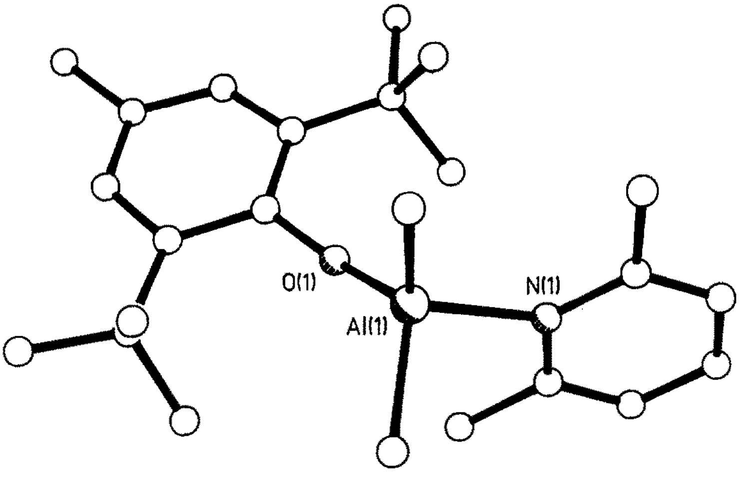


Fig. 10. The molecular structure of $AlMe_2(BHT)(2,6\text{-}Me_2py)$.

$AlR_x(BHT)_{3-x}$, (Table 1) but significantly shorter than reported for non-aryloxide compounds. In addition, the Al–O–C angles are all larger than previously observed for main group compounds. The bonding consequences of these unusual parameters is discussed in Section J.

The elimination-condensation reaction sequence (eqn. (16)) that occurs between an aluminum alkyl and a primary or secondary amine has been widely explored as a route to aluminum nitrogen ring and cluster compounds [37]. Similar condensation reactions have recently been exploited with ammonia as the nitrogen source for the low-temperature preparation of aluminum nitride (eqn. (17)) [38].

$$AlR_3 + HNR'_2 \longrightarrow [R_2AlNR'_2]_n + RH \tag{16}$$

$$AlR_3 + NH_3 \xrightarrow[>400^{\circ}C]{\Delta} AlN + 3RH \tag{17}$$

Reaction of aluminum alkyls with ammonia results in the initial formation of the simple Lewis acid-base adducts (eqn. (18)), which are ordinarily unstable with respect to condensation [39]. Furthermore, no organoaluminum-ammonia adducts had been structurally characterized.

$$AlR_3 + NH_3 \longrightarrow R_3Al(NH_3) \tag{18}$$

The addition of excess NH_3, a primary or secondary amine to $AlR_2(BHT)(OEt_2)$ results in the quantitative formation of the appropriate Lewis acid-base complex, i.e., $AlR_2(BHT)(NH_3)$ [40], $AlR_2(BHT)(H_2NR)$ [35] and $AlR_2(BHT)(HNR_2)$ [35], respectively (eqn. (19)).

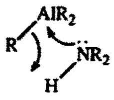
$$AlR_2(BHT)(OEt_2) + NH_3\ (excess) \xrightarrow[pentane]{-78^{\circ}C} AlR_2(BHT)(NH_3) \tag{19}$$

In contrast to previously reported organoaluminum-ammonia and amine complexes, the BHT substituted compounds show no propensity for alkane elimination, giving parent ions in the mass spectrum [35] and in the case of $AlMe_2(BHT)(NH_3)$ may be sublimed without decomposition [40]. Heating under an inert atmosphere beyond their melting point results in decomposition to multiple products including BHT-H.

It has been commonly assumed that the reaction of aluminum-alkyls and Brönsted acids proceeds via the prior formation of a Lewis acid-base adduct from which the elimination reaction occurs [41]. The differences in reactivity of various Brönsted acids are rationalized in terms of the acidity of the proton in the adduct molecule. Seminal work by Beachley et al. [42] has demonstrated, however, that although aluminum-alkyls and amines do form adducts, the important step for elimination is the prior dissociation of the adduct (eqn. (20)).

$$R_3Al\cdot N(H)R'_2 \longrightarrow AlR_3 + N(H)R'_2 \qquad (20)$$

If the recombination of the monomeric aluminum compound and the amine occurs with the appropriate orientation, elimination may occur, possibly via a four-centered S_Ei (substitution, electrophilic, internal) mechanism (I) [43].



I

The formation of a stable aluminum-amine adduct is therefore a “dead-end” path for alkane elimination [42]. Thus, if the Lewis acid-base adducts between AlR_2(BHT) and protic amines are undissociated in hydrocarbon solution, no alkane elimination can occur. However, at room temperature, Lewis base complexes of $AlMe_2$(BHT) do exist in equilibrium with the dissociated species (eqn. (21)) [35].

$$AlR_2(BHT)(L) \rightleftharpoons AlR_2(BHT) + L \qquad (21)$$

It would seem likely, therefore, that the lack of any reaction between the acidic N–H and the basic Al–R ligands is either because the sterically hindered aryloxide ligand precludes the approach of the amine to the aluminum atom in the orientation required for alkane elimination [44] or because the basicity, and therefore reactivity, of the aluminum-alkyl towards a Brönsted acid is reduced by the presence of the aryloxide substituent on the aluminum [45].

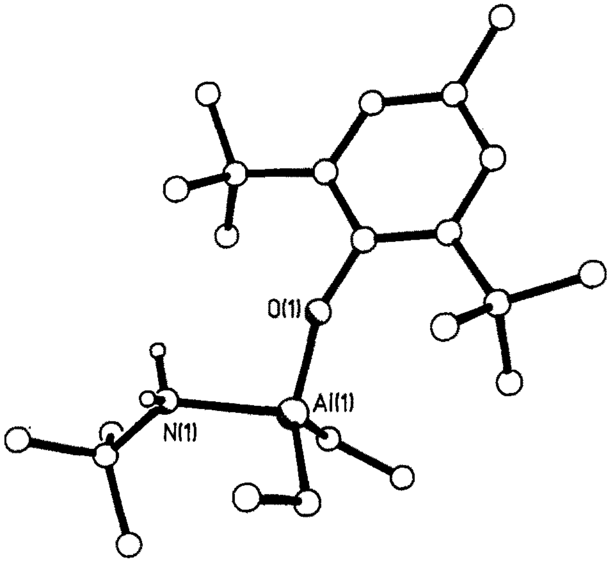


Fig. 11. The molecular structure of $AlEt_2(BHT)(H_2N^tBu)$.

In order to probe the relative importance of these steric and electronic effects involved in the stabilization of the amine/BHT compounds towards the thermal elimination of alkane, the structural and spectroscopic properties of one of these compounds, $AlEt_2(BHT)(H_2N^tBu)$ may be compared to the adducts $AlEt_2X(H_2N^tBu)$ (X = Et, Cl, Br, I) whose stability towards alkane elimination has been described in detail [46].

The molecular structure of $AlEt_2(BHT)(H_2N^tBu)$ is shown in Fig. 11. In order for alkane elimination to occur, either directly from the complex or via a four-membered S_Ei process, one of the amine N–H bonds must be oriented coplanar with the Al–C bond of the alkyl group to be eliminated. Such a conformation would require the amine ^{t}Bu group to eclipse either the BHT ligand or one of the ethyl groups. Although the former is undoubtedly disfavored on steric grounds, it is unlikely that the latter is sufficiently sterically hindered given that the elimination of ethane occurs readily from $AlEt_3(H_2N^tBu)$ [46] in which a similar conformation must occur. This suggests that steric inhibition of alkane elimination should not be present. In fact, any steric interaction in the isolated complex will be significantly reduced in a four-centered S_Ei type transition state.

Gosling and Bowen [46] reported the correlation between NMR spectral data and thermal stabilities of adducts of the general form $AlEt_2X(H_2N^tBu)$ (X = Et, Cl, Br, I). The corresponding data for $AlEt_2(BHT)(H_2N^tBu)$ are presented in Table 2. An estimate of the electronegativity of the aluminum atoms in the adducts should provide information concerning the relative degree of polarity of the Al–C bond and therefore the relative negative charge density at the α-carbon, which should be directly related to the basicity of the aluminum ethyl group. The electronegativity may readily be estimated by using the modified Dailey–Schoolery relationship (eqn. (22)) [47] where χ is the electronegativity of aluminum and Δ is the internal chemical shift (eqn. (23)) of an ethyl group bonded to aluminum.

TABLE 2

Decomposition temperature and ^{1}H NMR spectral data for the adduct $AlEt_2X(H_2N^tBu)$

X	Decomposition temperature (°C)	^{1}H NMR (ppm)[a]		$\delta(CH_3) - \delta(CH_2)$	χ	Ref.
		$AlCH_2CH_3$	$AlCH_2$			
Et	90	1.33	0.09	1.24	1.30	b
Cl	100	1.45	0.35	1.10	1.39	b
Br	120	1.62	0.57	1.05	1.42	b
I	~120	1.48	0.53	0.95	1.48	b
BHT	>120	1.02	0.07	0.95	1.48	c

[a] NMR spectra recorded in CCl_4 (10% $CDCl_3$).

[b] K. Gosling and R.E. Bowen, J. Chem. Soc. Dalton Trans., (1974) 1961.

[c] M.D. Healy, J.W. Ziller and A.R. Barron, Organometallics, 10 (1991) 597.

$$\chi = 0.62\Delta + 2.07 \qquad (22)$$

$$\Delta = \delta CH_3 - \delta CH_2 \qquad (23)$$

By use of this method, the calculated value of χ for $AlEt_2(BHT)(H_2N^tBu)$ is the same as that found for $AlEt_2I(H_2N^tBu)$ (see Table 2). This similarity is also reflected in the thermal stability of the two compounds. The high electronegativity of the aluminum atom in the BHT derivative would suggest an electron-rich aluminum center, consistent with ^{27}Al NMR studies [27] and the presence of π-donation of electron density from the BHT onto the aluminum (see Section J) [23,33]. It is reasonable to propose, therefore, that this donation of electron density accounts for the reduced basicity of the aluminum-alkyl and thus the lack of reactivity observed for the ammonia, primary and secondary amine adducts $AlR_2(BHT)(L)$.

(ii) Bis-aryloxide complexes

The bis-aryloxide compounds, $AlR(BHT)_2$ react readily with Lewis bases to yield the appropriate Lewis acid-base complex, e.g., eqn. (24) [23,33–35].

$$AlR(BHT)_2 + L \longrightarrow AlR(BHT)_2(L) \qquad (24)$$

$L = Et_2O$, THF, PMe_3, py, py·O, NH_3, H_2N^nBu, H_2N^tBu, HN^iBu_2, $HNEt_2$

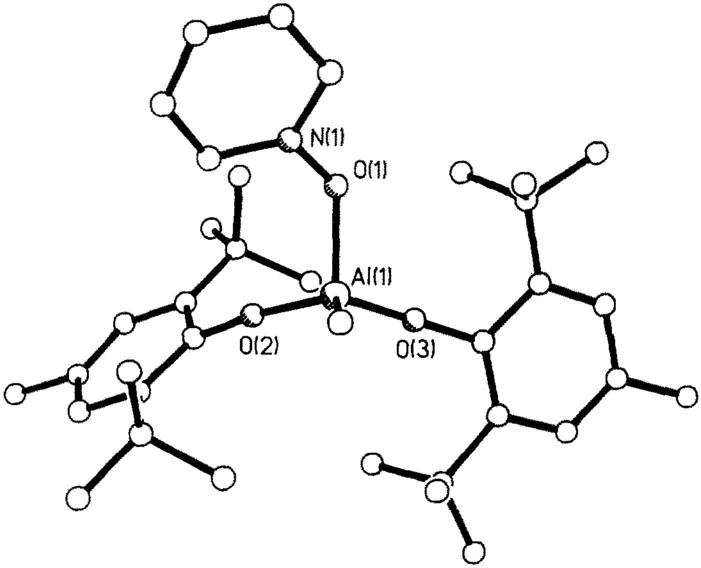


Fig. 12. The molecular structure of $AlMe(BHT)_2(py{\cdot}O)$.

TABLE 3

Selected equilibrium and thermodynamic data for Lewis base complexes of $AlMe_3$, $AlMe(BHT)_2$[a]

Compound	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
$AlMe_3(OEt_2)$[b]	84.6	
$AlMe(BHT)_2(OEt_2)$	63.8 (5)	179 (8)
$AlMe_3(THF)$[b]	95.8	
$AlMe(BHT)_2(THF)$	76.8 (3)	181(6)
$AlMe_3(py)$[b]	115.3	
$AlMe(BHT)_2(py)$	76.9 (5)	179 (9)

[a] Adapted from M.B. Power, J.R. Nash, M.D. Healy and A.R. Barron, Organometallics, 11 (1992) 1830. Error given in parentheses.

[b] C.H. Henrickson, D. Duffy and D.P. Eyman, Inorg. Chem., 7 (1968) 1047.

Crystallographic characterization has been obtained for several examples (e.g., Fig. 12), in particular those of organic carbonyls which are discussed separately (see Section F).

The ^1H NMR signals for the aluminum methyl ligand of $AlMe(BHT)_2(L)$ (δ –0.01 to –0.37) are downfield of that found for $AlMe(BHT)_2$ (δ –0.43) [23]. This downfield shift is consistent with an increasing p character in the Al–C bond in going from a planar sp^2 to a tetrahedral sp^3 aluminum center [48]. The magnitude of the shift is temperature dependent suggesting the presence of an equilibrium in solution (eqn. (25)) [49].

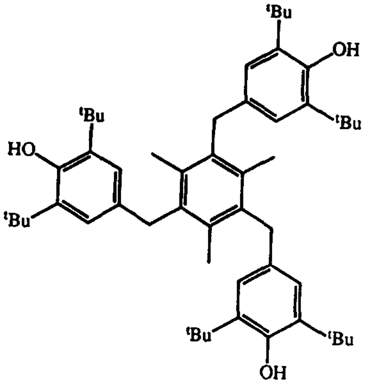
$$AlMe(BHT)_2(L) \rightleftharpoons AlMe(BHT)_2 + L \qquad (25)$$

Given the common occurrence of Lewis acid-base complexes for the Group 13 elements, it is perhaps surprising that reports of thermodynamic data such as bond-dissociation energies (BDEs) are sparse. The majority of studies have been carried out on the complexes of $AlMe_3$, $AlEt_3$ and $AlPh_3$ [50]. Unfortunately, the dissociation process for the complex is complicated by the dimerization of AlR_3 [51]. The measurement of any solution equilibrium process would, therefore, be greatly simplified for monomeric three-coordinate compounds whose steric bulk precludes dimerization. Thus, the bis-BHT compounds $AlR(BHT)_2$ makes an ideal subjects for study.

Table 3 lists the calculated ΔH_D and ΔS_D values for the dissociation of the Lewis base from $AlMe(BHT)_2(L)$ [49]. Also listed are the ΔH_D values determined for the corresponding $AlMe_3$ complex [50g]. From the NMR data, the following decreasing order of bond strength (ΔH_D) of ligand L, to $AlMe(BHT)_2$, has been determined: py ≈ THF > O_2N–C_6H_4–p-Me > O=CPh_2 > Et_2O [49]. Although the overall order is similar to that observed for $AlMe_3$, i.e., py > THF > Et_2O, the absolute values are significantly lower. This difference is consistent, not only with increased steric repulsion due to the steric bulk of the BHT ligand, but also other experimental and theoretical studies. Gas phase photoelectron spectral measurements [52] of the aluminum-ligand bonding energies in aluminum aryloxide complexes, and ab initio calculations [53] have both indicated that the R_3Al–L bond is significantly weakened with the replacement of alkyl with alkoxide or aryloxide ligands (see below). This weakening has been assigned to a π-type interaction between the aryloxide oxygen lone pair p orbital and the aluminum ligand σ^* orbital (see Section J).

The preferential complexation of a Lewis-base to the sterically demanding Lewis acid $AlMe(BHT)_2$, has been elegantly employed by Yamamoto et al. for the molecular recognition of ethers [54]. Using ^{13}C NMR spectroscopy, these workers investigated the recognition ability of $AlMe(BHT)_2$ with two different ether substrates, the results of this study are summarized in Table 4. The use of non-sterically demanding aluminum and boron Lewis acids resulted in poor selectivity.

The applicability of the selective coordination of $AlMe(BHT)_2$ towards methyl versus ethyl ethers was transferred to a polymeric $AlMe(OAr)_2$ system derived from the sterically hindered triphenol (II) [54].



II

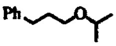
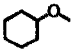
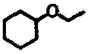
The polymeric aluminum aryloxide was successfully used as a column material for the chromatographic separation of structurally and/or electronically similar organic ethers [54].

(iii) *Tris-aryloxide complexes*

The formation of Lewis acid-base complexes of $Al(BHT)_3$ is not necessarily expected due to the steric congestion at the aluminum center provided by the propeller-like arrangement of the three 2,6-disubstituted aryloxide ligands (see Fig. 13) [29,30]. However, previous studies on transition metal and lanthanide analogs indicate that formation of the mono-adduct is facile. Thus, $Sc(BHT)_3$ reacts with THF and $O{=}PPh_3$ to form the appropriate complexes [15]. Similarly, $Ce(DBP)_3$ was shown to form 1:1 adducts with THF, $O{=}CPh_2$, $O{=}PEt_3$, $NH_2{}^nBu$, $NHEt_2$, MeCN, CN^tBu, and THT [16]. Furthermore, with "slender" ligands, an additional equivalent of the Lewis base may be added to the metal center, and the crystal structure of $Ce(DBP)_3(CN^tBu)_2$ was reported [16].

TABLE 4

Selective complexation of two different ethers with $AlMe(BHT)_2$[a]

Ethers		Complexation ratio[b]
		100:0
		100:0
		96:4
		100:0
		81:19
		100:0
		90:10
		100:0
		100:0

[a] K. Maruoka, S. Naghara and H. Yamamoto, J. Am. Chem. Soc., 112 (1990) 6115.
[b] As determined by ^{13}C NMR spectroscopy.

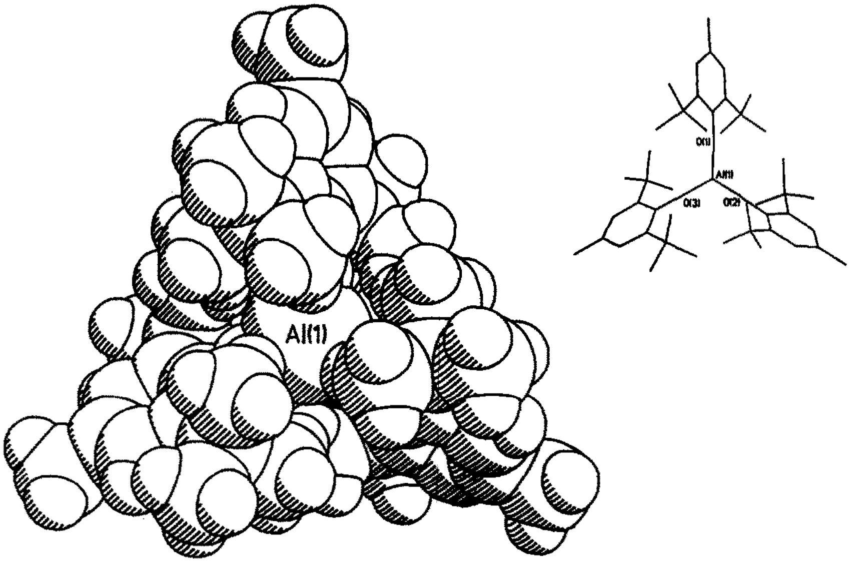


Fig. 13. Space filling representation of $Al(BHT)_3$ and its equivalent line drawing (inset), viewed perpendicular to the AlO_3 plane, showing the steric hinderance imposed on the aluminum center.

With pyridine, MeCN, $O{=}PPh_3$, and 4-tert-butylcyclohexanone, $Al(BHT)_3$ reacts to yield the appropriate Lewis acid-base complexes $Al(BHT)_3(L)$ (eqn. (26)). No evidence for adduct formation was observed for $O{=}CPh_2$, OEt_2, or THF [29].

$$Al(BHT)_3 + L \longrightarrow Al(BHT)_3(L) \tag{26}$$

$$L = MeCN,\ py,\ O{=}PPh_3,\ O{=}C(C_5H_9)\text{-}4\text{-}{}^tBu$$

By subjecting $Al(BHT)_3$ to a titration with up to 5 equiv. of acetonitrile (see Fig. 14), the ^1H NMR data shows that only 1 equiv. of MeCN is coordinated to each aluminum center, i.e., the formation of $Al(BHT)_3(NCMe)_2$ is not observed. Addition of less than 1 equiv. of MeCN gives two peaks in the tert-butyl region corresponding to $Al(BHT)_3$ and $Al(BHT)_3(NCMe)$ [29]. The exchange of MeCN between molecules of $Al(BHT)_3$ is therefore slow on the NMR timescale at 290 K. Warming a solution in C_6D_6 corresponding to the addition of ca. 2/3 equivalent of MeCN per aluminum allows for the activation energy for the degenerate exchange given in eqn. (27) to be calculated ($\Delta G^{\ddagger}$) of 18.2(3) kJ mol^{-1} [29].

$$Al^*(BHT)_3 + Al(BHT)_3(NCMe) \rightleftharpoons Al(BHT)_3 + Al^*(BHT)_3(NCMe) \tag{27}$$

Interestingly, this value is similar to that observed for the analogous exchanges between $AlMe(BHT)_2$ and $AlMe(BHT)_2(MeCN)$, i.e., 17(1) kJ mol^{-1} [55].

F. REACTIONS WITH ORGANIC CARBONYLS

Despite the diverse range of reactions reported to occur between organic carbonyls and organoaluminum compounds [56], the latter's use as reagents in organic synthesis has

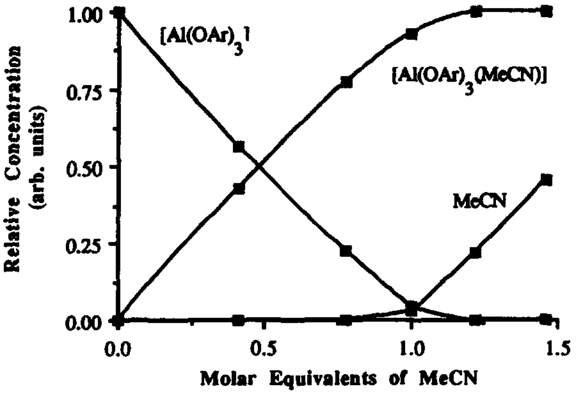


Fig. 14. Relative concentration of $Al(BHT)_3$, $Al(BHT)_3(NCMe)$ and MeCN as a function of MeCN/[$Al(BHT)_3$] molar ratio.

been traditionally limited due to the occurrence of multiple reaction products from a single substrate. For example, the reaction of acetaldehyde with $AlEt_3$ results in both alkyl addition to and reduction of the carbonyl group [57]. Secondary reactions include the Oppenauer oxidation, and the Tischenko reaction with both acetaldehyde and the primary reaction products [57]. It is therefore not surprising that much research effort has been aimed towards the development of new organoaluminum compounds, for use as both reaction-specific and also stereospecific reagents and catalysts. In this regard, sterically hindered aryloxide compounds have been one of the most extensively studied.

(i) Lewis acid-base complex formation

The initial products formed from the reaction of organic carbonyls with $AlR_x(BHT)_{3-x}$ ($x = 1,2$) are the Lewis acid-base complexes, $AlR_x(BHT)_{3-x}(O{=}CR'R'')$. In many cases, there is no further reaction and the complex may be isolated quantitatively, and crystallographically characterized. Even if further reaction is observed, the carbonyl complex may often be isolated due to the low solubility of the complexes in pentane, as compared to the reactants. Examples of complexes for which no subsequent reaction is observed are as follows: aldehyde complexes of $AlMe(BHT)_2$, e.g., Fig. 15; ketone complexes of $AlMe_2(BHT)$ and $AlMe(BHT)_2$, e.g., Figs. 16 and 17, respectively; all ester and amide complexes, e.g., Figs. 18 and 19 [58,59].

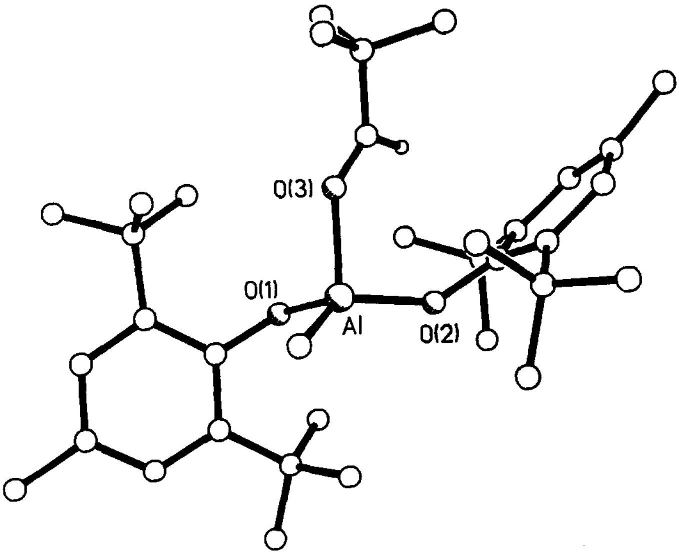


Fig. 15. The molecular structure of $AlMe(BHT)_2[O{=}C(H)^tBu]$.

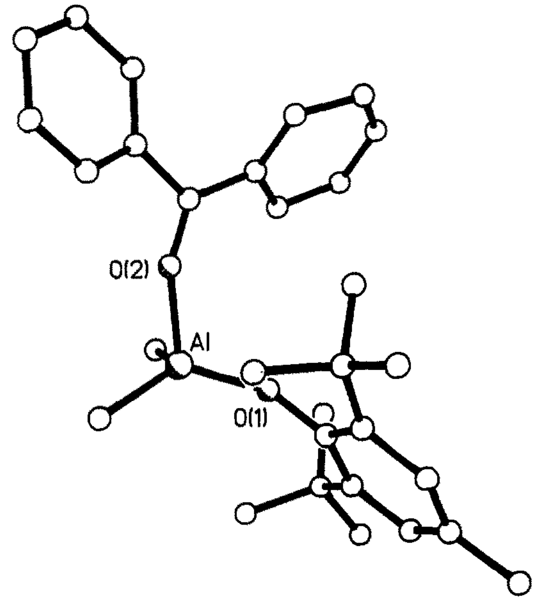


Fig. 16. The molecular structure of $AlMe_2(BHT)(O{=}CPh_2)$.

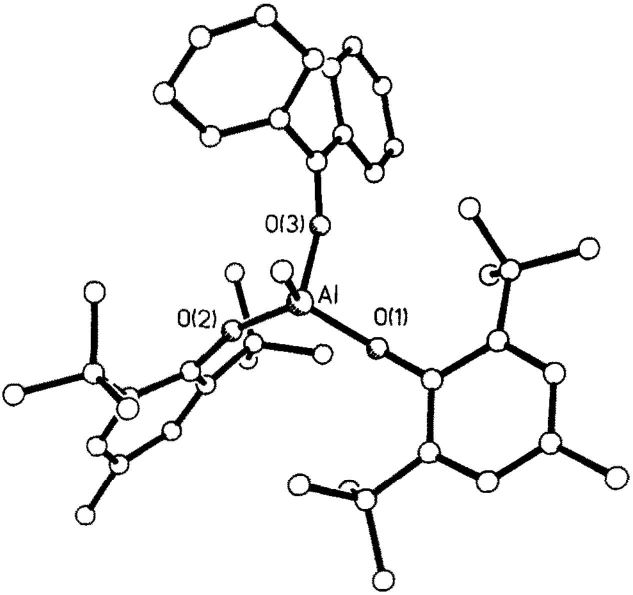


Fig. 17. The molecular structure of $AlMe(BHT)_2(O{=}CPh_2)$.

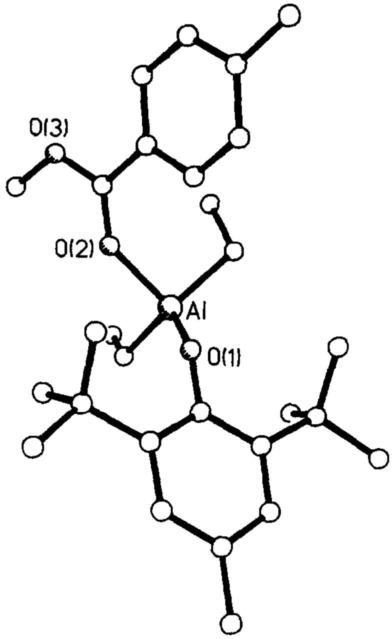


Fig. 18. The molecular structure of $AEt_2(BHT)[O{=}C(OMe)C_6H_4$-$p$-Me].

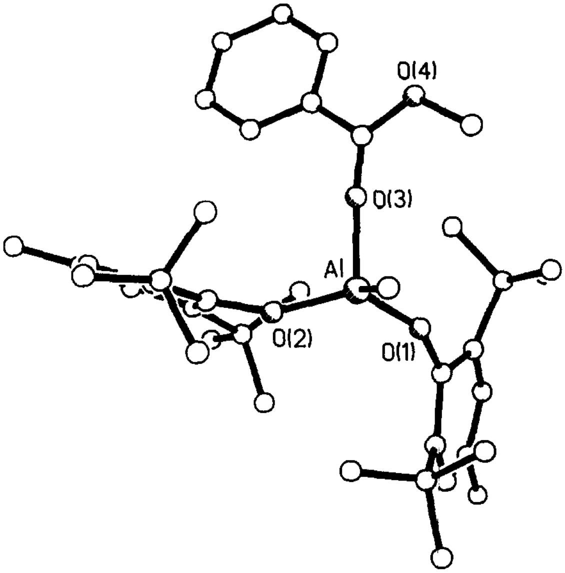
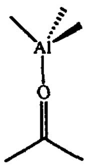
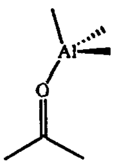


Fig. 19. The molecular structure of $AlMe(BHT)_2[O{=}C(OMe)Ph]$.

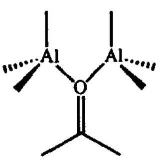
There are several different possible modes of coordination of aluminum Lewis acids to carbonyl groups [58]. One possibility is a purely electrostatic interaction, in which the aluminum is situated at the negative end of the C=O dipole, where C–O–Al = 180° (**III**). Another possibility is the coordination of the aluminum to one of the lone pairs on the carbonyl oxygen. This results in the aluminum being in the nodal plane of the C=O bond (**IV**). Ab initio calculations for the model system $H_3Al(O=CH_2)$ suggest that this bent mode is the energetically favored geometry [60]. Wuest et al. [61] have recently reported the coordination of two aluminum centers, one to each of the lone pairs of a ketone oxygen, i.e., **V**. A bent non-planar mode of bonding (**VI**) results from movement of the aluminum out of the carbonyl π nodal plane. Finally, η^2-coordination of a Lewis acid to the C=O π^* bond can be envisaged (**VII**) in which the carbonyl π orbital is the donor, but back-bonding into the C=O π^* orbital occurs. Although this mode has been reported for transition metals, it does not seem likely for main group metals.



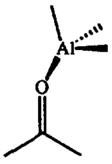
III



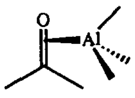
IV



V



VI

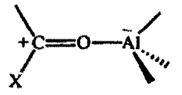


VII

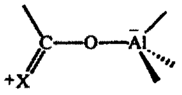
The structure of the aldehyde and ketone complexes (Figs. 15–17) are consistent with theoretical calculations, i.e., the carbonyl is coordinated such that the aluminum is in the π-nodal plane of the ketone. The Al–O–C angles range from 136.0(3) to 153.8(9)°, larger than the predicted range of 122° to 141° [58,59]. Wiberg has shown, however, that any steric effects at the α-carbon can be relieved by opening the Al–O–C angle, at a small energetic cost [60]. Thus, one would expect the Al–O–C angle in $AlMe(BHT)_2[O=C(H)^tBu]$ to be less than that for $AlMe(BHT)_2(O=CPh_2)$, and this is indeed observed, 136.0(3)° and 144.0(6)°, respectively. Although the *syn* conformation is predicted to be the most stable, both $AlMe(BHT)_2[O=C(H)^tBu]$ and $AlMe_2(BHT)(O=CPh_2)$ adopt *anti* conformations, presumably due to steric interactions [58].

The ester complex $AlMe(BHT)_2[O=C(OMe)Ph]$ (Fig. 19) [59] has a Al–O–C angle approaching linearity [168.4(3)°] while $AlEt_2(BHT)[O=C(OMe)C_6H_4\text{-}p\text{-}Me]$ (Fig. 18) appears to be a rare example of a bent non-planar mode of bonding, Al–O(2)–C(30) = 143.0(6)°, Al–O(2)–C(30)–O(3) = 130.1° [21]. Despite the proposal that this mode of coordination is important in the transition states for both the reduction and the alkylation of organic carbonyls by aluminum alkyls (see below), no other examples have been structurally characterized for aluminum complexes. It is apparent that the mode of coordination of organic carbonyls to aluminum is quite flexible, and that steric effects predominate. This is quite reasonable given the small barrier calculated for the distortion from bent to linear geometry for $AlH_3(O=CH_2)$ (6 kcal/mol at MP3/6-31G*) [60].

The IR C–O stretching frequency is strongly influenced by the C–O bond order; the higher the frequency the greater the bond order. There is a decrease in the carbonyl stretching frequency in the IR spectrum of the aluminum complexes when compared to the free carbonyls [58]. Although this shift in frequency is consistent with coordination of the carbonyl to aluminum, its magnitude appears to be characteristic of the class of carbonyl ligand, i.e., $\Delta\nu$ aldehydes: 55–70 cm^{-1}; ketones 45–70 cm^{-1}; esters 85–125 cm^{-1}; amides 80–125 cm^{-1}. This result can be rationalized as are the shifts observed for Lewis acid complexes of transition metal carbonyl and acetyl complexes [62]. If there is the possibility of electron donation from substituents X at the carbonyl α-carbon (**VIII**) then resonance from **IX** becomes a significant contributor for the carbonyl adducts.



VIII



IX

Not only is the shift in the C–O stretching frequency the largest for esters and amides, but also for aldehydes and ketones with strong electron donating substituents [58]. Thus, the *para*-methoxy benzaldehyde complex has a larger $\Delta\nu$ (100 cm^{-1}) than that observed for the other aldehydes. If this bonding picture is correct then the magnitude of the downfield shifts in the ^{13}C NMR for the carbonyl α-carbon, on coordination to aluminum, $\Delta\delta$, should decrease with an increase in the contribution of resonance from **IX**, i.e., the $\Delta\delta$ will decrease with an increase in $\Delta\nu$. Although a general trend is indeed observed for the changes in the ^{13}C NMR shift and the carbonyl $\nu(C{=}O)$ stretching frequency (Fig. 20), it is clear that other, possibly steric, factors are also important in determining the magnitude of either parameter.

It has been demonstrated that the ^{13}C NMR shift of the aluminum carbon resonance in Me_3AlPR_3 complexes is primarily dependent on the steric bulk of the phosphine ligand

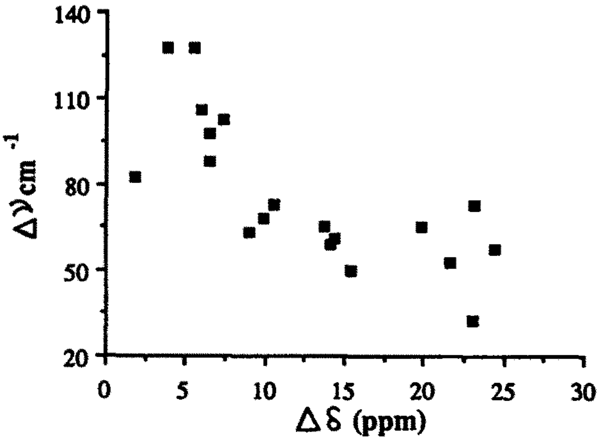


Fig. 20. Decrease in the IR carbonyl stretching frequency ($\Delta\gamma$) as a function of the downfield shift in the ^{13}C NMR resonances of the carbonyl α-carbon ($\Delta\delta$) for $AlMe_x(BHT)_{3-x}[O{=}C(X)Y']$.

[48]; the bulkier phosphines force the aluminum to become more distorted from planarity and the increased p character in the Al–C bond is reflected by the downfield shift of the Al–CH_3 carbon resonance [48]. As shown in Fig. 21, there is a similar dependence of the aluminum methyl ^{13}C shift on the steric bulk of the organic carbonyl for the complexes $AlMe_2(BHT)[O{=}C(X)Y]$ and $AlMe(BHT)_2[O{=}C(X)Y]$; that is, the greater the steric bulk of the α-carbon's substituents, the more downfield the shift of the methyl resonance. For simplicity the steric bulk of the organic carbonyls may be defined as the sum of their substituent's cone angles, as reported by Tolman, eqn. (28) [63].

$$\theta_{O=C(X)Y} \propto \theta_X + \theta_Y \qquad (28)$$

The aldehyde complexes are notable exceptions to the trends found for the ^{13}C NMR shifts for the Al–CH_3 groups in both $AlMe_2(BHT)[O{=}C(X)Y]$ and $AlMe(BHT)_2[O{=}C(X)Y]$ and therefore they are not included in the straight lines drawn in Fig. 21 [58]. From the ^{13}C NMR shift, it would appear that the aldehydes are sterically less hindered than their calculated values would suggest. Indeed, from Fig. 21, an effective cone angle between 140 and 150° can be estimated for all the aldehydes, which would correspond to that expected for $O{=}CH_2$, suggesting that the aldehyde complexes in solution retain the conformation observed in the solid state (see Fig. 15), in which the α-hydrogen is *syn* with respect to the aluminum [58]. This observation may be significant in the determination of the stereospecific nature of reactions of aldehydes coordinated to sterically-hindered aluminum Lewis acids.

(ii) Alkylation

The alkylation of organic carbonyls by aluminum alkyls (eqn. (29)) is undoubtedly the most common and best understood reaction pathway open to these reactants.

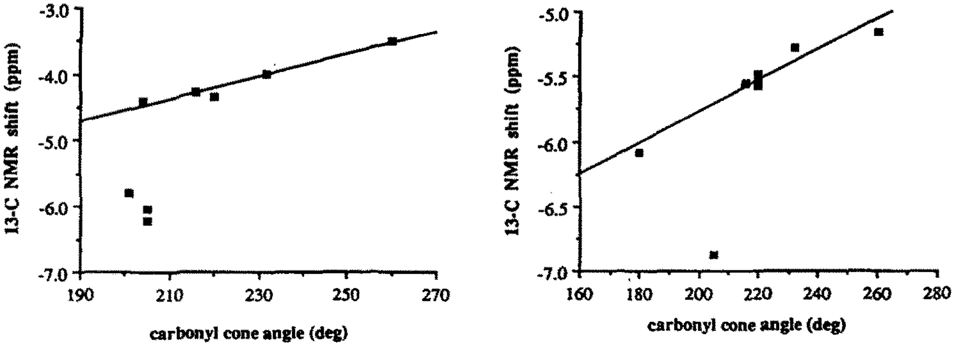
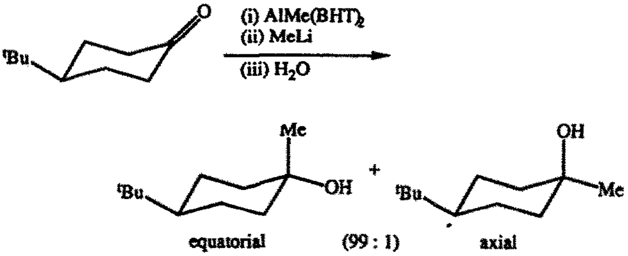


Fig. 21. Aluminum methyl ^{13}C NMR shift (d) as a function of the organic carbonyl ligands steric bulk (see text) for the complexes $AlMe(BHT)_2[O{=}C(X)Y]$ (a) and $AlMe_2(BHT)[O{=}C(X)Y]$ (b).

$$O{=}CR_2 \xrightarrow[(2)\ H_2O]{(1)\ AlR'_3} HOCR_2R' \qquad (29)$$

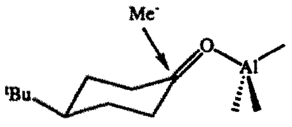
However, to date there have been no reports of alkylation occurring for any of the sterically hindered aryloxide compounds of aluminum. The reason for this lack of reactivity may be readily understood by a consideration of the reaction pathway. Ashby and co-workers [64] have proposed that the alkylation of ketones by $AlMe_3$ occurs via the dimeric cyclic transition state, i.e., Scheme 1. In the case of the BHT-substituted compounds, the steric bulk of the aryloxides and the ketones inhibits the formation of such an alkyl-bridged dimer, and thus alkyl transfer is procluded. It should be noted that alkyl transfer is observed for sterically less demanding aldehydes.

While intramolecular alkylation of ketones is not observed for the aryloxide compounds of aluminum, the stability of the Lewis acid-base complexes allows for regioselective control over intermolecular alkylation reactions. In this regard, Yamamoto and co-workers have reported that highly stereoselective equatorial (anti-Cram) alkylation of substituted cyclohexanones may be accomplished by the complexation of the ketone to $AlMe(BHT)_2$, with subsequent alkylation by an organolithium or magnesium reagent, e.g., eqn. (30) [65]; typical results are summarized in Table 5.



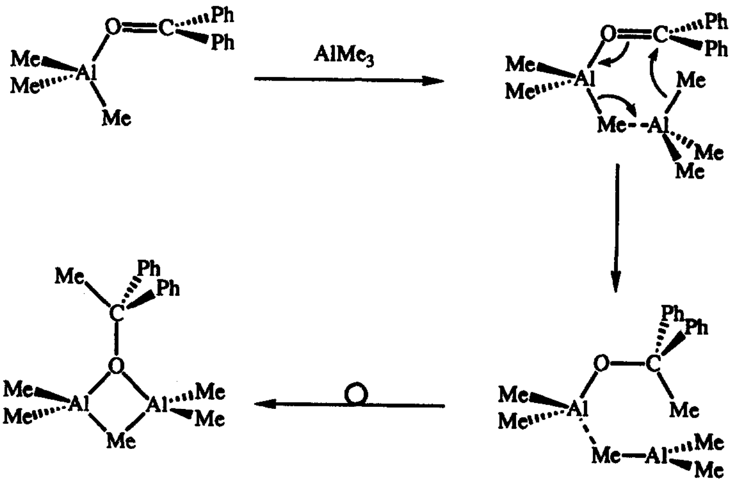
(30)

The high preference for alkyl addition to the equatorial diastereotopic π-face of the ketone was originally rationalized by postulating preferential complexation of $AlMe(BHT)_2$ to the opposing face of the ketone, i.e., **X** [65].



X

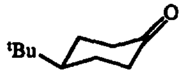
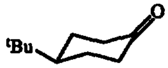
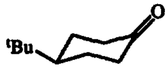
As discussed above, based upon ab initio calculations [60] and in comparison to experimentally determined structures [58,59], the preferred mode of complexation is in the π-nodal plane of the ketone. In this geometry, the aluminum methyl group would be eclipsed with respect to the ketone α-carbon in order to minimize steric repulsion. It is not apparent how this geometry would provide the experimentally observed stereoselectivity.



Scheme 1.

TABLE 5

Stereoselective alkylation of cyclohexanones[a,b]

Ketone	Nucleophile	Lewis acid	Ratio (ax/eq)[d]
	MeLi	None AlMe(BHT)$_2$ AlMe$_2$(BHT)[c]	79:21 1:99 5:95
	EtMgBr	None AlMe(BHT)$_2$	48:52 0:100
	BuMgBr	None AlMe(BHT)$_2$	6:44 0:100
	C$_3$H$_5$MgBr	None AlMe(BHT)$_2$	48:52 9:91
	MeLi	None AlMe(BHT)$_2$	92:8 7:93
	MeLi	None AlMe(BHT)$_2$	83:17 9:91

[a] K. Maruoka, T. Itoh and H. Yamamoto, J. Am. Chem. Soc. 107 (1985) 4573.
[b] Alkylation was carried out at −78°C using a ketone, nucleophile and Lewis acid in a 1:3:3 molar ratio.
[c] Not isolated, but formed by the addition of one molar equivalent of BHT-H to AlMe$_3$.
[d] See eqn. (30) for pictorial representation of axial and equitorial products.

On the basis of the structural data present on the carbonyl complexes of $AlMe(BHT)_2$, the stereoselectivity was explained in terms of the preferred orientation of the two aryloxide ligands [59]. The presence of two distinct aryloxide orientations can be clearly seen in Figs. 15, 17 and 19, resulting in steric protection of one face of the coordinated ketone ligand towards nucleophilic attack. Unfortunately, none of the $AlMe(BHT)_2$(ketone) complexes studied had two distinct faces, thus procluding direct confirmation that for a cyclohexanone the less bulky face of the ketone would be hindered by the *ortho*-tert butyl groups of one of the BHT ligands, leaving the sterically more demanding equatorial face open for alkylation. However, crystals of $Al(BHT)_3[O{=}C(C_5H_9)\text{-}4\text{-}{}^tBu]$ were grown suitable for X-ray crystallographic confirmation of such an effect [29]. The orientation of the aryloxide ligands with respect to the cyclohexanone may be clearly seen in Fig. 22. One of the *ortho*-tert-butyl groups for aryloxide, O(3), C(31), ... etc., is situated so as to provide steric protection of the axial face of the cyclohexanone, leaving the equatorial face open for external attack. This confirms that the mode of π-face selectivity of coordinated ketones is controlled by sterically hindered aryloxide compounds of aluminum [59].

The addition of ethereal MeLi to a pentane solution of the Lewis acid-base complex between a ketone and $AlMe(BHT)_2$ results in the alkylation of the coordinated ketone and the formation (in the absence of hydrolysis) of a dimetallic-heteronuclear complex (eqn. (31)) [59]. One example derived from the alkylation of benzophenone, has been characterized by X-ray crystallography (see Fig. 23) [59].

$$AlMe(BHT)_2(O{=}CR_2) + MeLi \xrightarrow[-Et_2O]{} AlMe(BHT)_2[OC(Me)R_2]Li(OEt_2) \qquad (31)$$

Although based upon the structure of this bimetallic compound a concerted aryloxide assisted alkyl addition may be proposed related studies (see below) suggest that the alkylation reaction is in fact radical in nature, and that the role of the aluminum Lewis acid is twofold. First, the steric bulk of the BHT ligands provides stereoselectivity (as described above) and, second, the coordination of the carbonyl to aluminum results in its chemical activation towards nucleophilic attack. Yamamoto and co-workers have applied this selectivity/activity duality to provide a route for the selective carbonyl alkylation of aldehydes in the presence of ketones [66].

In a typical reaction, an equimolar mixture of an aldehyde and a ketone were reacted with an alkyl lithium or Grignard reagent in the presence of $AlMe(BHT)_2$. In each case, the sterically less demanding aldehyde was activated with respect to alkylation in the absence of $AlMe(BHT)_2$, for example, reaction of a mixture of benzaldehyde and acetophenone with MeMgI results in the preferential alkylation of the aldehyde in the ratio of 22:1. This ratio is increased to 100:0 on addition of $AlMe(BHT)_2$. Perhaps more impressive is the chemoselectivity observed for polyfunctional molecules such as the keto-aldehyde **XI** (eqn. (32)) [66].

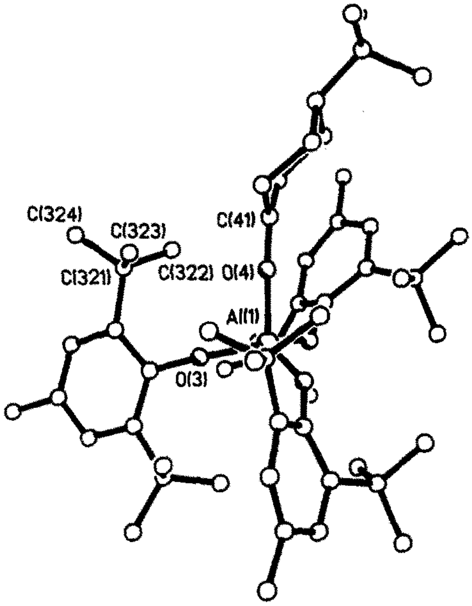


Fig. 22. Molecular structure of $Al(BHT)_3[O{=}C(C_5H_9)\text{-}4\text{-}^tBu]$, viewed parallel to the cyclohexanone ring, showing the steric inhibition to the carbonyl carbon C(41) by the *ortho*-tert-butyl group [C(322), C(323)] of one of the aryloxide ligands.

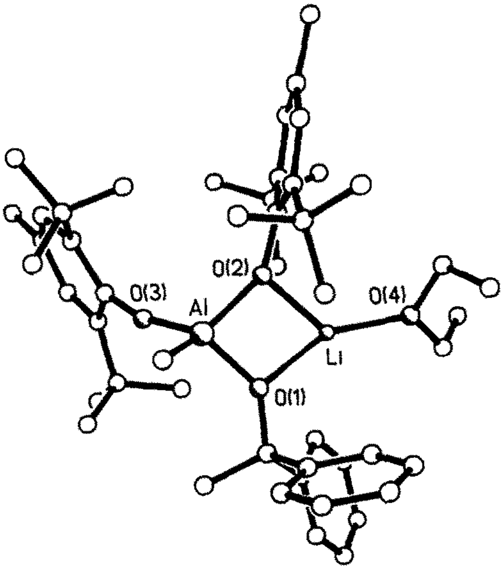
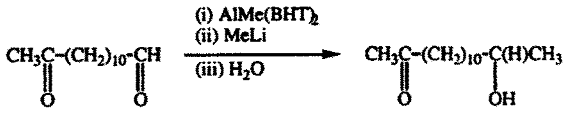


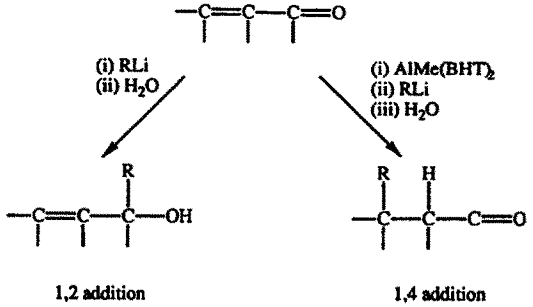
Fig. 23. The molecular structure of $AlMe(BHT)_2[OC(Me)Ph_2]Li(OEt_2)$.



XI 100%

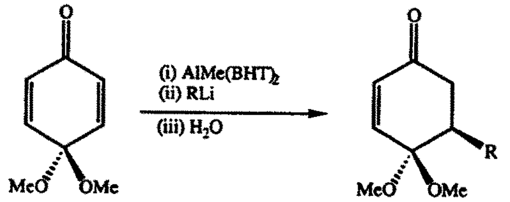
(32)

AlMe(BHT)$_2$ can also be used to promote a change in regioselectivity of alkyl additions to α,β-unsaturated ketones. Thus, 1,4-addition is observed upon alkyl lithium addition to α,β-unsaturated ketones in presence of AlMe(BHT)$_2$, while 1,2-addition is observed in the absence of AlMe(BHT)$_2$, e.g., eqn. (33) [67].

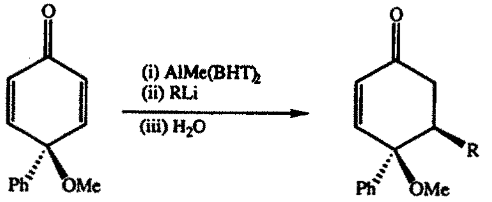


(33)

Swenton and co-workers have extended this concept to the regiospecific alkylation of quinone monoketals (eqn. (34)) and quinolethers (eqn. (35)) [68,69]. In the latter case, superb stereoselectivity as well as regioselectivity was observed.



(34)



(35)

(iii) Reduction

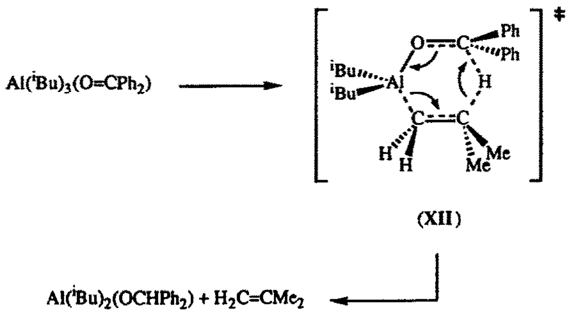
The reduction of an organic carbonyl by an aluminum alkyl group is conceptually simple: transfer of a β-hydride to give the aluminum alkoxide complex with concurrent loss of alkene. However, studies of this seemingly straightforward reaction are often complicated by competing alkylation reactions. For example, when using $AlEt_3$ as the aluminum source, both reduction of and alkyl addition to the carbonyl group occurs (eqn. (36)) [70].

$$O{=}CR_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } AlEt_3} HOC(H)R_2 + HOC(Et)R_2 \qquad (36)$$

These side reactions are readily negated by the use of branched alkyl derivatives, for example, the reaction of $Al(^iBu)_3$ with benzophenone results in the formation of only the reduction product, benzhydrol [70b,c]. This ability to confine exclusive reactivity to a single pathway through the choice of branched alkyl substituents enabled Ashby and Yu to perform a detailed mechanistic study of the reduction of ketones by aluminum alkyls, exclusive of the alkylation pathway [71]. Ketone reduction was proposed to involve a two step mechanism in which the first step involves a fast equilibrium to form a Lewis acid-base complex (eqn. (37)).

$$Al(^iBu)_3 + O{=}CPh_2 \rightleftharpoons Al(^iBu)_3(O{=}CPh_2) \qquad (37)$$

The second, rate-determining, step involves the transfer of the β-hydride to the ketone α-carbon (eqn. (38)) via a proposed six-membered transition state (**XII**) [71].



(XII)

(38)

The presence of aryloxide substituents on aluminum alkyls has been shown to result in the reduction of the reactivity of the Al–C bond (see above) [35]. As the cyclic six-membered transition state (**XII**), as proposed by Ashby [71], possibly involves partial Al–C bond cleavage, an interesting question arises: does the presence of aryloxide ligands on the aluminum effect the reactivity of the alkyl substituents towards the ketone reduction?

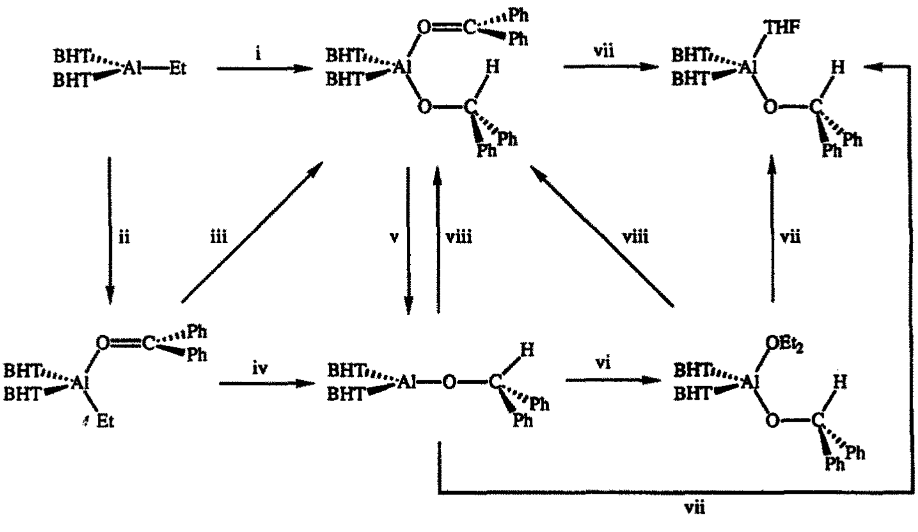
Interaction of $AlEt(BHT)_2$ with 1 equiv. of benzophenone, in pentane or benzene, results in the reduction of 1/2 an equivalent of the benzophenone and the formation of an equimolar mixture of $AlEt(BHT)_2$ and $Al(BHT)_2(OCHPh_2)(O{=}CPh_2)$, the latter is presumably formed as a result of the reduction of one coordinated benzophenone with the concomitant elimination of ethylene (eqn. (39)), followed by the subsequent coordination of a second ketone molecule (eqn. (40)) [49]. When the reaction is carried out with two equivalents of benzophenone, $Al(BHT)_2(OCHPh_2)(O{=}CPh_2)$ is the only product observed (Scheme 2(i)).

$$AlEt(BHT)_2 + O{=}CPh_2 \longrightarrow \text{“}Al(BHT)_2(OCHPh_2)\text{”} + C_2H_4 \tag{39}$$

$$\text{“}Al(BHT)_2(OCHPh_2)\text{”} + O{=}CPh_2 \longrightarrow Al(BHT)_2(OCHPh_2)(O{=}CPh_2) \tag{40}$$

The formation of an equimolar mixture of $Al(BHT)_2(OCHPh_2)(O{=}CPh_2)$ and $AlEt(BHT)_2$ from the interaction of the latter with one molar equivalent of benzophenone may be rationalized by a consideration of the equilibria present in solution, and an estimation of the appropriate bond dissociation energies [49].

The Lewis acid-base complex $AlEt(BHT)_2(O{=}CPh_2)$ may be isolated if $O{=}CPh_2$ is added to an Et_2O solution of $AlEt(BHT)_2$, in which the latter exists as the solvated complex, $AlEt(BHT)_2(OEt_2)$ (Scheme 2, path ii). Although indefinitely stable in Et_2O, $AlEt(BHT)_2(O{=}CPh_2)$ reacts either in the presence of excess $O{=}CPh_2$ to give $Al(BHT)_2(OCHPh_2)(O{=}CPh_2)$ (Scheme 2(iii)), or in benzene and pentane solutions to give an equimolar mixture of $Al(BHT)_2(OCHPh_2)(O{=}CPh_2)$ and $AlEt(BHT)_2$ (eqn. (41)) [49].



Scheme 2. Reagents and conditions: (i) $O{=}CPh_2$, 2 equiv., benzene or pentane; (ii) $O{=}CPh_2$, 1 equiv., Et_2O; (iii) $O{=}CPh_2$, benzene; (iv) hexane reflux; (v) $AlEt(BHT)_2$, hexane reflux; (vi) Et_2O; (vii) THF; (viii) $O{=}CPh_2$.

$$2AlEt(BHT)_2(O{=}CPh_2) \xrightarrow[\text{pentane or benzene}]{\Delta} AlEt(BHT)_2 + Al(BHT)(OCHPh_2)(O{=}CPh_2) + C_2H_4 \tag{41}$$

The isolation of $Al(Et)(BHT)_2(O{=}CPh_2)$ from an Et_2O solution of $AlEt(BHT)_2$ and $O{=}CPh_2$, but not when the reaction is carried out in pentane or benzene, may be explained by a consideration of the two concurrent equilibria occurring when $O{=}CPh_2$ reacts with $AlEt(BHT)_2$ in Et_2O solution [49]. One is due to the coordination of the solvent and a second to the coordination of benzophenone. The overall ligand exchange reaction thus takes the form shown in eqn. (42).

$$AlEt(BHT)_2(OEt_2) + O{=}CPh_2 \overset{K_{eq}}{\rightleftharpoons} AlEt(BHT)_2(O{=}CPh_2) + Et_2O \tag{42}$$

where

$$K_{eq} = \frac{[AlEt(BHT)_2(O{=}CPh_2)][Et_2O]}{[AlEt(BHT)_2(OEt_2)][O{=}CPh_2]} = \frac{K_1}{K_2} \tag{43}$$

Since the rate of benzophenone reduction is dependent on the concentration of the complex $AlEt(BHT)_2(O{=}CPh_2)$:

$$\text{Rate of } O{=}CPh_2 \text{ reduction} = k[AlEt(BHT)_2(O{=}CPh_2)] \tag{44}$$

and given eqn. (43):

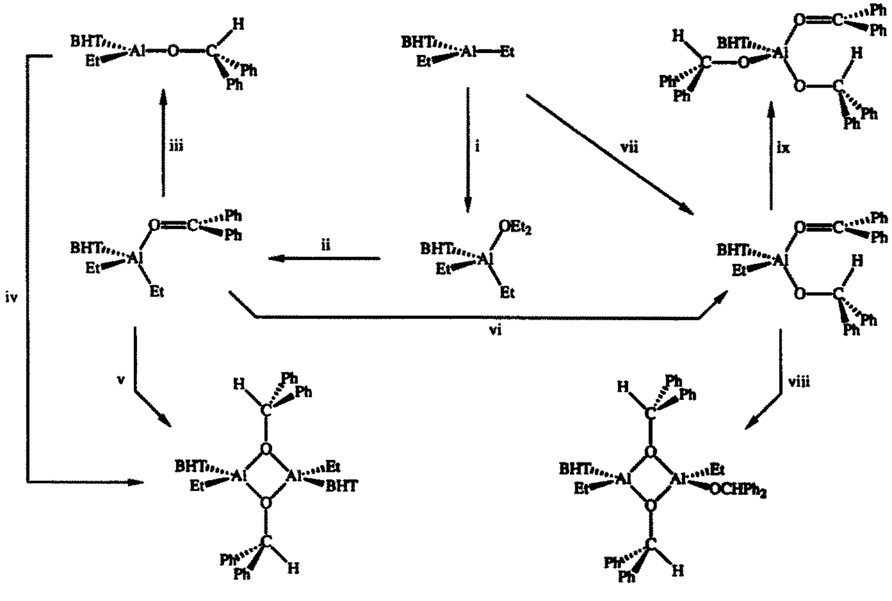
$$\text{Rate of } O{=}CPh_2 \text{ reduction} = k\left\{K_T \frac{[AlEt(BHT)_2(OEt_2)][O{=}CPh_2]}{[Et_2O]}\right\}$$

$$\text{Rate of } O{=}CPh_2 \text{ reduction} \propto \frac{1}{[Et_2O]} \tag{46}$$

Thus, when Et_2O, or any similar Lewis base is used as a solvent, the rate of benzophenone reduction becomes negligible, which enables the isolation of the Lewis acid-base adduct. Although a similar solvent dependence was observed in the rate of benzophenone reduction by $Al(^iBu)_3$, the complex $Al(^iBu)_3(O{=}CPh_2)$ could not be isolated, but was detected by UV-visible spectroscopy [71].

Thermolysis of a benzene solution of either $AlEt(BHT)_2(O{=}CPh_2)$ in the absence of excess benzophenone yields the alkoxide bis-aryloxide complex $Al(BHT)_2(OCHPh_2)$ as the only product (Scheme 2(iv)), which reacts readily with Et_2O, THF, or $O{=}CPh_2$ to give the respective Lewis acid-base complexes $Al(BHT)_2(OCHPh_2)(L)$, $L = Et_2O$, THF, $O{=}CPh_2$. The Et_2O ligand may be displaced by either THF or $O{=}CPh_2$ while THF displaces the coordinated O=CPh$_2$ (Scheme 2(vi–viii)). This ordering of affinities is consistent with the relative bond dissociation energies for the methyl AlMe(BHT)$_2$(L) complexes, i.e., OEt$_2$ < O=CPh$_2$ < THF (see above) [49].

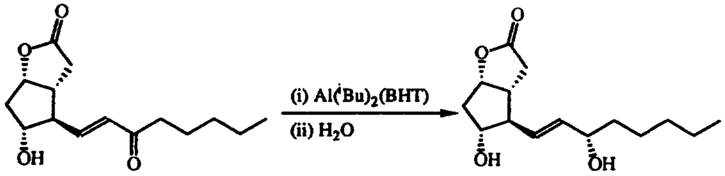
The reaction of AlEt$_2$(BHT)(OEt$_2$) with benzophenone in pentane yields the expected Lewis acid-base complex, AlEt$_2$(BHT)(O=CPh$_2$) (Scheme 3, path ii), which can be thermolyzed in the solid state to liberate ethylene and give the monomeric compound AlEt(BHT)(OCHPh$_2$) (Scheme 3(iii)) which rapidly dimerizes in solution (Et$_2$O, THF, benzene, or pentane) to give a product identified as the dimeric compound [AlEt(BHT)(μ-OCHPh$_2$)]$_2$ (Scheme 3, path iv). In the presence of excess benzophenone, AlEt$_2$(BHT)(O=CPh$_2$) undergoes reduction of the coordinated ketone losing ethylene, and subsequent coordination of a second molecule of benzophenone to give the monomeric complex AlEt(BHT)(OCHPh$_2$)(O=CPh$_2$) (Scheme 3, path vi) [49]. Thermolysis of AlEt(BHT) (OCHPh$_2$)(O=CPh$_2$) in hexane does not result in the reduction of the second benzophenone but in a disproportionation to give a moderate yield of the asymmetric dimer Et(BHT)Al(μ-OCHPh$_2$)$_2$AlEt(OCHPh$_2$) (Scheme 3, path viii), which contains both bridging and terminal diphenylmethoxy groups. In contrast, the thermolysis of AlEt(BHT)(OCHPh$_2$)(O=CPh$_2$) in the presence of excess benzophenone does result in the reduction of a second equivalent of benzophenone and the formation of the monomeric Al(BHT)(OCHPh$_2$)$_2$(O=CPh$_2$) (Scheme 3, path ix) [49].



Scheme 3. Reagents and conditions: (i) Et$_2$O; (ii) O=CPh$_2$; (iii) 90°C, no solvent; (iv) Et$_2$O or benzene; (v) 80°C, benzene; (vi) O=CPh$_2$, benzene; (vii) 2O=CPh$_2$, benzene; (viii) hexane reflux; (ix) >35°C, O=CPh$_2$, toluene.

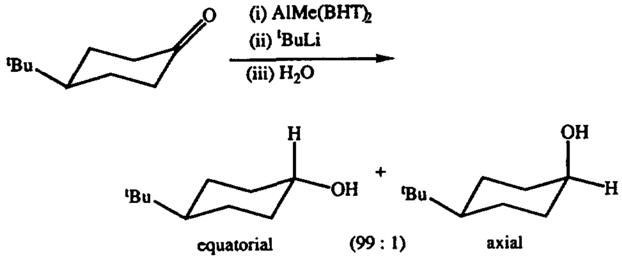
The kinetics of the reduction reactions shown in Scheme 2(iii) and Scheme 3(ix) were studied by ^{1}H NMR spectroscopy. The enthalpy of activation for the reduction of benzophenone by both AlEt(BHT)$_2$ (87.0 kJ mol^{-1}) and AlEt(BHT)(OCHPh$_2$) (102.8 kJ mol^{-1}) [49] are larger than that determined for the analogous reduction by Al(^{i}Bu)$_3$ (66.1 kJ mol^{-1}) [71]. Thus, it is clear that the presence of aryloxide and/or alkoxide ligands does indeed have a considerable effect on the energetics of the reduction reaction. However, based on these data, it is unclear whether this is steric, or electronic or both, in origin.

Despite the steric bulk of the aryloxide ligands, the reduction of benzophenone using AlEt(BHT)$_2$ or AlEt$_2$(BHT) is too complex to enable these aluminum complexes to be employed in organic synthesis. However, Yamamoto and co-workers [72] have demonstrated that Al(^{i}Bu)$_2$(BHT) is a highly stereoselective reducing agent with direct applicability in an important step in prostaglandin synthesis, i.e., eqn. (47).



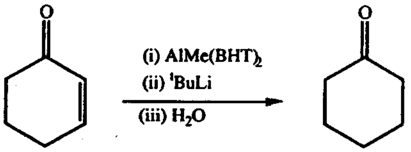
(47)

The stereo or regioselective reduction of ketones and enones may also be carried out employing a similar methodology to that discussed above for their alkylation in the presence of AlMe(BHT)$_2$. If either ^{t}BuLi [59] or ^{t}BuMgCl [65b] are added to a solution of AlMe(BHT)$_2$ and a substituted cyclohexanone, stereoselective reduction occurs, e.g., eqn. (48).



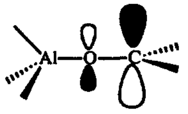
(48)

The use of a cyclohexenone as a substrate results in the preferential reduction of the olefinic residue not the ketone (eqn. (49)) [73].



(49)

The observation of identical stereoselective reduction of ketones using lithium metal (in place of ${}^tBuLi$) in concert with $AlMe(BHT)_2$ provides a useful insight to the mechanism of the Lewis acid assisted ketone reduction. The most plausible mechanism involves electron transfer from Li to the LUMO of the coordinated ketone, which is the carbon-centered carbonyl π^* orbital (XIII) [59].

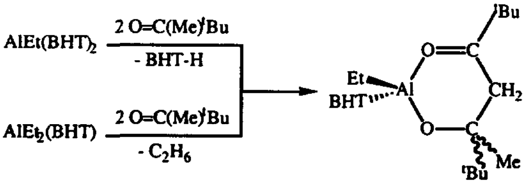


XIII

The resulting radical anion abstracts a hydrogen from the solvent to give the alkoxide complex, which is then hydrolyzed to give the alcohol. In the absence of $AlMe(BHT)_2$, no reaction is observed between Li metal and substituted-cyclohexanones, indicating that the aluminum activates the ketone towards reaction. Conformation of this is obtained from cyclovoltametric studies. The reduction potential of any given ketone is found to be reduced by up to 1 V upon complexation of the ketone to $AlMe(BHT)_2$ [74], thus it is apparent that the LUMO (carbonyl π^*) orbital is lowered upon complexation of a ketone to $AlMe(BHT)_2$ making it accessible for electron transfer from Li metal or an organolithium or Grignard reagent [59,65b]. The similarity of the stereoselectivity for ketone reduction and alkylation (see Section F(ii)) suggests that the latter also occurs via a one-electron-transfer mechanism [59].

(iv) Aldol condensation

Interaction of $AlEt(BHT)_2$ with 1 equiv. of $O{=}C(Me){}^tBu$ results in an equimolar mixture of $AlEt(BHT)_2$ and $AlEt(BHT)[O{=}C({}^tBu)CH_2C(Me)({}^tBu)O]$. If, however, the reaction is carried out with 2 equivalents of pinacolone the aluminum-β-oxo enolate is the only product observed in addition to 1 equiv. of BHT-H (eqn. (50)). The oxoenolate is also formed from the reaction of $AlEt_2(BHT)(OEt_2)$ with 2 equiv. of $O{=}C(Me){}^tBu$, presumably via the loss of ethane in place of BHT-H (eqn. (50)) [75].



(50)

The ${}^1H$ and ${}^{13}C$ NMR spectra of the aluminum-β-oxo enolate compound are consistent with the presence of two distinct isomers in a 2:1 ratio. The relative ratio is independent of the synthetic route. The molecular structures of the two isomers as determined by X-ray crystallography are shown in Fig. 24 [75].

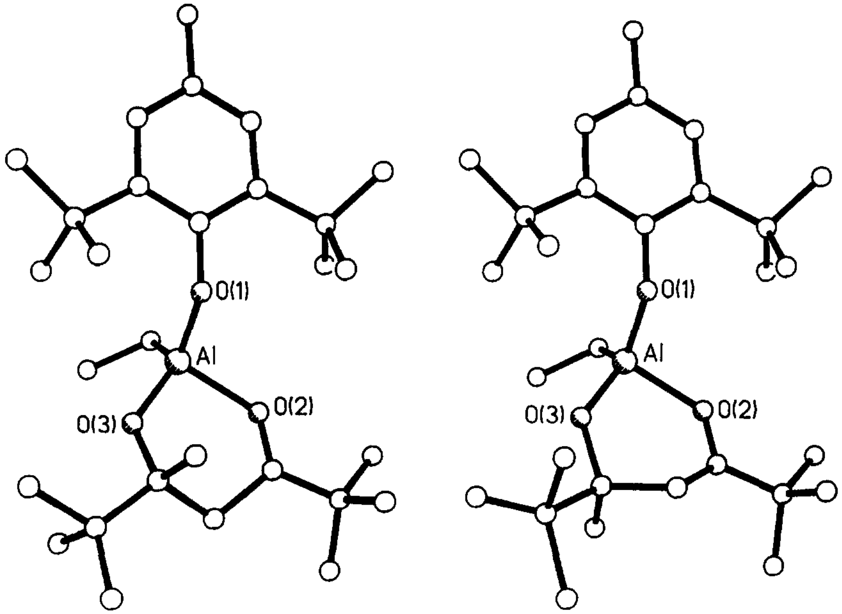
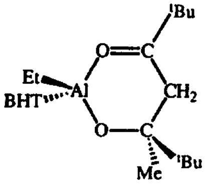
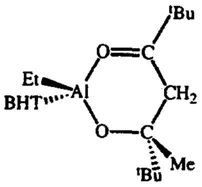


Fig. 24. Structures of the two isomers of $\overline{\text{AlEt(BHT)[O=C(}^t\text{Bu)CH}_2\text{C(Me)(}^t\text{Bu)O}}]$.

Based upon NOE experiments, the major isomer was determined to be the isomer in which the aluminum ethyl group is *cis* with respect to the alkoxide tert-butyl group of the oxo enolate, i.e., **XIV**, rather than **XV** [75].



XIV

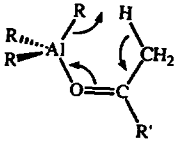


XV

The presence of two isomers formed from the enolization-condensation reaction with $O{=}C(Me)^tBu$ indicates that the condensation reaction is non-stereospecific. In an effort to determine the stereospecificity of the enolization, the reaction of $AlEt(BHT)_2$ with $O{=}C(Et)Ph$ and $O{=}CEt_2$ was investigated.

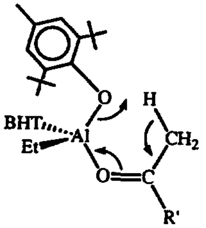
The reaction of $AlEt(BHT)_2$ or $AlEt_2(BHT)(OEt_2)$ with 2 equiv. of $O{=}C(Et)Ph$ yields the β-oxo enolate complex $\overline{\text{AlEt(BHT)[O=C(Ph)CH(Me)C(Et)(Ph)O}}]$. The ^1H and ^{13}C NMR spectra indicated the presence of a single isomer, in which the BHT and ring methyl and phenyl groups are therefore mutually *cis*. Both the enolization and condensation of O=C(Et)Ph are therefore stereospecific, as demonstrated by the presence of a single conformation at the central and alkoxide carbons of the oxo enolate. In contrast, the reaction of $AlEt(BHT)_2$ with a symmetric ketone, $O=CEt_2$, results in the formation of two isomers, arising from the nonstereospecific enolization of the ketone [75].

The accepted mechanism for the enolization of ketones by aluminum alkyls involves a six-membered transition state (**XVI**) with the concurrent loss of alkane [76].



XVI

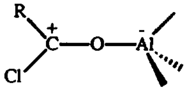
The reaction of $AlEt_2(BHT)$ with ketones likely occurs via a similar mechanism, whereby the ethyl group acts as an intramolecular base to assist in the enolization of the coordinated ketone [75]. In direct contrast to this usual mechanism is the enolization of ketones by $AlEt(BHT)_2$, in which one of the coordinated aryloxides is lost as the phenol, BHT-H. This reaction occurs via a unique intramolecular alkoxide-assisted enolization in which BHT acts as the base (**XVII**) [75].



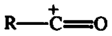
XVII

(v) Acylation and esterification

The interaction of acyl chlorides, O=C(Cl)R, with aluminum chloride, $AlCl_3$, results in the formation of an addition complex for which two structures are commonly proposed. Although structure **XVIII** was first suggested by Pfeiffer [77] upon noting that the addition compounds of aluminum halides with acid halides are similar to the addition compounds formed with ketones, ethers and other oxygen donor compounds, it was structure **XIX**, proposed by Meerwein [78] that was accepted for many years. Structural and spectroscopic investigations have now confirmed that both are indeed correct, that is, in some instances the compounds exist as acylium salts (**XIX**) and in others the aluminum is bonded to the carbonyl oxygen (**XVIII**) [79].



XVIII



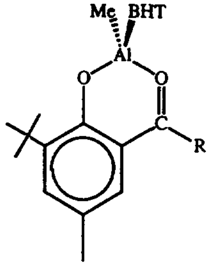
$R{-}\overset{+}{C}{\equiv}O$

XIX

In fact, mixtures are sometimes obtained. The distribution is dependent on whether the material is in the solid state or in solution, and even on the nature of the solvent [80]. In contrast, the interaction of acyl halides with organoaluminum compounds has been reported to result in alkyl-halide exchange (eqn. (51)).

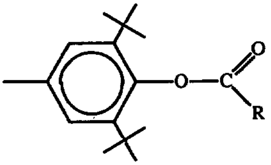
$$O{=}C(Cl)R + R'AlCl_2 \rightarrow AlCl_3[O{=}C(R')R] \tag{51}$$

The interaction of $AlMe(BHT)_2$, with $O{=}C(Cl)R$ (R = Me, Et, ^{i}Pr and Ph) results in the Friedel–Craft acylation of one of the aryloxide ligands, with concurrent elimination of ^{t}BuCl, to give the 3-tert-butyl-2-hydroxy-5-methylacetophenone-substituted products, **XX** [82].



R = Me, Et, ^{i}Pr, Ph

XX



XXI R = Me, Et, ^{i}Pr, ^{t}Bu

XXI

The molecular structure of the methyl derivative has been determined by X-ray diffraction (Fig. 25) [82]. While the acylation reaction is the major pathway, a side product may also be isolated from the reaction mixture in ca. 5% yield. Based upon NMR spectroscopy and mass spectrometry, this product is determined to be the ester, $O{=}C(BHT)R$ (**XXI**) [82]. The ratio of the ester to the acylation product increased with the increasing steric bulk of the alkyl substituent, R, i.e., Me < Et, ^{i}Pr. In fact, when the steric bulk of the alkyl substituent is sufficiently large, i.e., ^{t}Bu, then no acylation of the aryloxide ligand is observed.

In the reaction described above, as with any mechanistic discussion of Friedel–Craft acylation there is a dilemma as to whether the effective electrophile is the acylium ion **XIX** or a polarized complex **XVIII**. Although no direct evidence is available for either structure, the presence of a steric effect on the ratio of acylation versus esterification products, and the use of a non-polar solvent, suggests that a polarized complex **XVIII** is the more likely intermediate [82].

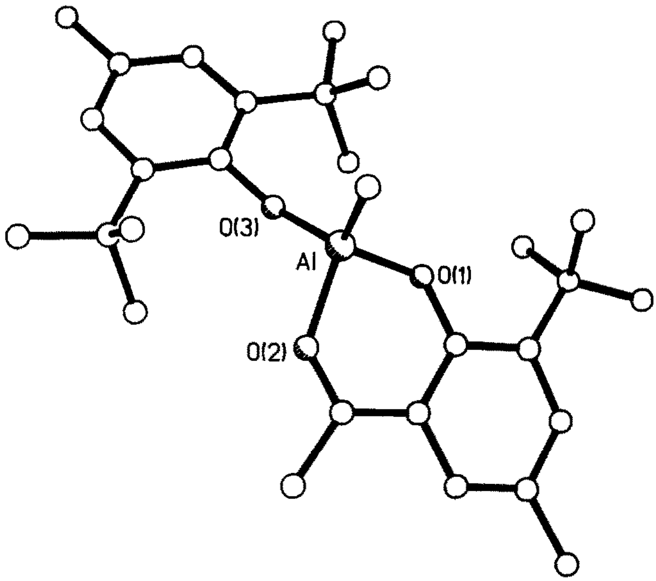


Fig. 25. Molecular structure of AlMe(BHT){OC_6H_2–3(^{t}Bu)[C(O)Me]-5-Me}.

The significant difference in reactivity between O=C(Cl)R (R = Me, Et, ^{i}Pr or Ph) and O=C(Cl)^{t}Bu is that the steric bulk of the electrophile in the latter is sufficient to inhibit completely electrophilic attack at the tert-butyl substituted *ortho*-carbons, and thus acylation does not occur. Instead electrophilic attack occurs at the BHT oxygen resulting in aryloxide substitution (eqn. (52)) [82].

$$AlMe(BHT)_2 + O{=}C(Cl)^tBu \rightarrow AlMe(Cl)(BHT) + O{=}C(BHT)^tBu \tag{52}$$

The subsequent reaction of the resulting alkyl chloride, AlMe(Cl)(BHT), with a second equivalent of O=C(Cl)^{t}Bu gives the dichloro compound, $AlCl_2$(BHT), which complexes with the O=C(Me)^{t}Bu produced (eqn. (53)) [82].

$$AlMe(Cl)(BHT) + O{=}C(Cl)^tBu \rightarrow AlCl_2(BHT)[O{=}C(Me)^tBu] \tag{53}$$

The ester formation reaction (eqn. (52)) can also be described as nucleophilic attack on the coordinated acyl chloride by the oxygen lone pair of BHT.

(vi) Aldehyde to ketone transformation

Treatment of benzaldehyde with 1:5 molar equivalents of $AlMe_2(BHT)(OEt_2)$ [34] gives, after hydrolysis, acetophenone in quantitative yield (eqn. (54)) [83,84]. Listed in Table 6 are the yields and reaction times for benzaldehyde and substituted benzaldehydes, as well as the effects of varying the aldehyde to aluminum ratio.

$$\mathrm{O{=}C(H)R} \xrightarrow[\text{(ii) } \mathrm{H_2O}]{\text{(i) } \mathrm{AlMe_2(BHT)(OEt_2)}} \mathrm{O{=}C(Me)R} \tag{54}$$

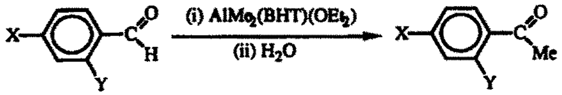
The initial step of this unique aldehyde to ketone conversion is undoubtedly the substitution of Et_2O resulting in the formation of the aldehyde complex. If the reaction is carried out in pentane, some of the aldehyde adducts have limited solubility and can be isolated quantitatively for $O{=}C(H)C_6H_4$-*p*-Me and $O{=}C(H)C_6H_4$-*p*-Cl [58]. The resulting complexes $AlMe_2(BHT)[O{=}C(H)C_6H_4$-*p*-Me] and $AlMe_2(BHT)[O{=}C(H)C_6H_4$-*p*-Cl] are stable as solids but slowly decompose in benzene, toluene or ether solution to give the corresponding methylketone complexes.

Based on (a) the required stoichiometry for the reaction (clearly from Table 5 a minimum of 1.5 equiv. of $AlMe_2(BHT)(OEt_2)$ is required for the reaction to proceed to completion), (b) literature precedent for the alkylation of organic carbonyls by $AlMe_3$, and (c) the presence of a transient species with a OCH(Me)R ligand and a possible bridging methyl, the mechanism shown in Scheme 4 has been proposed [84]. One molecule of $AlMe_2(BHT)(OEt_2)$ is required for the coordination of the aldehyde, while a second equivalent of $AlMe_2(BHT)(OEt_2)$ acts as the methyl source for two aldehyde to ketone conversions.

The rate-controlling step in the alkylation of ketones by trimethylaluminum (Scheme 1) is the attack of monomeric $AlMe_3$ on the complex $AlMe_3(O{=}CR_2)$ [64]. If this holds true for the reaction in Scheme 4, then the only assumption to be made is that the rotation of the oxygen–carbon single bond must be rapid in comparison to the rate of dissociation of the methyl bridged dimer. This is certainly plausible, given the activation

TABLE 6

Aldehyde to methyl ketone conversion[a]

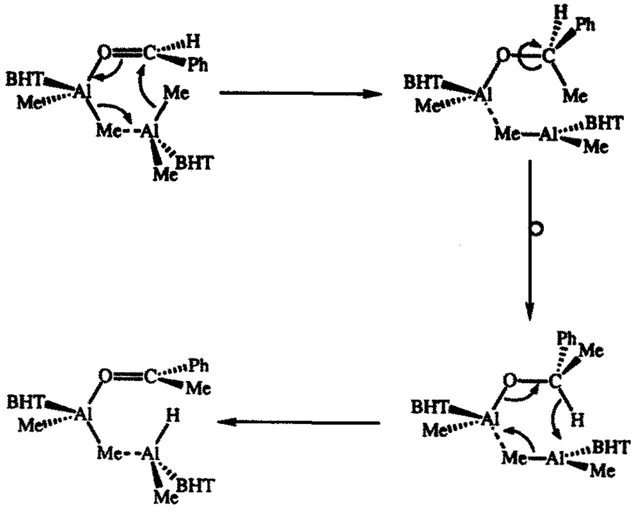


X	Y	$AlMe_2(BHT)(OEt_2)$:aldehyde	Time	% Yield[b]
H	H	1	1.5 h	72[c]
H	H	1.5	1.5 h	100
H	H	2	1 h	100
Me	H	1.5	1.5 h	100
H	Me	1.5	12 h	57[c]
Cl	H	1.5	45 min	100
NO_2	H	1.5	30 min	100

[a] M.B. Power and A.R. Barron, Tetrahedron Lett, 31(1990) 323.

[b] As determined by GC by comparison with authentic samples.

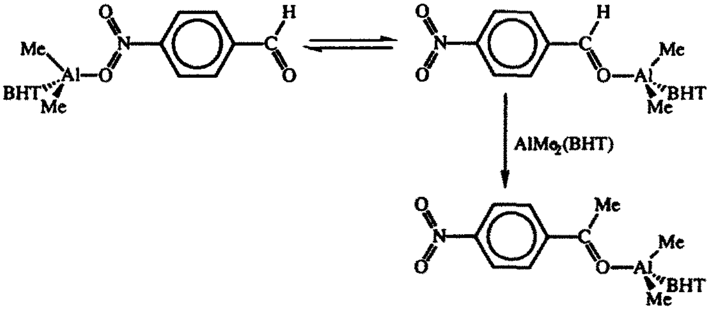
[c] Unreacted aldehyde the only other product observed.



Scheme 4.

energies of these processes can be estimated to be 3–8 and 11–15 kcal mol^{-1}, respectively [85]. If this proposed mechanism is correct, then the presence of electron-withdrawing substituents on the aldehyde should enhance the initial nucleophilic addition of methyl to the aldehyde, and this is indeed observed. Similarly, the opposite electronic effect should be present, i.e., electron-donating substituents should inhibit the reaction. In fact the addition of $O{=}C(H)C_6H_4$-*p*-OMe to a benzene solution of $AlMe_2(BHT)(OEt_2)$ results in the formation of the deep orange complex $AlMe_2(BHT)[O{=}C(H)C_6H_4$-*p*-OMe] which does not react further and is stable in refluxing toluene [58].

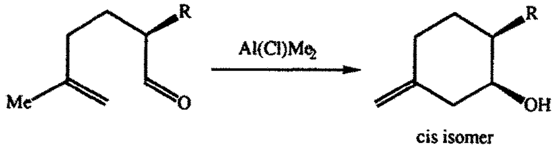
During the course of the conversion of $O{=}C(H)C_6H_4$-*p*-NO_2 to $O{=}C(Me)C_6H_4$-*p*-NO_2, the reaction solution changes from an initial deep blue to a dark brown of the ketone complex. In light of the isolation of the stable Lewis acid-base complex AlMe $(BHT)_2(O_2NC_6H_4$-*p*-Me) [58], it is likely that $O{=}C(H)C_6H_4$-*p*-NO_2 initially coordinates via a nitro oxygen to give the observed deep blue complex. This subsequently rearranges to, or is in equilibrium with, the aldehyde complex (eqn. (55)). The latter is rapidly converted to the ketone complex via the reaction discussed above.



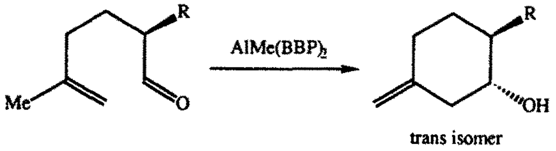
(55)

(vii) Ene reaction of δ,ε-unsaturated aldehydes

The Lewis acid promoted ene isomerization of unsaturated carbonyl compounds is a valuable route to the stereoselective synthesis of highly functionalized cyclic compounds [86]. Among these, type II intramolecular ene reactions of δ,ε-unsaturated aldehydes with α-substituents were reported to furnish *cis*-methylenecyclohexanols with high selectivity with non-sterically demanding Lewis acids (eqn. (56)). However, the use of $AlMe(BBP)_2$ results in an unprecedented stereochemical control, and the preferential formation of the *trans* isomer (eqn. (57)) [87].

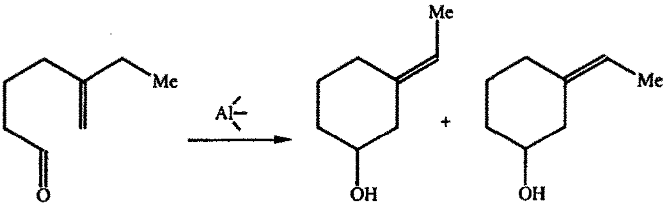


(56)



(57)

Another interesting feature of this chemistry is the remote stereochemical control imparted by $AlMe(BBP)_2$ as compared to non-sterically hindered Lewis acids such as $Al(Cl)Me_2$ (eqn. (58)) [87].



(58)

$Al(Cl)Me_2$ (88 : 12)

$AlMe(BBP)_2$ (100 : 0)

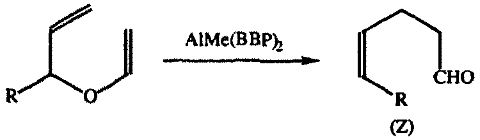
(viii) Miscellaneous

(a) Ethers

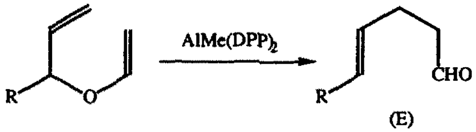
While simple dialkyl ether ligands readily coordinate to the mono- and bis-aryloxide compounds to form the stable Lewis acid-base complex (see Sections E(i),(ii)) [34], alkyl vinyl ethers readily undergo a Claisen rearrangement upon coordination [88].

The reaction of alkyl vinyl ethers with either $AlMe(BBP)_2$ or $AlMe(DPP)_2$ (DPP-H = diphenylphenol, see Fig. 1) results in clean generation of the appropriate alkyl-4-

octenal [88]. There is, however, distinct stereochemical control in the isomer produced upon the identity of the aryloxide ligand. The 4-bromo-2,6-di-tert-butylphenoxide compound shows a preference for the *Z* isomer (*E*/*Z* ≈ 1:9) (eqn. (59)). Although the origin of the high *E* selectivity with AlMe(DPP)$_2$ (eqn. (60)) is unclear, it is likely that a combination of steric and electronic factors are important [88].



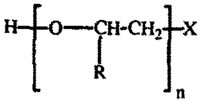
(59)



(60)

(b) Epoxides

Bifunctional oligoethers (**XXII**) have been prepared by the polymerization of epoxides using aluminum alkyl initiators, e.g., Al(Cl)Et$_2$ or aluminum Schiff base complexes [89].



$$H\left[O-\underset{R}{\underset{|}{CH}}-CH_2\right]_n X$$

X = Cl, OH, R'
R = alkyl, aryl
n < 10

XXII

While these initiators provide stereoselective polymers, the rates of polymerization are low; reactions to give the nonamer require over 110 h at 60°C. By contrast, AlMe$_2$(BHT)(L) (L = phosphine, amine) act as highly efficient polymerization catalysts; alkyl terminated dodecamers being formed within 12 h at 60°C [90]. No details of the stereoselectivity of the BHT based initiators are available as yet.

No or little polymerization is observed for epoxides with the bis-aryloxide compounds, however, epoxy silyl ethers are readily converted to β-siloxy aldehydes by AlMe(BHT)$_2$ or AlMe(BBP) (eqn. (61)) [91].

(61)

G. REACTIONS WITH MAIN GROUP CHLORIDES

The halodealumination of organoaluminum compounds by main group halides (eqn. (62)) is a class of reaction of industrial significance [36].

$$MX_n \xrightarrow[-AlXR_2]{AlR_3} MX_{n-1}R \xrightarrow{(n-1)AlR_3} MR_n \qquad (62)$$

The method has been successful for the preparation of organo-compounds of among others, zinc [92], mercury [93], boron [94], gallium [95], germanium [96], tin [97] and lead [98]. The aluminum alkyl chloride co-product formed often has commercial value. For example, $AlClEt_2$, formed in the preparation of $ZnEt_2$ (eqn. (63)) is recovered and sold as a Ziegler catalyst component.

$$2AlEt_3 + ZnCl_2 \rightarrow ZnEt_2 + 2AlClEt_2 \qquad (63)$$

Additionally, the reaction of $AlCl_3$ with aluminum alkyls has been employed in the synthesis of many alkylaluminum chlorides [99].

(i) Group 14 chlorides

The interaction of Me_3SnCl with either $AlMe(BHT)_2$ or $AlEt(BHT)_2$, in pentane, results in the rapid precipitation of the base free monochloride $AlCl(BHT)_2$ (eqn. (64)) [100].

$$AlR(BHT)_2 + Me_3SnCl \xrightarrow[R = Me, Et]{} AlCl(BHT)_2 + Me_3SnR \qquad (64)$$

The monochloride is very unstable and decomposes, even under an inert atmosphere in the solid state. However, addition of Et_2O to $AlCl(BHT)_2$ allows for the isolation of the Lewis acid-base complex, $AlCl(BHT)_2(OEt_2)$, which is stable in the solid state, under an inert atmosphere, for a period of weeks. $AlCl(BHT)_2(OEt_2)$ is also formed from the reaction of $SnCl_2$ with 1 equiv. of $AlR(BHT)_2$ (R = Me, Et) in Et_2O (eqn. (65)) [100].

$$AlR(BHT)_2 + SnCl_2 \xrightarrow[Et_2O]{} AlCl(BHT)_2(OEt_2) + \text{tin-containing products} \qquad (65)$$

The reaction of 1 equiv. of Me_3SnCl with $AlR_2(BHT)(OEt_2)$ in pentane leads to $AlClR(BHT)(OEt_2)$, R = Me, Et in good yield (eqn. (66)) [100]. N.B. $AlClMe(BHT)(OEt_2)$ is also formed from the reaction of BHT-H with $AlMe_2Cl$ in Et_2O (eqn. (67)).

$$AlR_2(BHT)(OEt_2) + Me_3SnCl \xrightarrow[R = Me, Et]{} AlClR(BHT)(OEt_2) + Me_3SnR \qquad (66)$$

$$AlMe_2Cl + BHT\text{-}H \xrightarrow[Et_2O]{} AlClMe(BHT)(OEt_2) + MeH \tag{67}$$

Use of 2 equiv. of Me_3SnCl leads in high yield to the dichloride compound, $AlCl_2(BHT)(OEt_2)$, the structure of which has been determined by X-ray crystallography (Fig. 26) (eqn. (68)) [100].

$$AlR_2(BHT)(OEt_2) + 2Me_3SnCl \rightarrow AlCl_2(BHT)(OEt_2) + 2Me_3SnR \tag{68}$$

The mono-BHT compounds are significantly more stable than their corresponding bis-BHT derivatives since, once they are isolated, they may be stored under an inert atmosphere at room temperature indefinitely.

(ii) Group 13 chlorides

The reaction of $AlMe(BHT)_2$ with one molar equivalent of BCl_3 in pentane/hexane mixture does not result in halodealumination as may be expected, but aryloxide-halide exchange (eqn. (69) [100]. Although there are no examples reported of BHT acting as a bridging ligand between two Group 13 elements, such a species, i.e., Al(μ-BHT)B, is clearly implicated in eqn. (69).

$$AlMe(BHT)_2 + BCl_3 \rightarrow \tfrac{1}{2}[Al(\mu\text{-}Cl)Me(BHT)] + BCl_2(BHT) \tag{69}$$

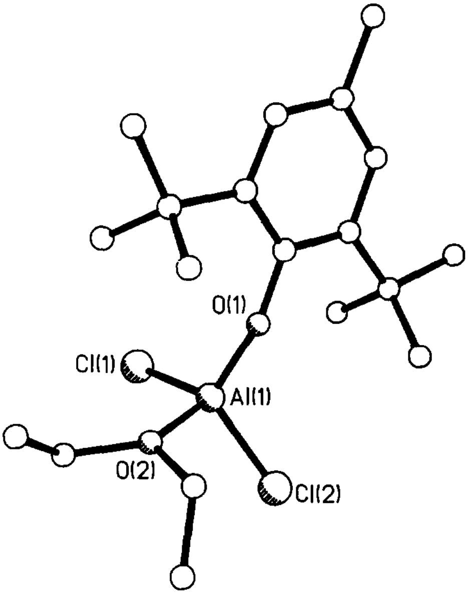
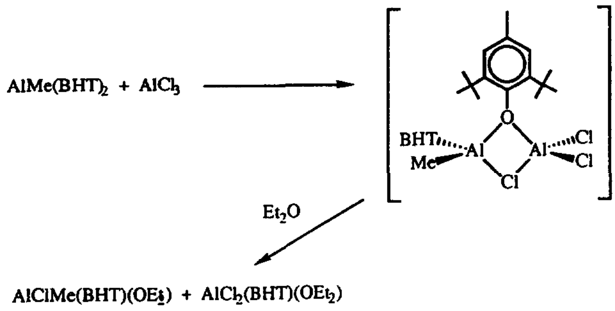


Fig. 26. The molecular structure of $AlCl_2(BHT)(OEt_2)$.

A more convenient synthesis of $[Al(\mu\text{-}Cl)Me(BHT)]_2$ is the reaction of $AlMe_2Cl$ with BHT-H (eqn. (70)) [24]. Based on molecular weight measurements, $[Al(\mu\text{-}Cl)Me(BHT)]_2$ was proposed to be dimeric in solution [24], however, X-ray crystallography analysis has since confirmed that, in the solid state, it does indeed exist as a chloride bridged dimer (Fig. 27) [100].

$$AlMe_2Cl + BHT\text{-}H \rightarrow \tfrac{1}{2}[Al(\mu\text{-}Cl)Me(BHT)]_2 + MeH \qquad (70)$$

The reaction of $AlMe(BHT)_2$ with $AlCl_3$ is highly solvent dependent. Reaction of $AlMe(BHT)_2$ with 1 equiv. of $AlCl_3$ in pentane leads to a complex mixture of products including a large quantity of BHT-H, indicative of decomposition. In Et_2O, this reaction also yields multiple products, however, from ^1H NMR compounds $AlClMe(BHT)(OEt_2)$ and $AlCl_2(BHT)(OEt_2)$ were determined to be the major constituents [100]. The pathway for the formation of these compounds is probably similar to that for BCl_3 with $AlMe(BHT)_2$, i.e., chloride/aryloxide ligand exchange, via an asymmetric dimer (eqn. (71)) [100]. N.B. Dimeric aluminum compounds with unlike bridging groups were first observed by Mole et al. [101].



(71)

Reaction of $AlMe(BHT)_2$ with $AlCl_3$ in CH_2Cl_2 at room temperature, leads, over the course of 12 h, to a light brown solution. Hydrolysis of the reaction mixture with

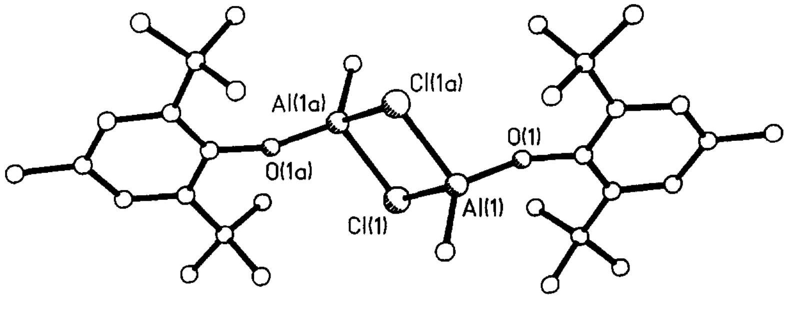
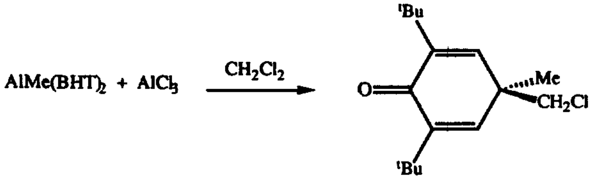


Fig. 27. The molecular structure of $[Al(\mu\text{-}Cl)Me(BHT)]_2$.

HCl/H_2O, extraction with Et_2O, followed by either crystallization from pentane, or vacuum sublimation, affords a single product (eqn. (72)) [100].



(72)

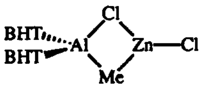
The stoichiometric nature of the reaction (eqn. (72)) is such that complete conversion of the BHT ligands in $AlMe(BHT)_2$ to the enone occurs with ca. 0.8 equiv. of $AlCl_3$. The source of the chloromethyl group was confirmed as the CH_2Cl_2 solvent, by carrying the reaction out in CD_2Cl_2, and isolating the appropriately deuterated product [100].

The reaction of $AlR(BHT)_2$ (R = Me, Et) with 1 equiv. of $InCl_3$ in Et_2O leads to the formation of $AlCl(BHT)_2(OEt_2)$ in high yield. While the reaction of $AlMe(BHT)_2$ in MeCN yielded the complex $AlCl(BHT)_2(NCMe)$ (eqn. (73)) [100].

$$AlMe(BHT)_2 + InCl_3 \rightarrow AlCl(BHT)_2(NCMe) + \text{indium containing products} \qquad (73)$$

(iii) Group 12 chlorides

The reaction of $AlMe(BHT)_2$ with $ZnCl_2$ in Et_2O is slow, resulting in only partial conversion to $AlCl(BHT)_2(OEt_2)$; the remaining aluminum containing product being $AlMe(BHT)_2(OEt_2)$ [100]. Given that this chloride/methyl exchange occurs, like those with Group 13 chlorides discussed above, through a dimeric intermediate, i.e., **XXIII**, then the lower Lewis acidity of zinc halides and alkyls as compared to B, Al or In may explain the low reactivity [102].



XXIII

(iv) Trimethylammonium and 2,6-dimethylpyridinium chloride

Trialkylammonium chloride salts have successfully been used in the synthesis of Group 13 chlorides from both hydrides and alkyls. Addition of 1 equiv. of Me_3NHCl to an Et_2O solution of $AlMe(BHT)_2$ yields the complex $AlCl(BHT)_2(NMe_3)$ [23]. A similar substitution is observed for the reaction of $AlMe_2(BHT)(PMe_3)$ with 1 equiv. of Me_3NH Cl to yield $AlClMe(BHT)(NMe_3)$ [23]. The addition of 2 equiv. of Me_3NHCl to $AlMe_2$ $(BHT)(PMe_3)$ does not yield the dichloride $AlCl_2(BHT)(NMe_3)$ as expected but rather yields the ionic complex $[Me_3NH][AlCl_2Me(BHT)]$ (eqn. (74)), the structure of which was confirmed by X-ray crystallography [23]. The substitution of NMe_3 for chloride suggests that reactivity of the Al–C bond is reduced by the presence of a halide ligand.

$$AlMe_2(BHT)(PMe_3) \rightarrow AlClMe(BHT)(NMe_3) \rightarrow [AlCl_2Me(BHT)]^- \qquad (74)$$

In a similar manner, the addition of 1 equiv. of 2,6-Me_2pyHCl to AlMe$(BHT)_2$ does not yield either the free, or even the complexed, chloride as expected, but rather a moderate yield of the ionic complex [2,6-Me_2pyH][$AlCl_2(BHT)_2$] (eqn. (75)) (Fig. 28) [100]. If 2 equiv. of 2,6-Me_2pyHCl are used, [2,6-Me_2pyH][$AlCl_2(BHT)_2$] is formed in essentially quantitative yield [100]. The complexation of chloride to AlCl$(BHT)_2$ as opposed to further reaction with AlMe$(BHT)_2$ may be attributed to the higher Lewis acidity of aluminum chlorides versus alkyls.

$$AlMe(BHT)_2 \rightarrow AlCl(BHT)_2 \rightarrow [AlCl_2(BHT)_2]^- \qquad (75)$$

The formation of chloroaluminate salts, such as [2,6-Me_2pyH][$AlCl_2(BHT)_2$] and [Me_3NH][$AlCl_2$Me(BHT)], is commonly observed in the reactions between $AlCl_3$ and MCl (M^+ being an alkali ion or an organic cation) [103].

H. ALANE DERIVATIVES

Although anionic alkoxy-alanes are readily prepared from the reaction of $LiAlH_4$ with alcohols (eqn. (76)), and the benzene soluble salts Na[AlH$(OMe)_2$OEt] (Red-Al) and Li[$AlH_2(OC_2H_4OMe)_2$] are commonly employed as reducing agents [104], examples of neutral alkoxide or aryloxide-alane derivations are rare.

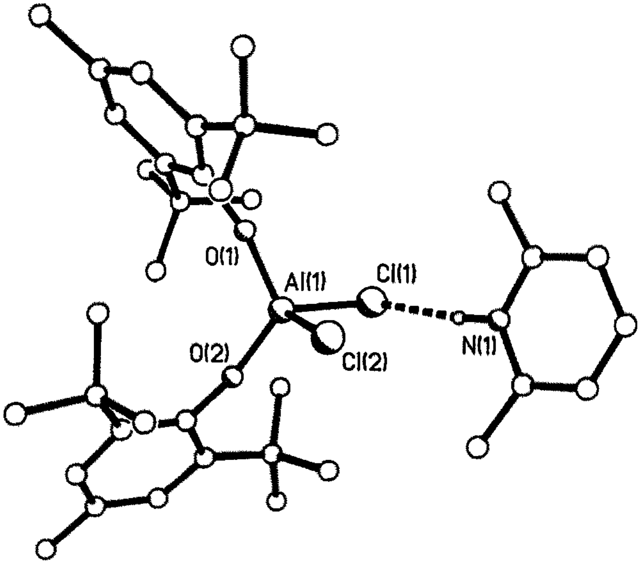
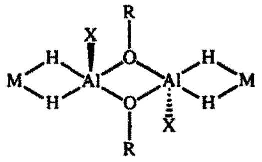


Fig. 28. The structure of [2,6-Me_2pyH][$AlCl_2$Me(BHT)] showing the inter-ion hydrogen bonding.

$$\mathrm{LiAlH_4 + 3ROH \rightarrow Li[AlH(OR)_3] + 3H_2} \quad (76)$$

Those previously reported include transition metal aluminopolyhydrides (**XXIV**) [105]. However, while these may be considered as an adduct of the aluminum Lewis acid with a neutral transition metal hydride, it is equally valid to regard them as being a transition metal salt of an anionic alane.



XXIV

X = OR, M = Ta; X = H, M = W, Re

Two examples of undisputedly neutral alkoxyhydrides were reported by Goel, Ashby and Mehrotra [106] to be formed as the result of the redistribution reaction between alane, AlH_3, and $Al(O^iPr)_3$ in THF (eqns. (77), (78)), however, no structural or reactivity data were reported.

$$\mathrm{AlH_3 + 2Al(O^iPr)_3 \rightarrow 3AlH(O^iPr)_2} \quad (77)$$

$$\mathrm{2AlH_3 + Al(O^iPr) \rightarrow 3AlH_2(O^iPr)} \quad (78)$$

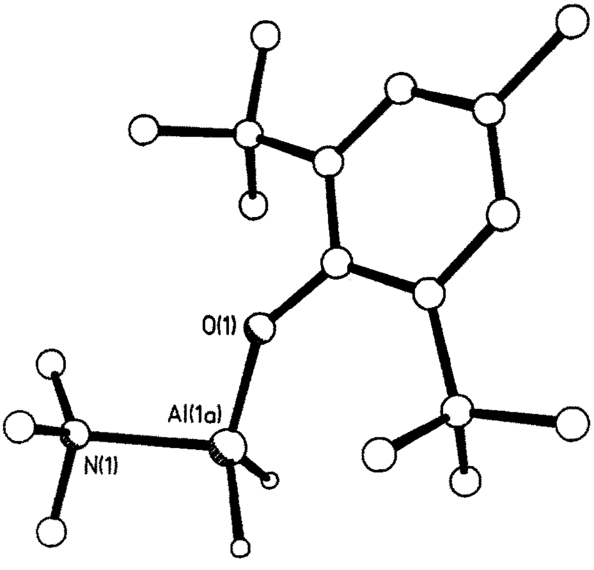


Fig. 29. The molecular structure of $AlH_2(BHT)(NMe_3)$.

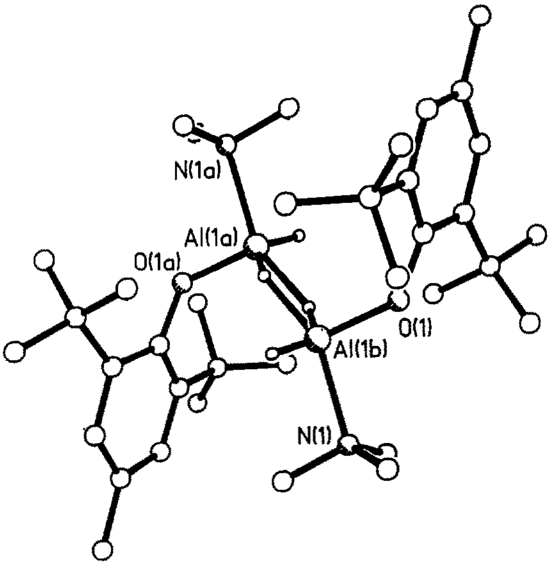
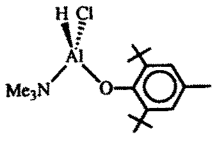


Fig. 30. The molecular structure of $[AlH_2(BHT)(NMe_3)]_2$.

(i) Mono-aryloxides

Interaction of $AlH_3(NMe_3)$ [107] with one molar equivalent of BHT-H resulted in the formation of $AlH_2(BHT)(NMe_3)$ as a colorless crystalline solid, the mass spectrum and low temperature ^{1}H NMR, of which are consistent with a monomeric structure [29]. However, the IR spectrum contains broad bands between 1880 and 1790 cm^{-1} due to the presence of both bridging and terminal hydrides [108] suggesting the formation of dimer. The presence of both monomeric and dimeric forms in the solid state has been confirmed by X-ray crystallography, as in Figs. 29 and 30, respectively [29]. Both monomer and dimer are present in the lattice as a disorder. The geometry around the aluminum in the monomer is highly distorted from tetrahedral, while that in the dimer approximates quite well to trigonal bipyramidal. Similar AlH_xL_{5-x} geometries have been reliably found in a number of transition metal aluminohydrides [105].

Interaction of $AlH_2Cl(NMe_3)$ [109] with 1 equiv. of BHT-H results in the formation of $AlHCl(BHT)(NMe_3)$, for which, unlike the dihydride, the IR spectrum contains a weak but sharp band at 1893 cm^{-1} due to terminal hydride consistent with a purely monomeric structure in the solid state (**XXV**).



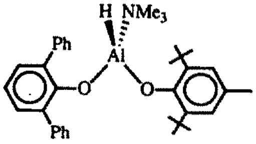
XXV

Repeated recrystallization of $AlH_2(BHT)(NMe_3)$ from Et_2O, or reaction with $^tBuNH_2$, results in ligand redistribution (eqns. (79) and (80), respectively) and allows for the isolation in low yield of the bis-aryloxide compounds $AlH(BHT)_2(L)$ ($L = OEt_2$, $^tBuNH_2$), whose structures have been determined by X-ray crystallography [29]. The etherate may be more conveniently prepared directly from the reaction of HOAr with $LiAlH_4$ in Et_2O (see below) [29,30].

$$AlH_2(BHT)(NMe_3) \xrightarrow{Et_2O} AlH(BHT)_2(OEt_2) + \text{unidentified products} \tag{79}$$

$$AlH_2(BHT)(NMe_3) + NH_2{}^tBu \rightarrow AlH(BHT)_2(NH_2{}^tBu) + \text{unidentified products} \tag{80}$$

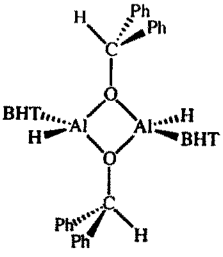
Reaction of $AlH_2(BHT)(NMe_3)$ with 2,6-diphenylphenol (DPP-H) allows the isolation of the mixed aryloxide, $AlH(BHT)(DPP)(NMe_3)$ (**XXVI**) [29].



XXVI

Interaction of $AlH_2(BHT)(NMe_3)$ with excess benzophenone in toluene results, upon hydrolysis, in the reduction of one molar equivalent of benzophenone per aluminum (eqn. (81)), while the reaction with one equivalent yields the dimeric compound $[AlH(BHT)(\mu\text{-}OCHPh_2)]_2$ (**XXVII**). No further reactivity is observed with excess ketone suggesting that complexation is required prior to hydrogen transfer [29].

$$O{=}CPh_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } AlH_2(BHT)(NMe_3)} HOC(H)Ph_2 \tag{81}$$



XXVII

(ii) Bis-aryloxides

In contrast to the reactions of sterically unhindered alcohols (eqn. (76)) when an

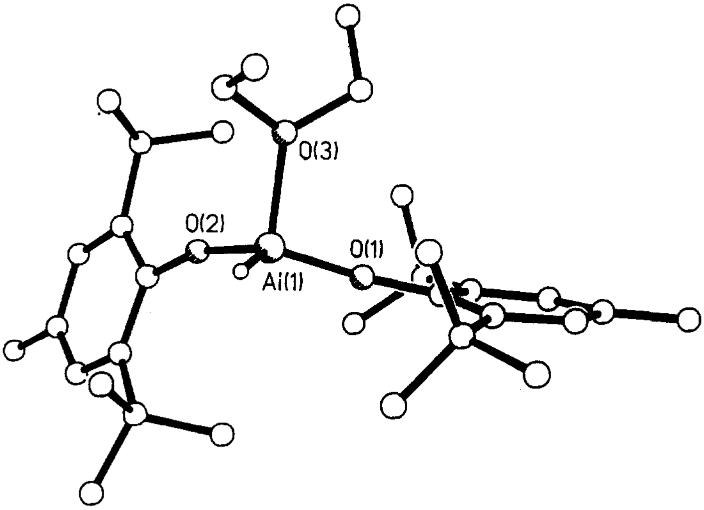


Fig. 31. The molecular structure of $AlH(BHT)_2(OEt_2)$.

equimolar amount of BHT-H is added to an Et_2O suspension of $LiAlH_4$, no gas evolution is observed, and subsequent work-up yields an equimolar quantity of alane, AlH_3, and the lithium aryloxide salt (eqn. (82)) [110].

$$LiAlH_4 + BHT\text{-}H \rightarrow AlH_3 + Li(BHT)(OEt_2) \qquad (82)$$

If the reaction is carried out with further equivalents of BHT-H gas evolution is observed, and a number of aluminum-aryloxide compounds may be observed by ^1H NMR. However, no single species could be isolated until addition of 3 equiv. of BHT-H per aluminum, at which point an equimolar mixture of $Li(BHT)(OEt_2)$ and $AlH(BHT)_2(OEt_2)$ are formed in quantitative yield (eqn. (83)), the structure of which is shown in Fig. 31.

$$LiAlH_4 + 3BHT\text{-}H \rightarrow AlH(BHT)_2(OEt_2) + Li(BHT)(OEt_2) + 3H_2 \qquad (83)$$

This observation is in contrast to the report by Haubenstock that the reaction of $LiAlH_4$ with 2 equiv. of DBP-H gives the lithium salt in quantitative yield, i.e., eqn. (84).

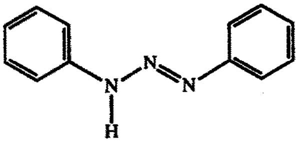
$$LiAlH_4 + 2DBP\text{-}H \rightarrow Li[AlH_2(DBP)_2] + H_2 \qquad (84)$$

However, Haubenstock and co-workers have noted that the reaction of $LiAlH_4$ with 4 equiv. of DBP-H does proceed in an analogous manner to that shown in eqn. (83), although it should be noted that they concluded that the resulting monohydride contained a tri-coordinate aluminum, i.e., $AlH(DBP)_2$ [112]. Based on subsequent data, it is most probable that the Et_2O solvate, was formed.

The interaction of $AlH(BHT)_2(OEt_2)$ with a further equivalent of BHT-H in refluxing toluene allows for the isolation of $Al(BHT)_3$ in quantitative yield (see above).

I. 1,3-DIPHENYLTRIAZENIDE DERIVATIVES

The triazenide anion, $[RN{=}N{-}NR]^-$, has been shown to strongly chelate Group 13 metals [113] and also stabilize the formation of a series of anionic radical complexes $[Al(dpt)_3]^{n-}$ ($n = 1,2,3$). Additionally the highly acidic nature of the parent triazene, e.g., 1,3-diphenyltriazene (dpt-H, **XXX**) promotes reactivity with Group 13 alkyls inert to aminolysis (see above).



XXX

(i) Mono-aryloxide compounds

The reaction of $AlMe_2(BHT)(OEt_2)$ with one molar equivalent of dpt-H yields AlMe(BHT)(dpt) in moderate yield (eqn. (85)) [114], however, if greater equivalents of dpt-H are employed, $Al(dpt)_3$ is the only aluminum-containing product isolated.

$$AlMe_2(BHT)(OEt_2) + dpt\text{-}H \rightarrow AlMe(BHT)(dpt) + CH_4 + Et_2O \qquad (85)$$

By contrast, the reaction of $AlH_2(BHT)(NMe_3)$ with dpt-H results in the near quantitative formation of $Al(BHT)(dpt)_2$ (eqn. (86)), which slowly (days at 25°C in toluene solution) undergoes ligand exchange to yield $Al(dpt)_3$ and $Al(BHT)_2(dpt)$ (eqn. (87)).

$$AlH_2(BHT)(NMe_3) + 2dpt\text{-}H \rightarrow Al(BHT)(dpt)_2 + 2H_2 + NMe_3 \qquad (86)$$

$$2Al(BHT)(dpt)_2 \rightarrow Al(dpt)_3 + 2Al(BHT)_2(dpt) \qquad (87)$$

(ii) Bis-aryloxide compounds

As noted above $Al(BHT)_2(dpt)$ is formed by the ligand redistribution reaction shown in eqn. (87), however, it may also be prepared directly from the reaction of $AlMe(BHT)_2$ with one equivalent of dpt-H (eqn. (88)).

$$AlMe(BHT)_2 + dpt\text{-}H \rightarrow Al(BHT)_2(dpt) + CH_4 \qquad (88)$$

The molecular structure of $Al(BHT)_2(dpt)$ has been determined by X-ray crystallography, and the structure is shown in Fig. 32. The compound contains a crystallographically im-

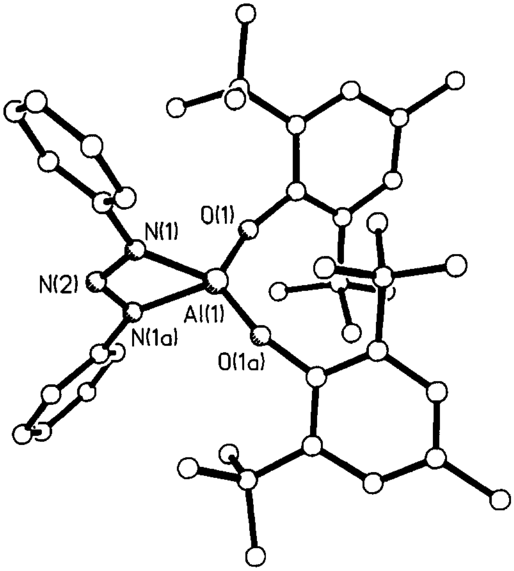


Fig. 32. The molecular structure of $Al(BHT)_2(dpt)$.

posed C_2 axis consistent with the Al(1)–N(2) vector. The aluminum atom is in a highly distorted tetrahedral environment, with the smallest angle being associated with the triazenide chelate [N(1)–Al(1)–N(la) = 64.7(1) Å]. In addition, the coordination geometry is further distorted as a consequence of the steric bulk of the aryloxide ligands such that the plane defined by the triazenide nitrogens and the aluminum atom is twisted ca. 15° away from perpendicular to the AlO_2 plane.

Electrochemical reduction of all the aryloxide-triazenide compounds results in their decomposition and the formation of BHT-H as the only isolable product.

J. THE AL–O BONDING INTERACTION IN FOUR-COORDINATE ALUMINUM ARYLOXIDES

In the structures of $AlMe_2(BHT)(L)$ and $AlMe(BHT)_2(L)$, the Al–O–C angles [140.6(6)–174.8(3)°] are much larger than usually observed for main-group alkoxides (121–129°) [14,115] although they are in the range found for those transition-metal alkoxide complexes (138–178°) [116] where significant $p\pi$–$d\pi$ bonding is present [117]. In addition, the Al–O distances [1.713(4)–1.749(5) Å] are short compared to the normal range [118] of 1.8–2.0 Å. For a summary of X-ray diffraction data, see Table 7.

Such a shortening with a concomitant increase in the Al–O–C angles would suggest the presence of some form of π-interaction. For transition metal aryloxide complexes, the short M–O bond distances and large M–O–C bond angles are frequently cited as being indicative of significant oxygen-p to metal-d π-bonding. A number of studies have shown that a definite correlation exists between the M–O bond distances and the electron configuration at the metal; i.e., the more electron-deficient the metal, the shorter the M–O

TABLE 7

Al–O bond distances and Al–O–C bond angles for selected derivatives of aluminum aryloxides

Compound	Ligand	Al–O (Å)	Al–O–C (°)	$\Delta_{O,C}$ (Å)	Ref.
$AlMe_2(BHT)(PMe_3)$	BHT	1.736(5)	164.5(4)	−0.234(5)	a
$[AlMeCl_2(BHT)][HNMe_3]$	BHT	1.713(4)	164.0(3)	0.282(5)	a
$AlMe_2(BHT)(py)$	BHT	1.740(4)	156.1(3)	−0.220(6)	b
$AlMe_2(BHT)(2,6\text{-}Me_2py)$	BHT	1.744(2)	158.0(3)	−0.224(3)	c
$AlMe_2(BHT)(O{=}CPh_2)$	BHT	1.731(8)	157.7(8)	−0.22(1)	d
	$O{=}CPh_2$	1.907(8)	153.8(9)	−0.04(1)	
$AlMe_2(OC_6F_5)[N(C_2H_4)_3CH]$	OC_6F_5	1.787(1)	128.8(1)	−0.163(2)	c
$AlEt_2(BHT)(H_2N^tBu)$	BHT	1.748(3)	151.3(2)	−0.222(5)	c
$AlEt_2(BHT)(py \cdot O)$	BHT	1.754(1)	144.1(1)	−0.220(2)	c
	$O \cdot py$	1.868(1)	128.8(1)[g]	−0.106 (2)	
$AlEt_2(BHT)[O{=}C(OMe)C_6H_4\text{-}p\text{-}Me]$	BHT	1.749(5)	145.6(5)	−0.215 (9)	e
	Ketone	1.887(6)	143.0(6)	−0.077(9)	
$AlMe(BHT)_2$	BHT	1.687(2)	140.5(2)	−0.240(3)	e
		1.685(2)	146.8(2)	−0.242(3)	e
$AlMe(OMes)_2(3,5\text{-}Me_2py)$	OMes	1.722(7)	140.6(6)	−0.22(1)	b
	OMes	1.714(6)	145.8(6)	−0.23(1)	
$AlMe(BHT)_2[O{=}C(OMe)Ph]$	BHT	1.714(9)	153.3(8)	−0.25(2)	d
	BHT	1.721(8)	156.3(6)	−0.24(2)	
	Ketone	1.851(7)	174(1)	−0.11(2)	
$AlMe(BHT)_2[O{=}C(H)^tBu]$	BHT	1.726(3)	131.3(2)	−0.229(4)	d
	BHT	1.729(3)	140.5(2)	−0.226(4)	
	Aldehyde	1.920(3)	136.0(3)	−0.035(4)	
$AlMe(BHT)_2(py \cdot O)$	BHT	1.739(4)	174.8(3)	−0.217(5)	c
	BHT	1.717(3)	167.9(3)	−0.239(5)	
	$O \cdot py$	1.854(4)	122.4(3)[g]	−0.102(5)	
$AlMe(BHT)_2[OC(Me)Ph_2]LiOEt_2$	BHT terminal	1.736(2)	165.6(2)	−0.233(4)	f
	BHT bridging		146.3(2)	−0.164(4)	
	OCR_3 bridging	1.808(2)	134.0(2)	−0.161(4)	

[a] M.D. Healy, D.A. Wierda and A.R. Barron, Organometallics, 7 (1988) 2543.

[b] M.D. Healy, J.W. Ziller and A.R. Barron, J. Am. Chem. Soc., 112 (1990) 2949.

[c] M.D. Healy, J.W. Ziller and A.R. Barron, Organometallics, 10 (1991) 597.

[d] M.B. Power, S.G. Bott, D.L. Clark, J.L. Atwood and A.R. Barron, Organometallics, 9 (1990) 3086.

[e] A.P. Shreve, R. Mulhaupt, W. Fultz, J. Calabrese, W. Robbins and S.D. Ittel, Organometallics, 7 (1988) 409.

[f] M.B. Power, S.G. Bott, J.L. Atwood and A.R. Barron, J. Am. Chem. Soc., 112 (1990) 3446.

[g] Al–O–N bond angle.

bond [119]. Recent studies by Rothwell et al. [116,120] have shown that there is no apparent correlation between the M–O bond distance and M–O–C bond angle for aryloxides of groups 4–6. They conclude that because the M–O–C bond angle is quite flexible only the M–O distance can be used as a basis for determining the amount of oxygen-to-metal π-bonding.

The Al–O bond distances and Al–O–C bond angles for a wide range of monomeric aluminum aryloxide compounds that have been structurally characterized are collected in Table 7 [58]. Figure 33 contains a plot of Al–O distances versus Al–O–C angles for monomeric four-coordinate aluminum aryloxides, $AlX_2Y(OR)$ (a) and $AlXY(OR)_2$ (b). There is clearly a near linear relationship between these two variable for the mono-alyloxide complexes $AlX_2Y(OR)$, suggesting that in less sterically congested complexes the Al–O bond length and the Al–O–C bond angle are related. A lack of correlation between the Al–O bond length and the Al–O–C bond angle exists, however, for compounds with more than one aryloxide bonded to aluminum. A similar result was

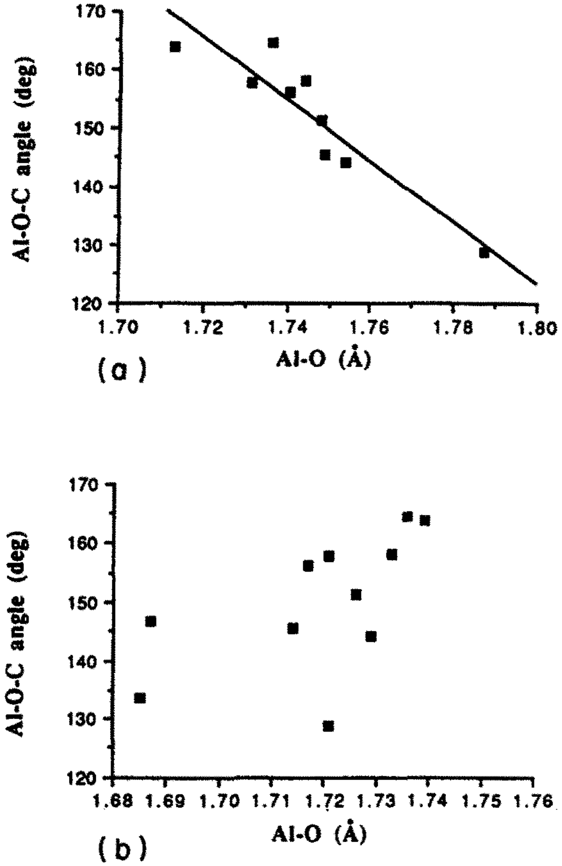
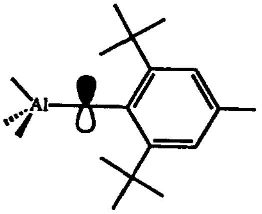


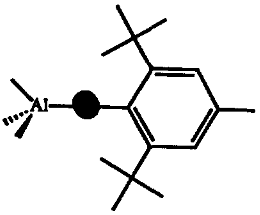
Fig. 33. Plot of Al–O bond length (Å) versus Al–O–C bond angle (deg) for the terminal aryloxide ligands in the compounds $AlX_2Y(BHT)$ (a) and $AlXY(BHT)_2$ (b) listed in Table 7.

obtained for the bis(aryloxides) of the d block metals [116,120]. We propose that when more than one aryloxide is present at the aluminum center, steric crowding constrains the Al–O–C bond angle but does not affect the magnitude of the Al–O bonding interaction. A possible explanation for the relative independence of the Al–O bond distance, and presumably any π–donation, from the Al–O-C bond angle is that the bond angle is controlled by the lone pair coplanar with the phenoxide ring, p_z (XXVIII), rather than the lone pair perpendicular to the phenoxide ring, p_y (XXIX).



Op_y

XXVIII



Op_z

XXIX

It is unlikely, however, that the Al–O distance would vary significantly between either of these interactions.

Rothwell et al. [120] noted that a consideration of the covalent radii and bond lengths reported for organic molecules would predict a metal alkoxide or aryloxide σ-bond length to be 0.10–0.15 Å shorter than a metal–alkyl bond. Therefore, the parameter $\Delta_{O,C}$ was proposed (eqn. (85)) as a probe for possible π-bonding between aryloxide, oxygen atoms, and electron-deficient metal centers [120].

$$\Delta_{O,C} = d(\text{M–O}) - d(\text{M–C}) \qquad (85)$$

In the case of Group 14 metals, $\Delta_{O,C}$ was found to be between –0.15 (Sn) and –0.17 (Ge), consistent with no π-bonding between oxygen and the metal center. On the other hand, average $\Delta_{O,C}$ values for Ti and Zr were –0.28 and –0.29, indicative of significant π-bonding [120].

The $\Delta_{O,C}$ values for aluminum aryloxide compounds are given in Table 7; also included for comparison are the values for a bridging aryloxide and other oxygen donor ligands within the same compounds. From the data, it is clear that pyridine-*N*-oxide ($\Delta_{O,C}$ = –0.102(5) Å for AlMe(BHT)$_2$(py·O); –0.106(2) Å for AlEt$_2$(BHT)(py·O)) is within the region expected for no π-interaction. The bridging aryloxide and alkoxide in AlMe(BHT)$_2$[OC(Me)Ph$_2$]LiOEt$_2$ ($\Delta_{O,C}$ = –0.164(4) and –0.161(4) Å, respectively) and the pentafluorophenoxide in AlMe$_2$(OC$_6$F$_5$)[N(C$_2$H$_4$)$_3$CH] ($\Delta_{O,C}$ = –0.163(2) Å) are also consistent with negligible π-bonding. By contrast, the terminal aryloxides have much shorter Al–O bond distances ($\Delta_{O,C}$ = –0.22(1) to –0.282(15) Å, average –0.23 Å) than predicted based on purely σ-bonding. The values of $\Delta_{O,C}$ for these latter ligands are similar to that observed for aryloxide compounds of d^0 titanium and zirconium in which significant pπ-dπ bonding is proposed [120].

For a transition-metal alkoxide, it is common for the lone pairs on oxygen to donate into a vacant d orbitals on the metal. In the case of $AlMe_2(BHT)(L)$ and $AlMe(BHT)_2(L)$ compounds, overlap between the oxygen p_x and p_y orbitals with the vacant $3d_{xz}$ and $3d_{yz}$ orbitals on aluminum is in principle possible (z axis along the Al–O vector) (i.e., **XXX** and **XXXI**). Such an interaction is unlikely, however, due to the relatively high energy of the Al 3d orbitals.

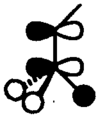
Al $3d_{xz}$ - O p_x

XXX

Al $3d_{yz}$ - O p_y

XXXI

An alternate bonding description involves π-donation from the oxygen p_x and p_y orbitals into the two π-acceptor orbitals $2e_x$ and $2e_y$ of the AlX_2Y moiety, which are Al–X and Al–Y σ-antibonding (i.e., **XXXII** and **XXXIII**) [121]. Either of the above bonding descriptions would account for the short Al–O distance and the large Al–O–C bond angles. Indeed, the latter structural feature may also be explained by invoking a π-interaction between the p_x orbital on oxygen and the antibonding (e_{2u}) orbital of the phenol ring. Such an interaction should shorten the O–C bond, however, and no appreciable shortening is observed.



$2e_x$ - p_x

XXXII

$2e_y$ - p_y

XXXIII

We note that σ^* orbitals have been invoked to explain the back-donation of electron density from transition metals to phosphines. Whereas the classical description involves the use of phosphorus d orbitals, recent results using quantum mechanical calculations indicate that the LUMO of the phosphine has substantial P–X σ^* character [122]. Thus, Orpen and Connelly [122b] were able to explain changes in M–P and P–X bond lengths upon oxidation of the metal center by invoking the participation of the P–X σ^* orbitals.

There has been some disagreement in the literature concerning this proposal of O p to Al–X σ^* donation [25]. It is not intended to propose an ethylene type interaction and therefore it is perhaps better to re-name this phenomenon as "forward donation". In this manner, the interaction is not dissimilar to the bonding in transition metal phosphines [122] and is also analogous to the orbital model often presented for the hyperconjugation observed in organic molecules [123].

It is worthwhile at this point before presenting evidence for this model to discuss other proposed explanations for the structural features observed in the solid state, i.e., short Al–O and large Al–O–C bond angles.

(i) Steric interactions

Since the aryloxides considered here are bulky, steric effects could provide a reasonable explanation for the enlarged angles, especially in the case of the 4-coordinate complexes. However, the similarity in the Al–O bond angles for the compounds $AlMe_2(BHT)(py)$ and $AlMe_2(BHT)(2,6\text{-}Me_2py)$ suggests that the magnitude of any Al–O π-interaction is largely independent of the steric bulk of the Lewis base. Furthermore, less sterically hindered aryloxides such as di-iso-propyl phenoxide and 2,4,6-tri-methyl phenode also show the similar effects of a short Al–O bond distance and a $\Delta_{O,C}$ e.g., for $AlMe(O\text{-}2,4,6\text{-}Me_3C_6H_2)_2(3,5\text{-}Me_2py)$ the $\Delta_{O,C}$ is comparable to that for $AlMe_2(BHT)(PMe_3)$ (see Table 7). The Al–O–C bond angle for the two less sterically hindered aryloxide compounds are considerably reduced from those observed for the BHT analogues. However, Rothwell et al. has previously shown that M–O–C bond angles are not necessarily a good indicator of π-interaction [116,120]. In addition, Francl et al. [53] have shown through ab initio studies on the structures of $H_2Al(OH)(PH_3)$ and $H_2Al(OMe)(PH_3)$ that small Al–O bond distances and large Al–O–C bond angles can be observed under conditions where minimal steric interaction can occur.

(ii) Bonding involving $d\pi$–$p\pi$ interactions

The second alternate explanation that could be considered is the interaction of Al d orbitals with the O p orbitals. As we have noted above, while the participation of the 3d-orbitals from the aluminum could conceivably be invoked, their energy relative to the valance molecular orbitals on the aryloxide ligands is such that it is most unlikely that they could be the source of the significant structural changes that are observed [53].

(iii) Ionic interaction

A purely, or largely, ionic model might be invoked to explain the short Al–O bond lengths, leaving the Al–O–C bond angle subject to considerable variance due to steric effects, packing forces in the solid state, or possible agostic Al···H interactions with the ligand *ortho*-tert-butyl groups. Power et al. [25] make this argument, noting a lack of observable splitting of ^1H NMR resonances upon cooling indicative of a lack of a rotational barrier in the Al–O bond, since such a barrier may be expected if a strong Al=O π-interaction is present. However, it is not clear that a barrier could in fact be observed in the NMR spectrum of $Al(^tBu)_2(BHT)$ since the BHT ligand can be fluxional without rotation around the Al–O bond. It should be noted that, to our knowledge, no such barrier has been measured for transition metal aryloxides where π-bonding is well accepted. A barrier to rotation about the Al–O–Si unit has been measured in the 4-coordinate siloxide $Al(OSiPh_3)_3(H_2O)(THF)_2$ and found to be $\Delta G^{\ddagger} = 9.7(\pm 0.2)$ kJ mol^{-1} [124].

To counter the argument involving ionic bonding, ab initio calculations have shown that the charges on the oxygen in AlH_2OH, AlH_2OCH_3, $AlH_2(OH)(PH_3)$, and $AlH_2(OCH_3)(PH_3)$ at the HF/3-21G(*) level are not in agreement with this model [53]. Charges for these species are shown in Table 8, along with the corresponding Al–O bond lengths. For comparison, the charge on oxygen in methanol at the same level is 0.705 [125]. The values found for the charges on oxygen in AlH_2OH and $AlH_2(OCH_3)(PH_3)$ charge (–0.127) found on the oxygen in $AlH_2(OCH_3)$ is also indicative of a covalent linkage. It is interesting to note that the negative charge on the oxygen in these aluminum complexes increases with increasing bond length [53]. This is the reverse of what would be expected for strongly ionic compounds, where in creasing charge should lead to tighter bonds and shorter bond lengths [53]. This observation further supports our contention that the geometrical distortions in aluminum alkoxides are the result of covalent interactions.

Additionally, ^1H NMR results previously discussed in Section E(i) show that the value of χ (the electronegativity of aluminum) for $AlEt_2(BHT)(H_2N^tBu)$ is calculated to be the same as that found for $AlEt_2I(H_2N^tBu)$ [58]. Thus, the high electronegativity of the aluminum atom in $AlEt_2(BHT)(H_2N^tBu)$ would suggest an electron-rich aluminum center inconsistent with an ionic model.

(iv) Bonding involving Al–X σ orbitals*

Having discussed other models for the π-interaction, it is now appropriate to discuss the model that we believe best fits the experimental and theoretical data. It has been proposed that the structural features are due to π-donation from O p to Al–X σ* orbitals. Supporting spectroscopic and theoretical evidence for this model is as follows.

TABLE 8

HF/3-21G(*) bond lengths in 3- and 4-coordinate aluminum alkoxides compared to net charges on oxygen[a]

Molecule	d(Al–O) (Å)	q(O)[b]
AlH_2OCH_3	1.649	–0.127
AlH_2OH	1.665	–0.828
$AlH_2(OCH_3)(PH_3)$	1.665	–0.854
$AlH_2(OH)(PH_3)$	1.690	–1.2275

[a] A.R. Barron, K.D. Dobbs and M.M. Francl, J. Am. Chem. Soc., 113 (1991) 39.

[b] Charges in fractions of an electron.

(a) NMR spectroscopy

^{1}H NMR spectroscopy allows for the electronegativity of the aluminum atom to be probed [58]. As discussed above, the presence of an electron-rich aluminum center as evidenced by the value of χ obtained is consistent with a donation of electron density from the oxygen to the aluminum [58]. Similarly, if π-donation is present from the aryloxide oxygen to the four-coordinate aluminum centers in $AlR_x(BHT)_{3-x}(L)$, then ^{27}Al NMR should be a useful technique to augment X-ray crystallographic data [27]. The ^{27}Al NMR shifts of the four-coordinate aryloxide compounds cover a wide range, δ 140 to 47. Within this range, however, there are three distinct groups. The mono-aryloxides δ 134–140; the bis-aryloxides δ 69–72; and the tris-aryloxides δ 47–50 [27]. The upfield shift of the ^{27}Al NMR signal with the substitution of a methyl group by an aryloxide is counterintuitive based on the relative electronegativity of the substituents. This trend is consistent, however, with the presence of π-donation of electron density onto the aluminum [27,29]. The similarity in the ^{27}Al NMR shifts for $Al(DIP)_3(py)$ (δ 48) and $Al(OMes)_3(py)$ (δ 50) is an indication that the steric hindrance at the *ortho* position on the phenol rings has little effect on the aluminum center.

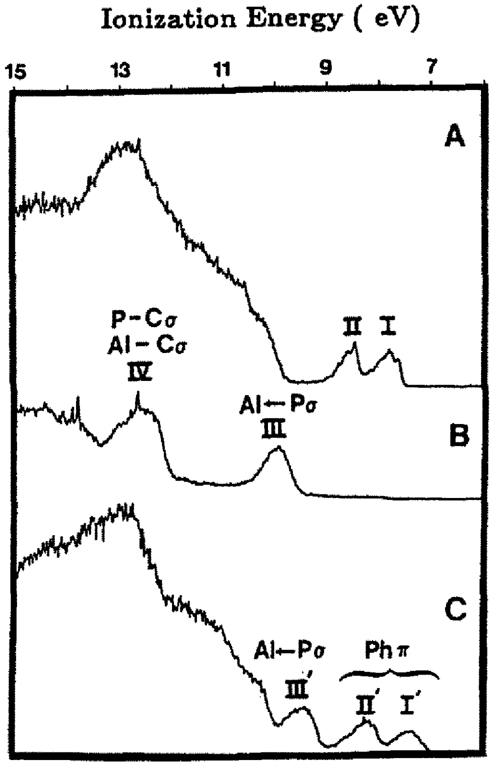


Fig. 34. Full HeI photoelectron spectrum of BHT-H (a), $AlMe_3(PMe_3)$ (b) and $AlMe_2(BHT)(PMe_3)$ (c).

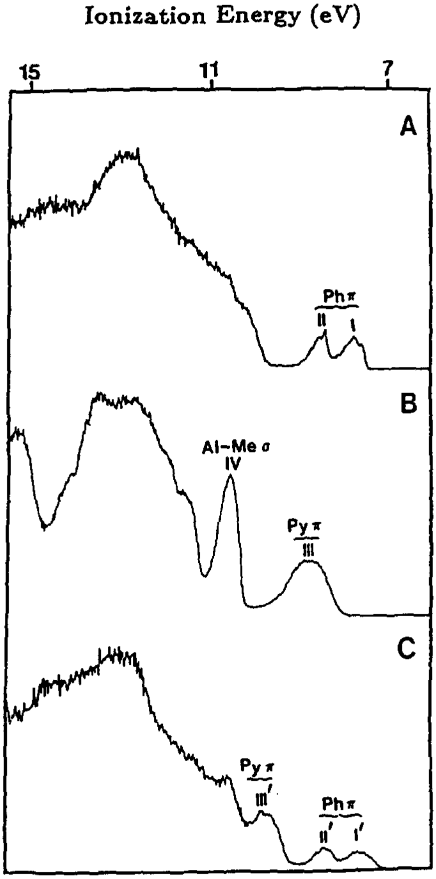


Fig. 35. Full HeI photoelectron spectrum of BHT-H (a), $AlMe_3(py)$, (b), and $AlMe_2(BHT)(py)$ (c).

Recently, Lehmkuhl et al. [27] published a study of the ^{27}Al NMR spectra of a series of aluminum aryloxide compounds of the type $[R_nAl(OAr)_{3-n}]_m$ (R = Me, ^iBu; $n = 0,1,2$; $m = 1,2,3$) where the 2 and 6 positions of the aryloxide are substituted with either H, Me, or ^tBu. These researchers found a progression in the ^{27}Al NMR in the series $Al(^iBu)_3$ (δ 276), $Al(^iBu)_2(BHT)$ (δ 196), $Al(^iBu)(BHT)_2$ (δ 109). The monomeric tris aryloxide $Al(BHT)_3$ (δ 3) can be added to this series and the aluminum center is very shielded in this species consistent with electron donation from the aryloxide ligands [29].

(b) Gas phase photoelectron spectroscopy

Evidence for the electronic structure of two of the aluminum aryloxide complexes, $AlMe_2(BHT)(PMe_3)$ and $AlMe_2(BHT)(py)$ has been obtained by use of gas phase photoelectron spectroscopy [52]. Both compounds are sufficiently volatile (both sublime in vacuo) to be suitable for gas phase study. The HeI valence photoelectron spectra of the Lewis acid-base adducts $AlMe_3(PMe_3)$, $AlMe_3(py)$, $AlMe_2(BHT)(PMe_3)$, and $AlMe_2(BHT)(py)$ were obtained. The spectra of the free ligand BHT-H was also obtained to aid in the assignment of the peaks. The HeI photoelectron spectra of these species are shown in Figs. 34 and 35. The first and second ionizations of free BHT-H show vibrational progressions associated with the symmetric C–C phenyl ring stretching modes, consistent with the b_1 and a_2 π ionizations, respectively, of monosubstituted phenyl rings. Figure 34(c), the spectrum of $AlMe_2(BHT)(PMe_3)$, shows that the corresponding phenoxide a_2 ionization retains the vibrational structure, but the peak corresponding to the b_1 ionization loses the individual vibrational components [52a]. This loss of vibrational fine structure of the phenyl π b_1 orbital in the coordinated phenoxide has been interpreted to mean that the phenoxide is involved in a π interaction with the $AlMe_2(PMe_3)$ fragment of the molecule. The situation for $AlMe_2(BHT)(py)$ [52b] is similar (Fig. 35(c)), and the loss of vibrational fine structure is again interpreted as indicative of a π-interaction between the phenoxide and the $AlMe_2(py)$ fragment of the molecule. Furthermore, the energy difference between the Phπ a_2 and b_1 ionizations for $AlMe_2(BHT)(PMe_3)$ and $AlMe_2(BHT)(py)$ indicate that the extent of π-inter action in the two species is about the same [52].

The Al–P σ ionization occurs at lower binding energy in $AlMe_2(BHT)(PMe_3)$ than in $AlMe_3(PMe_3)$, indicating that the aluminum center in $AlMe_2(BHT)(PMe_3)$ feels a more negative charge potential. This is counter to the expected σ inductive effects of an alkoxide compared to an alkyl and indicates that the BHT is acting as an electron donor, consistent with ^1H and ^{77}Al NMR spectroscopic investigations. Examination of the change in the band shape of the Al–P σ ionization between $AlMe_3(PMe_3)$ and $AlMe_2(BHT)(PMe_3)$ demonstrates that the oxygen p π orbital of the phenoxide is interacting directly with the Al–P σ^* orbital [52a]. This interaction is supported by the observation that the Al–P σ bond is stronger in $AlMe_3(PMe_3)$ than in $AlMe_2(BHT)(PMe_3)$ [49]. The better σ-donor ability of the trimethyl phosphine and the better π-acceptor ability of the pyridine ligand are indicated by an increase in negative charge potential at the metal center when pyridine is replaced by the phosphine.

The pyridine π-ionizations in $AlMe_3(py)$ and free pyridine indicate that the pyridine experiences a net negative charge potential upon coordination to the metal center [52b]. Comparison of the spectra of $AlMe_3(py)$ and $AlMe_2(BHT)(py)$ indicate that whereas the pyridine π ionizations show stabilization from the more positive potential at the metal center upon replacement of a methyl group with the more electronegative alkoxide, the coordinated lone pair shows no significant shift. As in the case of $AlMe_2(BHT)(PMe_3)$, this lack of stabilization is explained by a π type interaction between the O pπ orbitals and the Al–N σ^* orbital [52b].

(v) Theoretical calculations

The optimized structures and orbital description for AlH_2OCH_3, AlH_2OH, $AlH_2(OCH_3)(PH_3)$, and $AlH_2(OH)(PH_3)$ have been determined by ab initio molecular orbital calculations (Table 9) [53]. Both the short Al–O bonds and large Al–O–C angles are attributed to π-symmetry interactions between the oxygen lone pair and the empty

TABLE 9

HF/3-21G(*) structural parameters for aluminum alkoxides AlH_2OR and $AlH_2(OR)(PH_3)$ (R = H, CH_3)[a]

Molecule	Point group	Parameter[b]	HF/3-21G(*)
AlH_2OH[c]	C_s	r(Al–O)	1.665
		∠(HO–Al)	144.5
		r(Al–H_c)	1.589
		r(Al–H_{tr})	1.58 1
		r(OH)	0.953
		∠(H_c–Al–O)[c]	120.4
		∠(H_{tr}–Al–O)[c]	117.3
$AlH_2(OCH_3)$	C_s	r(Al–O)	1.649
		∠(C–O–Al)	176.2
		r(Al–O)	1.408
$AlH_2(OH)(PH_3)$	C_1	r(Al–O)	1.690
		∠(H–O–Al)	136.5
		r(Al–P)	2.659
		∠(H–P–H)	98.9
		∠(P–Al–O)	103.2
$AlH_2(OCH_3)(PH_3)$	C_1	r(Al–O)	1.665
		∠(C–O–Al)	175.5
		r(Al–P)	2.679
		∠(H–P–H)	98.9
		∠(P–Al–O)	103.3

[a] A.R. Barron, K.D. Dobbs and M.M. Francl, J. Am. Chem. Soc., 113 (1991) 39.

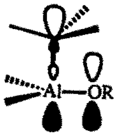
[b] Parameters in Angstroms and degrees.

[c] Subscripts c and tr refer to *cis* and *trans* orientation of the Al–H bond to the OH bond about the Al–O bond, respectively.

aluminum p-orbital in three-coordinate aluminum compounds and are expected not to be present in four-coordinate complexes. Optimization of the structures of $AlH_2(OCH_3)(PH_3)$ and $AlH_2(OH)(PH_3)$ revealed a slightly longer Al–O bond distance than in the corresponding three-coordinate complexes. In the hydroxide, the Al–O bond length is 0.024 Å longer, while in the methoxide the bond is 0.016 Å longer. Experimental results are in agreement with these results. The average Al–O bond distance in three-coordinate $AlMe(BHT)_2$ is 1.686 Å, while in $Al(BHT)_3$, the average bond length is 1.648(7) Å [21,29]. In four-coordinate compounds, the average length is 1.719 Å.

In neither $AlH_2(OH)(PH_3)$ nor $AlH_2(OCH_3)(PH_3)$ is any significant change in the Al–O–R bond angle relative to their three-coordinate analogues observed. Experimental results actually show that the Al–O–C bond angle can increase with complexation of a Lewis base. For example, the Al–O–C angles in $AlMe(BHT)_2$ (140.5(2) and 146.8(2)°), are similar to or smaller than those found in $AlMe(BHT)_2(O{=}CPh_2)$ (142.6(3) and 161.4(5)°) and $AlMe(BHT)_2(py \cdot O)$ (167.9(3) and 174.8(3)°) [21,35,59].

The addition of a Lewis base to either $AlH_2(OH)$ or $AlH_2(OCH_3)$ should effectively obstruct the interaction of the Al p with the appropriate O p [53]. What then is the source of the angular distortion in the four-coordinate complexes? The aluminum-Lewis base σ^* orbital is energetically accessible, though it lies some 0.05 au above the empty aluminum p, as Fig. 36 shows. Since the addition of a Lewis base does not result in a significant pyramidalization of the AlL_2OR fragment, either in the calculations (in both theoretical compounds the Al is shifted less than 0.2 Å out of the HHO plane) and experimentally, the σ^* Al–P orbital is also geometrically positioned for overlap with the oxygen lone pairs (XXXIV) [53].



XXXIV

The resulting interaction mimics the stabilizing interaction in three-coordinate aluminum complexes. Donation from the oxygen will not be as facile as in the three-coordinate systems due to the competition from the Lewis base. Thus, one would expect a longer Al–O bond than in the corresponding free molecule along with a smaller Al–O–C angle. In the AlH_2OH complex with phosphine, the Al–O bond is longer, as noted above, and the Al–O–H angle is found to be slightly smaller, 137° compared to 144°. The tightening of the Al–O–C angle is less pronounced in the four-coordinate methoxide complex with phosphine, which closes relative to the free $AlH_2(OCH_3)$ by less than 1°. The aluminum–oxygen bond distance in $AlH_2(OCH_3)(PH_3)$ is longer by 0.016 Å with respect to the corresponding three-coordinate molecule. One would expect the Al–P linkage to be lengthened relative to the simple Lewis acid-base complex due to the donation into the antibonding orbital. This is indeed found to be the case; the Al–P bond is approximately 0.1 Å longer in the alkoxide complexes than in the $AlH_3(PH_3)$. This is supported experimentally in the gas phase photoelectron spectra as the Al–P bond in $AlMe_2(BHT)(PMe_3)$ is significantly weaker than that in $AlMe_3(PMe_3)$ [52a]. Structural data are not inconsistent with this model, but the large uncertainty associated with the Al–P bond in $AlMe_3(PMe_3)$ (2.53(4) Å) determined by gas phase electron diffraction [126] precludes comparison with $AlMe_2(BHT)(PMe_3)$ (2.499(3) Å) [23]. Comparison with the cyclic dimer $(Me_2AlCH_2PMe_2)_2$ where the Al–P dative bond is 2.451(2) Å is, however, consistent with this model [127].

The ab initio calculations also indicated that electron density at the α-carbon of the aryloxide would have a substantial effect on the magnitude of the π-interaction [53]. Thus, based on this MO description, the opening of the Al–O–C angle and the shortening of the function of the π-donation capabilities of the R group of which the α-C is a part, then using an electron-withdrawing group should result in a more acute angle. This is in

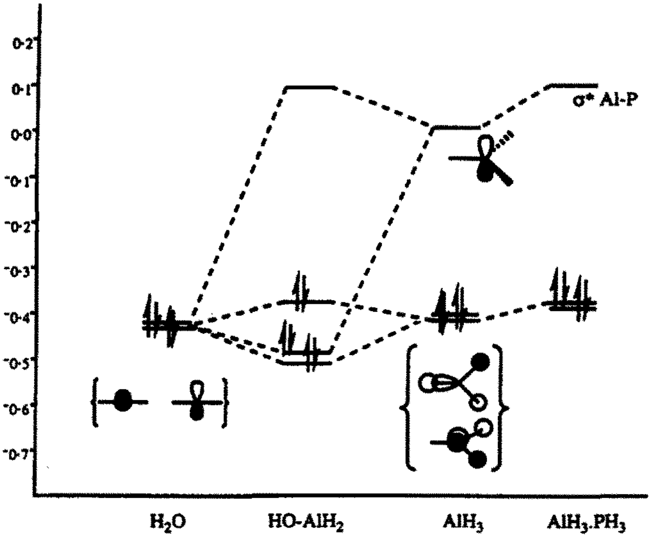


Fig. 36. MO interaction diagram for Al–O bonding in $AlH_2(OH)(PMe_3)$ energy of the σ* Al–P orbital and the π-AlH_2 orbital shown for comparison. Orbital energies are in atomic units and drawn from HF/3-21G(*) calculations.

fact observed for the perfluorinated phenoxide complex $AlMe_2(OC_6F_5)[N(C_2H_4)_3CH]$ [53] in which the Al–O–C angle of 128° is more than 20° smaller than the average angle in the corresponding BHT complexes. The Al–O bond distance is also significantly lengthened to 1.787(1) Å in this species. The $\Delta_{O,C}$ (Table 7) is also consistent with a lack of Al–O bonding.

(d) Bond dissociation energies

Further evidence that supports the results of the photoelectron spectroscopy and the ab initio calculations is the determination of Al–X bond dissociation energies [53]. Theory would predict that if the O p to Al–X σ* interaction is present, there would be a lengthening and thus a weakening of the Al–X bond. Difficulties encountered in the comparison of Al–P bond lengths are mentioned above. The weakening of the Al–X bond is observed in the photoelectron spectra and in the bond dissociation energies for a number of $AlMe(BHT)_2(L)$ complexes compared to their AlR_3 analogues. Thus, the absolute values for the dissociation of adduct ligands for $AlMe(BHT)_2$ is much lower (20–30%) than the corresponding trialkyl [49].

In conclusion, from spectroscopic and theoretical data, the model for a π-symmetry interaction between O p and Al–X σ* orbitals appears to be the best available.

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