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# Interaction of Organic Carbonyls with Sterically Crowded Aryloxide Compounds of Aluminum

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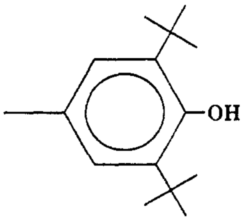
The interaction of $AlR(BHT)_2$ and $AlR_2(BHT)(OEt_2)$ (R = Me, Et) with organic carbonyls $O{=}C(X)R$ (X = H, R′, OR, $NR_2$) leads to the formation of the Lewis acid-base complexes $AlR(BHT)_2[O{=}C(X)R]$ and $AlR_2(BHT)[O{=}C(X)R]$, respectively. The aluminum-methyl $^{13}C$ NMR chemical shifts for the methyl aryloxide compounds $AlMe(BHT)_2[O{=}C(X)R]$ and $AlMe_2(BHT)[O{=}C(X)R]$ are found to be dependent primarily on the steric bulk of the substituents, X and R, on the carbonyl ligand. In contrast, the decrease in the carbonyl stretching frequency in the IR spectrum, and the downfield shift in the $^{13}C$ NMR spectrum for the carbonyl $\alpha$-carbon of the carbonyl adducts, when compared to those of the "free" carbonyls, is dependent on the electron-donating ability of X. The molecular structures of $AlMe(BHT)_2[O{=}C(H)Bu^t]$ (1), $AlMe_2(BHT)(O{=}CPh_2)$ (8), and $AlMe(BHT)_2[O{=}C(OMe)Ph]$ (17) have been determined by X-ray crystallography. The mode of coordination of the organic carbonyls to aluminum is discussed. Crystal data for 1: monoclinic, $P2_1/n$, $a$ = 10.0765 (5) Å, $b$ = 26.201 (2) Å, $c$ = 14.0106 (4) Å, $\beta$ = 103.638 (3)°, $Z$ = 4, $R$ = 0.0576, $R_w$ = 0.0623. Crystal data for 8: orthorhombic, $Pn2_1a$, $a$ = 19.133 (3) Å, $b$ = 14.638 (2) Å, $c$ = 10.022 (1) Å, $Z$ = 4, $R$ = 0.0552, $R_w$ = 0.0550. Crystal data for 17: triclinic, $P\bar{1}$, $a$ = 9.394 (2) Å, $b$ = 9.741 (3) Å, $c$ = 23.091 (7) Å, $\alpha$ = 91.43 (2)°, $\beta$ = 91.93 (2)°, $\gamma$ = 116.41 (2)°, $Z$ = 2, $R$ = 0.0599, $R_w$ = 0.0689.

## Introduction

Despite the diverse range of reactions reported to occur between organic carbonyls and organoaluminum compounds,[2,3] the latter's use as reagents in organic synthesis has been traditionally limited due to the occurrence of multiple reaction products from a single substrate. For example, the reaction of acetaldehyde with $AlEt_3$ results in both alkyl addition to and reduction of the carbonyl group.[4] Secondary reactions include the Meerwein–Ponndorf–Verley reduction, the Oppenauer oxidation, and the Tischenko reaction with both acetaldehyde and the primary reaction products. It is therefore not surprising that much research effort has been aimed toward the development of new organoaluminum compounds, for use as both reaction-specific and also stereospecific reagents and catalysts.[5] In this regard work in our laboratory has focused on the synthesis and characterization of monomeric aluminum complexes derived from the sterically hindered 2,6-di-*tert*-butyl-4-methylphenol (I; BHT-H, from the trivial name butylated hydroxytoluene).[6-8]



I

We believe that the future development of new organoaluminum reagents for organic synthesis must be based upon an intimate understanding of the steric and electronic effects controlling the coordination, and subsequent reactivity, of organic substrates with organoaluminum compounds. It is toward this end that we have undertaken a comprehensive investigation of the interaction of organic carbonyls with the organoaluminum aryloxide compounds $AlR_x(BHT)_{3-x}$ (R = Me, Et; $x$ = 1, 2), the results of which are the subject of this paper.

**Table I. Selected Bond Lengths (Å) and Angles (deg) in $AlMe(BHT)_2[O{=}C(H)^tBu]$ (1)**

| | | | |
|---|---|---|---|
| Al-O(1) | 1.726 (3) | Al-O(2) | 1.729 (3) |
| Al-O(3) | 1.920 (3) | Al-Me | 1.955 (4) |
| O(1)-C(1) | 1.372 (5) | O(2)-C(11) | 1.370 (4) |
| O(3)-C(31) | 1.164 (5) | C(31)-C(32) | 1.481 (6) |
| O(1)-Al-O(2) | 113.6 (1) | O(1)-Al-O(3) | 104.9 (1) |
| O(1)-Al-Me | 110.1 (2) | O(2)-Al-O(3) | 97.5 (1) |
| O(2)-Al-Me | 122.2 (2) | O(3)-Al-Me | 106.0 (2) |
| Al-O(1)-C(1) | 131.3 (2) | Al-O(2)-C(11) | 140.5 (2) |
| Al-O(3)-C(31) | 136.0 (3) | O(3)-C(31)-C(32) | 129.4 (5) |

## Results and Discussion

**Aldehydes.** The interaction of $AlMe(BHT)_2$[6,9] with $O{=}C(H)^tBu$, $O{=}C(H)C_6H_4$-*p*-Me, and $O{=}C(H)C_6H_4$-*p*-Cl

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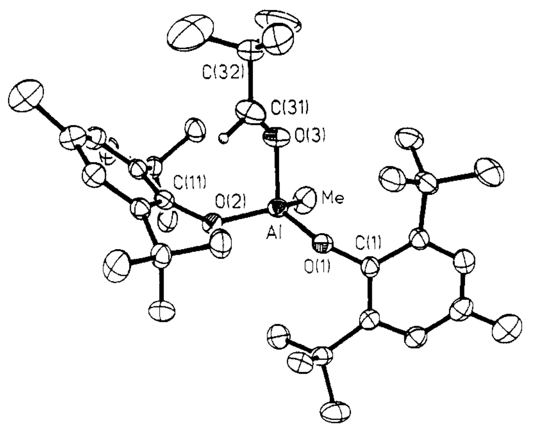


**Figure 1.** Structure of $AlMe(BHT)_2[O{=}C(H)^tBu]$ (1). Thermal ellipsoids are drawn at the 30% level, and the hydrogen atoms [except that bonded to C(31)] are omitted for clarity.

yields the Lewis acid–base complexes $AlMe(BHT)_2[O{=}C(H)^tBu]$ (1), $AlMe(BHT)_2[O{=}C(H)C_6H_4\text{-}p\text{-}Me]$ (2), and $AlMe(BHT)_2[O{=}C(H)C_6H_4\text{-}p\text{-}Cl]$ (3), respectively (eq 1).

$$AlMe(BHT)_2 + O{=}C(H)R \rightarrow AlMe(BHT)_2[O{=}C(H)R] \quad (1)$$

Compounds **1**–**3** have been characterized by elemental analysis and $^1H$ and $^{13}C$ NMR and IR spectroscopy (see Experimental Section). As we have observed previously for the ketone adducts $AlMe(BHT)_2(O{=}CR_2)$,[10] the aldehyde complexes exhibit a downfield shift in the $^{13}C$ NMR spectrum for the carbonyl $\alpha$-carbon and a decrease in the carbonyl stretching frequency when compared to those of the "free" aldehyde, consistent with the coordination of the carbonyl group of the aldehyde to aluminum. Compounds **1**–**3** are indefinitely stable under an inert atmosphere, showing no further reaction of the coordinated aldehyde.

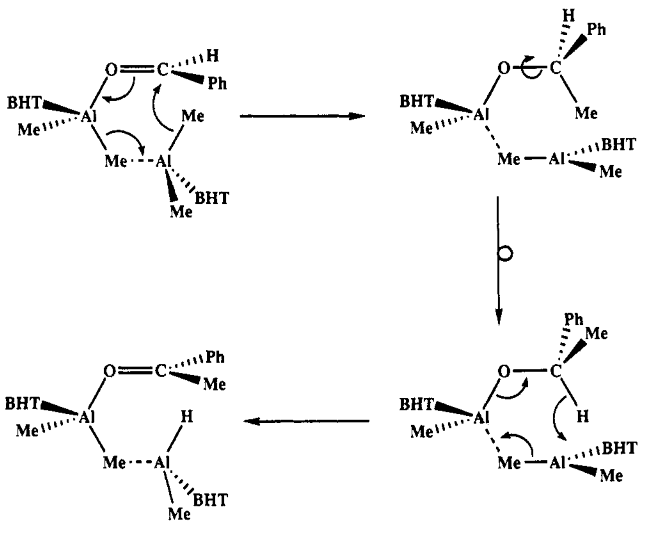
The molecular structure of **1** has been determined by X-ray crystallography and is shown in Figure 1. Selected bond lengths and angles are given in Table I. The geometry around aluminum is distorted from tetrahedral; the angles associated with the aldehyde oxygen are the most acute. The Al–C bond length in **1** [1.954 (4) Å] is slightly larger than that found for $AlMe(BHT)_2$ [1.927 (3) Å].[11] 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. The aldehyde Al–O bond distance [1.920 (3) Å] is within the normal range, 1.8–2.0 Å.[12] In contrast, the shorter aryloxide Al–O distances [1.766 (3), 1.729 (3) Å] indicate a degree of $\pi$-bonding between the oxygen lone pairs and aluminum-centered $\sigma^*$ orbitals.[6,7]

Adduct formation is not observed between $AlMe_2(BHT)$ and a wide range of aldehydes; instead a novel hydride-methyl exchange reaction occurs to give the corresponding methyl ketone upon hydrolysis (eq 2).[13,14] The initial step

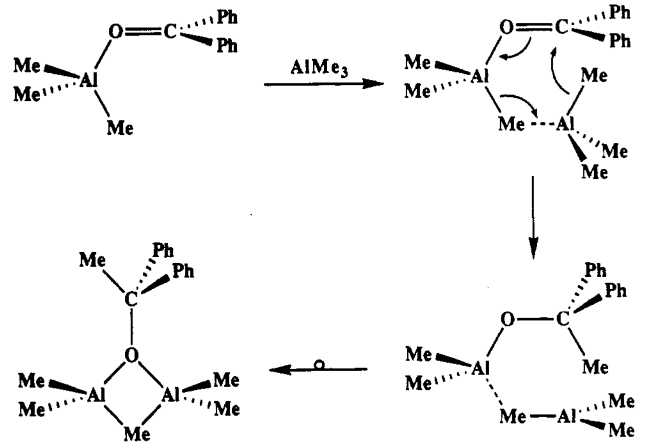
$$O{=}C(H)R \xrightarrow[\text{(ii) } H_2O]{\text{(i) } AlMe_2(BHT)(OEt_2)} O{=}C(Me)R \quad (2)$$

of this unique aldehyde to ketone conversion is undoubtedly the substitution of $Et_2O$, resulting in the formation of the aldehyde complex. If the reaction is carried out in pentane, some of the aldehyde adducts have limited solubility and can be isolated quantitatively for $O{=}C(H)C_6H_4\text{-}p\text{-}Me$ and $O{=}C(H)C_6H_4\text{-}p\text{-}Cl$. The resulting complexes $AlMe_2(BHT)[O{=}C(H)C_6H_4\text{-}p\text{-}Me]$ (**4**) and $AlMe_2(BHT)[O{=}C(H)C_6H_4\text{-}p\text{-}Cl]$ (**5**) are stable as solids but slowly decompose in benzene, toluene, or ether solution to give the corresponding methyl ketone complexes (vide infra).[13]

Scheme I



Scheme II



On the basis of (a) the required stoichiometry for the reaction, a minimum of 1.5 equiv of $AlMe_2(BHT)(OEt_2)$ being required for the reaction to proceed to completion,[13] (b) literature precedent for the alkylation of organic carbonyls by $AlMe_3$,[15–18] and (c) the presence of a transient species with a OCH(Me)R ligand and a possible bridging methyl, we have proposed the mechanism shown in Scheme I. One molecule of $AlMe_2(BHT)(OEt_2)$ is required for the coordination of the aldehyde, while a second equivalent of $AlMe_2(BHT)(OEt_2)$ acts as the methyl source for two aldehyde to ketone conversions.

Ashby et al.[15] have demonstrated that the rate-controlling step in the alkylation of benzophenone by trimethylaluminum (Scheme II) is the attack of monomeric

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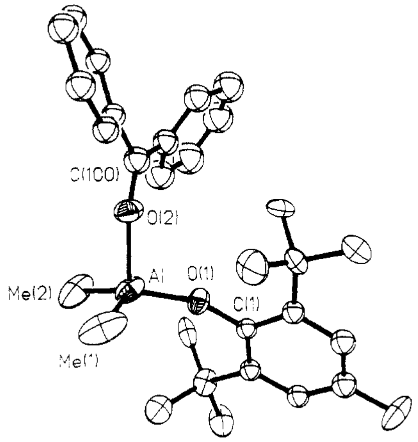


**Figure 2.** Structure of $AlMe_2(BHT)(O{=}CPh_2)$ (**8**). Thermal ellipsoids are drawn at the 30% level, and hydrogen atoms are omitted for clarity.

**Table II. Selected Bond Lengths (Å) and Angles (deg) in $AlMe_2(BHT)(O{=}CPh_2)$ (8)**

| | | | |
|---|---|---|---|
| Al-O(1) | 1.731 (8) | Al-O(2) | 1.907 (8) |
| Al-Me(1) | 1.96 (1) | Al-Me(2) | 1.94 (1) |
| O(1)-C(1) | 1.36 (1) | O(2)-C(100) | 1.24 (1) |
| C(100)-C(101) | 1.51 (2) | C(100)-C(107) | 1.47 (2) |
| O(1)-Al-O(2) | 103.1 (4) | O(1)-Al-Me(1) | 114.9 (6) |
| O(1)-Al-Me(2) | 119.4 (6) | O(2)-Al-Me(1) | 101.5 (5) |
| O(2)-Al-Me(2) | 101.2 (5) | Me(1)-Al-Me(2) | 113.1 (8) |
| Al-O(1)-C(1) | 157.7 (8) | Al-O(2)-C(100) | 153.8 (9) |
| O(2)-C(100)-C(101) | 116 (1) | O(2)-C(100)-C(107) | 124 (1) |

$AlMe_3$ on the complex $AlMe_3(O{=}CPh_2)$. If this holds true for the reaction shown in Scheme I, then the only assumption that must be made is that the rotation of the oxygen–carbon single bond must be rapid in comparison to the rate of dissociation of the methyl-bridged dimer. This is certainly plausible, given that the activation energies of these processes can be estimated to be 3–8 and 11–15 kcal $mol^{-1}$, respectively.[19]

The presence of electron-withdrawing substituents on the aldehyde should enhance the initial nucleophilic addition of methyl to the aldehyde, and this is indeed observed.[13] In order to ascertain if the opposite electronic effect is present, i.e., electron-donating substituents should inhibit the reaction, we have investigated the reaction of $AlMe_2(BHT)(OEt_2)$ with $O{=}C(H)C_6H_4\text{-}p\text{-}OMe$.

The addition of $O{=}C(H)C_6H_4\text{-}p\text{-}OMe$ to a benzene solution of $AlMe_2(BHT)(OEt_2)$ results in the formation of the stable deep orange complex $AlMe_2(BHT)[O{=}C(H)C_6H_4\text{-}p\text{-}OMe]$ (**6**). As predicted, compound **6** does not react further and is stable in refluxing toluene.

**Ketones.** Addition of cyclopentanone, $O{=}\overline{C(CH_2)_3C}H_2$, to a pentane solution of $AlMe(BHT)_2$ at room temperature results in the formation of $AlMe(BHT)_2[O{=}\overline{C(CH_2)_3C}H_2]$ (**7**), as a pale yellow crystalline solid. Compound **7** is chemically similar to the series of ketone adducts of $AlMe(BHT)_2$ that we have reported previously.[10] The ketone complexes of $AlMe(BHT)_2$ are all stable in solution, in direct contrast to the ketone complexes of $AlEt(BHT)_2$, in which the ketone readily undergoes reduction[20] or enolization.[21]

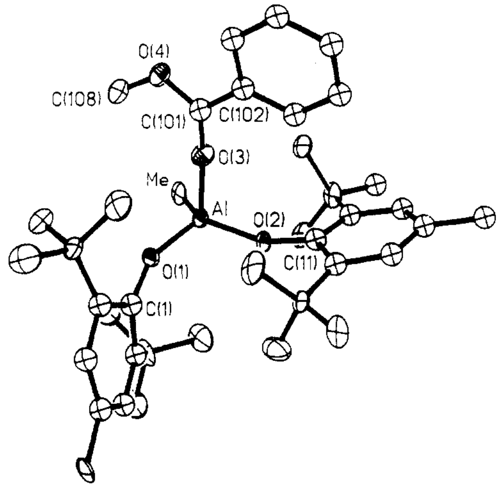


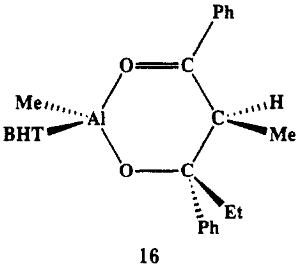
**Figure 3.** Structure of $AlMe(BHT)_2[O{=}C(OMe)Ph]$ (**17**). Thermal ellipsoids are drawn at the 30% level, and hydrogen atoms are omitted for clarity.

Addition of 1 equiv of a series of ketones, $O{=}CR_2$, to either an equimolar mixture of $AlMe_3$ and BHT-H or $AlMe_2(BHT)(OEt_2)$, at room temperature, yields the expected ketone complexes, $AlMe_2(BHT)(O{=}CR_2)$ (**8–15**; see Experimental Section). The molecular structure of one of these compounds, $AlMe_2(BHT)(O{=}CPh_2)$ (**8**), has been determined by X-ray crystallography.

The molecular structure of **8** is shown in Figure 2, and selected bond lengths and angles are given in Table II. Although the high standard deviations in the structural parameters (see Experimental Section) preclude a detailed comparison with other structures, the bond lengths and bond angles around aluminum are within the ranges observed previously for other complexes of $AlMe_2(BHT)$,[6,7] and the bond lengths and angles of the benzophenone are, within experimental error, identical with those observed for $AlMe(BHT)_2(O{=}CPh_2)$.[10]

In contrast to the $AlMe(BHT)_2$(ketone) complexes, the $AlMe_2(BHT)$(ketone) complexes (**8–15**) slowly decompose in pentane solution to give a complex mixture of products. The only exception is $AlMe_2(BHT)[O{=}C(Et)Ph]$ (**9**), which decomposes in the presence of a second equivalent of $O{=}C(Et)Ph$ to give the β-oxo enolate complex $\overline{AlMe(BHT)[O{=}C(Ph)CH(Me)C(Et)(Ph)O}]$ (**16**) (eq 3).

$$AlMe_2(BHT)[O{=}C(Et)Ph] + O{=}C(Et)Ph \rightarrow 16 + CH_4 \quad (3)$$



**16**

The $^1H$ and $^{13}C$ NMR spectra of **16** indicate the presence of a single isomer. We have previously observed the same reactivity and stereospecificity for the aluminum ethyl analogue.[21]

**Methyl Benzoate.** The interaction of $O{=}C(OMe)Ph$ in pentane with $AlR(BHT)_2$ and $AlR_2(BHT)$ (R = Me, Et) results in the formation of the aluminum ester complexes $AlR(BHT)_2[O{=}C(OMe)Ph]$ (R = Me (**17**), Et (**18**)) and $AlR_2(BHT)[O{=}C(OMe)Ph]$ (R = Me (**19**), Et (**20**)). The ester complexes undergo no further reaction and are in-

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**Table III. Selected Bond Lengths (Å) and Angles (deg) in $AlMe(BHT)_2[O{=}C(OMe)Ph]$ (17)**

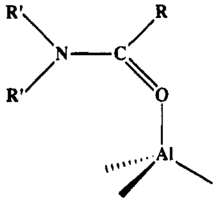
| | | | |
|---|---|---|---|
| Al-O(1) | 1.714 (9) | Al-O(2) | 1.721 (8) |
| Al-O(3) | 1.851 (7) | Al-Me | 1.96 (2) |
| O(1)-C(1) | 1.35 (2) | O(2)-C(11) | 1.35 (2) |
| O(3)-C(101) | 1.24 (1) | C(101)-O(4) | 1.31 (2) |
| O(4)-C(108) | 1.47 (2) | C(101)-C(102) | 1.44 (2) |
| O(1)-Al-O(2) | 116.0 (5) | O(1)-Al-O(3) | 105.7 (4) |
| O(1)-Al-Me | 109.4 (5) | O(2)-Al-O(3) | 100.4 (4) |
| O(2)-Al-Me | 119.4 (5) | O(3)-Al-Me | 103.7 (5) |
| Al-O(1)-C(1) | 153.3 (8) | Al-O(2)-C(11) | 156.3 (6) |
| Al-O(3)-C(101) | 174 (1) | O(3)-C(101)-O(4) | 123 (1) |
| O(3)-C(101)-C(102) | 124 (1) | C(101)-O(4)-C(108) | 118.0 (9) |

definitely stable as solids or in solution under an inert atmosphere.

The molecular structure of **17** has been confirmed by X-ray crystallography and is shown in Figure 3, with selected bond lengths and angles given in Table III. The geometry around aluminum in **17** is essentially the same as observed for **1** and $AlMe(BHT)_2(O{=}CPh_2)$,[10] while the aryloxide Al–O distances [Al–O(1) = 1.726 (3) Å, Al–O(2) = 1.729 (3) Å] are within the range for some degree of Al–O $\pi$ interaction.[6,7] The ester Al–O bond distance [1.857 (7) Å] is significantly shorter than those we have observed for the aldehyde and ketone analogues (see above and ref 10) but is within the expected range for a normal Al–O $\sigma$ bond (1.8–2.0 Å).[12]

**Amides.** The interaction of $AlMe(BHT)_2$ with $O{=}C(NH_2)Me$, $O{=}C(NPh_2)Me$, and $O{=}C(NMe_2)Ph$, in pentane, yields the corresponding Lewis acid–base complexes $AlMe(BHT)_2[O{=}C(NH_2)Me]$ (**21**), $AlMe(BHT)_2[O{=}C(NPh_2)Me]$ (**22**), and $AlMe(BHT)_2[O{=}C(NMe_2)Ph]$ (**23**), which have been characterized by $^1H$, $^{13}C$, and $^{27}Al$ NMR and IR spectroscopy.

Organic amides have lone pairs at both nitrogen and oxygen atoms and have the potential to act as ambidentate ligands, bonding through oxygen (II), nitrogen (III), or both nitrogen and oxygen (IV).



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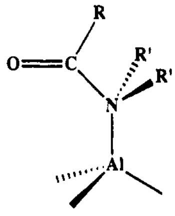

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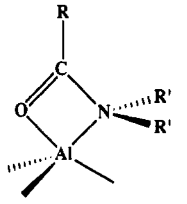


IV

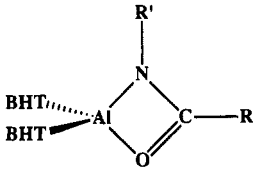
The $^{27}Al$ NMR spectra of **21**–**23** are consistent with four-coordinate aluminum centers (66–71 ppm),[7,22] which would preclude the bidentate coordination (IV) of the amide to aluminum. As has been observed for the aldehyde, ketone, and ester complexes, a decrease in the carbonyl stretching frequency and a downfield shift in the $^{13}C$ NMR resonances of the carbonyl $\alpha$-carbon in **21**–**23** (as compared to those of the free amide) indicates that the amide is bound via the carbonyl oxygen (II). In addition, the presence of dissimilar magnetic environments for the two substituents on nitrogen suggests that the $-NR_2$ moiety is rigid and coplanar with the coordinated carbonyl group. We have been unable, however, to confirm this proposal by X-ray crystallography.

We have shown that the elimination–condensation reaction sequence (eq 4) that commonly occurs between aluminum alkyls and primary or secondary amines does not occur with aluminum–BHT compounds.[23] In contrast, the reaction of $AlMe(BHT)_2$ with $O{=}C(NHMe)Ph$, in pentane, at ambient temperatures results in the elimination of methane and the formation of the amidate complex $Al(BHT)_2[O{=}C(NMe)Ph]$ (**24**; eq 5). Methane elimination from the acetamide complex (**21**) occurs in toluene solution at elevated temperatures (eq 6) to give $Al(BHT)_2[O{=}C(NH)Me]$ (**25**). The fact that the $^{27}Al$ NMR chemical shifts for **24** and **25** are consistent with a distorted four-coordinate aluminum and both are monomeric, as determined by solution molecular weight in benzene, suggests that the amidates act as bidentate chelating ligands, in contrast to the bidentate bridging mode previously reported for $\{Me_2Al[OC(Ph)NEt]\}_2$.[24]

$$AlR_3 + HNR'_2 \rightarrow [AlR_2(NR'_2)]_x + RH \qquad (4)$$

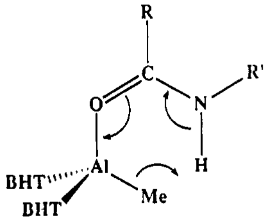
$$AlMe(BHT)_2 + O{=}C(NHMe)Ph \xrightarrow{25\ ^\circ C} \underset{\mathbf{24}}{Al(BHT)_2[O{=}C(NMe)Ph]} + MeH \qquad (5)$$

$$AlMe(BHT)_2[O{=}C(NH_2)Me] \xrightarrow{>80\ ^\circ C} \underset{\mathbf{25}}{Al(BHT)_2[O{=}C(NH)Me]} + MeH \qquad (6)$$



**24**: R = Ph, R' = Me
**25**: R = Me, R' = H

We have proposed that the observed lack of reactivity between the Al–C bonds in $AlMe(BHT)_2$ and primary and secondary amines is due to the reduced basicity of the aluminum methyl group arising from the presence of the electron-donating aryloxide substituents.[23] The difference in reactivity between $AlMe(BHT)_2$ and amides and amines may be ascribed to the increased acidity of amide protons ($pK_a$ = 15–17) as compared to those in primary or secondary amines ($pK_a$ = 27–30).[25] The small difference in acidity between $O{=}C(Me)NH_2$ ($pK_a$ = 17) and $O{=}C(Ph)NHMe$ ($pK_a$ = 16) is perhaps insufficient to explain that greater temperatures are required for alkane elimination from compound **21**. Given that the elimination reactions for amides undoubtedly proceed via a six-membered cyclic transition state (V; similar to that proposed for the enolization of coordinated ketones by aluminum alkyls[21]), the difference in steric bulk between the phenyl substituent and the methyl group is sufficient to favor a



V

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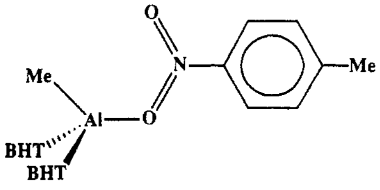
conformation in which the aluminum and nitrogen are cis with respect to the carbonyl C=O bond. Such a conformation would be required for the elimination of alkane. We propose, therefore, that a consideration of the increased steric bulk of phenyl versus that of methyl is sufficient to explain the enhanced tendency of O=C(Ph)N(H)Me to eliminate the aluminum methyl group.

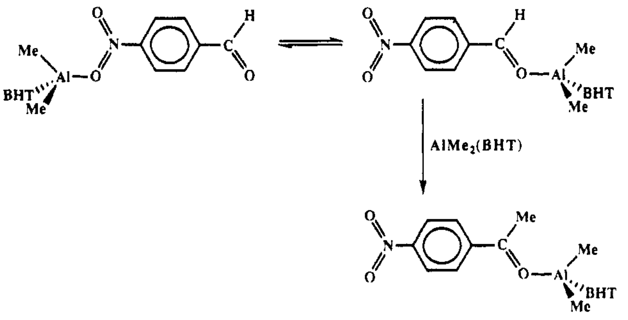
***p*-Nitrotoluene.** Organic nitro compounds are notoriously weak bases,[26] coordination by an $NO_2$ group occurring only when the ligand is anionic.[27] It is surprising, therefore, that the addition of *p*-nitrotoluene to a pentane solution of $AlMe(BHT)_2$ results in the formation of the deep blue Lewis acid–base adduct $AlMe(BHT)_2(O_2NC_6H_4\text{-}p\text{-}Me)$ (**26**).



**26**

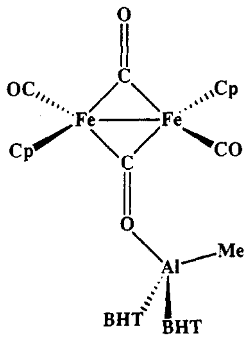
A recent X-ray crystallographic study of the first examples of complexes containing coordinated nitrobenzene, $[Zn(O_2NC_6H_5)_2(OTeF_5)_2]_2$ and $Zn(O_2NC_6H_5)_3(OTeF_5)_2$, has shown that organo nitro groups can function as either bidentate or monodentate ligands.[28] The IR spectrum of **26** exhibits $\nu(NO)$ bands (1517, 1510, 1340 and 1300 cm$^{-1}$) that are shifted with respect to those of free *p*-nitrotoluene [$\nu(NO)_{asym}$ 1596 cm$^{-1}$ and $\nu(NO)_{sym}$ 1366 cm$^{-1}$]. The bands in the spectra of **26** are similar to those reported[28] for $Zn(O_2NC_6H_5)_3(OTeF_5)_2$, in which the nitrobenzene groups are monodentate. In addition, the $^{27}$Al NMR shift (70 ppm) is consistent with a four-coordinate aluminum center,[7] confirming that the nitro group is bound through only one of the oxygen lone pairs.

During the course of the $AlMe_2(BHT)$-promoted conversion of $O{=}C(H)C_6H_4\text{-}p\text{-}NO_2$ to $O{=}C(Me)C_6H_4\text{-}p\text{-}NO_2$, the reaction solution changes from an initial deep blue to the dark brown of the ketone complex. In light of the above, we propose that $O{=}C(H)C_6H_4\text{-}p\text{-}NO_2$ initially coordinates via a nitro oxygen to give the observed deep blue complex. This subsequently rearranges to, or is in equilibrium with, the aldehyde-bound complex (eq 7). The latter is rapidly converted to the ketone complex via the reaction discussed above.



(7)

**Bis[cyclopentadienyldicarbonyliron].** The reaction of $AlMe(BHT)_2$ with $[CpFe(CO)_2]_2$ gives the red benzene- and toluene-soluble 1:1 adduct $[CpFe(CO)_2]_2AlMe(BHT)_2$ (**27**). Adduct formation is accompanied by a ca. 170-cm$^{-1}$ decrease in the asymmetric stretching frequency of one of the bridging carbonyls. We have been unable to confirm the structure of **27** by X-ray crystallography, but from $^1$H NMR and IR spectroscopy it appears to be analogous to the Lewis acid–base adducts of $[CpFe(CO)_2]_2$ reported by Shriver et al.[29] Compound **27** is stable in the solid state or in hexane or benzene solution but rapidly decomposes in coordinating solvent, e.g., $Et_2O$, to the solvent complex, e.g., $AlMe(BHT)_2(OEt_2)$.



**27**

In order to investigate the formation of a possible bis complex between $AlMe(BHT)_2$ and $[CpFe(CO)_2]_2$, the reaction has been monitored with use of variable-temperature $^1$H NMR spectroscopy. There is only a single aluminum methyl resonance observed, even as low as −80 °C, for a solution with an $AlMe(BHT)_2$:$[CpFe(CO)_2]_2$ molar ratio of 2:1, consistent with the formation of $[CpFe(CO)_2]_2 \cdot 2[AlMe(BHT)_2]$ (**28**).

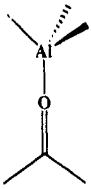
At $AlMe(BHT)_2$:$[CpFe(CO)_2]_2$ molar ratios greater than 2, there is only a single aluminum methyl resonance observed at room temperature, suggesting that free and coordinated $AlMe(BHT)_2$ are in rapid exchange (eq 8).

$$[CpFe(CO)_2]_2 \cdot 2[AlMe(BHT)_2] + Al^{*}Me(BHT)_2 \rightarrow [CpFe(CO)_2]_2[AlMe(BHT)_2][Al^{*}Me(BHT)_2] + AlMe(BHT)_2 \quad (8)$$

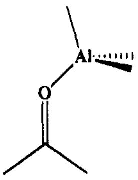
Cooling such a solution to −80 °C results in the observation of signals due to $AlMe(BHT)_2$ and a species consistent with **28**. We propose that solutions of $AlMe(BHT)_2$ and $[CpFe(CO)_2]_2$ are best described by equilibria between the 2:1 and 1:1 complexes and the free species (eq 9).

$$[CpFe(CO)_2]_2 \xrightleftharpoons{AlMe(BHT)_2} [CpFe(CO)_2]_2 \cdot AlMe(BHT)_2 \xrightleftharpoons{AlMe(BHT)_2} [CpFe(CO)_2]_2 \cdot 2[AlMe(BHT)_2] \quad (9)$$

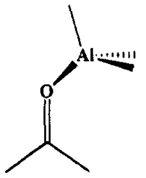
**Mode of Coordination of Organic Carbonyls to Aluminum Compounds.** There are several different possible modes of coordination of aluminum Lewis acids to carbonyl groups. One possibility is a purely electrostatic interaction, in which the aluminum is situated at the negative end of the C=O dipole, where C–O–Al = 180° (VI). Another possibility is the coordination of the alu-



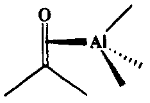
VI



VII



VIII



IX

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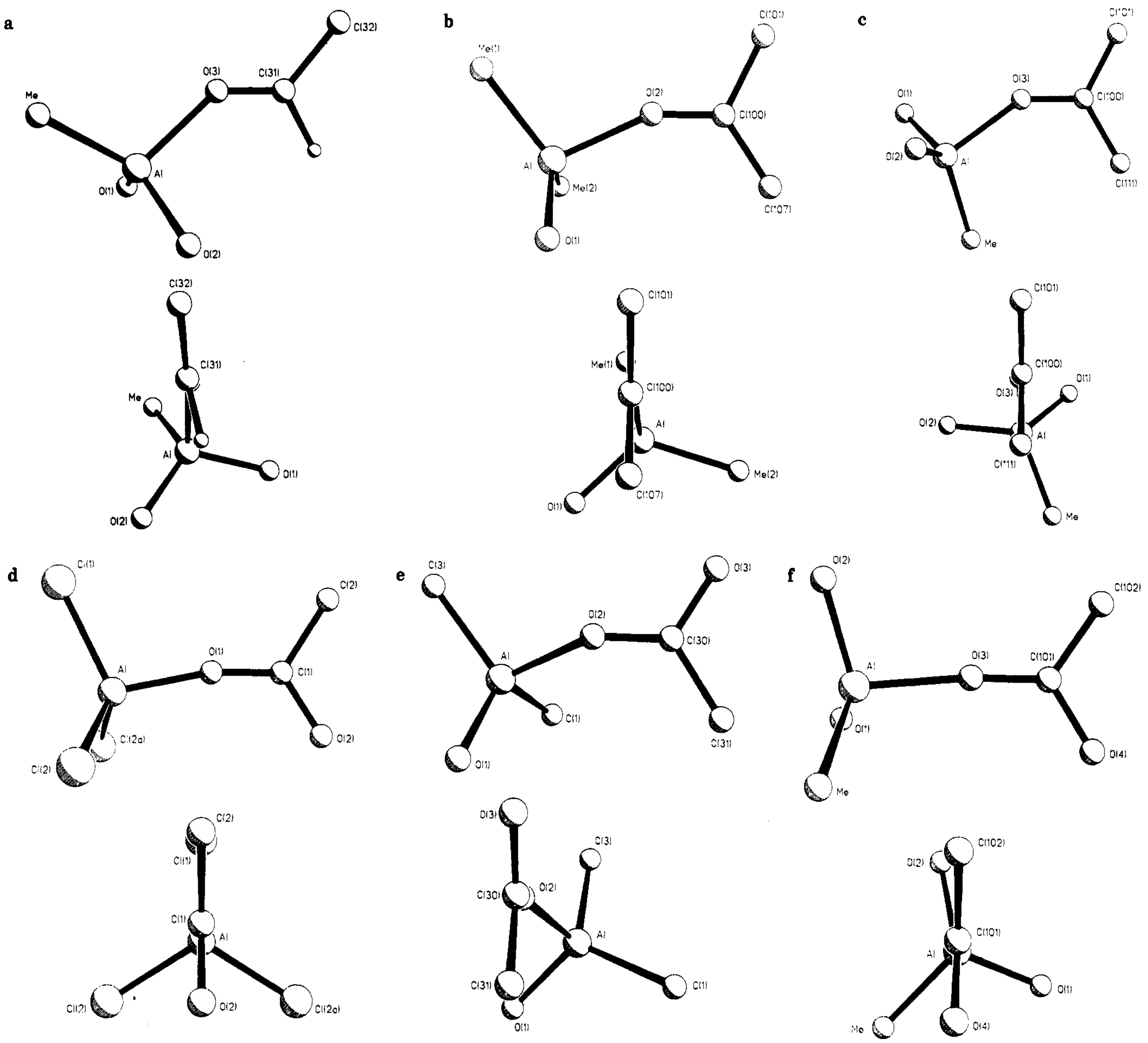

**Figure 4.** Partial coordination spheres of the organic carbonyl ligands for 1 (a), 8 (b), AlMe(BHT)$_2$(O=CPh$_2$) (c), AlCl$_3$[O=C(Me)OPh] (d), AlEt$_2$(BHT)[O=C(OMe)C$_6$H$_4$-*p*-Me] (e), and 17 (f), viewed perpendicular and parallel to the C=O vector.

minum to one of the lone pairs on the carbonyl oxygen. This results in the aluminum being in the nodal plane of the C=O $\pi$ bond (VII). Ab initio calculations for the model system H$_3$Al(O=CH$_2$)[30] suggest that this bent mode is the energetically favored geometry. A bent-nonplanar mode of bonding (VIII) results from movement of the aluminum out of the carbonyl $\pi$ nodal plane.[31] Finally a $\eta^2$ coordination of a Lewis acid to the C=O $\pi$ bond can be envisaged (IX) in which the carbonyl $\pi$ orbital is the donor but back-bonding into the C=O $\pi^*$ orbital occurs.[32] Although this mode has been reported for transition metals, it does not seem likely for main-group Lewis acids.

Figure 4 shows the partial coordination spheres of the organic carbonyl ligands, for a representative selection of monomeric aluminum complexes, viewed perpendicular and parallel to the C=O vector. The structures of the aldehyde and ketone[10] complexes (Figure 4a–c) are consistent with theoretical calculations;[30] i.e., the carbonyl is coordinated such that the aluminum is in the $\pi$ nodal plane of the ketone. The Al-O-C angles range from 136.0 (3) to 153.8 (9)°, larger than the predicted range of 122–141°. Wiberg[30] has shown, however, that any steric effects at the $\alpha$-carbon can be relieved by opening the Al-O-C angle, at a small energetic cost. Thus, one would expect the Al-O-C angle in 1 to be less than that for AlMe(BHT)$_2$(O=CPh$_2$),[10] and this is indeed observed [136.0 (3) and 144.0 (6)°, respectively]. Although the syn conformation is predicted to be the most stable,[30] both 1 and 8 adopt anti conformations, presumably due to steric interactions.

The ester complexes AlCl$_3$[O=C(Me)OPh][33] and 17 have Al-O-C angles approaching linearity, 168.4 (3) and 174 (1)°, respectively, while AlEt$_2$(BHT)[O=C(OMe)C$_6$H$_4$-*p*-Me][11] appears to be a rare example of a bent-nonplanar mode of bonding [Al-O(2)-C(30) = 143.0 (6)°, Al-O(2)-C(30)-O(3) = 130.1°]. Despite the proposal by Ashby et al.[15-18] that this mode of coordination is im-

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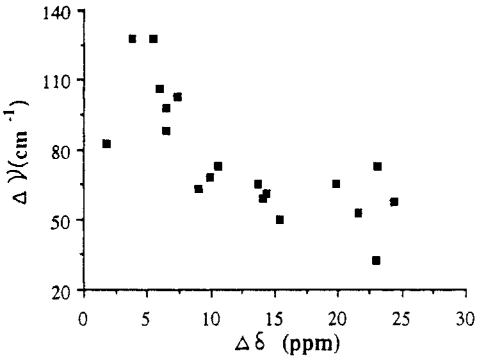
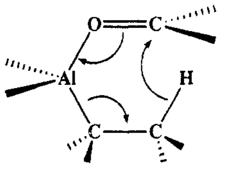
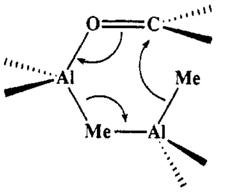


**Figure 5.** Decrease in the IR carbonyl stretching frequency (Δν) as a function of the downfield shift in the $^{13}$C NMR resonances of the carbonyl α-carbon (Δδ) for 1–3, 7–15, and 17–23.

portant in the transition states for both the reduction (X) and the alkylation (XI) of organic carbonyls by aluminum alkyl species, no other examples have been structurally characterized for aluminum complexes.



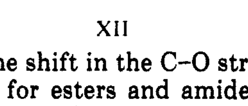
X



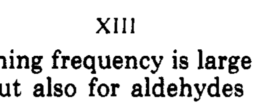
XI

It is apparent that the mode of coordination of organic carbonyls to aluminum is quite flexible. We propose that the control over the mode of bonding is predominantly steric. This is quite reasonable, given the small barrier calculated for the distortion from bent to linear geometry for $AlH_3(O{=}CH_2)$ (6 kcal/mol at MP3/6-31G*).[30]

**Effects on the Organic Carbonyl Ligand.** The IR C–O stretching frequency is strongly influenced by the C–O bond order; the higher the frequency, the greater the bond order. As we have previously observed,[10] there is a decrease in the carbonyl stretching frequency in the IR spectrum of the aluminum complexes when compared to those of the free carbonyls. Although this shift in frequency is consistent with coordination of the carbonyl to aluminum, the magnitude of Δν appears to be characteristic of the class of carbonyl ligand: aldehydes, 55–70 cm$^{-1}$; ketones, 45–70 cm$^{-1}$; esters, 85–125 cm$^{-1}$; amides, 80–125 cm$^{-1}$. This result can be rationalized as for the shifts observed for Lewis acid complexes of transition-metal carbonyl[29] and acetyl[34] complexes. If there is the possibility of electron donation from substituents X at the carbonyl α-carbon (XII), then resonance form XIII becomes a significant contributor for the carbonyl adducts.



XII



XIII

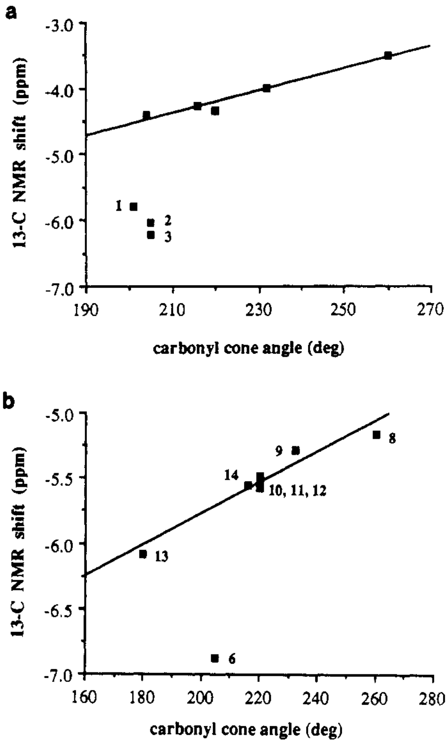


**Figure 6.** Aluminum methyl $^{13}$C NMR shift (δ) as a function of the organic carbonyl ligands' steric bulk (see text) for the complexes $AlMe(BHT)_2[O{=}C(X)Y]$ (a) and $AlMe_2(BHT)[O{=}C(X)Y]$ (b).

The shift in the C–O stretching frequency is large not only for esters and amides but also for aldehydes and ketones with strong electron-donating substituents. Thus, the *p*-methoxybenzaldehyde complex 6 has a larger Δν value (100 cm$^{-1}$) than that observed for the other aldehydes. If this bonding picture is correct, then the magnitude of the downfield shifts in the $^{13}$C NMR spectra for the carbonyl α-carbon, on coordination to aluminum (Δδ) should decrease with an increase in the contribution of resonance form XIII; i.e., Δδ will decrease with an increase in Δν. Although a general trend is indeed observed for the changes in the $^{13}$C NMR shift and the carbonyl ν(C=O) stretching frequency (Figure 5), it is clear that other, possibly steric, factors are also important in determining the magnitude of either parameter.

**Effects on Aluminum.** We have shown previously[35] that the $^{13}$C NMR shift of the aluminum carbon resonance in $Me_3AlPR_3$ complexes is primarily dependent on the steric bulk of the phosphine ligand; the bulkier phosphines force the aluminum to become more distorted from planarity, and the increased p character in the Al–C bond is reflected by the downfield shift of the $Al{-}CH_3$ carbon resonance. As shown in Figure 6, there is a similar dependence of the aluminum methyl $^{13}$C shift on the steric bulk of the organic carbonyl for the complexes $AlMe_2(BHT)[O{=}C(X)Y]$ (Figure 6a) and $AlMe(BHT)_2[O{=}C(X)Y]$ (Figure 6b); that is, the greater the steric bulk of the α-carbon's substituents, the more downfield the shift of the methyl resonance. For simplicity we have defined the steric bulk of the organic carbonyls to be proportional to the sum of their substituent cone angles as reported by Tolman (eq 10).

$$\theta_{O=C(X)Y} \propto \theta_X + \theta_Y \qquad (10)$$

The aldehyde complexes are notable exceptions to the trends found for the $^{13}$C NMR shifts for the $Al{-}CH_3$ groups in both $AlMe_2(BHT)[O{=}C(X)Y]$ and $AlMe(BHT)_2[O{=}C(X)Y]$, and therefore, they are not included in the straight lines drawn in Figure 6. From the $^{13}$C NMR shift, it would appear that the aldehydes are sterically less hindered than their calculated values would suggest. Indeed, from Figure 6, an effective cone angle between 140 and 150° can be estimated for all the aldehydes. On the basis of our me-

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thod of estimating the steric bulk of organic carbonyls, this value would correspond to that expected for $O{=}CH_2$, suggesting that the aldehyde complexes in solution retain the conformation observed in the solid state (see above), in which the $\alpha$-hydrogen is syn with respect to the aluminum. This observation may be significant in the stereospecific reactions of aldehydes coordinated to sterically hindered aluminum Lewis acids.

## Experimental Section

Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY. Melting points were determined in sealed capillaries and are uncorrected. IR spectra (4000–700 $cm^{-1}$) were recorded on a Nicolet 5ZDX FT-IR spectrometer as Nujol mulls (NaCl). NMR spectra, in $C_6D_6$ unless otherwise stated, were recorded on Bruker AM-500 ($^1H$ and $^{13}C$) and WM-300 spectrometers ($^{27}Al$) [$\delta$ in parts per million relative to $SiMe_4$ ($^1H$, $^{13}C$) and $Al(H_2O)_6{}^{2+}$ ($^{27}Al$)]. Molecular weight measurements were made in benzene with the use of an instrument similar to that described by Clark.[36] All manipulations were carried out under nitrogen. Solvents (pentane, unless otherwise indicated) were dried, distilled, and degassed before use. $AlMe(BHT)_2$[6] and $AlMe_2(BHT)(OEt_2)$[8] were prepared as described previously.

**AlMe(BHT)$_2$[O=C(H)$^t$Bu] (1).** $O{=}C(H)^tBu$ (0.426 mL, 6.24 mmol) in pentane (20 mL) was added dropwise to $AlMe(BHT)_2$ (3.0 g, 6.24 mmol) in pentane (30 mL). A bright yellow solution resulted. When the mixture was stirred for 2 h, the solvent was removed under vacuum to leave a bright yellow-orange powder. The yield of crude product was essentially quantitative. The powder was washed with pentane (20 mL), the washings were filtered, and the filtrate was reduced in volume and set aside in the freezer. Large orange crystals suitable for X-ray diffraction formed overnight: yield ca. 85%; mp 129–130 °C. Anal. Calcd for $C_{36}H_{59}AlO_3$: C, 76.28; H, 10.49. Found: C, 76.05; H, 10.10. IR: 1655 (s), 1290 (sh), 1258 (s), 1235 (s), 1215 (m), 1200 (s), 1120 (m) 1040 (w), 1030 (w), 950 (w), 920 (w), 890 (m), 870 (s), 860 (s), 810 (w), 770 (m), 710 (s), 670 (sh), 658 (s) $cm^{-1}$. $^1H$ NMR: $\delta$ 8.85 [1 H, s, $O{=}C(H)^tBu$], 7.18 (4 H, s, $C_6H_2$, BHT), 2.28 (6 H, s, $CH_3$, BHT), 1.59 [36 H, s, $C(CH_3)_3$, BHT], 0.537 [9 H, s, $O{=}C(H)C(CH_3)_3$], –0.14 (3 H, s, Al–$CH_3$). $^{13}C$ NMR: $\delta$ 223.78 (C=O) 154.65 (OC, BHT), 138.99 (*o*-C, BHT), 126.43 (*m*-C, BHT), 126.18 (*p*-C, BHT), 43.79 [$C(CH_3)_3$, $O{=}C(H)^tBu$], 35.57 [$C(CH_3)_3$, BHT], 31.96 [$C(CH_3)_3$, BHT], 22.47 [$C(CH_3)_3$, $O{=}C(H)^tBu$], 21.33 ($CH_3$, BHT), –5.80 (Al–$CH_3$).

**AlMe(BHT)$_2$[O=C(H)C$_6$H$_4$-*p*-Me] (2).** $O{=}C(H)C_6H_4$-*p*-Me (0.764 mL, 6.24 mmol) in pentane (30 mL) was added dropwise to $AlMe(BHT)_2$ (3.0 g, 6.24 mmol) in the same volume of pentane. A deep red solution resulted. As the addition proceeded, an orange precipitate formed. Upon completion of the addition, the resulting mixture was stirred for 1 h and then filtered. The precipitate was washed once with pentane, filtered, and dried under vacuum: yield ca. 73%; mp 138 °C. Anal. Calcd for $C_{39}H_{57}AlO_3$: C, 77.95; H, 9.56. Found: C, 78.14; H, 9.89. IR: 1630 (s), 1620 (s), 1595 (s), 1560 (s), 1335 (w), 1295 (sh), 1280 (s), 1260 (s), 1240 (sh), 1200 (m), 1170 (m), 1125 (m), 1025 (w), 1010 (w), 950 (w), 925 (w), 895 (s), 880 (s), 855 (s), 810 (m), 775 (m), 770 (m), 725 (w), 680 (s), 665 (s), 650 (s), 620 (m), 575 (w), 485 (m), 470 (w) $cm^{-1}$. $^1H$ NMR: $\delta$ 8.88 (1 H, s, O=C*H*), 7.35 (2 H, m, *o*-C*H*), 7.20 (4 H, s, $C_6H_2$, BHT), 6.58 [2 H, d, *J*(H–H) = 7.9 Hz, *m*-C*H*], 2.30 (6 H, s, $CH_3$, BHT), 1.78 (3 H, s, $CH_3$), 1.67 [36 H, s, $C(CH_3)_3$, BHT], 0.07 (3 H, s, Al–$CH_3$). $^{13}C$ NMR: $\delta$ 200.38 (O=C), 154.98 (OC, BHT), 153.17 (O=CC), 139.06 (*o*-C, BHT), 134.36 (*o*- and *m*-C), 130.57 (*p*-C), 126.39 (*m*-C, BHT), 125.79 (*p*-C, BHT), 35.46 [$C(CH_3)_3$, BHT], 31.91 [$C(CH_3)_3$, BHT], 22.12 ($CH_3$), 21.40 ($CH_3$, BHT), –6.04 (Al–$CH_3$).

**AlMe(BHT)$_2$[O=C(H)C$_6$H$_4$-*p*-Cl] (3)** was prepared in a manner analogous to that for **2**: yield 92%; mp 120 °C. Anal. Calcd for $C_{38}H_{54}AlClO_3$: C, 73.46; H, 8.76. Found: C. 73.28; H, 8.52. IR: 1630 (s), 1595 (s), 1565 (m), 1315 (sh), 1295 (sh), 1280 (s), 1260 (s), 1240 (sh), 1225 (sh), 1205 (m), 1170 (w), 1160 (w), 1125 (w), 1090 (m), 1030 (w), 1010 (w), 955 (w), 900 (m), 885 (m), 860 (m), 850 (m), 835 (m), 815 (m), 775 (w), 715 (w), 680 (m), 660 (m), 650 (m), 590 (m), 490 (m) $cm^{-1}$. $^1H$ NMR: $\delta$ 8.69 (1 H, s, O=C*H*), 7.19 (4 H, s, $C_6H_2$, BHT), 7.05 [2 H, d, *J*(H–H) = 8.72 Hz, *o*-C*H*], 6.65 [2 H, d, *J*(H–H) = 8.73 Hz, *m*-C*H*], 2.28 (6 H, s, $CH_3$, BHT), 1.65 [36 H, s, $C(CH_3)_3$, BHT], 0.038 (3H, s, Al–$CH_3$). $^{13}C$ NMR: $\delta$ 199.97 (O=C), 154.74 (OC, BHT), 147.20 (O=CC), 139.05 (*o*-C, BHT), 134.92 (*p*-C), 130.89 (*o*-C), 130.12 (*m*-C), 126.45 (*m*-C, BHT), 126.14 (*p*-C, BHT), 35.43 [$C(CH_3)_3$, BHT], 31.89 [$C(CH_3)_3$, BHT], 21.36 ($CH_3$, BHT), –6.22 (Al–$CH_3$).

**AlMe$_2$(BHT)[O=C(H)C$_6$H$_4$-*p*-Me] (4).** $O{=}C(H)C_6H_4$-*p*-Me (1.74 mL, 14.25 mmol) was added via syringe to a solution of $AlMe_2(BHT)(Et_2O)$ (5.0 g, 14.25 mmol) in pentane (40 mL). A large quantity of an orange-yellow precipitate resulted. The mixture was stirred for ca. 5 min and then filtered. The precipitate was dried under vacuum: yield ca. 80%; mp 82–86 °C. Anal. Calcd for $C_{25}H_{37}O_2Al$: C, 75.72; H, 9.40. Found: C, 75.55; H, 9.18. IR: 1640 (m), 1600 (s), 1570 (m), 1280 (s), 1260 (sh), 1240 (sh), 1220 (sh), 1190 (m), 1175 (m), 1130 (w), 1015 (w), 875 (s), 860 (sh), 810 (m), 780 (w), 770 (w), 710 (sh), 675 (s), 650 (sh), 625 (m) $cm^{-1}$. $^1H$ NMR: $\delta$ 9.02 (1 H, s, O=C*H*), 7.49 [2 H, d, *J*(H–H) = 8.17 Hz, *o*-C*H*], 7.30 (2 H, s, $C_6H_2$, BHT), 6.52 [2 H, d, *J*(H–H) = 8.1 Hz, *m*-C*H*], 2.39 (3 H, s, $CH_3$, BHT), 1.81 (3 H, s, $CH_3$), 1.68 [18 H, s, $C(CH_3)_3$, BHT], –0.035 (6 H, s, Al–$CH_3$).

**AlMe$_2$(BHT)[O=C(H)C$_6$H$_4$-*p*-Cl] (5)** was prepared in a manner analogous to that for **4**: yield ca. 86%; mp 85–87 °C. Anal. Calcd for $C_{24}H_{34}AlClO_2$: C, 69.13; H, 8.21. Found: C, 69.15; H, 8.37. IR: 1630 (s), 1585 (s), 1560 (m), 1285 (s), 1265 (sh), 1220 (m), 1190 (m), 1170 (w), 1085 (m), 1010 (w), 870 (m), 850 (m), 820 (m), 780 (w), 710 (m), 670 (s), 590 (m) $cm^{-1}$. $^1H$ NMR: $\delta$ 8.88 (1 H, s, OC*H*), 7.28 (2 H, s, $C_6H_2$, BHT), 6.91 [2 H, d, *J*(H–H) = 7.7 Hz, $C_6H_2$], 6.67 [2 H, d, *J*(H–H) = 7.7 Hz, $C_6H_2$], 2.38 (3 H, s, $CH_3$, BHT), 1.64 [18 H, s, $C(CH_3)_3$, BHT], –0.09 (6 H, s, Al–$CH_3$).

**AlMe$_2$(BHT)[O=C(H)C$_6$H$_4$-*p*-OMe] (6)** was prepared in a manner analogous to that for **4**: yield ca. 92%; mp 95–97 °C. Anal. Calcd. for $C_{25}H_{37}AlO_3$: C, 72.28; H, 9.03. Found: C, 72.79; H, 9.26. IR: 1625 (m), 1590 (s), 1550 (m), 1300 (sh), 1275 (s), 1220 (sh), 1200 (w), 1180 (w), 1155 (m), 1120 (w), 1020 (m), 860 (s), 840 (s), 810 (w), 780 (w), 770 (w), 700 (sh), 670 (s), 660 (s), 620 (m), 590 (sh), 545 (w), 520 (w) $cm^{-1}$. $^1H$ NMR: $\delta$ 8.99 (1 H, s, O=C*H*), 7.27 (2 H, s, $C_6H_2$, BHT), 6.31 [2 H, d, *J*(H–H) = 8.82 Hz, $C_6H_2$], 3.02 (3 H, s, $OCH_3$), 2.37 (3 H, s, $CH_3$, BHT), 1.69 [18 H, s, $C(CH_3)_3$, BHT], –0.049 (6 H, s, Al–$CH_3$). $^{13}C$ NMR: 196.82 (O=C), 169.15 (COMe), 155.79 (OC, BHT), 138.69 (*o*-C, BHT), 126.17 (OCC), 126.06 (*m*-C, BHT), 125.00 (*p*-C, BHT), 115.40 (*o*-C), 55.54 ($OCH_3$), 35.24 [$C(CH_3)_3$, BHT], 31.29 [$C(CH_3)_3$, BHT], 21.57 ($CH_3$, BHT), –6.88 (Al–$CH_3$).

**AlMe(BHT)$_2$[O=$\overline{\mathbf{C(CH_2)_3CH_2}}$] (7).** $O{=}\overline{C(CH_2)_3CH_2}$ (0.9 mL, 11.25 mmol) was added via syringe to a pentane (40 mL) solution of $AlMe(BHT)_2$ (5.25 g, 10.92 mmol). A pale yellow precipitate formed. After it was stirred for 15 min, the solution was filtered and the precipitate was dried under vacuum: yield 70–80%; mp 152–153 °C. Anal. Calcd for $C_{36}H_{57}AlO_3$: C, 76.55; H, 10.17. Found: C, 76.59; H, 10.20. IR: 1690 (sh), 1685 (s), 1660 (sh), 1598 (w), 1295 (s), 1285 (s), 1270 (s), 1250 (sh), 1235 (s), 1200 (sh), 1190 (m), 1155 (w), 1020 (w), 950 (w), 890 (s), 860 (m), 850 (m), 775 (w), 720 (m), 685 (sh), 665 (sh), 620 (w), 580 (m) $cm^{-1}$. $^1H$ NMR: $\delta$ 7.20 (4 H, s, $C_6H_2$, BHT), 2.29 (6 H, s, $CH_3$, BHT), 1.82 [4 H, m, $OCCH_2$], 1.59 [36 H, s, $C(CH_3)_3$, BHT], 1.02 [4 H, m, $OCCH_2CH_2$], –0.127 (3 H, s, Al–$CH_3$). $^{13}C$ NMR: $\delta$ 241.56 (C=O), 154.65 (OC, BHT), 138.86 (*o*-C, BHT), 126.33 (*m*-C, BHT), 125.75 (*p*-C, BHT), 40.73 ($OCCH_2$), 35.37 [$C(CH_3)_3$, BHT], 31.92 [$C(CH_3)_3$, BHT], 22.49 ($OCCH_2CH_2$), 21.39 ($CH_3$, BHT), –5.13 (Al–$CH_3$).

**AlMe$_2$(BHT)(O=CPh$_2$) (8). Method 1.** $O{=}CPh_2$ (1.82 g, 10.0 mmol) in pentane (40 mL) was added dropwise to an equimolar solution of $AlMe_3$ (5.0 mL, 2.0 M, 10.0 mmol) and BHT-H (2.2 g, 10.0 mmol) in pentane (20 mL). As the addition proceeded, an orange-red color developed. After the mixture was stirred for 1 h, the solvent was removed under vacuum to yield an orange-red residue. This was dissolved in pentane (10 mL) and the solution cooled to –20 °C. An orange oil formed, which crystallized after ca. 3 days. The crystalline material was filtered, and $^1H$ NMR spectroscopy showed it to consist of a 2:1 ratio of **8** and $AlMe(BHT)_2(O{=}CPh_2)$. Multiple fractional crystallization of this mixture gave pure **8**, yield ~40%.

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[36] Clark, E. P. *Ind. Eng. Chem., Anal. Ed.* **1941**, *13*, 820.

**Method 2.** To $AlMe_2(BHT)(OEt_2)$ (5.0 g, 14.25 mmol) in pentane (50 mL) was added solid $O{=}CPh_2$ (2.59 g, 14.25 mmol). A deep orange solution resulted. After the mixture was stirred for 20 min, crystalline $AlMe_2(BHT)(O{=}CPh_2)$ formed. This was filtered and dried under vacuum. More product was obtained by cooling the filtrate (−20 °C): yield ca. 90%; mp 98–102 °C. Anal. Calcd for $C_{30}H_{39}O_2Al$: C, 78.56; H, 8.57. Found: C, 78.15; H, 8.26. IR: 1605 (sh), 1590 (s), 1560 (s), 1550 (sh), 1330 (s), 1290 (sh), 1275 (s), 1255 (sh), 1195 (s), 1180 (s), 1160 (sh), 1120 (w), 1070 (w), 1020 (w), 1000 (w), 940 (m), 925 (m), 870 (s), 860 (sh), 805 (w), 770 (s), 700 (s), 660 (s), 630 (m) cm$^{-1}$. $^1$H NMR: δ 7.58 [4 H, d, *J*(H–H) = 8.3 Hz, *o*-C*H*], 7.31 (2 H, s, $C_6H_2$, BHT), 7.04 [2 H, t, *J*(H–H) = 8.3 Hz, *p*-C*H*], 6.86 [4 H, t, *J*(H–H) = 8.0 Hz, *m*-C*H*], 2.39 (3 H, s, $CH_3$, BHT), 1.66 [18 H, s, $C(CH_3)_3$, BHT], −0.137 (6 H, s, Al–$CH_3$). $^{13}$C NMR δ 204.18 (O=C), 155.88 (O*C*, BHT), 138.97 (*o*-*C*, BHT), 135.69 (O=C*C*, Ph), 135.17 (*p*-*C*, Ph), 132.87 (*o*-*C*, Ph) 128.74 (*m*-*C*, Ph), 126.15 (*m*-*C*, BHT), 125.12 (*p*-*C*, BHT), 35.18 [$C(CH_3)_3$, BHT], 31.37 [$C(CH_3)_3$, BHT], 21.57 ($CH_3$, BHT), −5.16 (Al–$CH_3$).

Compounds **9–15** were prepared in a manner analogous to that for **8** (method 2).

**$AlMe_2(BHT)[O{=}C(Et)Ph]$ (9)**: yield 80–90%; mp 93–94 °C. Anal. Calcd. for $C_{26}H_{39}AlO_2$: C, 76.06: H, 9.57. Found: C, 76.30; H, 9.24. IR: 1635 (s), 1595 (s), 1580 (s), 1310 (w), 1250 (s), 1215 (w), 1190 (m), 1125 (s), 1105 (w), 1085 (m), 1075 (sh), 1025 (m), 1000 (m), 950 (m), 935 (w), 920 (w), 885 (m), 865 (s), 835 (w), 805 (w), 775 (m), 745 (s), 700 (s, br), 610 (m), 575 (m), 565 (m), 540 (m), 495 (m) cm$^{-1}$. $^1$H NMR: δ 7.64 [2 H, d, *J*(H–H) = 7.8 Hz, *o*-C*H*], 7.23 (2 H, s, $C_6H_2$, BHT), 7.06 [1 H, t, *J*(H–H) = 7.7 Hz, *p*-C*H*], 6.87 [2 H, t, *J*(H–H) = 7.8 Hz, *m*-C*H*], 2.59 [2 H, q, *J*(H–H) = 7.5 Hz, $CH_2CH_3$], 2.34 (3 H, s, $CH_3$, BHT), 1.60 [18 H, s, $C(CH_3)_3$, BHT], 0.882 [3 H, t, *J*(H–H) = 7.5 Hz, $CH_2CH_3$], −0.119 (6 H, s, Al–$CH_3$). $^{13}$C NMR: δ 214.16 (*C*=O), 155.74 (O*C*, BHT), 138.79 (*o*-*C*, BHT), 137.38 (*C*C=O, Ph), 133.24 (*p*-*C*, Ph), 131.43 (*o*-*C*, Ph), 129.26 (*m*-*C*, Ph), 126.07 (*m*-*C*, BHT), 125.08 (*p*-*C*, BHT), 35.13 [$C(CH_3)_3$, BHT], 32.55 ($CH_2CH_3$), 31.34 [$C(CH_3)_3$, BHT], 21.55 ($CH_3$, BHT), 11.27 ($CH_2CH_3$), −5.28 (Al–$CH_3$).

**$AlMe_2(BHT)[O{=}C(Me)Ph]$ (10)**: yield 80–85%; mp 106–107 °C. Anal. Calcd for $C_{25}H_{37}O_2Al$: C, 75.72; H, 9.40. Found: C, 74.83; H, 9.06. IR: 1622 (s), 1600 (m), 1572 (s), 1275 (s), 1220 (w), 1185 (m), 1120 (w), 1100 (w), 1070 (w), 1020 (w), 1000 (w), 965 (w), 930 (w), 865 (s), 805 (w), 760 (w), 745 (w), 710 (m), 670 (s), 600 (m), 580 (m) cm$^{-1}$. $^1$H NMR: δ 7.50 [2 H, d, *J*(H–H) = 7.6 Hz, *o*-C*H*], 7.29 (2 H, s, $C_6H_2$, BHT), 6.98 [1 H, t, *J*(H–H) = 7.6 Hz, *p*-C*H*], 6.76 [2 H, t, *J*(H–H) = 7.6 Hz, *m*-C*H*], 2.38 (3 H, s, $CH_3$, BHT), 2.12 (3 H, s, $CH_3$), 1.65 [18 H, s, $C(CH_3)_3$, BHT], −0.05 (6 H, s, Al–$CH_3$). $^{13}$C NMR: δ 210.71 (O=*C*), 155.75 (O*C*, BHT), 138.77 (*o*-*C*, BHT), 137.42 (O=C*C*), 134.29 (*p*-*C*), 131.12 (*m*-*C*), 129.10 (*o*-*C*), 126.09 (*m*-*C*, BHT), 125.15 (*p*-*C*, BHT), 35.11 [$C(CH_3)_3$, BHT],31.30 [$C(CH_3)_3$, BHT], 26.00 ($CH_3$), 21.53 ($CH_3$, BHT), −5.52 (Al–$CH_3$).

**$AlMe_2(BHT)[O{=}C(Me)C_6H_4$-*p*-Me] (11)**: yield ~83%; mp 124 °C. Anal. Calcd for $C_{26}H_{39}O_2Al$: C, 76.06; H, 9.57. Found: C, 75.91; H, 9.20. IR: 1620 (m), 1595 (s), 1565 (s), 1320 (m), 1305 (m), 1290 (sh), 1280 (s), 1260 (sh), 1250 (sh), 1220 (w), 1220 (w), 1200 (w), 1183 (s), 1130 (w), 1020 (w), 1012 (w), 1000 (w), 965 (m), 950 (sh), 920 (w), 865 (s), 835 (w), 805 (m), 780 (m), 715 (m), 675 (s), 600 (m), 585 (sh) cm$^{-1}$. $^1$H NMR: δ 7.54 [2 H, d, *J*(H–H) = 8.2 Hz, *o*-C*H*], 7.27 (2 H, s, $C_6H_2$, BHT), 6.67 [2 H, d, *J*(H–H) = 8.2 Hz, *m*-C*H*], 2.36 (3 H, s, $CH_3$, BHT), 2.21 (3 H, s, O=C$CH_3$), 1.87 (3 H, s, $CH_3$), 1.65 [18 H, s, $C(CH_3)_3$, BHT], −0.08 (6 H, s, Al–$CH_3$). $^{13}$C NMR: δ 209.59 (*C*=O), 155.83 (O*C*, BHT), 149.71 (*C*C=O), 138.79 (*o*-*C*, BHT), 132.01 (*p*-*C*), 131.48 (*o*-*C*), 129.93 (*m*-*C*), 126.09 (*m*-*C*, BHT), 125.08 (*p*-*C*, BHT), 35.13 [$C(CH_3)_3$, BHT], 31.32 [$C(CH_3)_3$, BHT], 25.76 (O=C$CH_3$), 21.71 ($CH_3$, BHT), 21.54 ($CH_3$), −5.49 (Al–$CH_3$).

**$AlMe_2(BHT)[O{=}C(Me)C_6H_4$-*p*-Cl] (12)**: yield 83%; mp 123 °C. Anal. Calcd for $C_{25}H_{36}O_2AlCl$: C, 69.67; H, 8.41. Found: C, 69.61; H, 8.25. IR: 1630 (s), 1590 (s), 1565 (s), 1315 (m), 1300 (s), 1290 (sh), 1275 (s), 1255 (s), 1245 (sh), 1215 (w), 1190 (s), 1180 (m), 1125 (w), 1095 (m), 1080 (w), 1020 (w), 1010 (m), 975 (m), 950 (w), 920 (w), 885 (sh), 870 (sh), 865 (s), 835 (m), 827 (w), 805 (w), 780 (m), 710 (m), 675 (s), 640 (w), 620 (w), 590 (m), 580 (s), 545 (w), 465 (w) cm$^{-1}$. $^1$H NMR: δ 7.29 (2 H, s, $C_6H_2$, BHT), 7.21 [2 H, d, *J*(H–H) = 8.48 Hz, *o*-C*H*], 6.73 [2 H, d, *J*(H–H) = 8.5 Hz, *m*-C*H*], 2.38 (3 H, s, $CH_3$, BHT), 2.03 (3 H, s, $CH_3$), 1.64 [18 H, s, $C(CH_3)_3$, BHT], −0.088 (6 H, s, Al–$CH_3$). $^{13}$C NMR: δ 209.05 (*C*=O), 155.60 (O*C*, BHT), 144.30 (*C*C=O), 138.69 (*o*-*C*, BHT), 132.51 (Cl*C*), 132.29 (*o*-*C*), 129.45 (*m*-*C*), 126.17 (*m*–*C*, BHT), 125.42 (*p*-*C*, BHT), 35.11 [$C(CH_3)_3$, BHT], 31.30 [$C(CH_3)_3$, BHT], 25.86 (O=C$CH_3$), 21.51 ($CH_3$, BHT), −5.58 (Al–$CH_3$).

**$AlMe_2(BHT)(O{=}CMe_2)$ (13)**: yield 65–75%; mp 100–101 °C. Anal. Calcd for $C_{20}H_{35}AlO_2$: C, 71.81; H, 10.54. Found: C, 71.59; H, 9.74. IR: 1665 (s), 1270 (s), 1250 (s), 1215 (sh), 1190 (s), 1120 (w), 1080 (w), 1020 (w), 950 (w), 920 (w), 870 (s), 800 (w), 780 (w), 670 (s), 610 (w), 565 (m) cm$^{-1}$. $^1$H NMR: δ 7.24 (2 H, s, $C_6H_2$, BHT), 2.36 (3 H, s, $CH_3$, BHT), 1.60 [18 H, s, $C(CH_3)_3$, BHT], 1.45 [6 H, s, $CH_3$, $(CH_3)_2CO$], −0.281 (6 H, s, Al–$CH_3$). $^{13}$C NMR: δ 225.69 (O=*C*), 155.51 (O*C*, BHT), 138.58 (*o*-*C*, BHT), 126.06 (*m*-*C*, BHT), 125.13 (*p*-*C*, BHT), 35.04 [$C(CH_3)_3$, BHT], 31.28 [$C(CH_3)_3$, BHT], 30.87 ($CH_3$), 21.52 ($CH_3$, BHT), −6.09 (Al–$CH_3$).

**$AlMe_2(BHT)[O{=}C(Me)^tBu]$ (14)**: yield ~85%; mp 95–97 °C. Anal. Calcd for $C_{23}H_{41}O_2Al$: C, 73.36; H, 10.97. Found: C, 73.71; H, 10.27. IR: 1640 (s), 1385 (s), 1370 (s), 1350 (s), 1285 (sh), 1275 (s), 1255 (sh), 1215 (w), 1185 (w), 1150 (s), 1120 (w), 1040 (w), 1020 (w), 965 (w), 945 (w), 935 (w), 915 (w), 870 (s), 860 (s), 835 (w), 800 (w), 770 (m), 700 (sh), 670 (s), 610 (w), 570 (m), 540 (w), 475 (w) cm$^{-1}$. $^1$H NMR: δ 7.26 (2 H, s, $C_6H_2$, BHT), 2.36 (3 H, s, $CH_3$, BHT), 1.83 (3 H, s, $CH_3$, $^t$BuMeCO), 1.62 [18 H, s, $C(CH_3)_3$, BHT], 0.629 [9 H, s, $C(CH_3)_3$, $^t$BuMeCO], −0.227 (6 H, s, Al–$CH_3$). $^{13}$C NMR: δ 233.55 (*C*=O), 155.54 (O*C*, BHT), 138.70 (*o*-*C*, BHT), 126.10 (*m*-*C*, BHT), 125.32 (*p*-*C*, BHT), 46.23 ($CH_3$, $^t$BuMeCO), 35.24 [$C(CH_3)_3$, BHT], 31.59 [$C(CH_3)_3$, BHT], 26.22 [$C(CH_3)_3$, $^t$BuMeCO], 25.88 [$C(CH_3)_3$, $^t$BuCOMe], 21.67 ($CH_3$, BHT), −5.55 (Al–$CH_3$).

**$AlMe_2(BHT)[O{=}C(C_5H_9)$-4-Ph] (15)**: yield 73%; mp 96–97 °C. Anal. Calcd for $C_{29}H_{43}O_2Al$: C, 77.29; H, 9.61. Found: C, 77.08; H, 9.10. IR: 1670 (s), 1285 (s), 1265 (sh), 1220 (w), 1190 (m), 1170 (m), 1160 (sh), 1125 (w), 1065 (w), 1020 (w), 880 (s), 865 (m), 800 (w), 775 (w), 760 (m), 695 (s), 670 (s), 605 (w) cm$^{-1}$. $^1$H NMR: δ 7.26 (2 H, s, $C_6H_2$, BHT), 7.16–7.09 (4 H, m, *p*- + *m*-C*H*, Ph), 6.83 [2 H, d, *J*(H–H) = 6.8 Hz, *o*-C*H*, Ph], 2.42 (1 H, m, γ–C*H*), 2.36 (3 H, s, $CH_3$, BHT), 2.25, 1.8, 1.50 (8 H, m, β- + α-C*H*), 1.66 [18 H, s, $C(CH_3)_3$, BHT], −0.189 (6 H, s, Al–$CH_3$), $^{13}$C NMR: δ 230.38 (*C*=O), 155.53 (O*C*, BHT), 142.95 (*C*CH, Ph), 138.59 (*o*-*C*, BHT), 128.97 (*o*-*C*, Ph), 127.29 (*p*-*C*, Ph), 126.66 (*m*-*C*, Ph), 126.10 (*m*-*C*, BHT), 125.14 (*p*-*C*, BHT), 41.32 (*C*C=O), 41.12 (β-*C*), 35.27 [$C(CH_3)_3$, BHT], 33.30 (γ-*C*), 31.58 [$C(CH_3)_3$, BHT], 21.74 ($CH_3$, BHT), −5.46 (Al–$CH_3$).

**$\overline{AlMe(BHT)[O{=}C(Ph)HC(CH_3)C(Et)(Ph)O}]$ (16).** O=C(Et)Ph (1.54 mL, 11.37 mmol) was added via syringe to a toluene (30 mL) solution of $AlMe_2(BHT)OEt_2$ (2.0 g, 5.70 mmol), and the resulting orange solution was stirred for 4 h. The solvent was then removed under vacuum to leave an orange oil. This was washed with pentane, resulting in a yellow solid, which was recrystallized from a 50:50 pentane/ether solvent mixture (20 mL): yield ~70%; mp 159–161 °C. Anal. Calcd for $C_{34}H_{45}O_3Al$: C, 77.23; H, 8.57. Found: C, 77.29; H, 8.55. IR: 1600 (m), 1585 (m), 1558 (s), 1380 (s), 1358 (m), 1300 (m), 1280 (m), 1260 (m), 1250 (m), 1220 (w), 1210 (m), 1200 (m), 1190 (m), 1175 (w), 1165 (m), 1155 (m), 1125 (w), 1100 (w), 1090 (w), 1075 (w), 1060 (m), 1035 (w), 1005 (m), 985 (m), 955 (w), 930 (m), 895 (s), 865 (m), 840 (m), 835 (sh), 810 (w), 795 (sh), 780 (m), 755 (s), 730 (s), 700 (s), 670 (s), 660 (sh), 625 (m) cm$^{-1}$. $^1$H NMR: δ 7.85 [2 H, d, *J*(H–H) = 7.2 Hz, *o*-C*H*], 7.65 (2 H, m, *o*-C*H*), 7.32 (2 H, s, $C_6H_2$, BHT), 6.9–7.2 (6 H, m, *m*- + *p*-C*H*), 3.75 [1 H, q, *J*(H–H) = 6.4 Hz, *H*$CCH_3$], 2.39 (3 H, s, $CH_3$, BHT), 1.80 [18 H, s, $C(CH_3)_3$, BHT], 1.57 (3 H, m, $CH_2CH_3$), 1.14 [3 H, d, *J*(H–H) = 6.4 Hz, $HCCH_3$], 0.82 [3 H, t, *J*(H–H) = 6.67 Hz, $CH_2CH_3$], −0.088 (3 H, s, Al–$CH_3$). $^{13}$C NMR: δ 222.27 (*C*=O), 154.79 (O*C*, BHT), 146.08, 139.01, 138.03 (*o*-*C*, BHT), 134.29, 131.00, 129.69, 128.27, 126.78, 126.55, 126.10, 125.65, 80.82 [O*C*(Ph)Et], 50.99 ($CHCH_3$), 36.96 ($CHCH_3$), 35.02 [$C(CH_3)_3$, BHT], 31.52 [$C(CH_3)_3$, BHT], 21.60 ($CH_3$, BHT), 15.12 ($CH_2CH_3$), 8.14 ($CH_2CH_3$), −10.50 (Al–$CH_3$).

**$AlMe(BHT)_2[O{=}C(OMe)Ph]$ (17).** $AlMe(BHT)_2$ (1.0 g, 2.0 mmol) was dissolved in pentane (30 mL). O=C(OMe)Ph (0.26 mL, 2.0 mmol) in pentane (30 mL) was added slowly dropwise via cannula at room temperature under nitrogen. A clear pale yellow solution resulted. After the mixture was stirred for ca. 1.5 h, the solvent was removed under vacuum to leave a pale yellow residue. This was washed once with pentane (30 mL) and filtered.

The filtrate was reduced in volume and cooled (−20 °C) overnight. The remaining solid was recrystallized from a pentane/toluene solvent mixture. Crystalline product was also obtained from the filtrate: yield ~80%, mp 124–126 °C. Anal. Calcd for $C_{39}H_{57}AlO_4$: C, 75.93; H, 9.31. Found: C, 75.41; H, 9.38. IR: 1640 (s), 1600 (m), 1580 (m), 1250 (s), 1200 (s), 1180 (sh), 1155 (w), 1135 (w), 1120 (w), 1100 (sh), 1070 (w), 1020 (m), 1000 (sh), 940 (m), 920 (w), 875 (s), 850 (m), 800 (w), 770 (m), 715 (s), 670 (s), 650 (s) cm$^{-1}$. $^1$H NMR: δ 7.82 [2 H, d, *J*(H-H) = 8.0 Hz, *o*-$C_6H_2$], 7.18 (4 H, s, $C_6H_2$, BHT), 6.95 [1 H, t, *J*(H-H) = 8.0 Hz, *p*-$C_6H$], 6.79 [2 H, t, *J*(H-H) = 8.0 Hz, *m*-$C_6H_2$], 3.37 (3 H, s, $OCH_3$), 2.32 (6 H, s, $CH_3$, BHT), 1.55 [36 H, s, $C(CH_3)_3$, BHT], 0.093 (3 H, s, Al-$CH_3$). $^{13}$C NMR: δ 172.51 (C=O), 155.49 (OC, BHT), 138.77 (*o*-C, BHT), 136.12 (CC=O, Ph), 131.84 (*o*-C, Ph), 128.77 (*m*-C, Ph), 128.26 (*p*-C, Ph), 126.19 (*m*-C, BHT), 125.63 (*p*-C, BHT), 56.57 ($OCH_3$), 35.40 [$C(CH_3)_3$, BHT], 31.87 [$C(CH_3)_3$, BHT], 21.31 ($CH_3$, BHT), −3.12 (Al-$CH_3$).

**$AlEt(BHT)_2[O{=}C(OMe)Ph]$ (18)** was prepared in a fashion similar to that for the methyl analogue: mp 116–118 °C. Anal. Calcd for $C_{40}H_{59}O_4Al$: C, 76.15; H, 9.42. Found: C, 75.47; H, 9.35. IR: 1600 (s), 1575 (m), 1280 (sh), 1250 (s), 1220 (sh), 1200 (m), 1155 (w), 1145 (w), 1120 (w), 1070 (w), 1020 (w), 1000 (w), 990 (w), 965 (w), 945 (m), 920 (w), 880 (s), 860 (s), 800 (w), 770 (m), 720 (s), 670 (w), 620 (s) cm$^{-1}$. $^1$H NMR: δ 7.90 [2 H, d, *J*(H-H) = 7.5 Hz, *o*-$C_6H_2$], 7.17 (4 H, s, $C_6H_2$, BHT), 6.98 [1 H, t, *J*(H-H) = 7.5 Hz, *p*-$C_6H$], 6.85 [2 H, t, *J*(H-H) = 7.5 Hz, *m*-$C_6H_2$], 3.46 (3 H, s, $OCH_3$), 2.30 (6, H, s, $CH_3$, BHT), 1.56 (36 H, s, $C(CH_3)_3$, BHT), 1.32 [3 H, t, *J*(H-H) = 8 Hz, Al-$CH_2CH_3$], 0.682 (2 H, q, *J*(H-H) = 8.0 Hz, Al-$CH_2CH_3$). $^{13}$C NMR: δ 171.5 (C=O), 155.38 (OC, BHT), 138.73 (*o*-C, BHT), 135.37 (CC=O, Ph), 131.45 (*o*-C, Ph), 128.65 (*m*-C, Ph), 126.36 (*m*-C, BHT), 125.90 (*p*-C, BHT), 125.78 (*p*-C, Ph), 55.65 ($OCH_3$), 35.46 [$C(CH_3)_3$, BHT], 32.06 [$C(CH_3)_3$, BHT], 21.28 ($CH_3$, BHT), 9.86 (Al-$CH_2CH_3$), 5.43 (Al-$CH_2CH_3$).

**$AlMe_2(BHT)[O{=}C(OMe)Ph]$ (19).** BHT-H (2.2 g, 10.0 mmol) was dissolved in 20 mL of pentane. $AlMe_3$ (5 mL of a 2 M solution; 0.01 mmol) was added via syringe. The resulting solution was stirred for $^1/_2$ h. A pentane (20 mL) solution of O=C(OMe)Ph (1.25 mL, 0.01 mmol) was added dropwise to the reaction mixture. A white precipitate formed, which was filtered and recrystallized from pentane: yield ~70%; mp 109–112 °C. Anal. Calcd for $C_{25}H_{37}O_3Al$: C, 72.78; H, 9.03. Found: C, 72.12; H, 9.07. IR: 1640 (s), 1600 (m), 1580 (m), 1275 (s), 1190 (m), 1125 (w), 1020 (w), 1000 (sh), 930 (m), 870 (s), 860 (s), 805 (w), 775 (w), 710 (s), 665 (s), 610 (w) cm$^{-1}$. $^1$H NMR: δ 7.93 [2 H, d, *J*(H-H) = 7.3 Hz, *o*-$C_6H_2$], 7.27 (2 H, s, $C_6H_2$, BHT), 6.99 (1 H, t, *p*-$C_6H$), 6.85 (2 H, t, *m*-$C_6H_2$), 3.37 (3 H, s, $OCH_3$), 2.37 (3 H, s, $CH_3$, BHT), 1.62 [18 H, s, $C(CH_3)_3$, BHT], −0.109 (6 H, s, Al-$CH_3$). $^{13}$C NMR: δ 172.61 (C=O), 155.57 (OC, BHT), 138.77 (*o*-C, BHT), 136.15 (CC=O, Ph), 131.67 (*o*-C, Ph), 128.89 (*m*-C, Ph), 126.37 (*p*-C, Ph), 126.15 (*m*-C, BHT), 125.33 (*p*-C, BHT), 55.10 ($OCH_3$), 35.11 [$C(CH_3)_3$, BHT], 31.31 [$C(CH_3)_3$, BHT], 25.10 ($CH_3$, BHT), −5.23 (Al-$CH_3$).

**$AlEt_2(BHT)[O{=}C(OMe)(Ph)]$ (20).** To BHT-H (2.2 g, 10.0 mmol) in pentane (20 mL) was added $AlEt_3$ (10 mL of a 1 M solution, 10.0 mmol) slowly via syringe. The resulting solution was stirred for $^1/_2$ h. The O=C(OMe)Ph (1.24 mL, 10.0 mmol) in pentane (20 mL) was added dropwise via cannula. A clear pale yellow solution resulted. After the mixture was stirred for 2 h, the solvent was removed to yield a pale yellow residue. The residue was washed with pentane, and the washings were filtered, reduced in volume, and set aside in the freezer (−20 °C). A crystalline product formed overnight. The remaining white solid was recrystallized from a pentane/toluene (50:20) solvent mixture to yield more crystalline product: yield ~75%; mp 107–110 °C. Anal. Calcd for $C_{27}H_{41}O_3Al$: C, 73.60; H, 9.37. Found: C, 73.31; H, 9.20. IR: 1630 (s), 1600 (m), 1580 (m), 1270 (s), 1220 (w), 1190 (m), 1130 (w), 1125 (w), 1100 (w), 1080 (w), 1025 (w), 1000 (w), 985 (m), 975 (w), 940 (m), 925 (w), 865 (s), 800 (w), 775 (m), 715 (s), 680 (w), 635 (s), 600 (w), 575 (m) cm$^{-1}$. $^1$H NMR: δ 8.05 [2 H, d, *J*(H-H) = 7.25 Hz, *o*-$C_6H_2$, Ph], 7.26 (2 H, s, $C_6H_2$, BHT), 7.00 [1 H, t, *J*(H-H) = 7.25 Hz, *p*-$C_6H$], 6.88 [2 H, t, *J*(H-H) = 7.25 Hz, *m*-$C_6H_2$], 3.47 (3 H, s, $OCH_3$), 2.36 (3 H, s, $CH_3$, BHT), 1.60 [18 H, s, $C(CH_3)_3$, BHT], 1.33 [6 H, t, *J*(H-H) = 8.0 Hz, Al-$CH_2CH_3$], 0.55 [4 H, q, *J*(H-H) = 8.0 Hz, Al-$CH_2CH_3$]. $^{13}$C NMR: δ 172.61 (C=O), 155.77 (OC, BHT), 138.56 (*o*-C, BHT), 136.12 (CC=O, Ph), 131.53 (*o*-C, Ph), 128.91 (*m*-C, Ph), 126.55 (*p*-C, Ph), 126.14 (*m*-C, BHT), 125.30 (*p*-C, BHT), 55.89 ($OCH_3$), 35.07 [$C(CH_3)_3$, BHT], 31.32 [$C(CH_3)_3$, BHT], 21.47 ($CH_3$, BHT), 10.14 (Al-$CH_2CH_3$), 3.45 (Al-$CH_2CH_3$).

**$AlMe(BHT)_2[O{=}C(NH_2)Me]$ (21).** To $AlMe(BHT)_2$ (3.0 g, 6.24 mmol) and $O{=}C(NH_2)Me$ (0.368 g, 6.24 mmol) was added degassed pentane (30 mL). $AlMe(BHT)_2$ dissolved, leaving the insoluble acetamide. The resulting mixture was stirred overnight to give a white suspension, which was filtered and dried under vacuum: yield 92%; mp 147–149 °C. Anal. Calcd for $C_{33}H_{54}O_3NAl$: C, 73.42; H, 10.08; N, 2.59. Found: C, 72.55; H, 10.11; N, 2.36. IR: 3387 (s), 1546 (s), 1388 (s), 1377 (s), 1362 (s), 1297 (s), 1280 (s), 1266 (s), 1206 (m), 1188 (sh), 1168 (m), 1127 (m), 1043 (w), 1026 (w), 1010 (w), 964 (s), 935 (s), 924 (sh), 908 (s), 892 (m), 866 (m), 858 (m), 772 (m), 739 (s), 710 (w), 656 (s), 619 (s), 593 (m), 579 (w), 521 (w), 488 (s), 384 (m) cm$^{-1}$. $^1$H NMR ($CDCl_3$): δ 7.01 (4 H, s, $C_6H_2$, BHT), 6.50 (1 H, s, NH), 6.11 (1 H, s, NH), 2.25 (6 H, s, $CH_3$, BHT), 2.15 (3 H, s, $CH_3CONH_2$), 1.41 [36 H, s, $C(CH_3)_3$], −0.53 (3 H, s, Al-$CH_3$). $^{13}$C NMR ($CDCl_3$): δ 176.39 (O=C), 154.17 (OC, BHT), 139.04 (*o*-C, BHT), 126.06 (*m*-C, BHT), 125.23 (*p*-C, BHT), 35.03 [$C(CH_3)_3$, BHT], 31.39 [$C(CH_3)_3$, BHT], 22.43 ($O{=}CCH_3$), 21.03 ($CH_3$, BHT), −5.28 (Al-$CH_3$). $^{27}$Al NMR ($CDCl_3$): δ 66.0 ($w_{1/2}$ = 3660 Hz).

**$AlMe(BHT)_2[O{=}C(NPh_2)Me]$ (22)** was prepared in a manner analogous to that for **21**: yield ca. 90%; mp 228 °C. Anal. Calcd for $C_{45}H_{62}AlNO_3$: C, 78.09; H, 9.04; N, 2.02. Found: C, 78.18; H, 9.47; N, 1.81. IR: 1605 (s), 1589 (s), 1566 (s), 1279 (s), 1263 (s), 1243 (s), 1223 (sh), 1202 (s), 1172 (w), 1156 (w), 1124 (m), 1076 (m), 1035 (m), 1023 (sh), 1003 (s), 969 (w), 953 (w), 924 (w), 912 (w), 885 (s), 864 (s), 848 (s), 811 (w), 776 (s), 757 (s), 714 (s), 698 (s), 690 (s), 670 (s), 656 (s), 648 (s), 622 (w), 610 (w), 601 (m), 587 (m), 567 (m), 556 (m), 543 (w), 527 (w), 486 (s), 461 (s) cm$^{-1}$. $^1$H NMR ($CDCl_3$): δ 7.14–7.46 [10 H, m, $N(C_6H_5)_2$], 6.93 (4 H, s, $C_6H_2$, BHT), 2.24 (6 H, s, $CH_3$, BHT), 2.18 (3 H, s, $CH_3CO$), 1.29 [36 H, s, $C(CH_3)_3$, BHT], −0.50 (3 H, s, Al-$CH_3$). $^{13}$C NMR ($CDCl_3$): δ 175.71 (O=C), 155.15 (OC, BHT), 141.58, 140.15 (NC), 138.65 (*o*-C, BHT), 130.56, 129.89 (*o*-C), 129.63 (*m*-C), 126.71, 126.52 (*p*-C), 125.57 (*m*-C, BHT), 124.38 (*p*-C, BHT), 34.88 [$C(CH_3)_3$, BHT], 31.39 [$C(CH_3)_3$, BHT], 23.58 ($OCCH_3$), 21.03 ($CH_3$, BHT), −4.29 (Al-$CH_3$). $^{27}$Al NMR ($CDCl_3$): δ 70.2 ($w_{1/2}$ = 4240 Hz).

**$AlMe(BHT)_2[O{=}C(NMe_2)Ph]$ (23)** was prepared in a manner analogous to that for **21**: yield ca. 85%; mp 160 °C. Anal. Calcd for $C_{40}H_{60}AlNO_3$: C, 76.27; H, 9.60; N, 2.22. Found: C, 76.35; H, 9.79; N, 1.91. IR: 1603 (s), 1578 (sh), 1520 (s), 1290 (sh), 1277 (s), 1260 (s), 1247 (s), 1217 (sh), 1200 (s), 1160 (w), 1122 (w), 1104 (w), 1075 (w), 1050 (w), 1028 (w), 1001 (w), 971 (w), 967 (w), 953 (w), 924 (w), 909 (w), 881 (s), 859 (s), 848 (s), 810 (w), 779 (s), 749 (m), 727 (m), 697 (s), 667 (s), 640 (s), 579 (m), 564 (m), 461 (m), 442 (m) cm$^{-1}$. $^1$H NMR ($CDCl_3$): δ 7.49 [1 H, t, *J*(H-H) = 7.83 Hz, *p*-CH], 7.41 [2 H, t, *J*(H-H) = 7.83 Hz, *m*-CH], 7.20 [2 H, d, *J*(H-H) = 7.8 Hz, *o*-CH], 6.93 (4 H, s, $C_6H_2$, BHT), 3.35 (3 H, s, $NCH_3$), 2.98 (3 H, s, $NCH_3$), 2.22 (6 H, s, $CH_3$, BHT), 1.32 [36 H, s, $C(CH_3)_3$, BHT], −1.12 (3 H, s, Al-$CH_3$). $^{13}$C NMR ($CDCl_3$): δ 172.64 (C=O), 155.36 (OC, BHT), 138.46 (*o*-C, BHT), 131.26 (NC), 131.04 (*o*-C), 129.04 (*m*-C), 126.54 (*p*-C), 125.57 (*m*-C, BHT), 124.22 (*p*-C, BHT), 41.08, 38.32 ($NCH_3$), 34.96 [$C(CH_3)_3$, BHT], 31.51 [$C(CH_3)_3$], 21.00 ($CH_3$, BHT), −5.33 (Al-$CH_3$). $^{27}$Al NMR ($CDCl_3$): δ 71.2 ($w_{1/2}$ = 4245 Hz).

**$\overline{Al(BHT)_2[O{=}C(N}Me)Ph]$ (24)** was prepared in a manner analogous to that for **21**: yield ca. 90%; mp 209–211 °C. Anal. Calcd for $C_{38}H_{54}AlNO_3$: C, 76.08; H, 9.08; N, 2.33. Found: C, 76.01; H, 9.36; N, 2.20. IR: 1597 (m), 1584 (m), 1547 (s), 1209 (m), 1202 (sh), 1173 (w), 1156 (w), 1125 (m), 1074 (m), 1031 (w), 1001 (w), 984 (w), 964 (s), 934 (s), 911 (s), 905 (s), 888 (m), 865 (m), 860 (m), 845 (m), 832 (w), 772 (m), 752 (m), 722 (w), 695 (s), 661 (s), 626 (s), 618 (s), 596 (m) cm$^{-1}$. $^1$H NMR: δ 7.18 (4 H, s, $C_6H_2$, BHT), 6.99 [2 H, t, *J*(H-H) = 7.63 Hz, *m*-$C_6H$], 6.87–6.91 [3 H, m, *o*- + *p*-$C_6H$], 2.26 (6 H, s, $CH_3$, BHT), 1.54 [39 H, s, $C(CH_3)_3$ and $CH_3CO$]. $^{13}$C NMR: δ 185.26 (C=O), 152.65 (OC, BHT), 139.87, 138.65 (*o*-C, BHT), 129.34, 127.38, 126.73, 126.31 (*m*-C, BHT), 125.21 (*p*-C, BHT), 35.18 [$C(CH_3)_3$, BHT], 31.52 [$C(CH_3)_3$, BHT], 21.40 ($CH_3$, BHT), 16.09 ($CH_3CONPh$). $^{27}$Al NMR: δ 35.9 ($w_{1/2}$ = 6652 Hz). Molecular weight (benzene): calcd for $C_{38}H_{54}AlNO_3$, 599.9; found, 597.

**Table IV. Summary of X-ray Diffraction Data**

| compd | $\mathrm{AlMe(BHT)_2[O{=}C(H)^tBu]}$ (1) | $\mathrm{AlMe_2(BHT)(O{=}CPh_2)}$ (8) | $\mathrm{AlMe(BHT)_2[O{=}C(OMe)Ph]}$ (17) |
|---|---|---|---|
| formula | $\mathrm{C_{36}H_{59}AlO_3}$ | $\mathrm{C_{30}H_{39}AlO_2}$ | $\mathrm{C_{39}H_{57}AlO_4}$ |
| space group | $P2_1/n$ | $Pn2_1a$ | $P\bar{1}$ |
| $a$, Å | 10.0765 (5) | 19.133 (3) | 9.394 (2) |
| $b$, Å | 26.201 (2) | 14.638 (2) | 9.741 (3) |
| $c$, Å | 14.0106 (4) | 10.022 (1) | 23.091 (7) |
| $\alpha$, deg | | | 91.43 (2) |
| $\beta$, deg | 103.638 (3) | | 91.93 (2) |
| $\gamma$, deg | | | 116.41 (2) |
| $V$, Å$^3$ | 3595 (3) | 2807 (2) | 1889 |
| $Z$ | 4 | 4 | 2 |
| $D$(calcd), g cm$^{-3}$ | 1.051 | 1.089 | 1.089 |
| cryst dimens, mm | 0.20 × 0.24 × 0.32 | 0.15 × 0.18 × 0.22 | 0.22 × 0.24 × 0.33 |
| temp, °C | 23 | 23 | 23 |
| radiation[a] | Cu K$\alpha$ ($\lambda$ = 1.5418 Å) | Cu K$\alpha$ ($\lambda$ = 1.5418 Å) | Mo K$\alpha$ ($\lambda$ = 0.71069 Å) |
| $\mu$, cm$^{-1}$ | 6.91 | 7.70 | 0.85 |
| $2\theta$ limits, deg | 2.0–110.0 | 2.0–110.0 | 0.0–40.0 |
| no. of collected data | 5040 | 2098 | 3907 |
| no. of unique data | 4717 | 2098 | 3714 |
| no. of obsd data [$I > 3\sigma(I)$] | 3475 | 968 | 1095 |
| $R$[b] | 0.0576 | 0.0552 | 0.0599 |
| $R_w$[c] | 0.0623 | 0.0550 | 0.0689 |
| final residual, e Å$^{-3}$ | 0.24 | 0.19 | 0.21 |

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

**$\overline{\mathrm{Al(BHT)_2[O{=}C(N}}\mathrm{H)Me]}$ (25).** A toluene solution (50 mL) of **21** (4.0 g, 7.63 mmol) was heated overnight (80 °C). The solvent was removed under vacuum, giving a white solid, which was recrystallized from pentane (30 mL): yield ca. 75%; mp 200–205 °C. Anal. Calcd for $\mathrm{C_{32}H_{50}AlNO_3}$: C, 73.38; H, 9.62; N, 2.67. Found: C, 73.57; H, 9.80; N, 2.72. IR: 3387 (m), 1633 (s), 1532 (s), 1293 (sh), 1262 (s), 1226 (sh), 1204 (m), 1157 (w), 1125 (m), 1043 (w), 1024 (w), 957 (m), 914 (s), 890 (s), 861 (s), 772 (s), 700 (w), 641 (s), 608 (s), 576 (w), 540 (w), 524 (w), 405 (m), 388 (m) cm$^{-1}$. $^1$H NMR: $\delta$ 7.16 (4 H, s, $\mathrm{C_6}H_2$, BHT), 6.66 (1 H, s, N$H$), 2.26 (6 H, s, C$H_3$, BHT), 1.76 (3 H, s, O=CC$H_3$), 1.44 [36 H, s, C(C$H_3$)$_3$, BHT]. $^{13}$C NMR: $\delta$ 178.47 (O=$C$), 153.60 (O$C$, BHT), 138.35 ($o$-$C$, BHT), 126.80 ($p$-$C$, BHT), 126.46 ($m$-$C$, BHT), 35.11 [$C$(CH$_3$)$_3$, BHT], 32.01 [C($C$H$_3$)$_3$, BHT], 26.74 (O=C$C$H$_3$), 21.25 ($C$H$_3$, BHT). $^{27}$Al NMR: $\delta$ 37.1 ($w_{1/2}$ = 6720 Hz). Molecular weight (benzene): calcd for $\mathrm{C_{32}H_{50}AlNO_3}$, 523.7; found, 483.

**$\mathrm{AlMe(BHT)_2(O_2NC_6H_4}$-*p*-Me) (26).** A pentane (50 mL) solution of $\mathrm{O_2NC_6H_4}$-*p*-Me (0.85 g, 6.19 mmol) was added dropwise to $\mathrm{AlMe(BHT)_2}$ (3.0 g, 6.24 mmol) in pentane (25 mL). A deep blue-black color developed immediately, and as the addition proceeded, a brown-black precipitate formed. Upon completion of the addition the resulting solution was stirred for 1 h and then filtered. The black precipitate was washed once with pentane (30 mL) and then dried under vacuum: yield ca. 90%; mp 110–112 °C. Anal. Calcd for $\mathrm{C_{38}H_{56}O_4AlN}$: C, 73.87: H, 9.13; N, 2.26. Found: C, 73.58; H, 8.49; N, 2.01. IR: 1600 (w), 1517 (m), 1510 (sh), 1340 (w), 1300 (sh), 1290 (sh), 1265 (s), 1230 (w), 1205 (w), 1185 (m), 1130 (w), 1110 (w), 1020 (w), 960 (w), 900 (sh), 890 (s), 860 (m), 840 (w), 780 (w), 740 (w), 700 (sh), 665 (m), 630 (w) cm$^{-1}$. $^1$H NMR: $\delta$ 7.72 [2 H, d, $J$(H–H) = 8.5 Hz, $\mathrm{C_6}H_2$], 7.20 (4 H, s, $\mathrm{C_6}H_2$, BHT), 6.39 [2 H, d, $J$(H–H) = 8.5 Hz, $\mathrm{C_6}H_2$], 2.30 (6 H, s, C$H_3$, BHT), 1.68 (3 H, s, C$H_3$), 1.64 [36 H, s, C(C$H_3$)$_3$, BHT], 0.045 (3 H, s, Al–C$H_3$). $^{13}$C NMR: $\delta$ 154.02 (O$C$, BHT), 149.12 (NO$_2$$C$), 144.70 (CH$_3$$C$), 138.73 ($o$-$C$, BHT), 130.21 ($o$-$C$), 126.63 ($p$-$C$, BHT), 126.30 ($m$-$C$, BHT), 124.56 ($m$-$C$), 35.28 [$C$(CH$_3$)$_3$, BHT], 31.92 [C($C$H$_3$)$_3$, BHT], 21.38 ($C$H$_3$, BHT), 21.32 ($C$H$_3$), –6.68 (Al–$C$H$_3$). $^{27}$Al NMR: $\delta$ 70.3 ($w_{1/2}$ = 3418 Hz).

**$\mathrm{[CpFe(CO)_2]_2AlMe(BHT)_2}$ (27).** $\mathrm{AlMe(BHT)_2}$ (2.0 g, 4.16 mmol) and $\mathrm{[CpFe(CO)_2]_2}$ (1.47 g, 4.15 mmol) were stirred under nitrogen in pentane (50 mL). The deep red-black color of the $\mathrm{[CpFe(CO)_2]_2}$ gradually lightened, and a bright red precipitate formed. The reaction mixture was stirred overnight and filtered, and the residue was washed once with pentane (50 mL) and dried under vacuum: yield 92%; mp 199–200 °C. Anal. Calcd for $\mathrm{C_{55}H_{69}O_6Fe_2Al}$: C, 79.14; H, 8.33. Found: C, 78.82; H, 8.01. IR: 2030 (s), 1985 (s), 1815 (s), 1600 (s), 1290 (sh), 1275 (s), 1240 (sh), 1225 (w), 1205 (m), 1125 (w), 1065 (w), 1015 (w), 1005 (w), 955 (w), 880 (s), 870 (s), 855 (m), 840 (w), 830 (m), 780 (w), 770 (w), 695 (s), 660 (s), 625 (m), 610 (sh), 575 (w), 555 (w), 535 (m), 490 (m) cm$^{-1}$. $^1$H NMR: $\delta$ 7.25 (4 H, s, $\mathrm{C_6}H_2$, BHT), 4.23 (10 H, s, Cp), 2.31 (6 H, s, C$H_3$, BHT), 1.68 [36 H, s, C(C$H_3$)$_3$, BHT], 0.14 (3 H, s, Al–C$H_3$). $^{13}$C NMR: $\delta$ 153.98 (O$C$, BHT), 138.72 ($o$-$C$, BHT), 126.38 ($m$-$C$, BHT), 125.81 ($p$-$C$, BHT), 89.06 ($C_5$H$_5$), 35.41 [$C$(CH$_3$)$_3$, BHT], 32.08 [C($C$H$_3$)$_3$, BHT], 21.38 ($C$H$_3$, BHT), –3.56 (Al–$C$H$_3$).

**Table V. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å$^2$) of the Non-Hydrogen Atoms in $\mathrm{AlMe(BHT)_2[O{=}C(H)^tBu]}$ (1)**

| atom | $x/a$ | $y/b$ | $z/c$ | $U$(eqv) |
|---|---|---|---|---|
| Al(1) | 0.0760 (1) | 0.36781 (5) | 0.74792 (9) | 0.043 (4) |
| O(1) | 0.0407 (3) | 0.4282 (1) | 0.6993 (2) | 0.045 (1) |
| O(2) | 0.0977 (3) | 0.3228 (1) | 0.6626 (2) | 0.045 (1) |
| O(3) | 0.2626 (3) | 0.3709 (1) | 0.8211 (2) | 0.061 (13) |
| Me | −0.0322 (5) | 0.3541 (2) | 0.8440 (3) | 0.078 (4) |
| C(1) | −0.0499 (4) | 0.4647 (1) | 0.7145 (3) | 0.045 (8) |
| C(2) | −0.1856 (4) | 0.4645 (2) | 0.6558 (3) | 0.047 (2) |
| C(3) | −0.2796 (5) | 0.4970 (2) | 0.6831 (3) | 0.057 (2) |
| C(4) | −0.2445 (5) | 0.5308 (2) | 0.7596 (3) | 0.063 (6) |
| C(5) | −0.1090 (5) | 0.5347 (2) | 0.8080 (3) | 0.061 (19) |
| C(6) | −0.0082 (5) | 0.5029 (2) | 0.7858 (3) | 0.052 (11) |
| C(21) | −0.2290 (4) | 0.4315 (2) | 0.5626 (3) | 0.051 (3) |
| C(22) | −0.3747 (5) | 0.4462 (2) | 0.5030 (4) | 0.074 (11) |
| C(23) | −0.1332 (5) | 0.4421 (2) | 0.4951 (3) | 0.061 (12) |
| C(24) | −0.2342 (5) | 0.3745 (2) | 0.5854 (4) | 0.070 (9) |
| C(41) | −0.3518 (6) | 0.5633 (2) | 0.7903 (4) | 0.090 (13) |
| C(61) | 0.1420 (5) | 0.5119 (2) | 0.8421 (3) | 0.060 (9) |
| C(62) | 0.1619 (6) | 0.5665 (2) | 0.8839 (5) | 0.101 (17) |
| C(63) | 0.1806 (5) | 0.4754 (2) | 0.9294 (3) | 0.076 (21) |
| C(64) | 0.2415 (5) | 0.5062 (2) | 0.7744 (4) | 0.076 (15) |
| C(11) | 0.1934 (4) | 0.2892 (1) | 0.6449 (3) | 0.042 (3) |
| C(12) | 0.2659 (4) | 0.3018 (2) | 0.5719 (3) | 0.047 (6) |
| C(13) | 0.3794 (4) | 0.2720 (2) | 0.5683 (3) | 0.057 (3) |
| C(14) | 0.4189 (5) | 0.2306 (2) | 0.6287 (3) | 0.062 (3) |
| C(15) | 0.3357 (5) | 0.2153 (2) | 0.6890 (3) | 0.056 (5) |
| C(16) | 0.2197 (4) | 0.2429 (2) | 0.6965 (3) | 0.045 (6) |
| C(121) | 0.2206 (5) | 0.3447 (2) | 0.4965 (3) | 0.055 (9) |
| C(122) | 0.2438 (5) | 0.3982 (2) | 0.5416 (3) | 0.067 (10) |
| C(123) | 0.0688 (5) | 0.3371 (2) | 0.4455 (3) | 0.063 (12) |
| C(124) | 0.3008 (5) | 0.3425 (2) | 0.4144 (3) | 0.083 (15) |
| C(141) | 0.5487 (5) | 0.2008 (2) | 0.6274 (4) | 0.092 (11) |
| C(161) | 0.1295 (4) | 0.2206 (2) | 0.7618 (3) | 0.055 (4) |
| C(162) | −0.0243 (5) | 0.2287 (2) | 0.7122 (3) | 0.069 (6) |
| C(163) | 0.1488 (6) | 0.1624 (2) | 0.7737 (4) | 0.078 (20) |
| C(164) | 0.1686 (5) | 0.2437 (2) | 0.8657 (3) | 0.067 (11) |
| C(31) | 0.3690 (5) | 0.3635 (2) | 0.8048 (4) | 0.075 (15) |
| C(32) | 0.5055 (5) | 0.3617 (2) | 0.8733 (4) | 0.065 (11) |
| C(33) | 0.4940 (7) | 0.3576 (4) | 0.9751 (4) | 0.198 (158) |
| C(34) | 0.5810 (6) | 0.4083 (2) | 0.8547 (5) | 0.110 (20) |
| C(35) | 0.5754 (7) | 0.3154 (3) | 0.8458 (7) | 0.177 (113) |

**Crystallography.** Crystals sealed in a glass capillary under

**Table VI. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å$^2$) of the Non-Hydrogen Atoms in $AlMe_2(BHT)(O{=}CPh_2)$ (8)**

| atom | *x/a* | *y/b* | *z/c* | *U*(eqv) |
|---|---|---|---|---|
| Al | 0.5956 (2) | 0.6801 | 0.1065 (4) | 0.069 (13) |
| O(1) | 0.5969 (4) | 0.6110 (6) | 0.2467 (7) | 0.058 (13) |
| O(2) | 0.5253 (4) | 0.6252 (6) | −0.0022 (8) | 0.075 (9) |
| Me(1) | 0.6781 (6) | 0.670 (1) | −0.009 (1) | 0.123 (58) |
| Me(2) | 0.5607 (8) | 0.804 (1) | 0.121 (1) | 0.119 (42) |
| C(1) | 0.6247 (6) | 0.5641 (8) | 0.351 (1) | 0.044 (2) |
| C(2) | 0.6280 (6) | 0.4686 (8) | 0.344 (1) | 0.052 (3) |
| C(3) | 0.6566 (6) | 0.4226 (9) | 0.455 (1) | 0.063 (3) |
| C(4) | 0.6812 (6) | 0.4688 (9) | 0.567 (1) | 0.066 (3) |
| C(5) | 0.6752 (6) | 0.5617 (9) | 0.570 (1) | 0.053 (3) |
| C(6) | 0.6472 (6) | 0.6118 (8) | 0.467 (1) | 0.049 (2) |
| C(21) | 0.5991 (7) | 0.4108 (9) | 0.230 (1) | 0.067 (17) |
| C(22) | 0.6067 (7) | 0.3091 (9) | 0.250 (1) | 0.095 (17) |
| C(23) | 0.5195 (6) | 0.431 (1) | 0.221 (1) | 0.077 (6) |
| C(24) | 0.6343 (7) | 0.435 (1) | 0.095 (1) | 0.103 (27) |
| C(41) | 0.7096 (7) | 0.417 (1) | 0.684 (1) | 0.109 (9) |
| C(61) | 0.6384 (7) | 0.7125 (7) | 0.480 (1) | 0.061 (25) |
| C(62) | 0.5607 (7) | 0.7405 (9) | 0.462 (1) | 0.081 (25) |
| C(63) | 0.6592 (7) | 0.747 (1) | 0.621 (1) | 0.094 (47) |
| C(64) | 0.6851 (6) | 0.7647 (9) | 0.383 (1) | 0.080 (16) |
| C(100) | 0.4655 (6) | 0.5964 (9) | −0.025 (1) | 0.069 (3) |
| C(101) | 0.4509 (6) | 0.5684 (8) | −0.166 (1) | 0.055 (3) |
| C(102) | 0.3823 (6) | 0.5740 (9) | −0.217 (1) | 0.059 (3) |
| C(103) | 0.3735 (7) | 0.5502 (9) | −0.352 (1) | 0.073 (3) |
| C(104) | 0.4272 (6) | 0.5207 (9) | −0.430 (1) | 0.076 (3) |
| C(105) | 0.4947 (6) | 0.5139 (9) | −0.377 (1) | 0.073 (3) |
| C(106) | 0.5056 (6) | 0.5395 (8) | −0.244 (1) | 0.060 (3) |
| C(107) | 0.4100 (6) | 0.5900 (9) | 0.076 (1) | 0.069 (3) |
| C(108) | 0.3641 (6) | 0.521 (1) | 0.073 (1) | 0.077 (3) |
| C(109) | 0.3161 (7) | 0.506 (1) | 0.180 (1) | 0.104 (4) |
| C(110) | 0.3150 (8) | 0.572 (1) | 0.272 (2) | 0.108 (5) |
| C(111) | 0.3581 (8) | 0.642 (1) | 0.279 (2) | 0.117 (5) |
| C(112) | 0.4099 (7) | 0.655 (1) | 0.179 (1) | 0.095 (4) |

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 [$2\theta > 70°$ (**1**, **8**), $2\theta > 35°$ (**17**)], and other experimental data are given in Table IV. Typical data collection procedures in our laboratory have been described previously.[37] Examination of the data, which were corrected for Lorentz and polarization effects but not for absorption, revealed the space groups to be $P2_1/n$ (**1**), $Pn2_1a$ (nonstandard setting of $Pna2_1$) (**8**), and $P\bar{1}$ (**17**). The space groups for the last two structures were determined by symmetry considerations and confirmed by successful structure solution and refinement.

Structure solutions were readily accomplished with use of the direct-methods option of SHELX-86,[38] through which the bulk of the molecule was located. The remaining atomic coordinates were determined through the generation of difference Fourier maps with SHELX-76.[39]

Appropriate atoms were treated with anisotropic thermal parameters (all non-hydrogen atoms for **1**, all non-aromatic, non-hydrogen atoms in **8** and **17**), and hydrogen atoms were included in the models in calculated positions. Due to the low scattering power of the crystals of **8** and **17**, final refinement of these structures was performed by using blocked-matrix least squares.

**Table VII. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å$^2$) of the Non-Hydrogen Atoms in $AlMe(BHT)_2[O{=}C(OMe)Ph]$ (17)**

| atom | *x/a* | *y/b* | *z/c* | *U*(eqv) |
|---|---|---|---|---|
| Al | 0.4196 (5) | 0.4191 (4) | 0.7192 (2) | 0.040 (5) |
| O(1) | 0.3458 (9) | 0.4735 (8) | 0.6599 (3) | 0.043 (6) |
| O(2) | 0.2988 (9) | 0.3628 (8) | 0.7771 (3) | 0.040 (5) |
| O(3) | 0.585 (1) | 0.5970 (8) | 0.7509 (3) | 0.058 (7) |
| O(4) | 0.834 (1) | 0.7757 (8) | 0.7389 (3) | 0.055 (3) |
| Me | 0.525 (1) | 0.296 (1) | 0.6935 (5) | 0.061 (13) |
| C(1) | 0.229 (2) | 0.486 (1) | 0.6284 (5) | 0.042 (3) |
| C(2) | 0.086 (2) | 0.354 (1) | 0.6091 (5) | 0.045 (3) |
| C(3) | −0.039 (2) | 0.380 (1) | 0.5873 (5) | 0.048 (3) |
| C(4) | −0.026 (2) | 0.521 (2) | 0.5774 (5) | 0.051 (3) |
| C(5) | 0.118 (2) | 0.648 (1) | 0.5870 (5) | 0.053 (3) |
| C(6) | 0.250 (2) | 0.631 (1) | 0.6105 (5) | 0.042 (3) |
| C(11) | 0.260 (1) | 0.363 (1) | 0.8328 (6) | 0.040 (3) |
| C(12) | 0.304 (2) | 0.286 (1) | 0.8744 (5) | 0.048 (3) |
| C(13) | 0.275 (2) | 0.299 (1) | 0.9319 (5) | 0.057 (4) |
| C(14) | 0.206 (2) | 0.392 (2) | 0.9492 (6) | 0.076 (4) |
| C(15) | 0.154 (2) | 0.457 (1) | 0.9083 (6) | 0.061 (4) |
| C(16) | 0.173 (1) | 0.447 (1) | 0.8488 (5) | 0.038 (3) |
| C(21) | 0.079 (2) | 0.194 (1) | 0.6064 (6) | 0.054 (24) |
| C(22) | 0.073 (2) | 0.123 (1) | 0.6655 (6) | 0.076 (18) |
| C(23) | 0.227 (2) | 0.203 (1) | 0.5730 (6) | 0.062 (12) |
| C(24) | −0.064 (2) | 0.082 (1) | 0.5691 (6) | 0.085 (12) |
| C(41) | −0.167 (2) | 0.539 (2) | 0.5523 (5) | 0.093 (48) |
| C(61) | 0.416 (2) | 0.769 (1) | 0.6102 (6) | 0.048 (4) |
| C(62) | 0.524 (2) | 0.716 (1) | 0.5765 (5) | 0.056 (8) |
| C(63) | 0.417 (2) | 0.903 1) | 0.5761 (6) | 0.084 (25) |
| C(64) | 0.489 (2) | 0.836 (1) | 0.6706 (6) | 0.067 (17) |
| C(101) | 0.703 (2) | 0.716 (2) | 0.7677 (6) | 0.054 (4) |
| C(102) | 0.713 (2) | 0.800 (1) | 0.8212 (5) | 0.050 (3) |
| C(103) | 0.603 (2) | 0.737 (1) | 0.8620 (5) | 0.063 (3) |
| C(104) | 0.610 (2) | 0.817 (1) | 0.9133 (5) | 0.070 (4) |
| C(105) | 0.730 (2) | 0.962 (2) | 0.9231 (6) | 0.077 (4) |
| C(106) | 0.841 (2) | 1.028 (2) | 0.8827 (6) | 0.092 (5) |
| C(107) | 0.834 (2) | 0.949 (1) | 0.8314 (5) | 0.067 (4) |
| C(108) | 0.839 (2) | 0.696 (1) | 0.6849 (5) | 0.077 (16) |
| C(121) | 0.384 (2) | 0.183 (2) | 0.8594 (6) | 0.067 (13) |
| C(122) | 0.294 (2) | 0.070 (1) | 0.8082 (6) | 0.071 (7) |
| C(123) | 0.556 (2) | 0.279 (2) | 0.8454 (5) | 0.077 (20) |
| C(124) | 0.382 (2) | 0.080 (2) | 0.9090 (6) | 0.128 (33) |
| C(141) | 0.179 (2) | 0.408 (2) | 1.0126 (6) | 0.127 (6) |
| C(161) | 0.100 (2) | 0.515 (2) | 0.8055 (6) | 0.058 (23) |
| C(162) | −0.003 (2) | 0.583 (2) | 0.8358 (5) | 0.087 (17) |
| C(163) | 0.226 (2) | 0.644 (1) | 0.7746 (5) | 0.076 (10) |
| C(164) | −0.011 (2) | 0.391 (2) | 0.7619 (6) | 0.082 (13) |

Final residuals are listed in Table IV.

Scattering factors were taken from ref 40. Final atomic positional parameters are given in Tables V–VII. 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:** Tables of positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, and full bond lengths and angles for **1**, **8**, and **17** and a table of best planes for **8** (17 pages); listings of observed and calculated structure factors for **1**, **8**, and **17** (34 pages). Ordering information is given on any current masthead page.

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