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THE Al—O BOND INTERACTION IN FOUR-COORDINATE ALUMINUM ARYLOXIDE COMPOUNDS

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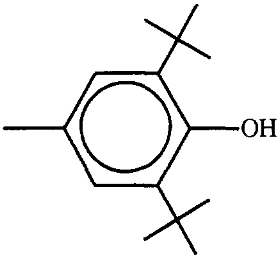
Abstract—What is a normal Al—O bond? The nature of this common chemical bond is discussed with respect to the observed structural and spectroscopic parameters for monomeric aluminum aryloxide compounds, e.g. $AlR_x(OAr)_{3-x}(L)_n$ ($x = 0, 1, 2$ and $n = 0, 1$). Experimental evidence for the presence of short Al—O bond distances, the low reactivity of residual aluminum-alkyl groups, the electron rich nature of the aluminum center, and the weakening of Al—X bonding by the aryloxide ligand are presented. Based upon the experimental observations and theoretical studies, models for the Al—O bond are presented and discussed: steric effects, highly ionic bonding, $d\pi$–$p\pi$ interactions and π-bonding via donation into Al—X σ^* orbitals.

The tendency of aluminum alkoxide and aryloxide compounds to maximize their coordination number by associating to give aggregates containing tetrahedral and octahedral centers is well documented.[1] The use of sterically hindered aryloxide ligands, in particular that derived from 2,6-di-tert-butylmethylphenol (**I**, BHT-H from the trivial name butylated hydroxytoluene), results in the isolation of monomeric aryloxide compounds of aluminum.[2]



(**I**)

The X-ray determinations of $Al(^tBu)_2(BHT)$,[3] $AlMe(BHT)_2$,[4] and $Al(BHT)_3$[5] have been reported, and confirm the monomeric nature of these compounds. The isolation of these monomeric compounds is undoubtedly due to the steric hindrance of the aryloxide precluding dimerization via bridging by the aryloxides, however, the short Al—O distances and large Al—O—C bond angles observed in the solid state are consistent with some form of π-interaction between the vacant p orbital on aluminum and the lone pairs on the aryloxide oxygens.[2] Such a bonding scheme is compatible with the commonly accepted concept that the presence of any form of π-bonding to a group 13 element requires a trigonal planar coordinatively unsaturated metal center.

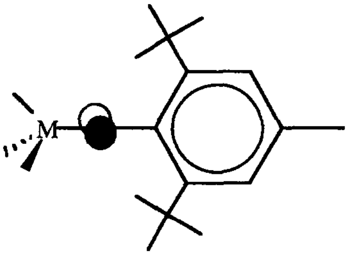
Despite their steric hindrance all the monomeric aryloxide compounds readily form Lewis acid–base complexes, in which the aluminum is four-coordinate. The traditional view of such compounds, $AlR_x(OAr)_{3-x}(L)$ ($x = 0$–3), is that they are electron precise; the aluminum having an octet electron environment. However, the X-ray structural characterization of several of these compounds opened up the possibility that the Al—O bonding interaction in four-coordinate aluminum compounds may not be as simple as expected.[6] The presence of shorter than expected Al—O bonds is typical of a π interaction, while spectroscopic data are indicative of an electron rich aluminum center.[2] A number of proposals have been made by us and other workers to account for the observed experimental data. While some of these proposals are contradictory in nature, it is clear that a better understanding of the bonding between aluminum and oxygen is required. It is, therefore, the goal of this review to discuss the experimental data for the

Al—O bond in four-coordinate aluminum compounds, and place the various bonding models in perspective.

EXPERIMENTAL OBSERVATIONS

Al—O *vs.* Al—C *bond distances*

In the molecular structures of $AlR_2(BHT)(L)$ and $AlR(BHT)_2(L)$, as determined by X-ray crystallography, the Al—O distances [1.713(4)–1.749(5) Å][6] are short compared to the normal range 1.8–2.0 Å.[7] In addition, the Al—O—C angles [140.6(6)–174.8(3)°] are much larger than usually observed for main-group alkoxides (121–129°),[8] although they are in the range found for those transition-metal alkoxide complexes (138–178°)[9] where significant *pπ–dπ* bonding is present.[10] However, Rothwell and co-workers[11] have shown that there is no apparent correlation between the M—O bond distance and M—O—C bond angle for aryloxides of group 4–6 elements. A possible explanation for the relative independence of the M—O bond distance, and presumably any π donation, from the M—O—C bond angle is that the bond angle is controlled by the lone pair perpendicular to the phenoxide ring, **(II)**, rather than the lone pair parallel to the phenoxide ring, **(III)**.[2]



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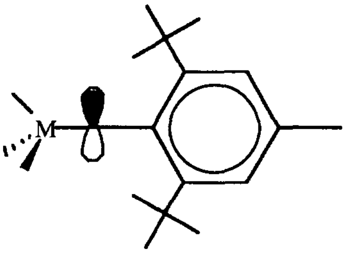


(III)

It is unlikely, however, that the M—O distance would vary significantly between either of these interactions. A similar conclusion was reached by Rothwell and co-workers.[11] They proposed that only the M—O distance can be used as a basis for determining the extent of oxygen-to-metal bonding.

Rothwell and co-workers[11] 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 [eq. (1)] as a qualitive probe for possible π-bonding between aryloxide, oxygen atoms, and electron-deficient metal centers.[11]

$$\Delta_{O,C} = d(M{-}O) - d(M{-}C) \qquad (1)$$

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.[11]

Based on a radius of 1.3 Å for Al, 0.77 Å for C, and 0.66 Å for O,[12] Power and co-workers[3] calculated theoretical Al—C and Al—O bond lengths to be 2.07 Å and 1.96 Å, respectively.[13] Thus, on purely electrostatic arguments the difference between an Al—O and Al—C bond should be *ca* 0.11 Å. This correlates well with the $\Delta_{O,C}$ reported for the group 14 metals (*vide supra*). Selected $\Delta_{O,C}$ values for aluminum mono-aryloxide compounds are given in Table 1; also included for comparison are the values for other oxygen donor ligands within the same compounds.[2] From the data, it is clear that pyridine-*N*-oxide [$\Delta_{O,C} = -0.106(2)$ Å for $AlEt_2(BHT)(py{\cdot}O)$] is within the region expected for a usual Al—O bonding interaction. The pentafluorophenoxide in $AlMe_2(OC_6F_5)[N(C_2H_4)_3CH]$ [$\Delta_{O,C} = -0.163(2)$ Å] is also consistent with negligible additional bonding. By contrast, the terminal aryloxides have much shorter Al—O bond distances [$\Delta_{O,C} = -0.215(1)$ to $-0.282(5)$ Å, average -0.229 Å] than predicted based on purely σ-bonding. The values of $\Delta_{O,C}$ for these latter ligands are similar to those observed for aryloxide compounds of d^0 titanium and zirconium, in which *pπ–dπ* bonding is proposed.

Low reactivity of aluminum alkyl substituents in $AlR_x(BHT)_{3-x}(L)$ (x = 1, 2)

In contrast to tri-alkyl aluminum compounds, AlR_3, the aryloxide substituted compounds show a low propensity for alkane elimination. Two significant examples involve the reaction with enolizable ketones, and the formation of stable amine complexes.

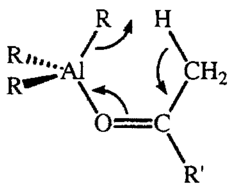
Interaction of $AlEt(BHT)_2$ with 2 equivalents of $O{=}C(Me)^tBu$ results in the formation of the aluminum-β-oxo enolate, in addition to 1 equivalent of BHT-H [eq. (2)].[14] Similar aldol condensation

Table 1. Al—O bond distances and $\Delta_{O,C}$ for selected derivatives of aluminum aryloxides

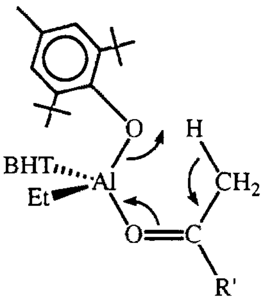
Compound	Ligand	Al—O (Å)	$\Delta_{O,C}$ (Å)	Ref.
$Al(^tBu)_2(BHT)$	BHT	1.710(2)	−0.266	3
$Al(^tBu)_2(IBP)$	IBP	1.709	−0.286, −0.278	3
$AlMe_2(BHT)(PMe_3)$	BHT	1.736(5)	−0.234(5)	6(a)
$[AlMeCl_2(BHT)][HNMe_3]$	BHT	1.713(4)	−0.282(5)	6(a)
$AlMe_2(BHT)(py)$	BHT	1.740(4)	−0.220(6)	6(b)
$AlMe_2(BHT)(2,6\text{-}Me_2py)$	BHT	1.744(2)	−0.224(3)	6(c)
$AlMe_2(BHT)(O{=}CPh_2)$	BHT	1.731(8)	−0.22(1)	32
	$O{=}CPh_2$	1.907(8)	−0.04(1)	
$AlMe_2(OC_6F_5)[N(C_2H_4)_3CH]$	OC_6F_5	1.787(1)	−0.163(2)	6(c)
$AlEt_2(BHT)(H_2N^tBu)$	BHT	1.748(3)	−0.222(5)	6(c)
$AlEt_2(BHT)(py{\cdot}O)$	BHT	1.754(1)	−0.220(2)	6(c)
	O·py	1.868(1)	−0.106(2)	
$AlEt_2(BHT)[O{=}C(OMe)C_6H_4\text{-}p\text{-}Me]$	BHT	1.749(5)	−0.215(9)	4
	Ketone	1.887(6)	−0.077(9)	

products are observed with $O{=}C(Et)Ph$ and $O{=}CEt_2$.

The accepted mechanism for the enolization of ketones by aluminum alkyls involves a six-membered transition state (**IV**) with the concurrent loss of alkane.[15] 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 (**V**).

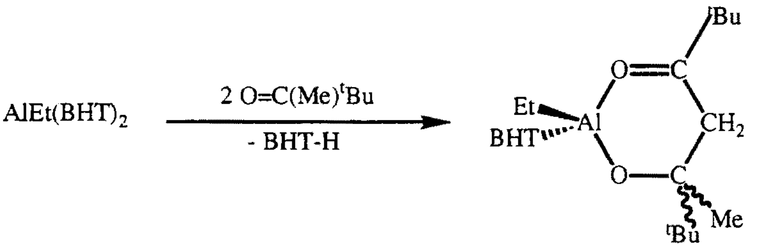


(**IV**)



(**V**)

In contrast to previously reported organoaluminum–ammonia complexes, the aryloxide substituted compounds, $AlMe_2(BHT)(NH_3)$ and $AlMe(BHT)_2(NH_3)$, show no propensity for alkane elimination, giving parent ions in the mass spectrum, and in the case of $AlMe_2(BHT)(NH_3)$ may be sublimed without decomposition.[16] Heating under an inert atmosphere beyond their melting point results in decomposition to multiple products, including BHT-H.



(2)

The lack of alkane elimination is clearly not due to the steric approach of the ketone or ammonia. It would seem likely, therefore, that the lack of any reaction with the Al—R ligands is because the basicity, and therefore reactivity, of the aluminum-alkyl toward a Brönsted acid is reduced by the presence of the aryloxide substituent on the aluminum.[17]

^1H *NMR spectroscopy*

Gosling and Bowen[18] 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 [eq. (3)],[19] where χ is the electronegativity of aluminum, and Δ is the internal chemical shift [eq. (4)] of an ethyl group bonded to aluminum.

$$\chi = 0.62\Delta + 2.07 \tag{3}$$

$$\Delta = \delta CH_3 - \delta CH_2 \tag{4}$$

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 the lack of reactivity of the aluminum alkyls (*vide supra*), and the ^{27}Al NMR studies.

^{27}Al *NMR spectroscopy*

While ^{27}Al NMR spectroscopy has become a near routine technique for the characterization of aluminum compounds in solution, there are a number of misconceptions that have become propagated in the literature. The major mistake in assignments has been the assumption that the chemical shift is highly dependent of the coordination number of aluminum, and only slightly on the coordination environment. Thus, peaks in the range 300–200 ppm were assigned as being due to three-coordinate, 200–70 ppm due to four-coordinate, *ca* 50 ppm due to five-coordinate, and *ca* 0 ppm due to six-coordinate aluminum. However, we have demonstrated that while there is a dependence of coordination number on the ^{27}Al NMR shift, there is also a significant effect of coordination environment, especially paramagnetic shifts due to non-σ-interactions.[2] Thus, if electron 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.

Perhaps the best example of the dependence on electronic ligand effects is the change in chemical shift for a series of monomeric three-coordinate aluminum compounds (characterized by mass spectrometry, solution molecular weights, and X-ray crystallography) upon substitution of an aryloxide group for an alkyl group, see Fig. 1. There is a clear 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), and $Al(BHT)_3$ (δ 3).[5,20] We note that the aluminum center is very shielded in the tris-aryloxide species consistent with significant electron donation from the aryloxide ligands.

Although the shift range upon aryloxide substitution for four-coordinate compounds is not as great as for three-coordinate compounds, the ^{27}Al NMR shifts of the former still cover a wide range, δ 140–47 ppm. Within this range, there are three distinct groups (Fig. 1). The mono aryloxides δ 134–140 ppm; the bis-aryloxides δ 69–72 ppm; and the tris-aryloxides δ 47–50 ppm. The upfield shift of the ^{27}Al NMR signal with the substitution of a methyl group by an aryloxide is counter intuitive based on the relative electronegativity of the substituents. This trend is consistent, however, with the presence of donation of electron density on to the aluminum from the BHT ligand as observed by ^1H NMR. 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.[6b] Furthermore, it is interesting to note that the chemical shifts for $Al(BHT)_3(L)$ are downfield of that for $Al(BHT)_3$

Table 2. Decomposition temperature and ^1H NMR spectral data for the adduct $AlEt_2X(H_2N^tBu)$

X	Dec. temp (°C)	^1H NMR (ppm) $AlCH_2CH_3$	$AlCH_2$	$\delta CH_3 - \delta CH_2$	χ	Ref.
Et	90	1.33	0.09	1.24	1.30	18
Cl	100	1.45	0.35	1.10	1.39	18
Br	120	1.62	0.57	1.05	1.42	18
I	*ca* 120	1.48	0.53	0.95	1.48	18
BHT	> 120	1.02	0.07	0.95	1.48	6(c)

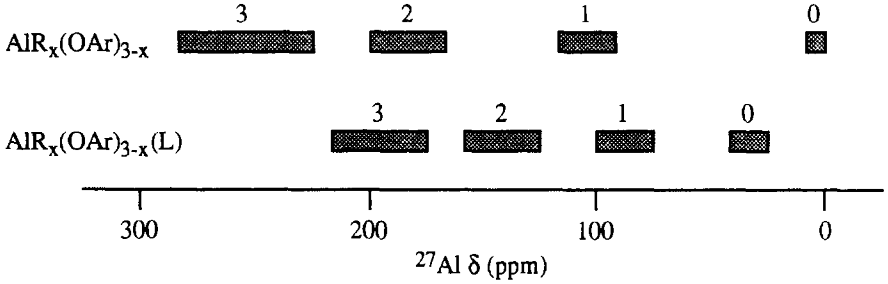


Fig. 1. ^{27}Al NMR spectroscopic shifts of three- and four-coordinate aluminum aryloxide compounds. The number of alkyl substituents, x, is given above the grey bars.

Gas-phase photoelectron spectroscopy

Despite the usefulness of ^1H and ^{27}Al NMR spectroscopy as an indication of electron density on the aluminum center in aryloxide compounds, a direct measure of the electronic structure is desirable. 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.[21] 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 2 and 3. The first and second ionizations of free BHT-H [Fig. 2(a)] 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 substituted phenyl rings. Figure 2(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. 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 $AlMe_2(BHT)(py)$ is similar [Fig. 3(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 differences 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 interaction in the two species is about the same.[21]

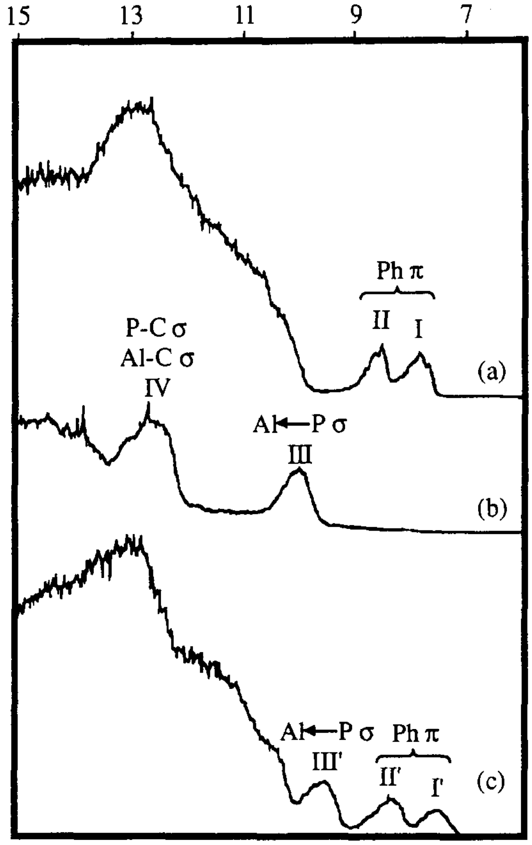


Fig. 2. Full HeI photoelectron spectrum of BHT-H (a), $AlMe_3(PHe_3)$ (b), and $AlMe_2(BMT)(PMe_3)$ (c).

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, consistent with the ^1H and ^{27}Al NMR data. 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. 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 $p\pi$ orbital of the phenoxide is interacting directly with the Al—P σ^* orbital. This interaction is supported by the observation that the Al—P σ bond is stronger in $AlMe_3(PMe_3)$

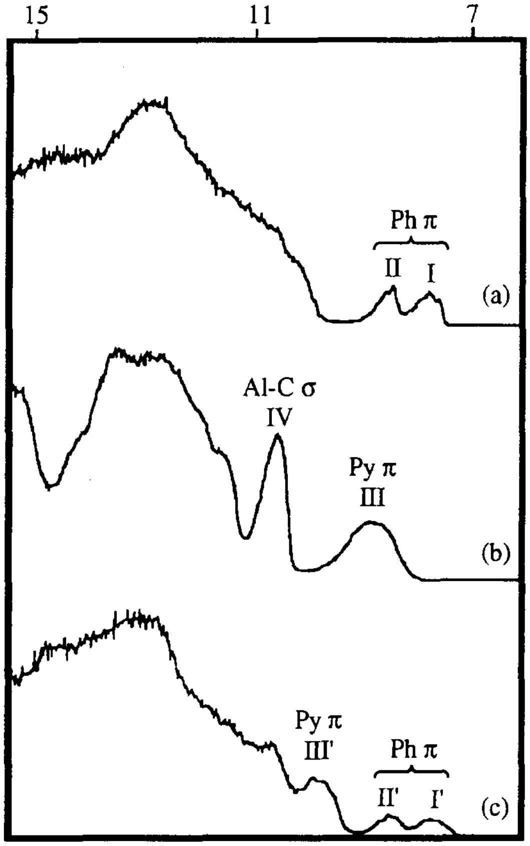


Fig. 3. Full HeI photoelectron spectrum of BHT-H (a), $AlMe_3(py)$ (b), and $AlMe_2$ (BHT)(py) (c).

than in $AlMe_2(BHT)(PMe_3)$. The better σ donor ability of the trimethylphosphine 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.[21a]

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. 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.[21b]

Bond dissociation energies

Further evidence that supports the results of the photoelectron spectroscopy for the weakening of Al—ligand σ bonds is the determination of Al—X bond dissociation energies. Theory would predict that if the Op to Al—X σ^* interaction is present, there would be a weakening of the Al—X bond. The weakening of the Al—X bond is observed in the bond dissociation energies determined for a number of $AlMe(BHT)_2(L)$ complexes as compared to their AlR_3 analogues.[22]

Table 3 lists the calculated ΔH_D and ΔS_D values for the dissociation of the Lewis base from AlMe $(BHT)_2(L)$. Also listed are the ΔH_D values determined for the corresponding $AlMe_3$ complex. From the NMR data the following decreasing order of bond strength (ΔH_D) of ligand L, to $AlMe(BHT)_2$, has been determined: py $\approx$ THF > $O_2NC_6H_4$-*p*-Me > O=CPh$_2$ > Et_2O. Although the overall order is similar to that observed for $AlMe_3$, i.e. py > THF > Et_2O, the absolute values are significantly lower. In fact, the absolute value for the dissociation of adduct ligands for $AlMe(BHT)_2$ is much lower (20–30%) than the corresponding trialkyl. It is possible to rationalize such a difference in terms of increased steric hindrance, however, the ΔH_D values for $AlMe_3(L)$ and $Al(^tBu)_3(L)$ complexes are similar.

RATIONALIZATION OF AL—O BONDING INTERACTIONS IN FOUR-COORDINATE COMPOUNDS

Having set out the experimental results of studies on aluminum aryloxide compounds, it is worthwhile at this point to discuss proposed explanations for the structural features observed by X-ray crystallography (short Al—O), by NMR spectroscopy (electron rich aluminum center), and PES (weakening of the Al—X bond). Each of the following models is able to explain some (or all) of the experimental data, and each has its merits.

Steric interactions

Since the aryloxides considered here are bulky, steric effects could provide a reasonable explanation for the enlarged Al—O—C bond angles,

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] See ref. 22. Error given in parenthesis.
[b] See ref. 33.

especially in the case of the four-coordinate complexes and the sterically congested $Al(BHT)_3$. 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 interaction is largely independent of the steric bulk of the Lewis base.[6c] Furthermore, less sterically hindered aryloxides such as DIP and OMes also show the similar effects of a short Al—O bond distance,[6b] and a $\Delta_{O\text{-}C}$ [$-0.22(1)$ and $-0.23(1)$ Å for $AlMe(OMes)_2(3,5\text{-}Me_2py)$] comparable to that for $AlMe_2(BHT)(PMe_3)$ (see Table 1).[6c] The Al—O—C bond angles for the two less sterically hindered aryloxide compounds are considerably reduced from those observed for the BHT analogues. However, as noted above the M—O—C bond angles are not necessarily a good indicator of π interaction. In addition, Francl and co-workers[23] 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.

Ionic interactions

A purely, or largely, ionic bonding model has been invoked to explain the short Al—O bond lengths observed by X-ray crystallography, leaving the Al—O—C bond angle subject to considerable variance due to sterics, packing forces in the solid state, or possible agostic Al···H interactions with the ligand *ortho*-tert-butyl groups. Power and co-workers[3] 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. Such a barrier may be expected if a strong, ethylene-like, Al=O π interaction was present. However, it is not clear that a barrier could be observed in the NMR as 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. Such a barrier to rotation, however, has been measured in the four-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}.[24] Given that this value is undoubtedly steric in nature we can infer 10 kJ mol^{-1} to be an upper value for any rotational barrier about an Al—O bond.

Using Fenske–Hall and *ab initio* techniques Chisholm and co-workers[25] have calculated the atomic charges on aluminum and oxygen in $Al_2(OH)_6$, basing the structural parameters on the X-ray crystallographic determination of $Al_2(O^tBu)_6$. Both methods gave significant ionic character to the Al—O bond, with a total charge on O of -0.95 and -1.16 for Fenske–Hall and *ab initio* calculations, respectively. In addition, they found the Al—O π overlap to be small.[25] However, it should be noted that $Al_2(OH)_6$ is very different from the $AlR_x(BHT)_{3-x}(L)$ compounds. First, gas-phase photoelectron spectroscopy clearly indicated that in the aryloxide compounds the π orbital of the BHT ligand's phenyl ring (Phπ b_1) is involved in the interaction with the Al—P bonding orbital, and hydroxide may not be expected to have as significant an interaction.[21] Secondly, in $Al_2(OH)_6$ any π donation (see below) would involve the Al—O π^* orbitals, which are much higher in energy than a dative Al—ligand σ^* orbital.

A counter to the purely ionic bonding model is the relative charges on the oxygen in AlH_2OH, AlH_2OCH_3, $AlH_2(OH)(PH_3)$, and $AlH_2(OCH_3)(PH_3)$ as calculated by *ab initio* methods.[23] Charges for these species are shown in Table 4, along with the corresponding Al—O bond lengths. While the magnitude of the charges on oxygen are in broad agreement with the previous results, it is interesting to note, however, that the negative charge on the oxygen in these aluminum complexes increases with increasing bond length. This is the reverse of what would be expected for strongly ionic compounds, where increasing charge should lead to tighter bonds and shorter bond lengths.

While the ionic model can possibly be used to explain (rationalize) the observed structural data, it does not readily allow for the observed weakening of Al—ligand bonds upon substitution of alkyl for aryloxide, and the apparent electron rich environment about aluminum as determined by NMR spectroscopy.

Bonding involving dπ–pπ interactions

For a transition-metal alkoxide, it is common for the lone pairs of oxygen to donate into a vacant *d*

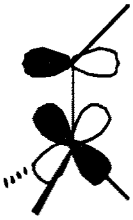
Table 4. HF/3-21G(*) bond lengths in three- and four-coordinate aluminum alkoxides compared to net charges on oxygen[a]

Molecule	r(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] Table 4 taken from ref. 23.

[b] Charges in fractions of an electron.

orbital on the metal. In the case of $AlR_2(BHT)(L)$ and $AlR(BHT)_2(L)$ 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. **VI** and **VII**). Such an interaction is unlikely, however, due to the relatively high energy of the Al $3d$ orbitals.



Al $3d_{xz}$-Op_x

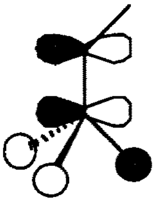
(VI)

Al $3d_{yz}$-Op_y

(VII)

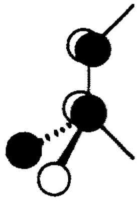
Bonding involving Al—X *σ* orbitals*

An alternate π-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. **VIII** and **IX**).[26] This bonding description would account for the short Al—O bonding distances observed by X-ray crystallography, as well as the presence of an electron-rich aluminum center. In addition, the donaton of electron density into the Al—L σ* orbital would result in its weakening; an effect observed by photoelectron spectroscopy and bond dissociation energy measurements.



$2e_x$ - p_x

(VIII)

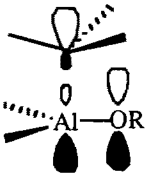


$2e_y$ - p_y

(IX)

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.[23] 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 aryloxide 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 data are in agreement with these results. The average Al—O bond distance in three-coordinate $AlMe(BHT)_2$ is 1.686 Å,[4] while in $Al(BHT)_3$ the average bond length is 1.648(7) Å.[5] In four-coordinate compounds, the average length is 1.791 Å.[2]

Ab initio molecular oribtal calculations of the model compounds, AlH_2OCH_3, AlH_2OH, $AlH_2(OCH_3)(PH_3)$, and $AlH_2(OH)(PH_3)$ indicate that in the four-coordinate compounds, the aluminum–Lewis base σ* orbital is energetically accessible, though it lies some 0.05 au above the empty aluminum p orbital in a three-coordinate aluminum compound, as Fig. 4 shows.[23] 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 aluminum is shifted less than 0.2 Å out of the HHO plane) and experimentally (see Fig. 5), the σ* Al—P orbital is also geometrically positioned for overlap with the oxygen lone pairs (**X**). 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 the case; the calculated Al—P bond is approximately 0.1 Å longer in the alkoxide complexes than in the $AlH_3(PH_3)$. This supports the experimental gas phase photoelectron spectra in which the Al—P bond in $AlMe_2(BHT)(PMe_3)$ is significantly weaker than that in Me_3AlPMe_3.[21a]



(X)

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.[23] 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. The X-ray crystallographic structure of the fluoro-substituted aryloxide, $AlMe_2(OC_6F_5)[N(C_2H_4)_3CH]$,[6c] reveals an Al—O—C angle of 128°, 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 1) is also consistent with a lack of Al—O π-bonding.[6c]

We note that σ* orbitals have been invoked to explain the back-donation of electron density from

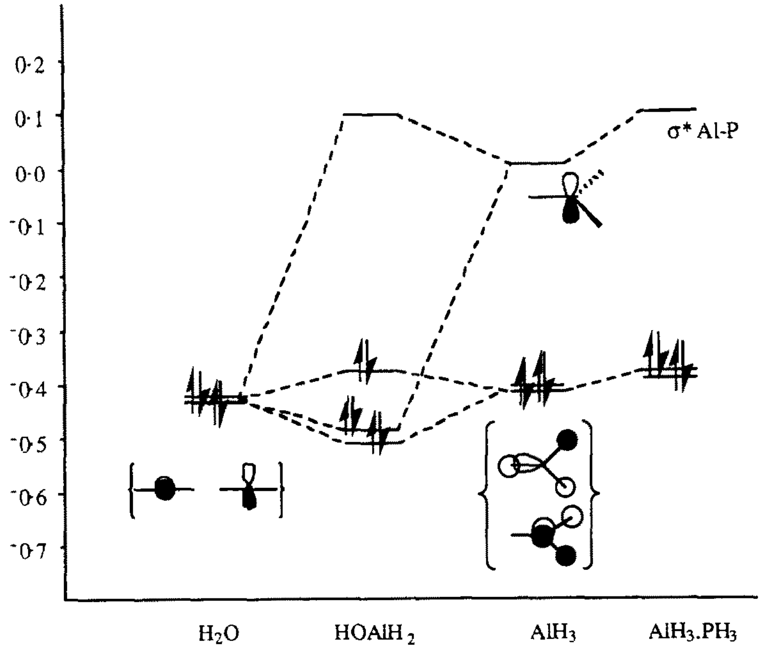


Fig. 4. MO interaction diagram for Al—O bonding in $HOAlH_2$, energy of the σ* Al—P orbital and the π AlH_2 orbital shown for comparison. Orbital energies are in atomic units and drawn from HF/3-21G(*) calculations.

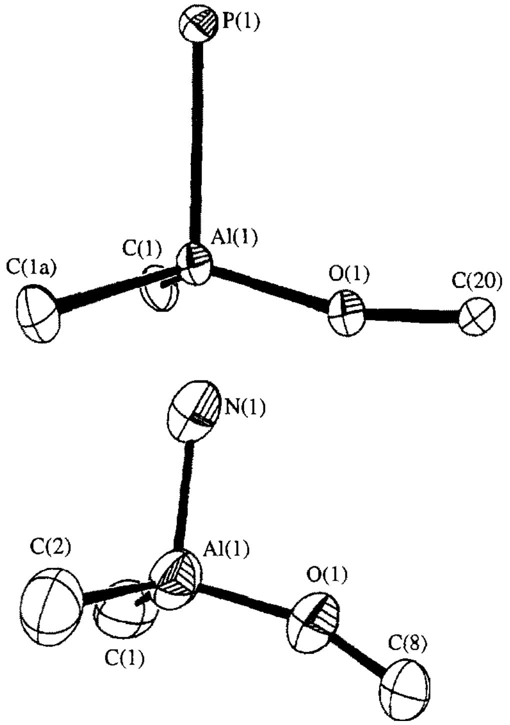
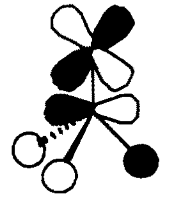


Fig. 5. The partial coordination sphere of the aluminum atoms in $AlMe_2(BMT)$ (PMe_3) and $AlMe_2(BMT)(py)$. These views emphasize the lack of pyramidalization of the $Air_2(BHT)$ fragment.

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 (**XI**).[27] Thus, Orpen and Connelly[27b] 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.

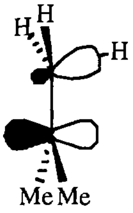


(**XI**)

It is also interesting to note that π back-donation from a transition metal to the phosphine (P—X σ*) can also be correlated with the ^{31}P NMR chemical shift for the phosphine. Thus, the chemical shifts for a series of tungsten compounds of PMe_3 are dependent on the oxidation state (and hence back-donation) of the tungsten; tungsten(II) −33 ppm, tungsten(IV) −24 ppm, and tungsten(VI) −18 ppm.[28] This upfield shift with increased π back-bonding is exactly the same as the trend observed for the ^{27}Al NMR spectra of aluminum aryloxide compounds.

The hyperconjugative stabilization of carbocations, e.g. $[CMe_3]^+$ (**XII**),[29,30] is also related to the

O p to Al—X σ^* donation, except the interaction is between an empty p orbital and a full C—H σ bond.



(XII)

CONCLUSION

In considering the interaction between aluminum and an aryloxide oxygen one question that should be asked is, what is a normal Al—O bonding interaction? Clearly an Al—O bond is covalent with a significant polar, *ionic*, contribution. As such many of the structural observations, such as short Al—O bonds, can be rationalized. However, such a simplistic model does not fully explain all of the observed spectroscopic data. An ionic (or polar covalent) bond cannot account for the presence of an electron-rich aluminum center, and weakening of the Al—ligand bonds. Thus, an additional electronic interaction must be postulated. At present the spectroscopic and theoretical data is consistent with a model including a π-interaction between the O p and Al—X σ^* orbitals. We note that there has been some disagreement in the literature concerning this proposal of O p to Al—X σ^* donation. It does not suggest an ethylene-type interaction, and should be considered to be similar to the bonding in transition metal phosphines and is also analogous to the orbital model often presented for the hyperconjugation observed in stable carbocations.

If we accept the presence of some π interaction in an Al—O bond then returning to the question of the identity of a normal Al—O bond, Haaland[31] has described a normal (non-dative) Al—O bond to be 1.69 Å in length. This is clearly similar to that observed for terminal aluminum aryloxides. Thus, we propose that a "normal" Al—O bond is a polar covalent σ-bond with an additional π interaction involving the antibonding orbitals of the aluminum.

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