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Sterically Crowded Aryloxide Compounds of Aluminum

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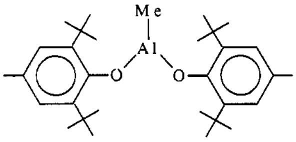
The interaction of $AlMe_3$ with 2 equiv of the sterically hindered phenol 2,6-di-*tert*-butyl-4-methylphenol (BHT-H) gives the disubstituted compound $AlMe(BHT)_2$ (**1**), whereas the use of an excess of $AlMe_3$ leads to the compound $AlMe_2(BHT)$ (**4**). Addition of PMe_3 to **1** and **4** yields $AlMe(BHT)_2(PMe_3)$ (**2**) and $AlMe_2(BHT)(PMe_3)$ (**3**), respectively. The addition of 1 equiv of Me_3NHCl to **1** and **3** results in the formation of $AlCl(BHT)_2(NMe_3)$ (**5**) and $AlClMe(BHT)(NMe_3)$ (**6**); reaction of a further equivalent of Me_3NHCl to **6** affords the ionic complex $[Me_3NH][AlMeCl_2(BHT)]$ (**7**). The molecular structures of **3** and **7** have been confirmed by X-ray crystallography. The Al–O distances are shorter and Al–O–C angles larger than usually found for aluminum alkoxides. The possibility of a π-type interaction between aluminum and oxygen is discussed. The compound $AlMe_2(BHT)PMe_3$ (**3**) crystallizes in the monoclinic space group $P2_1/m$ with unit cell dimensions $a = 7.427$ (2) Å, $b = 15.735$ (2) Å, $c = 9.430$ (3) Å, $\beta = 96.37$ (2)°, $Z = 2$, observed data 1071, $R = 0.0572$, and $R_w = 0.0417$. The compound $[Me_3NH][AlMeCl_2(BHT)]$ (**7**) crystallizes in the orthorhombic space group $P2_12_12_1$ with unit cell dimensions $a = 15.251$ (4) Å, $b = 15.218$ (5) Å, $c = 9.680$ (4) Å, $Z = 4$, observed data 2459, $R = 0.0499$, and $R_w = 0.0417$.

Introduction

The reaction of aluminum alkyls with 1 equiv of phenol, and substituted phenols, was first demonstrated, by Mole,[1] to yield bridging phenoxide compounds (eq 1). Addition

$$AlR_3 + PhOH \rightarrow {}^1\!/_2[R_2Al(\mu\text{-}OPh)]_2 \qquad (1)$$

of 2 and 3 equiv of phenol yields the di- and trisubstituted complexes $AlR(OPh)_2$ and $Al(OPh)_3$, respectively.[2] Analogous reactions with the sterically hindered 2,6-di-*tert*-butyl-4-methylphenol (BHT-H, from the trivial name butylated hydroxytoluene) result in the monomeric products $AlR_2(BHT)$ and $AlR(BHT)_2$ (R = Et, Bu).[3-5] For R = Me, however, the bis(phenoxide) complex **1** is the only product isolated even when 1 equiv of BHT-H is used in the preparation.



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It was suggested[4] that **1** was formed by disproportionation of $AlMe_2(BHT)$ (eq 2) upon removal of volatile Al_2Me_6 during workup of the reaction.

$$2AlMe_2(BHT) \rightarrow {}^1\!/_2Al_2Me_6 + AlMe(BHT)_2 \qquad (2)$$

A recent NMR study by Ittel et al.[5] of the species present in solutions of $AlMe_xBHT_{3-x}$ showed that this was not the case. They proposed that two concurrent disproportionations occur in solutions (eq 3 and 4). The publication of this result has prompted us to report our work on the synthesis and characterization of methyl- and chloro-substituted complexes of aluminum containing the sterically hindering aryloxide ligand BHT.

$$Al_2Me_5(BHT) \rightleftharpoons {}^1\!/_2Al_2Me_6 + AlMe_2(BHT) \qquad (3)$$

$$3AlMe_2(BHT) \rightleftharpoons Al_2Me_5(BHT) + AlMe(BHT)_2 \qquad (4)$$

Results and Discussion

Interaction of $AlMe_3$ with 2 equiv of BHT-H in benzene allows the isolation of $AlMe(BHT)_2$ (**1**). Addition of PMe_3 to a benzene solution of **1** results in the formation of the Lewis acid–base adduct $AlMe(BHT)_2(PMe_3)$ (**2**), which can be recrystallized from pentane. In contrast to **1**, solid **2** can be handled in air for several minutes without appreciable decomposition.

The ^1H NMR signal for the aluminum methyl ligand of **2** (δ –0.17) is downfield of that found for **1** (δ –0.43). This downfield shift is consistent with an increase in p character in the Al–C bond in going from a planar sp^2 to a tetrahedral sp^3 aluminum center.[6]

The room-temperature ^1H NMR spectrum of an equimolar solution of $AlMe_3$ and BHT-H contains a single peak due to Al–Me protons (δ –0.38); integration is consistent with a stoichiometry $AlMe_2(BHT)$. If, however, the sample is cooled to –80 °C, four peaks are observed that have been assigned by Ittel et al.[5] as **1**, $AlMe_2(BHT)$, $Al_2Me_5(BHT)$, and Al_2Me_6.

Addition of 1 equiv of PMe_3 to an equimolar mixture of $AlMe_3$ and BHT-H at room temperature, results in the isolation of a single product, $AlMe_2(BHT)(PMe_3)$ (**3**), as a white crystalline solid which has moderate stability in air. The ^1H NMR signal for the aluminum methyls of **3** (δ –0.27) is *upfield* of that assigned to $AlMe_2(BHT)$ at –80 °C by Ittel et al. (δ –0.20). This is in the opposite direction to that expected in going from sp^2 to sp^3 aluminum center. Note, however, that at –80 °C the methyl groups of $AlMe_2(BHT)$ are probably still exchanging with those on $Al_2Me_5(BHT)$.[5]

If PMe_3 is added to the $AlMe_3$/BHT (1:1) solution at –80 °C, the major product is **2**, with **3** and Me_3AlPMe_3 as minor constituents. This mixture of products and their approximate ratios (7:1:2) is consistent with the proposal of four species in solution at equilibrium, i.e., $AlMe(BHT)_2$ (**1**), $AlMe_2(BHT)$, $Al_2Me_5(BHT)$, and Al_2Me_6. Addition of $AlMe_3$ to a benzene solution of **1** followed by addition of PMe_3, at room temperature also yields **3** as the only product.

The preferential formation of **3** upon addition of PMe_3 to the reaction mixture at room temperature suggests that

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$AlMe_2(BHT)$ is a coordinatively unsaturated monomer in solution. NMR results indicate it to be a minor constituent (ca. 15%) in equilibrium, with the sterically more demanding bis(aryloxide) (**1**) or the dimers $Al_2Me_5(BHT)$ and Al_2Me_6.

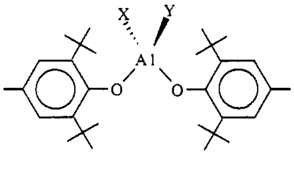
When PMe_3 is added to a solution containing BHT-H with a fourfold excess of $AlMe_3$, compound **3** is formed along with Me_3AlPMe_3 (eq 5). If, on the other hand, the

$$4AlMe_3 + BHT\text{-}H \xrightarrow{PMe_3} AlMe_2(BHT)(PMe_3) + 3Me_3AlPMe_3 + CH_4 \quad (5)$$

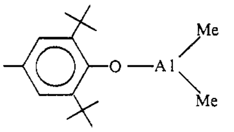
phosphine is not added to the above mixture and the solvent is simply removed under vacuum, white $AlMe_2(BHT)$ (**4**) is isolated (eq 6), which can be subsequently converted to **3** by the addition of PMe_3.

$$4AlMe_3 + HBHT \rightarrow AlMe_2(BHT) + \tfrac{3}{2}Al_2Me_6 \quad (6)$$

The mass spectrum of **4** shows peaks due to parent ion (*m/z* 276) and the consecutive loss of methyl groups (*m/z* 261, 246). The fragmentation pattern is identical with that found for **3** with the exception of peaks due to coordinated and free PMe_3.



2 X = Me, Y = PMe_3
5 X = Cl, Y = NMe_3



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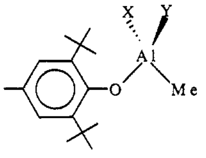

3 X = Me, Y = PMe_3
6 X = Cl, Y = NMe_3
7 X = Y = Cl

Attempted syntheses of the chloride analogues of **1** and **4** by reaction of $AlCl_3$ with LiBHT resulted in a mixture of products. The reaction of **1** with HCl gas does lead to chlorinated products, but careful control of stoichiometry is required. Trialkylammonium chloride salts, which have been used previously in the synthesis of aluminum chlorides from hydrides,[7] permitted more convenient stoichiometric control.

Addition of 1 equiv of Me_3NHCl to an Et_2O solution of **1** yields the complex $AlCl(BHTe_2(NMe_3)$ (**5**). A similar substitution is observed for the reaction of **3** with 1 equiv of Me_3NHCl to yield $AlClMe(BHT)(NMe_3)$ (**6**). The presence of coordinated NMe_3 was confirmed by ^1H NMR and elemental analysis. Neither **5** nor **6** show a parent ion in the mass spectra, the highest mass peak being due to $M^+ - NMe_3$. Compounds with the general formula $AlClMe(OR)$ have been prepared previously via the alcoholysis of $AlClMe_2$ and are dimeric, containing alkoxide bridges.[4,8]

The addition of 2 equiv of Me_3NHCl to **3** does not yield the dichloride $AlCl_2(BHT)$ as expected but rather yields the ionic complex $[Me_3NH][AlCl_2Me(BHT)]$ (**7**) (eq 7). The substitution of NMe_3 for chloride in **6** suggests that reactivity of the Al–C bond is reduced by the presence of a halide ligand.

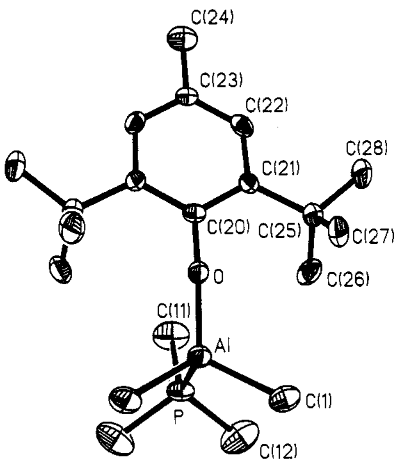

Figure 1. The structure of $AlMe_2(BHT)(PMe_3)$ (**3**). Thermal ellipsoids are drawn at the 50% level, and hydrogen atoms are omitted for clarity.

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) in $AlMe_2(BHT)(PMe_3)$

Bond Lengths			
P–Al	2.499 (3)	Al–C(1)	1.970 (4)
P–C(11)	1.800 (6)	Al–C(1A)	1.970 (4)
P–C(12)	1.809 (5)	Al–O	1.736 (5)
P–C(12A)	1.810 (5)	O–C(20)	1.343 (7)
C(20)–C(21)	1.421 (5)	C(20)–C(21A)	1.421 (5)
C(21)–C(22)	1.400 (6)	C(21)–C(25)	1.536 (6)
C(22)–C(23)	1.374 (5)	C(23)–C(24)	1.520 (9)
C(23)–C(22A)	1.374 (5)	C(25)–C(26)	1.537 (6)
C(25)–C(27)	1.552 (6)	C(25)–C(28)	1.536 (7)

Bond Angles			
P–Al–C(1)	101.9 (1)	P–Al–O	104.5 (2)
C(1)–Al–O	117.9 (1)	P–Al–C(1A)	101.9 (1)
C(1)–Al–C(1A)	111.7 (3)	O–Al–C(1A)	117.0 (1)
C(11)–P–C(12)	104.2 (2)	C(11)–P–Al	118.8 (2)
C(12)–P–Al	112.5 (2)	C(11)–P–C(12A)	104.1 (2)
C(12)–P–C(12A)	103.3 (3)	Al–P–C(12A)	112.5 (2)
Al–O–C(20)	164.5 (4)	O–C(20)–C(21)	120.2 (3)
O–C(20)–C(21A)	120.2 (3)	C(21)–C(20)–C(21A)	119.6 (5)
C(20)–C(21)–C(22)	118.2 (4)	C(20)–C(21)–C(25)	122.1 (4)
C(22)–C(21)–C(25)	119.7 (4)	C(21)–C(22)–C(23)	122.8 (4)
C(22)–C(23)–C(24)	120.8 (3)	C(22)–C(23)–C(22A)	118.3 (6)
C(24)–C(23)–C(22A)	120.9 (3)	C(21)–C(25)–C(26)	110.1 (3)
C(21)–C(25)–C(27)	110.6 (3)	C(26)–C(25)–C(27)	111.5 (4)
C(21)–C(25)–C(28)	112.8 (4)	C(26)–C(25)–C(28)	105.7 (4)
C(27)–C(25)–C(28)	106.0 (4)		

$$AlMe_2(BHT)(PMe_3) \rightarrow AlClMe(BHT)(NMe_3) \rightarrow [AlCl_2Me(BHT)]^- \quad (7)$$

The ^1H NMR signal for the aluminum methyl of **7** (δ −0.06) is downfield of that found for **6** (δ −0.18), a consequence of the greater electronegativity of Cl^- as compared to NR_3.

X-ray Crystallographic Studies. The molecular structure of **3** is shown in Figure 1; selected bond lengths and angles are given in Table I. The structure consists of discreet monomeric units which have a crystallographically imposed mirror plane. As is common with essentially all four-coordinate aluminum compounds, the geometry around aluminum is distorted tetrahedral, with the angles associated with phosphine being the most acute. The Al–C bonds in **3** [1.970 (4) Å] are longer than those found for $AlMe_3$[9] [1.957 (3) Å] or $AlMe(BHT)_2$[5] [1.927 (3) Å]. This

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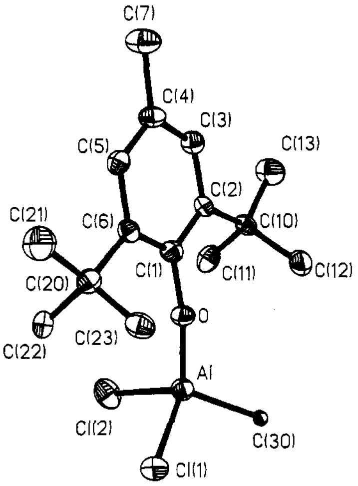

Figure 2. The structure of the anion [AlMeCl$_2$(BHT)]$^-$ (7). Thermal ellipsoids are drawn at the 50% level, and hydrogen atoms are omitted for clarity.

change is in the direction predicted on the basis of increased p character in the Al–C bonds on changing from a planar to tetrahedral geometry and is consistent with the observed chemical shifts in the ^{1}H NMR spectrum. The C–P–C angles of the coordinated PMe$_3$ in **3** [C(11)–P–C(12) = 104.2 (2)°, C(12)–P–C(12A) = 103.3 (3)°] are larger than that found for the free phosphine [98.9 (2)°],[9] which is in agreement with the positive $\Delta(^{31}P)$ ($\Delta = \delta_{\text{complex}} - \delta_{\text{free phosphine}}$), i.e., a downfield shift on coordination.[11] In contrast to the staggered conformations observed for the structures of Me$_3$AlPMe$_3$[12] and Me$_3$AlPPh$_3$,[13] the P–Me groups are eclipsed with respect to the substituents on aluminum. This is undoubtedly a consequence of the sterically demanding *tert*-butyl groups on the phenoxide ring. In addition the PMe$_3$ is tilted away from the phenoxide, resulting in large Al–P–C(11) angle, 118.8 (2)°, [Al–P–C = 115.0 (7)° in Me$_3$AlPMe$_3$].[12] The Al–P distance [2.499 (3) Å] is within the range previously reported for aluminum phosphine complexes.[12,13] The Al–O–C angle of the phenoxide is much larger than has been previously observed for main group compounds (see below).

The structure of the complex anion of **7** is shown in Figure 2; selected bond lengths and angles are given in Table II. The structure consists of discrete monomeric units; the geometry around the aluminum atom is distorted tetrahedral. The arrangement of the substituents around the aluminum is similar to that found for **3**; i.e., the most acute angles to the aryloxide are made by the substituents perpendicular to the aryl ring, i.e., P–Al–O = 104.5 (2)° (**3**) and Cl(2)–Al–O = 109.5 (1)° (**7**); this similarity can be seen clearly by a comparison of the aluminum coordination spheres in **3** and **7** (Figure 3).

The Al–C(30) bond distance in **7** is longer than is usual for aluminum methyl groups. Despite a slight disordering with the chlorides (see Experimental Section), this lengthening is not inconsistent with the large upfield shift of the methyl resonance in the ^{1}H NMR (δ −0.06).

In the structures of both **3** and **7** the Al–O–C angles are much larger than previously observed for main-group alkoxides, although they are in a region commonly found for transition-metal alkoxide complexes,[14] where significant pπ–dπ bonding is present. In addition the Al–O distances are short compared to the normal range of 1.8–2.0 Å.[15]

Table II. Selected Bond lengths (Å) and Bond Angles (deg) in [AlMeCl$_2$(BHT)][Me$_3$NH]

	Bond Lengths		
Al–Cl(2)	2.199 (2)	Al–Cl(1)	2.190 (2)
Al–C(30)	1.995 (5)	Al–O	1.713 (4)
O–C(1)	1.370 (6)	C(1)–C(2)	1.418 (7)
C(1)–C(6)	1.414 (7)	C(2)–C(3)	1.393 (7)
C(2)–C(10)	1.549 (7)	C(3)–C(4)	1.383 (8)
C(4)–C(5)	1.389 (8)	C(4)–C(7)	1.517 (7)
C(5)–C(6)	1.401 (7)	C(6)–C(20)	1.540 (8)
C(10)–C(11)	1.546 (8)	C(10)–C(12)	1.523 (8)
C(10)–C(13)	1.542 (8)	C(20)–C(21)	1.539 (8)
C(20)–C(22)	1.539 (8)	C(20)–C(23)	1.513 (8)
N–C(43)	1.464 (8)	N–C(42)	1.493 (7)
N–C(41)	1.469 (7)		
	Bond Angles		
Cl(2)–Al–Cl(1)	101.2 (1)	Cl(2)–Al–C(30)	111.1 (2)
Cl(1)–Al–C(30)	105.3 (1)	Cl(2)—Al–O	109.5 (1)
Cl(1)–Al–O	111.2 (1)	C(30)–Al–O	117.2 (2)
Al–O–C(1)	164.0 (3)	O–C(1)–C(2)	120.3 (5)
O–C(1)–C(6)	119.2 (5)	C(2)–C(1)–C(6)	120.4 (5)
C(1)–C(2)–C(3)	117.8 (5)	C(1)–C(2)–C(10)	123.1 (5)
C(3)–C(2)–C(10)	119.8 (5)	C(2)–C(3)–C(4)	123.4 (5)
C(3)–C(4)–C(5)	117.5 (5)	C(3)–C(4)–C(7)	121.3 (5)
C(5)–C(4)–C(7)	121.1 (5)	C(4)–C(5)–C(6)	122.7 (5)
C(1)–C(6)–C(5)	118.1 (5)	C(1)–C(6)–C(20)	123.3 (4)
C(5)–C(6)–C(20)	118.6 (4)	C(2)–C(10)–C(11)	110.1 (4)
C(2)–C(10)–C(12)	110.2 (4)	C(11)–C(10)–C(12)	111.8 (4)
C(2)–C(10)–C(13)	112.5 (4)	C(11)–C(10)–C(13)	105.5 (4)
C(12)–C(10)–C(13)	106.5 (5)	C(6)–C(20)–C(21)	112.5 (4)
C(6)–C(20)–C(22)	111.0 (4)	C(21)–C(20)–C(22)	106.1 (4)
C(6)–C(20)–C(23)	109.6 (4)	C(21)–C(20)–C(23)	105.6 (5)
C(22)–C(20)–C(23)	111.9 (4)	C(41)–N–C(42)	110.7 (5)
C(41)–N–C(43)	112.0 (5)	C(42)–N–C(43)	111.3 (5)

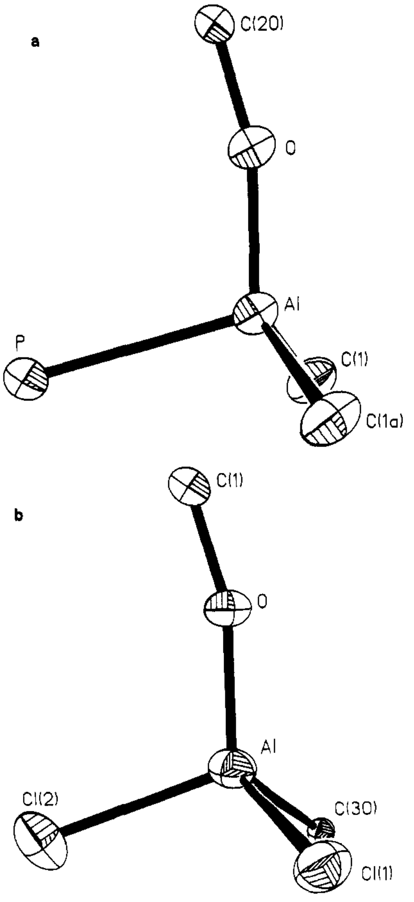

Figure 3. The partial coordination sphere of the aluminum atoms in compounds **3** (a) and **7** (b).

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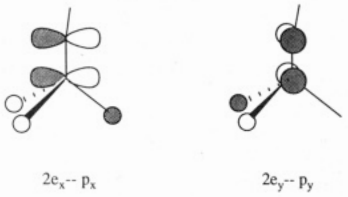
Such a shortening with a concomitant increase in the Al–O–C angles would suggest the presence of some form of π-interaction. For a transition-metal alkoxide, it is common for the lone pairs on oxygen to donate into a vacant d orbitals on the metal. In the case of **3** and **7**, overlap between the oxygen p_x and p_y orbitals with the vacant $3d_{xz}$ and $3d_{yz}$ orbitals on aluminum is possible (z axis along the Al–O vector). Such an interaction is unlikely, however, due to the relatively high energy of the Al 3d orbitals.

An alternative 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. 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. Finally, it should be noted that steric effects cannot be ignored. In order to ascertain which factors predominate, we are studying complexes of the type $AlMe_2(OR)PMe_3$ in which R is not as sterically demanding.



Experimental Section

Microanalyses were performed by Multichem Laboratories, Lowell, MA. Melting points were determined in sealed capillaries and are uncorrected. IR spectra (4000–700 cm^{-1}) were recorded on a Perkin-Elmer 137 grating spectrometer as Nujol mulls. NMR spectra, in C_6D_6, were recorded on Bruker AM-250 (^1H) and Bruker WM-300 ($^{31}P\{^1H\}$) spectrometers [δ in parts per million relative to $SiMe_4$(^1H) and 85% H_3PO_4, external (^{31}P)]. All manipulations were carried out under nitrogen. Solvents were dried, distilled, and degassed before use.

Trimethylaluminum (2.0 M solution in hexane) was used as supplied (Aldrich). BHT-H (Aldrich) was sublimed, and NMe_3HCl (Aldrich) was dried under vacuum prior to use.

AlMe(BHT)$_2$ (1). The synthesis of **1** was carried out by a modification of the literature procedure.[5] To a benzene (50-mL) solution of BHT-H (1.37 g, 6.23 mmol), at room temperature, was added a hexane solution of $AlMe_3$ (1.6 mL, 2.0 M). The solution was refluxed for 3 h, cooled, and evaporated to give a white solid. Recrystallization from boiling pentane resulted in colorless crystals: yield 1.37 g, 91%; mp 164 °C; mass spectrum, m/z 480 (M^+), 465 ($M^+ - Me$), 246 [Al(BHT)]. IR and NMR were in full agreement with published data.[5]

AlMe(BHT)$_2$(PMe$_3$) (2). PMe_3 (1.0 mL, 10.0 mmol) was added to a benzene (30 mL) solution of **1** (2.44 g, 5.0 mmol) and the resulting mixture stirred for 2 h. Removal of the solvent and drying under vacuum gave a white solid, which was extracted with pentane (2 × 20 mL). The extracts were reduced in volume and cooled to −20 °C, affording colorless crystals: yield 2.72 g, 96%; mp 89–91 °C; mass spectrum, m/z 556 (M^+), 480 ($M^+ - PMe_3$), 465 [$Al(BHT)_2$], 220 (BHTH); IR 1405 (s), 1350 (m), 1300 (sh), 1265 (s), 1180 (m), 1155 (w), 1125 (m), 1025 (m), 965 (m), 955 (m), 885 (s), 865 (s), 815 (w), 775 (m), 735 (m) cm^{-1}; ^1H NMR δ 6.98 (4 H, s, C_6H_2), 2.24 (6 H, s, $C_6H_2CH_3$), 1.49 (36 H, s, CCH_3), 0.65 [9 H, d, J(P–H) = 5.4 Hz, PCH_3], −0.17 (3 H, s, $AlCH_3$); $^{31}P\{^1H\}$ NMR δ −52.27 (s). Anal. Calcd for $C_{34}H_{58}AlO_2P$: C, 73.38; H, 10.43. Found: C, 73.54; H, 10.64.

AlMe$_2$(BHT)(PMe$_3$) (3). Method 1. To a solution of BHT-H (1.20 g, 5.45 mmol) in benzene (35 mL) was added $AlMe_3$ in hexane (3.5 mL, 2.0 M). After the solution was stirred for 4 h, PMe_3 (2.0 mL, 20 mmol) was added. The resulting solution was stirred for 12 h and reduced to dryness under vacuum. Extraction of the white solid with pentane gave on cooling (−20 °C) colorless crystals, yield 1.70 g, 89%.

Method 2. $AlMe_3$ (1.8 mL, 2.0 M) was added to a toluene (30 mL) solution of **1** (1.63 g, 3.40 mmol). The solution was refluxed for 12 h. After the solution was cooled to 0 °C, PMe_3 (1.5 mL, 15 mmol) was added, and the solution was stirred for 2 h. The solvent was removed under vacuum, and the white solid recrystallized from pentane (−20 °C): yield 2.18 g, 91%; mp 162 °C; mass spectrum, m/z 352 (M^+), 276 ($M^+ - PMe_3$), 261 [Al(BHT)Me], 246 [Al(BHT)]; IR 1425 (s), 1350 (m), 1300 (sh), 1280 (s), 1255 (s), 1200 (m), 1175 (m), 1125 (w), 1025 (w), 975 (m), 955 (m), 885 (s), 870 (m), 758 (m), 745 (m) cm^{-1}; ^1H NMR δ 7.07 (2 H, s, C_6H_2), 2.26 (3 H, s, $C_6H_2CH_3$), 1.50 (18 H, s, CCH_3), 0.46 [9 H, d, J(P–H) = 6.9 Hz, PCH_3], −0.27 (6 H, s, $AlCH_3$); $^{31}P\{^1H\}$ NMR δ −50.45 (s). Anal. Calcd for $C_{20}H_{38}AlOP$: C, 68.18; H, 10.79. Found: C, 67.66; H, 10.63.

AlMe$_2$(BHT) (4). To a solution of BHT-H (0.60 g, 273 mmol) in benzene (25 mL) was added $AlMe_3$ (5.5 mL, 2.0 M) in hexane. The solution was stirred for 12 h, and then the solvent was removed under vacuum affording a white powder: yield 0.59 g, 78%; mp 146–147 °C; mass spectrum, m/z 276 (M^+), 261 ($M^+ - CH_3$), 246 [Al(BHT)]; IR 1405 (s), 1350 (m), 1295 (sh), 1255 (s), 1205 (m), 1120 (m), 1075 (m), 960 (m), 925 (s), 895 (m), 855 (s), 815 (s), 775 (m) cm^{-1}. Anal. Calcd for $C_{17}H_{29}AlO$: C, 73.91; H, 10.50. Found: C, 74.02; H, 10.51.

AlCl(BHT)$_2$(NMe$_2$) (5). To a solution of **1** (0.67 g, 1.39 mmol) in Et_2O (50 mL) was added Me_3NHCl (0.13 g, 1.39 mmol) as a solid. After the solution was stirred for 5 h, a white precipitate was formed. Filtration, followed by washing with Et_2O (2 × 10 mL), and then recrystallization from CH_2Cl_2 resulted in a white microcrystalline solid: yield 0.61 g, 78%; mp 190 °C; mass spectrum, m/z 500 ($M^+ - NMe_3$), 465 [$Al(BHT)_2$]; IR 1405 (s), 1350 (m), 1265 (s), 1215 (w), 1160 (m), 1100 (s), 1020 (s), 980 (w), 885 (s), 870 (s), 835 (sh), 810 (s), 780 (w), 745 (m) cm^{-1}; ^1H NMR δ 6.93 (4 H, s, C_6H_2), 2.79 (9 H, s, NCH_3), 2.19 (6 H, s, $C_6H_2CH_3$), 1.43 (36 H, s, CCH_3). Anal. Calcd for $C_{33}H_{55}AlClNO_2$: C, 72.86; H, 10.12. Found: C, 73.00; H, 10.43.

AlClMe(BHT)(NMe$_3$) (6). To a solution of **3** (1.91 g, 5.43 mmol) in Et_2O (40 mL) at −78 °C was added Me_3NHCl (0.52 g, 5.44 mmol) as a solid. On warming to room temperature and stirring for 3 h, all the solid dissolved. Removal of the solvent followed by extraction with pentane/CH_2Cl_2 (2:1) and cooling to −20 °C resulted in the formation of colorless crystals: yield 1.35 g, 70%; mp 223 °C; mass spectrum, m/z 296 ($M^+ - NMe_3$), 281 [AlCl(BHT)], 246 [Al(BHT)]; IR 1420 (s), 1250 (s), 1200 (m), 1115 (m), 1010 (m), 970 (m), 965 (w), 895 (s), 875 (m), 810 (m), 785 (w) cm^{-1}; ^1H NMR δ 7.14 (2 H, s, C_6H_2), 2.30 (3 H, s, $C_6H_2CH_3$), 1.88 (9 H, s, NCH_3), 1.59 (18 H, s, CCH_3), −0.18 (3 H, s, $AlCH_3$). Anal. Calcd for $C_{19}H_{35}AlClNO$: C, 64.13; H, 9.84. Found: C, 64.22; H, 9.72.

[Me$_3$NH][AlCl$_2$Me(BHT)] (7). A solution of **3** (1.91 g, 5.43 mmol) in Et_2O (40 mL) was cooled to −78 °C. To this was added solid Me_3NHCl (1.04 g, 10.8 mmol). The reaction mixture was warmed to room temperature and stirred for 12 h. Subsequently the solvent was removed and the residue extracted with pentane/CH_2Cl_2 (2:1). Cooling to −20 °C resulted in the formation of colorless crystals: yield 0.88 g, 38%; mp > 300 °C; mass spectrum, m/z 246 [Al(BHT)], 220 (H-BHT); IR 3105 (m), 1410 (m), 1265 (s), 1200 (2), 1180 (w), 1025 (w), 975 (m), 880 (s), 800 (m), 756 (w) cm^{-1}; ^1H NMR δ 7.04 (2 H, s, C_6H_2), 2.33 (3 H, s, $C_6H_2CH_3$), 2.22 (1 H, s, NH), 1.82 (9 H, s, NCH_3), 1.59 (18 H, s, CCH_3), −0.06 (3 H, s, $AlCH_3$). Anal. Calcd for $C_{19}H_{36}AlCl_2NO$: C, 53.33; H, 8.42. Found: C, 53.16; H, 8.52.

Crystallography. A crystal data summary is given in Table III; fractional atomic coordinates are listed in Tables IV and V. X-ray data were collected on a Nicolet R3m/V four-circle diffractometer equipped with a LT-1 low-temperature device. Data collection was controlled by using the Nicolet P3 program.[17]

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Table III. Summary of X-ray Diffraction Data

complex	$AlMe_2(BHT)(PMe_3)$	$[Me_3NH][AlMeCl_2(BHT)]$
formula	$C_{20}H_{38}AlOP$	$C_{19}H_{36}AlCl_2NO$
space group	$P2_1/m$	$P2_12_12_1$
a, Å	7.427 (2)	15.251 (4)
b, Å	15.735 (2)	15.218 (5)
c, Å	9.430 (3)	9.680 (4)
β, deg	96.37 (2)	
V, Å^3	1095.2	2246.5
Z	2	4
D(calcd), g cm^{-3}	1.068	1.160
cryst dimen, mm	0.31 × 0.22 × 0.29	0.28 × 0.23 × 0.18
temp, °C	−80 (1)	−80 (1)
radiatn	Mo Kα (0.71073 Å, graphite monochromater)	
N, cm^{-1}	1.64	3.33
2θ limits, deg	4.0–50.0	3.03–48.0
no. of collected	5790	7653
no. of unique	2013	3541
obsd data	1071	2459
R	0.0572	0.0499
R_w	0.0417	0.0564
GOF	1.69	1.30
final residual, e Å^{-3}	0.35	0.81

Table IV. Fractional Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (×10^3 Å^2) of the Non-Hydrogen Atoms in $AlMe_2(BHT)(PMe_3)$

	x	y	z	U(eq)
Al	4 (3)	2500	9488 (2)	23 (1)
C(1)	−1429 (5)	3536 (3)	9707 (5)	36 (2)
P	2114 (2)	2500	11744 (2)	28 (1)
C(11)	4517 (8)	2500	11630 (7)	48 (3)
C(12)	1761 (6)	3402 (3)	12872 (5)	58 (2)
O	1418 (5)	2500	8142 (4)	22 (1)
C(20)	2862 (8)	2500	7401 (6)	20 (2)
C(21)	3609 (6)	3281 (3)	6984 (4)	21 (1)
C(22)	5121 (6)	3250 (3)	6221 (4)	25 (1)
C(23)	5896 (8)	2500	5853 (6)	20 (2)
C(24)	7577 (8)	2500	5069 (7)	37 (3)
C(25)	2856 (6)	4145 (3)	7395 (5)	31 (2)
C(26)	3104 (6)	4254 (3)	9025 (5)	35 (2)
C(27)	839 (6)	4236 (3)	6781 (5)	39 (2)
C(29)	3851 (7)	4898 (3)	6799 (6)	54 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table V. Fractional Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (×10^3 Å^2) of the Non-Hydrogen Atoms in $[AlMeCl_2(BHT)][Me_3NH]$

	x	y	z	U(eq)
Al	801 (1)	8209 (1)	730 (2)	24 (1)
Cl(1)	−318 (1)	9111 (1)	759 (2)	31 (1)
Cl(2)	1846 (1)	9072 (1)	−50 (2)	39 (1)
C(40)	490 (3)	7289 (3)	−655 (5)	11 (1)
O	1060 (2)	7859 (2)	2362 (3)	23 (1)
C(1)	1493 (3)	7666 (4)	3564 (6)	22 (2)
C(2)	2045 (3)	6918 (3)	3642 (5)	20 (2)
C(3)	2440 (3)	6732 (4)	4906 (6)	23 (2)
C(4)	2321 (3)	7238 (4)	6078 (5)	24 (2)
C(5)	1783 (3)	7971 (3)	5968 (5)	23 (2)
C(6)	1351 (3)	8197 (3)	4741 (5)	21 (2)
C(7)	2747 (4)	6992 (4)	7441 (6)	29 (2)
C(10)	2237 (3)	6316 (3)	2388 (5)	22 (2)
C(11)	2712 (4)	6843 (4)	1246 (6)	31 (2)
C(12)	1391 (4)	5902 (4)	1862 (6)	33 (2)
C(13)	2858 (4)	5551 (4)	2754 (7)	40 (2)
C(20)	744 (4)	9005 (3)	4742 (5)	26 (2)
C(21)	701 (4)	9456 (4)	6164 (6)	44 (2)
C(22)	1073 (4)	9708 (4)	3723 (6)	30 (2)
C(23)	−185 (3)	8721 (4)	4425 (6)	28 (2)
N	674 (3)	10925 (3)	−495 (4)	30 (2)
C(41)	−215 (4)	11120 (4)	−991 (7)	43 (2)
C(42)	790 (4)	11235 (4)	957 (6)	44 (2)
C(43)	1349 (4)	11291 (4)	−1405 (7)	49 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Unit-cell symmetry was checked with the program XCELL. Raw diffractometer data was processed with the program XDISK. An empirical absorption correction was performed with the program PSICOR. The structure was solved by use of the SHELXTL-PLUS[18] package of programs. Drawings were produced by using the Nicolet program XP.

$AlMe_2(BHT)(PMe_3)$. The unit cell was indexed by using 20 reflections obtained from a rotation photograph. A lattice determination using both the P3 program and XCELL suggested a monoclinic cell. Examination of the axial photographs confirmed this assignment. Systematic absences where consistent with space groups $P2_1/m$ and $P2_1$. Successful solution in $P2_1/m$ confirmed its choice as being correct. The final unit cell parameters were obtained by a least-squares refinement of 50 selected reflections, including two Friedel pairs, in the range 15° < 2θ < 30°.

A total of 5790 reflections were collected in the range 4° < 2θ < 50° (h,k,l, plus Friedel pairs). Of these, 2013 were unique reflections and 1071 with $F_o > 6\sigma(F_o)$ were used in the structure solution. The intensities of three check reflections were measured after every 60 reflections; the intensities did not vary significantly during the data collection. A semiempirical absorption correction based on scans from six reflections in the range 16° < 2θ < 40°, and Lorentz and polarization corrections were applied to the data.

Use of direct methods readily revealed the positions of the Al, P, O, and the aromatic ring. Standard difference map techniques were used to find the remaining non-hydrogen atoms. After all of the non-hydrogen atoms were located and refined anisotropically, a difference map revealed all of the hydrogen atom positions. Insufficient data were available to refine the positions of the hydrogens; therefore, all of the hydrogen atoms were placed in calculated positions [$U_{iso}(H) = 1.2U_{iso}(C)$; $d_{C-H} = 0.96$ Å] for refinement. Refinement was performed to convergence ($\Delta/\sigma(\max) < 0.01$) with this model. The weighting scheme was $w = [\sigma^2(F) + gF^2]^{-1}$. The final difference map was essentially featureless with all peaks less than 0.35 e Å^{-3}.

$[Me_3NH][AlMeCl_2(BHT)]$. The unit cell was indexed by using 15 reflections obtained from a rotation photograph. A lattice determination using both the P3 program and XCELL sugested an orthorhombic cell. Examination of the axial photographs confirmed this assignment. Systematic absences determined the space group to be $P2_12_12_1$. The final unit cell parameters were obtained by a least-squares refinement of 50 selected reflections, including two Friedel pairs, in the range 15° < 2θ < 30°.

A total of 7053 reflections were collected in the range 4° < 2θ < 48° (h,k,l, plus Friedel pairs). Of these, 3541 were unique reflections and 2459 with $F_o > 6\sigma(F_o)$ were used in the structure solution. The intensities of three check reflections were measured after every 60 reflections; the intensities did not vary significantly during the data collection. A semiempirical absorption correction based on scans from 6 reflections in the range 10° < 2θ < 40°, and Lorentz and polarization corrections were applied to the data.

Use of direct methods readily revealed the positions of the Al, Cl, O, and the aromatic ring. Standard difference map techniques were used to find the remaining non-hydrogen atoms. After all of the non-hydrogen atoms were located and refined anisotropically, C(30) refined to a nonpositive definite thermal parameter [U(eq) = 0.019], and a difference map revealed a peak in the appropriate location for a Cl atom attached to Al. Refinement of the occupancy of C(30) and this position (assigned as Cl with fixed position and $U = U_{iso}(Cl_{av})$) indicated the possibility of a 1% component. This could be due to a slight disorder between C(30) and Cl(2) or possibly the presence of a small amount of trichloro product. In the final model, C(30) was refined isotropically. A difference map phased on the non-hydrogen atoms revealed most, but not all of the hydrogen atom positions. Therefore, all of the hydrogen atoms were placed in calculated positions [$U_{iso}(H) = 1.2U_{iso}(C)$; $d_{C-H} = 0.96$ Å] for refinement.

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(17) *P3/R3 Data Collection Manual*; Nicolet Instrument Corp.: Madison, WI, 1987.

(18) *SHELXTL-PLUS Users Manual*; Nicolet Instrument Corp.: Madison, WI, 1988.

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Refinement was performed to convergence ($\Delta/\sigma(\max) < 0.01$) with this model. The weighting scheme was $w = [\sigma^2(F) + gF^2]^{-1}$. The final difference map was essentially featureless with all peaks less than 0.81 e Å^{-3} [near C(30)]. Inversion of configuration confirmed that the correct enantiomorph had been chosen.

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Supplementary Material Available: Listings of anisotropic thermal parameters and hydrogen atom parameters (4 pages); tables of calculated and observed structure factors (21 pages). Ordering information is given on any current masthead page.

Phase Transfer Catalyzed Generation of the (η^5-Cyclopentadienyl)tricarbonylhydridovanadate Anion. Applications to the Reduction of Halides, Sterically Encumbered Nitro Compounds, and the Cyclodehydration of α,β-Unsaturated Ketones

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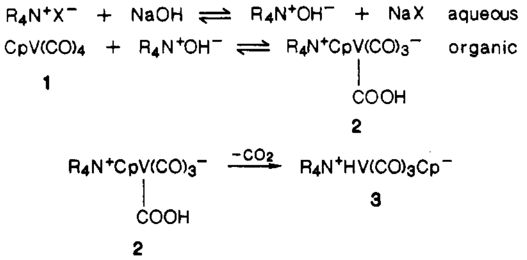
The first examples of the application of phase transfer catalysis to early-transition-metal organometallic chemistry are described. Reaction of (η^5-cyclopentadienyl)vanadium tetracarbonyl with 5 N sodium hydroxide, benzene, and tetrabutylammonium hydrogen sulfate affords the (η^5-cyclopentadienyl)tricarbonylhydridovanadate anion. The latter is capable of effecting, under mild phase transfer conditions, the reduction of sterically encumbered nitro compounds, the semicatalytic, stereospecific, cyclodehydration of acyclic α,β-unsaturated ketones, and the reduction of the double bond of cyclic ketones, as well as the dehalogenation of a wide range of halides. The reactions may proceed via electron transfer pathways.

The use of phase transfer catalysis for the reduction of organic substrates by metal complexes has been extensively investigated in recent years. Examples include the rhodium-catalyzed hydrogenation of aromatic hydrocarbons and heterocyclic compounds,[2,3] and the conversion of nitro compounds to amines. With reference to the latter reactions, triiron dodecacarbonyl,[4] ruthenium carbonyl,[5] dichlorotris(triphenylphosphine)ruthenium(II),[6] and chloro(1,5-hexadiene)rhodium(I) dimer, together with cobalt carbonyl,[7] are effective for the phase transfer catalyzed reactions. However, none of these systems are of value when nitroarenes, containing one sizable orthosubstituent or methyl groups at the 2,6-positions, are used as substrates.

There are no examples, to our knowledge, of the use of phase transfer catalysis for reactions involving complexes of early transition metals. It seemed conceivable that commercially available cyclopentadienylvanadium tetracarbonyl (1, Cp = C_5H_5), when subjected to phase transfer conditions (aqueous base, organic phase, and quaternary ammonium salt), would experience nucleophilic attack by the quaternary ammonium hydroxide to give the vanadium anion 2 bearing a carboxyl ligand. Loss of carbon dioxide from 2 may then generate the (η^5-cyclopentadienyl)tricarbonylhydridovanadate anion (3), previously prepared by the use of sodium amalgam or dispersion techniques.[8] Synthetic applications of anionic transition-metal carbonyl hydrides have also attracted considerable recent interest,[9a] and several such anions have been synthesized by phase transfer techniques.[9b] We now wish to report that phase transfer catalysis is an excellent, experimentally simple method for the generation of the vanadium hydride 3. Furthermore, 3 is capable of reducing sterically encum-



$$R_4N^+X^- + NaOH \rightleftharpoons R_4N^+OH^- + NaX \quad \text{aqueous}$$

$$\underset{1}{CpV(CO)_4} + R_4N^+OH^- \rightleftharpoons \underset{2}{R_4N^+Cp\underset{COOH}{V}(CO)_3^-} \quad \text{organic}$$

$$\underset{2}{R_4N^+Cp\underset{COOH}{V}(CO)_3^-} \xrightarrow{-CO_2} \underset{3}{R_4N^+HV(CO)_3Cp^-}$$

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