

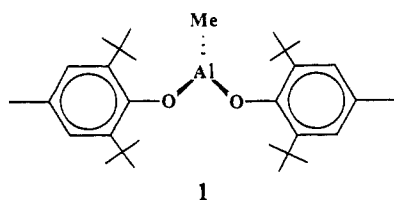
π -Face Selectivity of Coordinated Ketones to Nucleophilic Additions: The Importance of Aluminum–Oxygen π -Bonding

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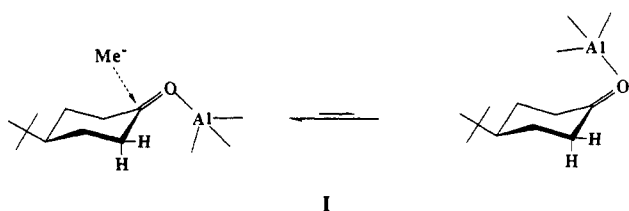
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Abstract: The interaction of $\text{AlMe}(\text{BHT})_2$ with ketones $\text{O}=\text{CRR}'$ yields the Lewis acid–base complexes $\text{AlMe}(\text{BHT})_2(\text{O}=\text{CRR}')$. The X-ray crystallographic determination of $\text{AlMe}(\text{BHT})_2(\text{O}=\text{CPh}_2)$ shows that the ketone coordinates such that the aluminum is in the nodal plane of the $\text{C}=\text{O}$ π -bond. The importance of the orientation of the aryl oxides toward π -face selective nucleophilic addition to the coordinated ketone is discussed. The reaction of $\text{AlMe}(\text{BHT})_2(\text{O}=\text{CRR}')$ with 1 equiv of MeLi , in Et_2O , yields $\text{AlMe}(\text{BHT})_2[\text{OC}(\text{Me})\text{RR}']\text{Li}(\text{OEt}_2)$, the structure of which has been confirmed by X-ray crystallography for $\text{R} = \text{R}' = \text{Ph}$. Addition of an excess of MeLi yields $\text{AlMe}_2(\text{BHT})[\text{OC}(\text{Me})\text{RR}']\cdot\text{Li}(\text{OEt}_2)$ and $[\text{Li}(\text{BHT})\text{OEt}_2]_2$. The reaction of $\text{AlMe}(\text{BHT})_2(\text{O}=\text{CRR}')$ with $^t\text{BuLi}$ or Li metal, in Et_2O , yields $\text{AlMe}(\text{BHT})_2[\text{OC}(\text{H})\text{RR}']\text{Li}(\text{OEt}_2)$. A possible electron-transfer mechanism for methyl and hydride addition to the coordinated ketone is presented. The compound $\text{AlMe}(\text{BHT})_2(\text{O}=\text{CPh}_2)$ crystallizes in the monoclinic space group $P2_1/n$, $a = 12.002$ (2) Å, $b = 24.881$ (2) Å, $c = 13.767$ (3) Å, $\beta = 90.573$ (9)°, $z = 4$, observed data = 1836, $R = 0.061$, $R_w = 0.068$. The compound $\text{AlMe}(\text{BHT})_2[\text{OC}(\text{Me})\text{Ph}_2]\text{Li}(\text{OEt}_2)$ crystallizes in the monoclinic space group $P2_1/c$, $a = 13.789$ (1) Å, $b = 19.676$ (2) Å, $c = 17.835$ (2) Å, $\beta = 105.389$ (7)°, $z = 4$, observed data = 4427, $R = 0.056$, $R_w = 0.060$.

Any chemical protocol that turns over π -face selectivity of a reaction is of great importance to stereoselective organic synthesis. An important development in this area has been the utilization, by Yamamoto and co-workers, of the bulky organoaluminum compound, $\text{AlMe}(\text{BHT})_2$ (**1**) (BHT-H, from the trivial name



butylated hydroxytoluene), for the stereoselective activation of carbonyl moieties.² In this system the stereoselective, equatorial (anti-Cram) alkylation of a substituted cyclohexanone was rationalized by postulating preferential complexation of $\text{AlMe}(\text{BHT})_2$ to the equatorial diastereotopic π -face of the ketone (**I**).



Ab initio calculations,³ however, suggest that the preferred geometry of the ketone–aluminum complex has aluminum in the π -nodal plane of the ketone (**II**). In this geometry the aluminum methyl group would be syn (eclipsed) with respect to the ketone α -carbon in order to minimize steric repulsion. It is, however, not apparent how this geometry would provide the experimentally observed stereoselectivity.

We describe here the synthesis and structural characterization of several ketone adducts of $\text{AlMe}(\text{BHT})_2$ in which the asymmetric orientation of the aryl oxide ligands, due to aluminum–oxygen π -bonding, sterically hinders one face of the ketone. In addition,

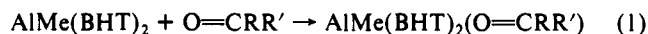


II

the products formed from the interaction of the coordinated ketone with MeLi are reported.

Results and Discussion

Ketone Adducts of $\text{AlMe}(\text{BHT})_2$. The interaction of $\text{AlMe}(\text{BHT})_2$ (**1**) with a series of ketones, $\text{O}=\text{CRR}'$, yields the Lewis acid–base complexes $\text{AlMe}(\text{BHT})_2(\text{O}=\text{CRR}')$, **2–9** (eq 1), which have been fully characterized by elemental analysis, ^1H and ^{13}C NMR, and infrared spectroscopy (see Experimental Section and Table I). All the complexes show a decrease in the carbonyl stretching frequency in the IR spectrum and a downfield shift in the ^{13}C NMR for the carbonyl α -carbon, when compared to the “free” ketone, consistent with coordination of the ketone to aluminum.



We have shown previously⁴ that the ^{13}C NMR shift of the methyl ligands in Me_3AlPR_3 complexes is primarily dependent on the steric bulk of the phosphine ligand; that is, the greater the steric bulk of the phosphine, the more the downfield shift of the methyl resonance. A similar dependence of the methyl ^{13}C shift on the steric bulk of the coordinated ketones is found for the complexes **2–9**.

The paucity of structural data for organo–carbonyl complexes of aluminum prompted us to investigate the X-ray structure of one of these complexes. The molecular structure of $\text{AlMe}(\text{BHT})_2(\text{O}=\text{CPh}_2)$ (**2**) is shown in Figure 1, and selected bond lengths and angles are given in Table II. It is noteworthy that despite the interest in aluminum/ketone systems, **2** is the first example of an aluminum–ketone complex to be structurally characterized. The geometry around aluminum is highly distorted from tetrahedral, with the angles associated with benzophenone being the most acute. The Al–C bond length in **2** [1.942 (8) Å] is slightly larger than that found for $\text{AlMe}(\text{BHT})_2$ [1.927 (3) Å];⁵

(1) (a) Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. (b) Department of Chemistry, University of Alabama, Tuscaloosa, Alabama 35487.

(2) (a) Maruoka, K.; Itoh, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1985**, *107*, 4573. (b) Maruoka, K.; Itoh, T.; Sakurita, M.; Nanoshita, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 3588.

(3) LePage, T. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 6642.

(4) Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1988**, 3047.

Table I. Selected NMR and IR Spectroscopic Data for Aluminum–Ketone Compounds^a

compound	¹³ C NMR (ppm)		IR (cm ⁻¹) (C=O)
	Al–Me	O=CR ₂	
2, AlMe(BHT) ₂ (O=CPh ₂)	-3.51 (-8.79)	205.5 (195.6)	1550 (1650)
3, AlMe(BHT) ₂ [O=C(Ph)Et]	-4.01	216.9 (199.3)	1565 (1682)
4, AlMe(BHT) ₂ [O=C(Ph)Me]	-4.34	212.1 (196.9)	1565 (1680)
5, AlMe(BHT) ₂ (O=CEt ₂)	-4.41	235.2 (209.5)	1660 (1715)
6, AlMe(BHT) ₂ [O=C(Me) ^t Bu]	-4.27	236.54 (211.26)	1650 (1710)
7, AlMe(BHT) ₂ (O=CC ₅ H ₁₀)	-4.44	232.76 (209.62)	1650 (1705)
8, AlMe(BHT) ₂ [O=C(C ₃ H ₉)-4- ^t Bu]	-4.52	233.4 (208.8)	1655 (1720)
9, AlMe(BHT) ₂ [O=C(C ₃ H ₉)-4-Ph]	-4.51	232.19 (107.94)	1655 (1700)

^a Values in parentheses are for the uncoordinated ketone and AlMe(BHT)₂.

Table II. Selected Bond Lengths (Å) and Angles (deg) in AlMe(BHT)₂(O=CPh₂) (2)

Bond Lengths			
Al–O(1)	1.733 (5)	Al–O(2)	1.721 (6)
Al–O(3)	1.903 (6)	Al–C	1.942 (8)
O(1)–C(1)	1.362 (9)	O(2)–C(11)	1.355 (9)
O(3)–C(100)	1.264 (9)	C(100)–C(101)	1.44 (1)
C(100)–C(111)	1.49 (1)		
Bond Angles			
O(1)–Al–O(2)	116.8 (3)	O(1)–Al–O(3)	99.5 (3)
O(1)–Al–C	112.5 (3)	O(2)–Al–O(3)	96.0 (3)
O(2)–Al–C	118.2 (3)	O(3)–Al–C	110.3 (3)
Al–O(1)–C(1)	142.6 (3)	Al–O(2)–C(11)	161.4 (5)
Al–O(3)–C(100)	144.0 (6)	O(3)–C(100)–C(101)	118.4 (8)
O(3)–C(100)–C(111)	118.9 (8)		

this change is in the direction predicted on the basis of increased p character in the Al–C bond on changing from planar to pseudotetrahedral geometry and is consistent with observed chemical shifts in the ¹³C NMR spectrum.⁵

As predicted by theoretical calculations,³ the ketone is coordinated such that the aluminum atom is in the π -nodal plane of the ketone and oriented syn with respect to the aluminum methyl. The aryl oxide Al–O distances [Al–O(1) = 1.733 (5) Å, Al–O(2) = 1.721 (6) Å] are in the range observed previously and are consistent with some degree of π -bonding between oxygen and aluminum.⁶ The aryl oxide Al–O–C angles are different; the larger of the two, Al–O(2)–C(11) [161.4 (5)°], is comparable to that found in AlMe(BHT)₂(PMe₃) [164.5 (54)°].⁶ In this compound there is significant π -bonding between the oxygen lone pair, which is perpendicular to the aryl ring and the Al–P σ^* orbital (III).⁷ By contrast, the second aryl oxide has a more acute Al–O–C angle [142.6 (5)°] comparable to AlMe(BHT)₂ [140.5 (2)°, 146.8 (2)°],⁵ whereas the lone pairs parallel to the aryl ring are involved in π -bonding to the vacant aluminum p_z orbital (IV).

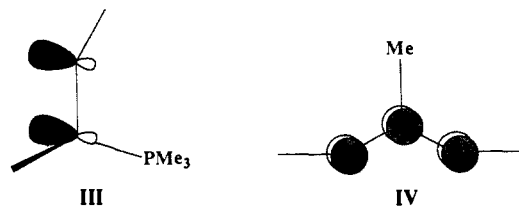
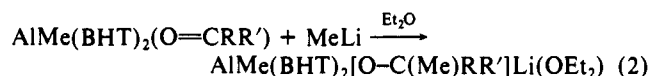


Figure 1. The structure of AlMe(BHT)₂(O=CPh₂) (2). Thermal ellipsoids are drawn at the 50% level, and hydrogen atoms are omitted for clarity.

On the basis of our structural data we propose that the presence of the π -bonding between the aryl oxide lone pairs and the benzophenone Al–O(3) σ^* orbital accounts for the preferred orientation of the two aryl oxides.

The presence of the two distinct aryl oxide orientations results in steric protection for one face of the coordinated ketone ligand (Figure 2) toward nucleophilic attack. In the case of *tert*-butylcyclohexanone² (8) the less bulky face of the ketone would be the one hindered by the *ortho-tert*-butyl groups leaving the sterically more demanding face open for nucleophilic attack.⁸ It is important to note that although the benzophenone in 2 is coordinated coplanar to the aluminum (II), such a coordination is not a requirement for π -face selectivity. We propose therefore that the stereoselectivity observed by Yamamoto and co-workers² is controlled by the preferred orientation of the aryl oxide ligands due to oxygen–aluminum π -bonding.

Reaction of Coordinated Ketones with MeLi. Addition of ethereal MeLi to a pentane solution of 2 or 8 results in the alkylation of the coordinated ketone and the formation of the dinuclear complexes AlMe(BHT)₂[O–C(Me)Ph₂]Li(OEt₂) (10) and AlMe(BHT)₂[O–C(Me)C₃H₉^tBu]Li(OEt₂) (11), respectively (eq 2). Compounds 10 and 11 have been characterized by elemental analysis, ¹H, ¹³C, and ⁶Li NMR, and infrared spectroscopy. It should be noted that if the alkylation is carried out in hexane with nonsolvated MeLi, the reaction proceeds slowly and does not go to completion.



The alkylation of the coordinated ketone at the α -carbon was confirmed by the observation of a resonance in the ¹³C NMR for a quaternary carbon [78.5 ppm (10), 71.7 ppm (11)], and the loss of both the carbonyl $\nu(\text{C=O})$ stretch in the IR spectra and the C=O resonance in the ¹³C spectra. The low field shift of the Al–Me ¹³C shift for compounds 10 and 11, as compared to the ketone complexes 2 and 8, respectively, is suggestive of increased steric congestion at the aluminum center. Heterobimetallic aluminum/lithium alkoxides have been previously reported as having a Al(μ -OR)₂Li bridging unit.⁹ It is reasonable therefore to propose a similar structure for 10 and 11. The presence of a single set of resonances for the BHT ligands in the ¹H and ¹³C NMR spectra would suggest that a symmetrical Al(μ -BHT)₂Li bridge (V) is present in compounds 10 and 11. On steric grounds,

(5) Shreve, A. P.; Mulhaupt, R.; Fultz, W.; Calabrese, J.; Robbins, W.; Ittel, S. D. *Organometallics* 1988, 7, 409.

(6) Healy, M. D.; Wierda, D. A.; Barron, A. R. *Organometallics* 1988, 7, 2543.

(7) Lichtenberger, D. L.; Hogan, R. H.; Healy, M. D.; Barron, A. R. Submitted for publication.

(8) Addition of MeLi to a pentane solution of 6 results in the same product distribution reported by Yamamoto and co-workers. See ref 1 and 2.

(9) Mehrotra, R. C. *Adv. Inorg. Chem. Radiochem.* 1983, 26, 269.

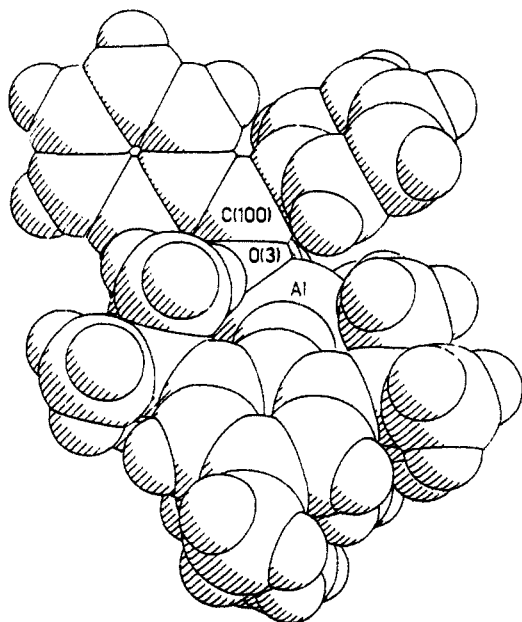
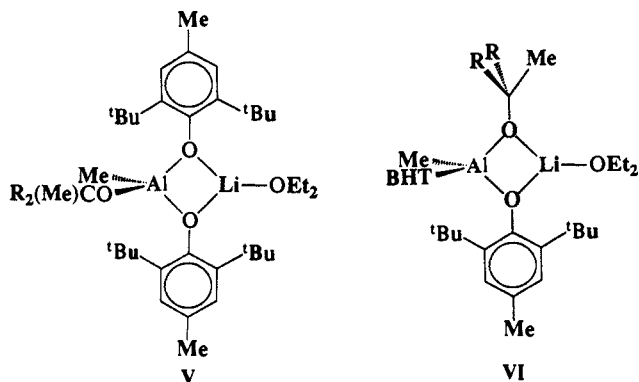


Figure 2. Space-fitting representation of $\text{AlMe}(\text{BHT})_2(\text{O}=\text{CPh}_2)$ (**2**) viewed perpendicular to the nodal plane of the $\text{C}=\text{O}$ π -bond, showing the difference in the steric hindrance of $\text{C}(100)$.

however, one would expect bridging by the less sterically hindered alkoxide (VI).



In order to confirm the heterobimetallic nature of these compounds and investigate the nature of the alkoxide bridges, the

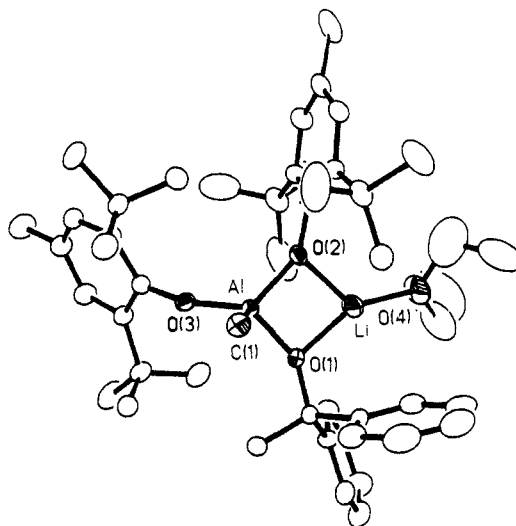


Figure 3. The structure of $\text{AlMe}(\text{BHT})_2[\text{OC}(\text{Me})\text{Ph}_2]\text{Li}(\text{OEt}_2)$ (**10**). Thermal ellipsoids are drawn at the 30% level, and the hydrogen atoms are omitted for clarity.

Table III. Selected Bond Lengths (\AA) and Angles (deg) in $\text{AlMe}(\text{BHT})_2[\text{OC}(\text{Me})\text{Ph}_2]\text{Li}(\text{OEt}_2)$

Bond Lengths			
Al-O(1)	1.808 (2)	Al-O(2)	1.805 (2)
Al-O(3)	1.736 (2)	Al-C(1)	1.969 (4)
Li-O(1)	1.922 (7)	Li-O(2)	1.910 (7)
Li-O(4)	1.933 (7)	O(1)-C(32)	1.436 (4)
O(2)-C(2)	1.374 (4)	O(3)-C(8)	1.357 (4)
C(32)-C(33)	1.537 (5)	C(32)-C(34)	1.530 (5)
C(32)-C(40)	1.541 (5)		
Bond Angles			
O(1)-Al-O(2)	88.0 (1)	O(1)-Al-O(3)	116.7 (1)
O(1)-Al-C(1)	110.8 (1)	O(2)-Al-O(3)	114.5 (1)
O(2)-Al-C(1)	119.1 (2)	O(3)-Al-C(1)	107.2 (2)
O(1)-Li-O(2)	81.8 (3)	O(1)-Li-O(4)	147.8 (4)
O(2)-Li-O(4)	128.3 (4)	Al-O(1)-Li	94.4 (2)
Al-O(2)-Li	94.9 (2)	Al-O(1)-C(32)	134.0 (2)
Li-O(1)-C(32)	121.0 (3)	Al-O(2)-C(2)	146.3 (2)
Li-O(2)-C(2)	118.8 (3)	Al-O(3)-C(8)	165.6 (2)
O(2)-C(32)-C(33)	110.1 (3)	O(1)-C(32)-C(34)	110.0 (3)
O(1)-C(32)-C(40)	108.0 (3)		

structure of **10** was determined by X-ray crystallography. The molecular structure of **10** is shown in Figure 3, with selected bond lengths and angles given in Table III.

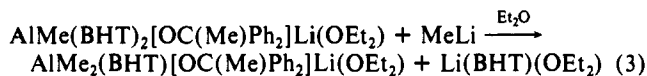
The structure of **10** exists as a bimetallic alkoxide bridged dimer, with one BHT and the alkylated benzophenone acting as the bridging ligands (VI). The geometry around aluminum and lithium are distorted tetrahedral and trigonal planar, respectively, with the most acute angles associated with the $\text{Al}(\mu\text{-O})_2\text{Li}$ bridge. The terminal aryl oxide $\text{Al}-\text{O}(3)$ distance [1.736 (2) \AA] and $\text{Al}-\text{O}(3)-\text{C}(8)$ [165.6 (2) $^\circ$] are consistent with some degree of $\text{Al}-\text{O}$ π bonding.⁶ The $\text{Al}-\text{O}$ distances for the bridging aryl oxide and alkoxide are somewhat larger [$\text{Al}-\text{O}(1) = 1.808$ (2) \AA , $\text{Al}-\text{O}(2) = 1.805$ (2) \AA] and are within the range associated with no π interaction.¹⁰ The $\text{Li}-\text{O}$ bond lengths and the geometry around Li are similar to those reported for the structurally related compound $[\text{Li}(\text{BHT})(\text{OEt}_2)]_2$.

It should be noted that either addition of MeLi to a pentane solution of **8** followed by hydrolysis or hydrolysis of **11**, at either -78 $^\circ\text{C}$ or room temperature, results in the same or better product distribution of syn and anti as reported previously.⁸

In the "one-pot" alkylation of ketones, described by Yamamoto and co-workers, an excess of MeLi is employed. In order to

(10) (a) Zaworotko, M. J.; Rogers, R. D.; Atwood, J. L. *Organometallics* **1982**, *1*, 1179. (b) Atwood, J. L.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 302.

ascertain the effect of excess MeLi we have studied the reaction of **2** with greater than 1 equiv of MeLi. The addition of an excess of MeLi to **2** results in the formation of an inseparable mixture of compounds, **10**, $[\text{Li}(\text{BHT})(\text{OEt}_2)]_2$, and a heterobimetallic compound, proposed from ^1H NMR to be $\text{AlMe}_2(\text{BHT})[\text{OC}(\text{Me})\text{Ph}_2]\text{Li}(\text{OEt}_2)$ (**12**), whose formulation is consistent with the reaction of **10** with MeLi (eq 3).

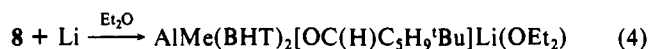


Nucleophilic Attack vs Electron Transfer? It is clear from the X-ray structural study of compound **2** that there are two distinct aryl oxides (see above), one of which is clearly oriented so as to act as a steric hindrance to attack on one side of the coordinated ketone. It is not clear, however, what, if any, purpose the second aryl oxide serves. One possibility is that the second aryl oxide may assist in stabilizing the incoming MeLi unit. This assumes that the alkylation proceeds via a concerted nucleophilic attack. The alkylation could, however, proceed via an electron-transfer mechanism.

In order to ascertain whether the alkyl addition is concerted or not, and if the second aryl oxide takes an active part in the reaction pathway, we have investigated the reaction of **8** with the more sterically hindered lithium reagent, $^t\text{BuLi}$.

The reaction of **8** with 1 equiv of $^t\text{BuLi}$ in pentane/ Et_2O solution does not result in alkyl addition to the carbonyl α -carbon but leads to the reduction of the ketone and formation of the heterobimetallic compound $\text{AlMe}(\text{BHT})_2[\text{O}-\text{C}(\text{H})\text{C}_5\text{H}_9^t\text{Bu}]\text{Li}(\text{OEt}_2)$ (**13**), which has been characterized by elemental analysis and NMR and IR spectroscopy. The structure of **13** is probably similar to that of **11**; unfortunately crystals suitable for an X-ray diffraction could not be obtained.

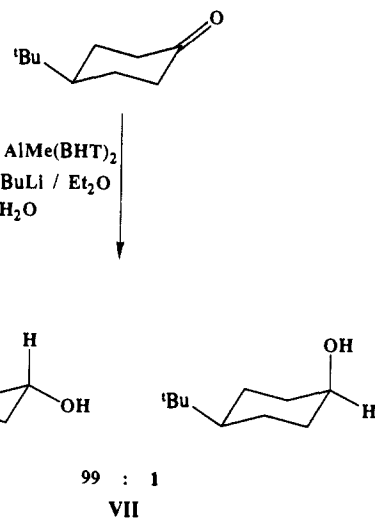
Compound **13** is also the only product from the reduction of **8** in Et_2O by Li metal (eq 4). It should be noted that this reduction cannot proceed via a nucleophilic addition.



The formation of **13** from the reaction of **8** with Li metal is an important observation and would suggest that the mechanism of reduction involves electron transfer from Li to the LUMO of **8**, the carbon-centered carbonyl π^* orbital. The resulting radical anion abstracts a hydrogen from the solvent to give the alkoxide complex. It is possible that the reaction of **8** with $^t\text{BuLi}$ most likely proceeds via an analogous pathway due to the steric bulk of the ^tBu radical precluding alkyl addition to the coordinated ketone.

Despite this evidence for a one electron-transfer mechanism for the reaction of **8** with $^t\text{BuLi}$ and Li metal, it is possible that the MeLi reaction may proceed by a different pathway. If the methyl addition is a radical pathway, and the observed stereoselectivity is high, which it is, then the regioselectivity of the reduction reaction should be comparable. Hydrolysis of **13** yields 4-*tert*-butylcyclohexanol (**VII**) in a *cis*:*trans* ratio of 1:99 (see Experimental Section), which is comparable to the selectivity observed not only for the methyl addition but also for the hydride addition to coordinated ketones reported using $^t\text{BuMgCl}$ in the presence of $\text{AlMe}(\text{BHT})_2$.¹¹

The high regioselectivity of the reduction and alkyl addition reactions can, we believe, be explained by assuming that the structure of the radical anion, formed by electron transfer, is structurally similar to the parent ketone complex. This should indeed be true because the radical would be centered on the carbonyl α -carbon in the $\text{C}=\text{O}$ π^* bonding orbital and as such should not significantly affect the bonding to aluminum or the geometry around the α -carbon. The radical anion reacts further to combine with the methyl radical or, where steric bulk precludes recombination, abstracts a hydrogen from the solvent.



Conclusion

We propose therefore that the mechanism for the π -face selective alkyl addition to the coordinated ketone is likely to involve an electron-transfer mechanism. The radical anion formed would have essentially the same geometry as observed for the neutral complex, involving steric hindrance of the less bulky face of the coordinated ketone. It is still unclear what effect the second aryl oxide would have on the π -face selectivity. Yamamoto and co-workers observed comparable selectivity when the monoaryl oxide $\text{AlMe}_2(\text{BHT})$ was employed for the methyl addition to 4-*tert*-butylcyclohexanone but a dramatic reduction for 2-methyl- and 3-methylcyclohexanone.² If a sterically hindered alkyllithium or lithium metal is used in place of MeLi, π -face selective reduction of the ketone occurs.

Experimental Section

Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY. Melting points were determined in sealed capillaries and are uncorrected. IR spectra ($4000\text{--}700\text{ cm}^{-1}$) were recorded on a Perkin-Elmer 137 grating spectrometer as Nujol mulls (NaCl). NMR spectra, in C_6D_6 , were recorded on Bruker AM-250 (^1H), AM-500 (^{13}C), and WM-300 (^6Li) spectrometers [δ in parts per million relative to SiMe_4 (^1H , ^{13}C) and LiCl in D_2O (^6Li external)]. GC were performed on a Perkin-Elmer 900 gas chromatograph with an 8 mm \times 6 ft glass column packed with SE30 adsorbed on Chromosorb P. Injection port and oven temperatures were 100 and 105 $^\circ\text{C}$, respectively. All manipulations were carried out under nitrogen. Solvents and ketones were dried, distilled, and degassed before use. $\text{AlMe}(\text{BHT})_2$ was prepared as previously described.⁶

$\text{AlMe}(\text{BHT})_2(\text{O}=\text{CPh}_2)$. To $\text{AlMe}(\text{BHT})_2$ (1.0 g, 2.0 mmol) in pentane (10 mL) was added a pentane solution (40 mL) of $\text{O}=\text{CPh}_2$ (0.364 g, 2.0 mmol) dropwise at room temperature under nitrogen atmosphere. An orange-red color formed which deepened considerably as the addition proceeded. Upon completion of the addition the resulting solution was stirred for 1–2 h during which time an orange precipitate formed. The crude product was filtered, dried under vacuum, and recrystallized from hexane ($-20\text{ }^\circ\text{C}$): yield 80–90%; mp 176–178 $^\circ\text{C}$; IR (cm^{-1}) 1600 (m), 1585 (m), 1555 (m), 1455 (s), 1420 (s), 1335 (s), 1300 (m), 1285 (sh), 1270 (m), 1255 (s), 1215 (w), 1190 (w), 1160 (w), 1120 (w), 1075 (w), 1020 (w), 1000 (w), 940 (w), 920 (w), 880 (s), 855 (s), 810 (w), 765 (m), 715 (s); ^1H NMR (δ , C_6D_6) 7.48 [4 H, d, $J(\text{H}-\text{H}) = 7.5\text{ Hz}$, *o*-CH], 7.21 [4 H, s, C_6H_2 , BHT], 7.02 [2 H, t, $J(\text{H}-\text{H}) = 7.5\text{ Hz}$, *p*-CH], 6.83 [4 H, t, $J(\text{H}-\text{H}) = 7.5\text{ Hz}$, *m*-CH], 2.34 (6 H, s, CH_3 , BHT), 1.57 [36 H, s, $\text{C}(\text{CH}_3)_3$], -0.05 (3 H, s, $\text{Al}-\text{CH}_3$); ^{13}C NMR 205.48 ($\text{C}=\text{O}$), 155.77 (CO , BHT), 138.96 (*o*-C, BHT), 136.06 ($\text{C}-\text{O}$), 135.05 (*o*-C), 133.33 (*m*-C), 128.65 (*p*-C), 126.20 (*m*-C, BHT), 125.38 (*p*-C, BHT), 35.45 [$\text{C}(\text{CH}_3)_3$, BHT], 31.96 [$\text{C}(\text{CH}_3)_3$, BHT], 21.39 (CH_3 , BHT), -3.50 ($\text{Al}-\text{CH}_3$). Anal. Calcd for $\text{C}_{44}\text{H}_{59}\text{O}_3\text{Al}$: C, 79.71; H, 8.97. Found: C, 79.13; H, 9.03.

$\text{AlMe}(\text{BHT})_2[\text{O}=\text{C}(\text{C}_5\text{H}_9)^t\text{Bu}]$ (**8**). Procedures were done in an analogous manner to **2**: mp 110 $^\circ\text{C}$; IR (cm^{-1}) 1655 (s), 1240 (s), 1215 (sh), 1200 (sh), 1120 (m), 1020 (w), 940 (w), 915 (w), 870 (s), 855 (s), 770 (m), 680 (sh), 650 (s), 575 (w), 550 (m); ^1H NMR (δ , C_6D_6) 7.18 (4 H, s, C_6H_2 , BHT), 2.43–2.46 (2 H, m, β -CH), 2.29 (6 H, s, CH_3 , BHT), 1.61 [36 H, s, $\text{C}(\text{CH}_3)_3$, BHT], 1.24–1.28 (2 H, m, β -CH), 0.92–0.97 (2 H, m, γ -CH), 0.87 (3 H, m, $\gamma + \delta$ -CH), 0.61 [9 H, s,

(11) Maruoka, K.; Sakurai, M.; Yamamoto, H. *Tetrahedron Lett.* **1985**, 26, 3853.

Table IV. Summary of X-ray Diffraction Data

compound	AlMe(BHT) ₂ (O=CPh ₂)	AlMe(BHT) ₂ [OC(Me)-Ph ₂ Li(OEt ₂)
formula	C ₄₄ H ₃₉ AlO ₃	C ₄₉ H ₇₂ AlLiO ₄
space group	P2 ₁ /n	P2 ₁ /c
a, Å	12.002 (2)	13.789 (1)
b, Å	24.881 (2)	19.676 (2)
c, Å	13.767 (3)	17.835 (2)
β, deg	90.573 (9)	105.389 (7)
V, Å ³	4111 (1)	4665 (9)
Z	4	4
D(calcd), g cm ⁻³	1.075	1.075
cryst dimen, mm	0.15 × 0.18 × 0.52	0.18 × 0.15 × 0.22
temp, °C	25	25
radiation	Cu Kα (1.5418 Å, graphite monochromator)	
μ, cm ⁻¹	6.71	6.53
2θ limits, deg	2.0–110.0	2.0–110.0
no. of collected	5759	6548
no. of unique	5417	6240
obsd data	1836	4427
R ^a	0.0614	0.0559
R _w ^b	0.0636	0.0595
final residual	0.43	0.23
eÅ ⁻³		

$$^a R = \sum |F_o - F_c| / \sum |F_o| \quad ^b R_w = [\sum (w|F_o - F_c|^2) / \sum w(F_o)^2]^{1/2}$$

C(CH₃)₃, -0.11 (3 H, s, Al-CH₃); ¹³C NMR 233.42 (C=O), 154.74 (CO, BHT), 138.88 (*o*-C, BHT), 126.32 (*m*-C, BHT), 125.68 (*p*-C, BHT), 45.01 (*δ*-C), 41.32 [C(CH₃)₃], 35.41 [C(CH₃)₃, BHT], 34.42 [C(CH₃)₃], 32.07 [C(CH₃)₃, BHT], 27.28 (*γ*-C), 27.22 (*β*-C), 21.43 (CH₃, BHT), -4.52 (Al-CH₃). Anal. Calcd for C₄₁H₆₇O₃Al: C, 77.55; H, 10.63. Found: C, 77.15; H, 10.43.

Full spectroscopic and analytical data for compounds 3–7 and 9 are available as Supplementary Material.

AlMe(BHT)₂[OC(Me)Ph₂Li(OEt₂)] (10). To a suspension of 2 (5.0 g, 7.5 mmol) in an ether/pentane solvent mixture (50:50, 50 mL) cooled to -78 °C under nitrogen was added MeLi (5.4 mL of a 1.4 M solution in ether). The resulting mixture was allowed to warm slowly to room temperature during which time the orange suspension gradually disappeared resulting in a clear colorless solution. This was reduced in volume to ≈40 mL and set aside in the freezer (-20 °C) overnight. White crystalline material was deposited. The crude product was filtered, dried under vacuum, and recrystallized from pentane: yield 90%; mp 152–153 °C; IR (cm⁻¹) 1600 (w), 1260 (s), 1240 (s), 1200 (s), 1145 (m), 1110 (s), 1080 (s), 1040 (s), 990 (w), 940 (s), 910 (m), 860 (s), 850 (sh), 830 (s), 800 (sh), 770 (s), 750 (s), 700 (s), 680 (s), 640 (s), 610 (m), 590 (s); ¹H NMR (δ, C₆D₆) 7.33 [4 H, d, J(H-H) = 7.5 Hz, *o*-CH], 7.12 [4 H, t, J(H-H) = 7.5 Hz, *m*-CH], 7.06 [4 H, s, C₆H₂, BHT], 7.05 [2 H, t, J(H-H) = 7.5 Hz, *p*-CH], 2.74 [4 H, q, J(H-H) = 7.5 Hz, CH₂, Et₂O], 2.31 [3 H, s, OC(CH₃)₃], 2.23 [6 H, s, CH₃, BHT], 1.44 [36 H, s, C(CH₃)₃, BHT], 0.47 [6 H, t, J(H-H) = 7.5 Hz, CH₃, Et₂O], -0.06 (3 H, s, Al-CH₃); ¹³C NMR 154.94 (CO, BHT), 151.74 (C-CO, Ph), 138.92 (*o*-C, BHT), 128.22 (*o*-C), 127.22 (*m*-C), 126.99 (*m*-C, BHT), 126.81 (*p*-C), 126.10 (*p*-C, BHT), 78.54 (OCPh₂Me), 62.99 (CH₂, Et₂O), 35.98 [C(CH₃)₃, BHT], 32.86 [C(CH₃)₃, BHT], 21.30 (CH₃, BHT), 13.48 (CH₃, Et₂O), 0.339 (Al-CH₃); ⁶Li NMR -2.36 (s). Anal. Calcd for C₄₉H₇₂L₄AlLi: C, 77.53; H, 9.56. Found: C, 77.26; H, 9.65.

AlMe(BHT)₂[OC(Me)C₆H₅BuLi(OEt₂)] (11). Procedures were done in an analogous manner to 10: mp 129–131 °C; IR (cm⁻¹) 1600 (w), 1270 (s), 1250 (s), 1230 (s), 1150 (sh), 1135 (s), 1120 (s), 1090 (m), 1050 (m), 1010 (sh), 1000 (m), 990 (sh), 930 (m), 865 (s), 855 (s), 830 (s), 800 (sh), 770 (m), 740 (m), 690 (s), 660 (s), 650 (sh), 620 (s), 590 (m), 570 (m), 550 (m), 480 (w); ¹H NMR (δ, C₆D₆) 7.10 (4 H, s, C₆H₂, BHT), 3.01 [4 H, q, J(H-H) = 7.5 Hz, CH₂, Et₂O], 2.27 [6 H, s, CH₃, BHT], 2.05–2.07 (2 H, m, *β*-CH), 1.77–1.81 (2 H, m, *β*-CH), 1.70–1.72 (2 H, m, *γ*-CH), 1.52 [36 H, s, C(CH₃)₃, BHT], 1.48 [3 H, s, OC(CH₃)₃], 1.10–1.15 (3 H, m, *γ* + *δ*-CH), 0.88 [9 H, s, C(CH₃)₃], 0.68 [6 H, t, J(H-H) = 7.5 Hz, CH₃, Et₂O], 0.225 (3 H, s, Al-CH₃); ¹³C NMR 155.03 (CO, BHT), 138.91 (*o*-C, BHT), 126.84 (*m*-C, BHT), 125.92 (*p*-C, BHT), 71.72 (CO), 64.51 (CH₂, Et₂O), 48.33 (*δ*-C), 42.89 [C(CH₃)₃], 35.75 [C(CH₃)₃, BHT], 32.59 [C(CH₃)₃, BHT], 32.33 [C(CH₃)₃, Bu], 27.82 (*γ*-C), 27.06 (*β*-C), 25.72 [OC(CH₃)₃], 21.20 (CH₃, BHT), 13.96 (CH₃, Et₂O), 1.36 (Al-CH₃); ⁶Li NMR -2.28 (s). Anal. Calcd for C₄₆H₈₀O₄AlLi: C, 75.57; H, 11.02. Found: C, 75.25; H, 10.91.

AlMe₂(BHT)[OC(Me)Ph₂Li(OEt₂)] (12). Procedures were done in analogous manner to 10 but with an excess of MeLi. The crude reaction mixture gave a mixture of products: 10 (80%), [Li(BHT)(OEt₂)]₂ (10%), and 12 (10%): ¹H NMR (δ, C₆D₆) 7.26 [4 H, d, J(H-H) = 7.5

Table V. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å²) of the Non-Hydrogen Atoms in AlMe(BHT)₂(O=CPh₂)

atom	x/a	y/b	z/c	U (eqv)
Al	0.0577 (2)	0.3155 (1)	0.0240 (2)	0.048 (2)
O(1)	0.0896 (4)	0.2548 (2)	0.0793 (4)	0.055 (7)
O(2)	0.1147 (5)	0.3724 (2)	0.0755 (4)	0.055 (3)
O(3)	-0.0885 (5)	0.3261 (2)	0.0729 (4)	0.059 (5)
Me	0.0535 (7)	0.3102 (4)	-0.1167 (5)	0.070 (5)
C(1)	0.1244 (8)	0.2038 (3)	0.0601 (6)	0.053 (2)
C(2)	0.2397 (7)	0.1910 (4)	0.0550 (6)	0.055 (2)
C(3)	0.2692 (8)	0.1397 (3)	0.0254 (6)	0.062 (2)
C(4)	0.1926 (8)	0.1004 (4)	0.0057 (6)	0.061 (2)
C(5)	0.0821 (8)	0.1113 (4)	0.0210 (6)	0.063 (2)
C(6)	0.0437 (7)	0.1619 (3)	0.0507 (6)	0.055 (2)
C(11)	0.1859 (7)	0.4056 (3)	0.1234 (6)	0.050 (2)
C(12)	0.1817 (7)	0.4103 (3)	0.2259 (6)	0.056 (2)
C(13)	0.2676 (7)	0.4373 (3)	0.2736 (6)	0.059 (2)
C(14)	0.3533 (8)	0.4631 (4)	0.2241 (6)	0.064 (2)
C(15)	0.3451 (7)	0.4641 (3)	0.1248 (6)	0.063 (2)
C(16)	0.2629 (7)	0.4377 (3)	0.0707 (6)	0.053 (2)
C(21)	0.3317 (8)	0.2318 (4)	0.0806 (7)	0.065 (14)
C(22)	0.3093 (8)	0.2604 (4)	0.1773 (7)	0.091 (13)
C(23)	0.4461 (8)	0.2044 (4)	0.0966 (7)	0.091 (18)
C(24)	0.3459 (9)	0.2723 (4)	0.0007 (8)	0.110 (18)
C(41)	0.2293 (9)	0.0458 (3)	-0.0318 (7)	0.099 (27)
C(61)	-0.0792 (8)	0.1691 (4)	0.0747 (7)	0.063 (11)
C(62)	-0.1389 (8)	0.2012 (4)	-0.0071 (7)	0.079 (23)
C(63)	-0.0949 (8)	0.1954 (4)	0.1729 (7)	0.080 (15)
C(64)	-0.1421 (8)	0.1143 (4)	0.0796 (7)	0.093 (30)
C(100)	-0.1869 (8)	0.3393 (3)	0.0497 (6)	0.055 (2)
C(101)	-0.2712 (7)	0.3379 (3)	0.1238 (6)	0.052 (2)
C(102)	-0.2467 (8)	0.3180 (3)	0.2148 (6)	0.069 (2)
C(103)	-0.3261 (8)	0.3193 (4)	0.2871 (7)	0.073 (2)
C(104)	0.4288 (9)	0.3418 (4)	0.2672 (7)	0.084 (3)
C(105)	-0.4545 (8)	0.3613 (4)	0.1778 (7)	0.076 (2)
C(106)	-0.3761 (7)	0.3602 (3)	0.1032 (6)	0.062 (3)
C(111)	0.2099 (8)	0.3594 (4)	-0.0506 (6)	0.065 (2)
C(112)	-0.1484 (8)	0.4030 (4)	-0.0803 (7)	0.087 (3)
C(113)	-0.168 (1)	0.4276 (5)	-0.1745 (9)	0.127 (4)
C(114)	-0.246 (1)	0.4013 (5)	-0.2246 (9)	0.112 (4)
C(115)	-0.309 (1)	0.3619 (5)	-0.2022 (9)	0.122 (4)
C(116)	-0.294 (1)	0.3360 (4)	-0.1064 (8)	0.107 (3)
C(121)	0.0795 (7)	0.3918 (4)	0.2855 (6)	0.059 (5)
C(122)	-0.0262 (7)	0.4173 (4)	0.2411 (6)	0.069 (3)
C(123)	0.0866 (8)	0.4121 (4)	0.3916 (6)	0.090 (22)
C(124)	0.0695 (7)	0.3308 (4)	0.2907 (6)	0.072 (12)
C(141)	0.4483 (8)	0.4902 (4)	0.2795 (7)	0.090 (17)
C(161)	0.2562 (8)	0.4465 (3)	-0.0394 (7)	0.061 (9)
C(162)	0.1370 (8)	0.4578 (4)	-0.0726 (6)	0.087 (6)
C(163)	0.3242 (8)	0.4958 (4)	-0.0709 (7)	0.095 (2)
C(164)	0.3018 (8)	0.3990 (4)	-0.0952 (6)	0.090 (14)

Hz, *o*-CH], 7.12 [4 H, t, J(H-H) = 7.5 Hz, *m*-C₆H₂], 7.06 [2 H, s, C₆H₂, BHT], 7.05 [2 H, t, J(H-H) = 7.5 Hz, *p*-CH], 3.04 [4 H, q, J(H-H) = 7.5 Hz, CH₂, Et₂O], 2.33 [3 H, s, OCCH₃], 2.23 [3 H, s, CH₃, BHT], 1.57 [18 H, s, C(CH₃)₃, BHT], 0.66 [6 H, t, J(H-H) = 7.5 Hz, CH₃, Et₂O], -0.30 (6 H, s, Al-CH₃); ⁶Li NMR -1.72 (s).

AlMe(BHT)₂[OC(H)C₆H₅BuLi(OEt₂)] (13). Method 1. To a suspension of 8 (5.00 g, 7.87 mmol) in pentane/Et₂O (50:50, 50 mL), at -78 °C, was added ^tBuLi solution 4.63 mL, 1.7 M). Immediately the suspension dissolved to give a clear pale yellow solution. The reaction was warmed to room temperature, reduced in volume, under vacuum, to ca. 20 mL, and cooled (-20 °C). The resulting white crystalline precipitate was filtered and dried under vacuum: yield 80%.

Method 2. Excess Li metal (0.3 g, 4.32 mmol) was added to an ether solution (50 mL) of 8 (5.00 g, 7.87 mmol). The initial pale yellow color immediately turned yellow-green. On stirring for 0.5 h the solution became colorless. The excess Li metal was removed by filtration, and the resulting solution was reduced in volume and cooled (-20 °C). Colorless crystals of [Li(BHT)(OEt₂)]₂ were deposited. These were removed by filtration. The filtrate was evaporated to dryness, and the resulting residue was recrystallized from pentane (-20 °C): yield 80%; mp >260 °C; IR (cm⁻¹) 1280 (s), 1260 (sh), 1235 (s), 1220 (s), 1200

Table VI. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (\AA^2) of the Non-Hydrogen Atoms in $\text{AlMe}(\text{BHT})_2[\text{OC}(\text{Me})\text{Ph}_2]\text{Li}(\text{OEt}_2)$

atom	x/a	y/b	z/c	U (eqv)
Al	0.81792 (8)	0.03767 (5)	0.28229 (6)	0.031 (1)
Li	0.6515 (5)	-0.0380 (4)	0.2828 (5)	0.064 (19)
O(1)	0.6982 (2)	0.0539 (1)	0.3024 (1)	0.037 (2)
O(2)	0.7726 (2)	-0.0464 (1)	0.2507 (1)	0.038 (6)
O(3)	0.8473 (2)	0.0872 (1)	0.2108 (1)	0.043 (3)
O(4)	0.5403 (3)	-0.1011 (2)	0.2662 (3)	0.104 (51)
C(1)	0.9290 (3)	0.0477 (2)	0.3773 (2)	0.048 (6)
C(2)	0.7917 (3)	-0.1065 (2)	0.2182 (2)	0.036 (2)
C(3)	0.8471 (3)	-0.1583 (2)	0.2658 (2)	0.038 (3)
C(4)	0.8757 (3)	-0.2148 (2)	0.2304 (2)	0.051 (14)
C(5)	0.8461 (4)	-0.2240 (2)	-0.1506 (3)	0.062 (24)
C(6)	0.4843 (3)	-0.1761 (2)	0.1064 (2)	0.054 (19)
C(7)	0.7536 (3)	-0.1175 (2)	0.1375 (2)	0.041 (4)
C(8)	0.8677 (3)	0.1109 (2)	0.1452 (2)	0.041 (2)
C(9)	0.9491 (3)	0.0842 (2)	0.1190 (2)	0.041 (3)
C(10)	0.9577 (3)	0.1048 (2)	0.0459 (2)	0.051 (3)
C(11)	0.8947 (4)	0.1511 (2)	0.0002 (2)	0.059 (14)
C(12)	0.8234 (3)	0.1819 (2)	0.0305 (2)	0.058 (8)
C(13)	0.8097 (3)	0.1646 (2)	0.1032 (2)	0.049 (4)
C(14)	0.8825 (4)	-0.1586 (2)	0.3562 (2)	0.055 (20)
C(15)	0.8174 (4)	-0.1161 (2)	0.3969 (2)	0.066 (23)
C(16)	0.8772 (6)	-0.2322 (2)	0.3862 (3)	0.122 (97)
C(17)	0.9907 (4)	-0.1342 (3)	0.3822 (3)	0.108 (43)
C(18)	0.8768 (5)	-0.2865 (2)	0.1121 (3)	0.116 (72)
C(19)	0.6808 (3)	-0.0718 (2)	0.0776 (2)	0.053 (7)
C(20)	0.5982 (4)	-0.1152 (3)	0.0266 (4)	0.102 (10)
C(21)	0.7381 (5)	-0.0364 (3)	0.0268 (3)	0.112 (10)
C(22)	0.6282 (5)	-0.0158 (3)	0.1123 (3)	0.107 (19)
C(23)	1.0325 (3)	0.0402 (2)	0.1703 (2)	0.048 (7)
C(24)	1.0794 (3)	0.0800 (2)	0.2451 (2)	0.059 (10)
C(25)	0.9936 (3)	-0.0295 (2)	0.1880 (3)	0.062 (17)
C(26)	1.1188 (3)	0.0260 (2)	0.1319 (3)	0.071 (16)
C(27)	0.9034 (4)	0.1719 (3)	-0.0801 (3)	0.097 (31)
C(28)	0.7407 (4)	0.2092 (2)	0.1379 (3)	0.066 (14)
C(29)	0.6964 (5)	0.2696 (3)	0.0838 (3)	0.124 (30)
C(30)	0.6517 (3)	0.1692 (2)	0.1503 (3)	0.073 (10)
C(31)	0.8051 (4)	0.2395 (2)	0.2149 (3)	0.084 (25)
C(32)	0.6669 (3)	0.0955 (2)	0.3579 (2)	0.039 (2)
C(33)	0.7282 (3)	0.1618 (2)	0.3720 (2)	0.050 (7)
C(34)	0.5563 (3)	0.1152 (2)	0.3261 (2)	0.044 (5)
C(35)	0.4999 (3)	0.0978 (2)	0.2522 (3)	0.054 (10)
C(36)	0.3993 (4)	0.1178 (3)	0.2254 (3)	0.072 (18)
C(37)	0.3551 (4)	0.1554 (3)	0.2745 (4)	0.083 (80)
C(38)	0.4106 (4)	0.1731 (3)	0.3469 (4)	0.080 (19)
C(39)	0.5097 (3)	0.1530 (2)	0.3735 (3)	0.061 (9)
C(40)	0.6787 (3)	0.0536 (2)	0.4327 (2)	0.042 ()
C(41)	0.6099 (3)	0.0020 (2)	0.4331 (3)	0.058 ()
C(42)	0.6203 (4)	-0.0380 (3)	0.4998 (3)	0.079 (7)
C(43)	0.6978 (4)	-0.0267 (3)	0.5648 (3)	0.084 (15)
C(44)	0.7658 (4)	0.0237 (3)	0.5644 (3)	0.080 (21)
C(45)	0.7568 (3)	0.0641 (2)	0.4983 (2)	0.059 (8)
C(46)	0.4374 (5)	-0.0841 (4)	0.2521 (7)	0.181 (129)
C(47)	0.3776 (7)	-0.1027 (6)	0.1806 (8)	0.301 (178)
C(48)	0.5629 (6)	-0.1728 (3)	0.2706 (6)	0.178 (124)
C(49)	0.5588 (7)	-0.2022 (4)	0.3490 (7)	0.293 (225)

(m), 1190 (sh), 1115 (w), 1090 (sh), 1070 (s), 1060 (sh), 1025 (w), 985 (w), 950 (w), 925 (w), 880 (s), 860 (m), 840 (s), 775 (w), 755 (w), 705 (s), 675 (m), 660 (m), 615 (m), 590 (w), 550 (w); ^1H NMR (δ , C_6D_6) 7.14 (4 H, s, C_6H_5 , BHT), 4.07 (1 H, m, OCH), 2.94 [4 H, q, $J(\text{H}-\text{H}) = 7.0$ Hz, CH_2 , Et_2O], 2.47–2.49 (2 H, m, β -CH), 2.25 (6 H, s, CH_3 , BHT), 1.75–1.77 (2 H, m, β -CH), 1.56 [36 H, s, $\text{C}(\text{CH}_3)_3$, BHT],

1.07–1.16 (5 H, m, $\gamma + \delta$ -CH), 0.86 [9 H, s, $\text{C}(\text{CH}_3)_3$], 0.63 [6 H, t, $J(\text{H}-\text{H}) = 7.0$ Hz, CH_3 , Et_2O], 0.15 (3 H, s, $\text{Al}-\text{CH}_3$); ^{13}C NMR 154.75 (CO, BHT), 138.88 (o -C, BHT), 126.71 (m -C, BHT), 126.00 (p -C, BHT), 70.57 (OCH), 64.77 (CH_2 , Et_2O), 48.71 (δ -C), 38.55 [$\text{C}(\text{CH}_3)_3$], 35.61 [$\text{C}(\text{CH}_3)_3$, BHT], 32.42 [$\text{C}(\text{CH}_3)_3$], 32.28 (CH_3 , BHT), 27.89 (γ -C), 26.46 (β -C), 21.31 [$\text{C}(\text{CH}_3)_3$, BHT], 14.02 (CH_3 , Et_2O), -2.85 ($\text{Al}-\text{CH}_3$); ^{13}C NMR (^1H coupled) 70.57 [d, $J(\text{C}-\text{H}) = 551.6$ Hz, α -C]; ^6Li NMR -2.19 (s). Anal. Calcd for $\text{C}_{45}\text{H}_{78}\text{O}_4\text{AlLi}$: C, 75.37; H, 10.96. Found C, 75.21; H, 10.50.

Hydrolysis of 13. To an Et_2O solution of 13 was added 1 M HCl (50 mL). The aqueous layer was separated and washed with Et_2O (2×10 mL). The Et_2O extracts were combined, washed with brine solution, dried over MgSO_4 , and filtered, and the solvent was removed by using a water aspirator. The residue was determined to contain BHT-H and *tert*-butylcyclohexanol (cis:trans 1:99) by GC analysis and ^{13}C NMR in C_6D_6 .¹³

Crystallography. Crystals sealed in a glass capillary under argon were mounted on the goniometer of an Enraf-Nonius CAD-4 automated diffractometer. Final lattice parameters, as determined from a least-squares fit of the setting angles of 25 accurately centered reflections ($2\theta > 70^\circ$) and other experimental data, are given in Table IV. Typical data collection procedures in our laboratory have been described previously.¹⁴ Examination of the data, which was corrected for Lorentz and polarization effects but not for absorption, revealed the space groups to be uniquely defined, $P2_1/n$ (2), $P2_1/c$ (10).

Structure solution were readily accomplished by using the direct methods option of SHELXS,¹⁵ through which the bulk of the molecules were located. The remaining atomic coordinates were determined through the generation of difference Fourier maps using SHELX-76.¹⁶ Not unexpectedly, the ethyl groups of the coordinated solvent in 10 showed high thermal motion, but attempts at various stages of the refinement to resolve this into positions of partial occupancy failed. Treatment of all the non-hydrogen atoms except the phenyl carbon atoms in 2 with anisotropic thermal parameters revealed the location of most of the hydrogen atoms and enabled the geometric generation of the remainder. Inclusion of these in "riding" positions into the structure factor calculation and refinement led to converged R and R_w values of 0.061 (2), 0.056 (10) and 0.068 (2), 0.060 (10); respectively. Scattering factors were taken from ref 17. Final atomic positional parameters are given in Tables V and VI. Anisotropic thermal parameters, hydrogen positions, structure factors, and full bond lengths and angles are available as Supplementary Material.

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Supplementary Material Available: Full ^1H and ^{13}C NMR and IR spectroscopic data of compounds 3–7 and 9 and tables of atomic positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, and full bond distances and angles (18 pages); listing of observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

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