by a least-squares method using 25 independent reflections with $20° < 2\theta < 25°$ (3) and $12° < 2\theta < 20°$ (8). Data were collected with the ω–2θ scan technique. If $\sigma(F)/F$ was more than 0.1, a scan was repeated up to three times and the results were added to the first scan. Three standard reflections were monitored at every 100 measurements. All data processing was performed on a FACOM A-70 computer by using the R-CRYSTAN structure solving program system obtained from Rigaku Corp., Tokyo, Japan. Neutral scattering factors were obtained from the standard sources.[20] In the reduction of data, Lorentz and polarization corrections were made and no absorption correction was made. Full-matrix least-squares refinement minimized the function $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/[\sum(F_o)^2 + (pF_o)^2]$, the parameter p being automatically optimized.

3 and 8 crystallized in a triclinic and monoclinic system, respectively. The positions of the metal atoms were located by direct methods (SAPI 85). Subsequent difference Fourier maps revealed the positions of all the non-hydrogen atoms. For 3 all the non-hydrogen atoms were refined anisotropically, and the positions of the hydrogen atoms were confirmed by using isotropic thermal parameters with $B(H) = B(C)$. For 8 the non-hydrogen atoms other than the Cp* groups were refined anisotropically and the carbon atoms of the Cp* groups were refined isotropically, because enough data could not be obtained owing to the small size of the crystal.

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Acknowledgment. We are grateful to Prof. D. F. Shriver for sending us a reprint of ref 16. This research was financially supported by a Grant-in-Aid from the Ministry of Education, Science, and Technology of the Japanese Government.

Registry No. 1, 33029-77-5; 2, 125453-83-0; 3, 140362-50-1; 4, 140362-51-2; 7, 134153-80-3; 8, 140362-52-3; $Co_2(CO)_8$, 10210-68-1; Fe, 7439-89-6; CO, 7440-48-4.

Supplementary Material Available: Tables of anisotropic thermal parameters and bond lengths and angles for 3 and 8 (13 pages). Ordering information is given on any current masthead page.

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Sterically Crowded Aryloxide Compounds of Aluminum: Reduction of Coordinated Benzophenone

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The interaction of $AlEt(BHT)_2$ with benzophenone, $O{=}CPh_2$, in pentane or benzene yields as the sole product $Al(BHT)_2(OCHPh_2)(O{=}CPh_2)$ (1). In diethyl ether, however, the Lewis acid–base complex $AlEt(BHT)_2(O{=}CPh_2)$ (2) is isolated. Thermolysis of 2 yields $Al(BHT)_2(OCHPh_2)$ (3), which reacts rapidly with Et_2O, THF, or $O{=}CPh_2$ to give the acid–base complexes $Al(BHT)_2(OCHPh_2)(L)$ (L = Et_2O (4), THF (5), $O{=}CPh_2$ (1)). Interaction of $AlEt_2(BHT)(OEt_2)$ with 1 equiv of benzophenone in diethyl ether produces the isolable complex $AlEt_2(BHT)(O{=}CPh_2)$ (6). Solid-phase thermolysis of 6 yields the monomer $AlEt(BHT)(OCHPh_2)$ (7), which dimerizes upon dissolution in organic solvents to give $[AlEt(BHT)(\mu\text{-}OCHPh_2)]_2$ (8). In the presence of excess benzophenone in benzene solution, $AlEt_2(BHT)(OEt_2)$ gives $AlEt(BHT)(OCHPh_2)(O{=}CPh_2)$ (9), which rearranges when heated in hexane to the bridged dimer $(BHT)(Et)Al(\mu\text{-}OCHPh_2)_2Al(OCHPh_2)(Et)$ (10). Thermolysis of 7 in the presence of excess benzophenone results in the reduction of a second ketone to give $Al(BHT)(OCHPh_2)_2(O{=}CPh_2)$ (11). Unlike the benzophenone derivatives, the reaction of acetophenone with $AlEt(BHT)_2$ and $AlEt_2(BHT)(OEt_2)$ does not result in ketone reduction but rather in the formation of the thermally stable Lewis acid–base adducts $AlEt(BHT)_2[O{=}C(Me)Ph]$ (12) and $AlEt_2(BHT)[O{=}C(Me)Ph]$ (13), respectively. The solvent-dependent formation of the benzophenone adducts 2 and 6 has been related to the solution equilibria and the relative metal–ligand bond dissociation energies (the BDE's) of the methyl compounds $AlMe(BHT)_2L$ (L = Et_2O, THF, py, $O{=}CPh_2$, $O_2N\text{-}C_6H_4\text{-}p\text{-}Me$) and 1 which have been obtained from variable-temperature ^1H NMR data. The kinetics of the conversion of 2 to 1 and 9 to 11 have been investigated and the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values determined. Interaction of 2,6-diphenylphenol (DPP-H) with AlR_3 in a 1:1 molar ratio allows for the isolation of the dimeric compounds $[R_2Al(\mu\text{-DPP})]_2$ (R = Me (14), Et (15)). The reaction of 15 with $O{=}CPh_2$ results after hydrolysis in the formation of approximately 1 equiv of $HOCHPh_2$ per aluminum; however, no intermediate could be isolated.

Introduction

Organoaluminum compounds undergo a wide range of reactions with organic carbonyls.[1] Much of their reactivity, including the undesirable presence of multiple reaction pathways, is dependent on the dimeric nature of many organoaluminum compounds. In order for future development of new organoaluminum compounds with a broad synthetic utility to be possible, a detailed knowledge of their mechanisms and the factors controlling product distribution is required. Toward this end, recent work in our laboratory has explored the reactivity of organic carbonyls with monomeric aluminum complexes derived from the sterically hindered phenol 2,6-di-*tert*-butyl-4-methylphenol (BHT-H, from the trivial name butylated hydroxytoluene).[2-7]

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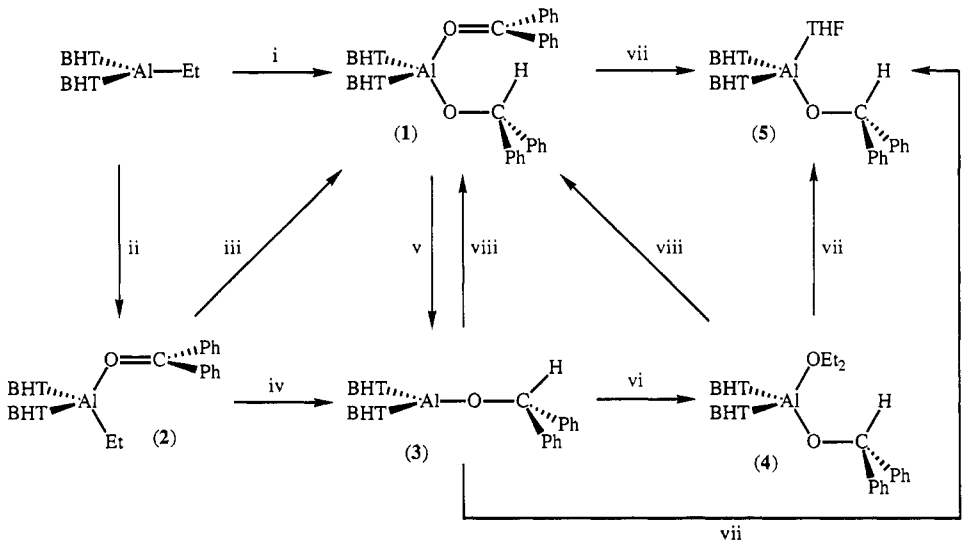
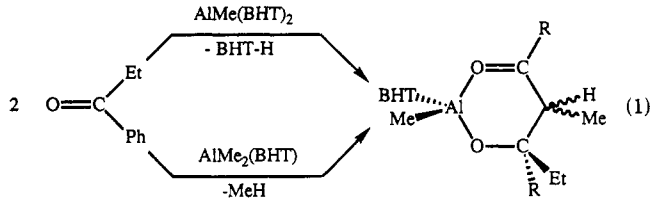
Scheme I[a]



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

The reaction of $AlMe(BHT)_2$ or $AlMe_2(BHT)$ with the majority of ketones results in the formation of stable Lewis acid–base adducts,[4,6] while an aldol condensation occurs for enolizable ketones, i.e., those with at least one aliphatic β-hydrogen (e.g. eq 1).[5,6] Although the interaction of



(1)

aldehydes with $AlMe(BHT)_2$ also results in complex formation,[2,6] a unique aldehyde to ketone interconversion occurs with $AlMe_2(BHT)$ (eq 2).[2,3]

$$1.5AlMe_2(BHT) + O{=}C(H)R \rightarrow AlMe_2(BHT)[O{=}C(Me)R] + 0.5[AlH_2(BHT)] \quad (2)$$

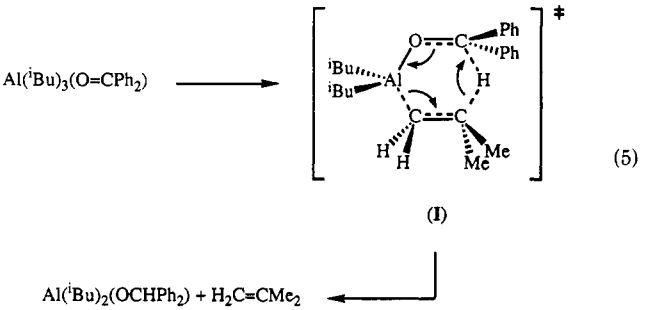
Recent work by Yamamoto and co-workers[8] has shown that the reduction of ketones may readily be carried out in high yield by the use of the isobutyl-BHT derivative $Al(^iBu)_2(BHT)$. The reduction of an organic carbonyl by an aluminum alkyl group is conceptually simple: transfer of a β-hydride to give the aluminum alkoxide complex with concurrent loss of ethylene. However, studies of this seemingly straightforward reaction are often complicated by competing alkylation reactions. For example, when $AlEt_3$ is used as the aluminum source, both reduction of and alkyl addition to the carbonyl group occurs (eq 3).[9]

$$O{=}CR_2 \xrightarrow[(ii)\ H_2O]{(i)\ AlEt_3} HOC(H)R_2 + HOC(Et)R_2 \quad (3)$$

To complicate matters further, secondary reactions occur. These include the Meerwein–Ponndorf–Verley reduction, the Oppenauer oxidation, and the Tishenko reaction.[10] These side reactions are negated by the use of branched alkyl derivatives.[11] For example, the reaction of $Al(^iBu)_3$ with benzophenone results in the formation of the reduction product, benzhydrol.[9b,c] This ability to confine reactivity exclusively to a single pathway through the choice of branched alkyl substituents enabled Ashby and Yu to perform a detailed mechanistic study of the reduction of ketones by aluminum alkyls,[12] exclusive of the alkylation pathway.[13] Ketone reduction was proposed to involve a two-step mechanism in which the first step involves a fast equilibrium to form a Lewis acid–base complex (eq 4). The second, rate-determining step involves

$$Al(^iBu)_3 + O{=}CPh_2 \rightleftharpoons Al(^iBu)_3(O{=}CPh_2) \quad (4)$$

the transfer of the β-hydride to the ketone α-carbon (eq 5) via a proposed six-membered transition state (I).



(I)

(5)

We have observed that the presence of aryloxide substituents on aluminum alkyls results in the reduction of

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the reactivity of the Al–C bond.[14] Since the cyclic six-membered transition state I, as proposed by Ashby,[12] possibly involves partial Al–C bond cleavage, an interesting question arises. *Does the presence of aryloxide ligands on aluminum alkyls affect the reduction reactivity of the alkyl substituents toward ketone reduction*? In order to answer this question, we have investigated the course of the reduction of benzophenone with $AlEt_x(BHT)_{3-x}$ (x = 1, 2), and results of this study, along with those for the related 2,6-diphenylphenoxide (DPP) derivatives $[R_2Al(\mu\text{-DPP})]_2$ (R = Me, Et) are presented herein.

Results and Discussion

Reaction of Benzophenone with $AlEt(BHT)_2$ (Scheme I). We have previously reported[4] that the interaction of $AlMe(BHT)_2$ with benzophenone, in pentane, allows the isolation of the appropriate Lewis acid–base complex (eq 6). Under corresponding conditions, the aluminum ethyl analogue cannot be isolated. Instead, reduction of the ketone occurs to give a coordinated alkoxide. Interaction of $AlEt(BHT)_2$ with 1 equiv of benzophenone, in pentane or benzene, results in the reduction of $^1/_2$ equiv of the benzophenone and the formation of an equimolar mixture of $AlEt(BHT)_2$ and $Al(BHT)_2(OCHPh_2)(O{=}CPh_2)$ (1). Compound 1 presumably is formed as a result of the reduction of one coordinated benzophenone with the concomitant elimination of ethylene (eq 7), followed by the subsequent coordination of a second ketone molecule (eq 8). When the reaction is carried out with 2 equiv of benzophenone, 1 is the only product observed (Scheme I, path i).

$$AlMe(BHT)_2 + O{=}CPh_2 \xrightarrow[\text{pentane or benzene}]{} AlMe(BHT)_2(O{=}CPh_2) \quad (6)$$

$$AlEt(BHT)_2 + O{=}CPh_2 \rightarrow \text{“}Al(BHT)_2(OCHPh_2)\text{”} + C_2H_4 \quad (7)$$

$$\text{“}Al(BHT)_2(OCHPh_2)\text{”} + O{=}CPh_2 \rightarrow Al(BHT)_2(OCHPh_2)(O{=}CPh_2) \quad (8)$$

The formation of an equimolar mixture of 1 and $AlEt(BHT)_2$ from the interaction of the latter with 1 molar equiv of benzophenone may be rationalized by a consideration of the equilibria present in solution and an estimation of the appropriate bond dissociation energies (see below). In solution Lewis base complexes of $AlR(BHT)_2$ exist as equilibrium mixtures such that, in the present case, the reaction mixture will involve two concurrent equilibria, i.e., one due to the coordination of benzophenone (eq 9)

$$AlEt(BHT)_2 + O{=}CPh_2 \overset{K_1}{\rightleftharpoons} AlEt(BHT)_2(O{=}CPh_2) \quad (9)$$

where

$$K_1 = \frac{[AlEt(BHT)_2(O{=}CPh_2)]}{[AlEt(BHT)_2][O{=}CPh_2]} \quad (10)$$

and a second involving the competitive binding of benzophenone with the product from the reduction reaction, i.e. eq 11

$$Al(BHT)_2(OCHPh_2) + O{=}CPh_2 \overset{K_2}{\rightleftharpoons} Al(BHT)_2(OCHPh_2)(O{=}CPh_2) \quad (11)$$

where

$$K_2 = \frac{[Al(BHT)_2(OCHPh_2)(O{=}CPh_2)]}{[Al(BHT)_2(OCHPh_2)][O{=}CPh_2]} \quad (12)$$

Given a steady-state approximation for the concentration of uncomplexed benzophenone, the overall exchange will be

$$AlEt(BHT)_2(O{=}CPh_2) + Al(BHT)_2(OCHPh_2) \overset{K_T}{\rightleftharpoons} AlEt(BHT)_2 + Al(BHT)_2(OCHPh_2)(O{=}CPh_2) \quad (13)$$

where

$$K_T = \frac{[AlEt(BHT)_2][Al(BHT)_2(OCHPh_2)(O{=}CPh_2)]}{[AlEt(BHT)_2(O{=}CPh_2)][Al(BHT)_2(OCHPh_2)]} = \frac{K_2}{K_1} \quad (14)$$

Although it is difficult to obtain reliable values of K_1 and K_2 and, therefore, the overall equilibrium constant K_T from NMR measurements (see below), it is possible to estimate the enthalpy of the overall reaction if it is assumed that the bond dissociation energy (BDE) for methyl and ethyl analogues are comparable; i.e., the BDE for $AlMe(BHT)_2(O{=}CPh_2)$ is close to that of 2. Given this assumption, the ΔH and ΔS values for the forward reaction as written in eq 13 can be calculated as ca. −25 kJ mol^{-1} and −70 J K^{-1} mol^{-1}, respectively. From this it can be concluded that, as is observed experimentally, the equilibrium in eq 13 should indeed be significantly shifted to the formation of 1 and $AlEt(BHT)_2$.

The Lewis acid–base complex $AlEt(BHT)_2(O{=}CPh_2)$ (2) may be isolated if $O{=}CPh_2$ is added to an Et_2O solution of $AlEt(BHT)_2$, in which the latter exists as the solvated complex $AlEt(BHT)_2(OEt_2)$[15] (Scheme I, path ii). Although indefinitely stable in Et_2O, compound 2 reacts either in the presence of excess $O{=}CPh_2$ to give 1 (Scheme I, path iii), or in benzene and pentane solutions to give an equimolar mixture of 1 and $AlEt(BHT)_2$ (eq 15).

$$2AlEt(BHT)_2(O{=}CPh_2) \xrightarrow[\text{pentane or benzene}]{\Delta} AlEt(BHT)_2 + Al(BHT)(OCHPh_2)(O{=}CPh_2) + C_2H_4 \quad (15)$$

The isolation of 2 from an Et_2O solution of $AlEt(BHT)_2$ and $O{=}CPh_2$, but not when the reaction is carried out in pentane or benzene, may readily be explained by a consideration of the possible exchange equilibria occurring in solution. Thus, two concurrent equilibria occur when $O{=}CPh_2$ reacts with $AlEt(BHT)_2$ in Et_2O. As before, one is due to the coordination of the solvent and a second to the coordination of benzophenone; thus, the overall ligand exchange reaction takes the form shown in eq 16

$$AlEt(BHT)_2(OEt_2) + O{=}CPh_2 \overset{K_{eq}}{\rightleftharpoons} AlEt(BHT)_2(O{=}CPh_2) + Et_2O \quad (16)$$

where

$$K_{eq} = \frac{[AlEt(BHT)_2(O{=}CPh_2)][Et_2O]}{[AlEt(BHT)_2(OEt_2)][O{=}CPh_2]} = \frac{K_1}{K_2} \quad (17)$$

As discussed below, we have shown that the rate of benzophenone reduction is dependent on the concentration of the complex 2:

$$\text{rate of } O{=}CPh_2 \text{ reduction} = k[AlEt(BHT)_2(O{=}CPh_2)] \quad (18)$$

Therefore, given eq 16:

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rate of $O{=}CPh_2$ reduction =

$$k\left\{K_T\frac{[AlEt(BHT)_2(OEt_2)][O{=}CPh_2]}{[Et_2O]}\right\} \quad (19)$$

$$\therefore \text{ rate of } O{=}CPh_2 \text{ reduction} \propto \frac{1}{[Et_2O]} \quad (20)$$

Thus, when Et_2O, or any similar Lewis base is used as a solvent, the rate of benzophenone reduction becomes negligible, which along with the lower solubility of the $AlEt(BHT)_2(O{=}CPh_2)$ adduct, compared to that of either $AlEt(BHT)_2(OEt_2)$ or $AlEt(BHT)_2$, enables its isolation. Although a similar solvent dependence was observed on the rate of benzophenone reduction by $Al(^iBu)_3$,[9c] the complex $Al(^iBu)_3(O{=}CPh_2)$ could not be isolated, but it was detected by UV–visible spectroscopy.

All NMR and IR spectra are consistent with the proposed monomeric structures of **1** and **2** (see Experimental Section). It is worth noting that both compounds show a decreased carbonyl stretching frequency in their IR spectra (1615 (**1**), 1570 (**2**) cm^{-1}) and a downfield shift in the ^{13}C NMR signals for their carbonyl α-carbon (206.9 (**1**), 206.0 (**2**) ppm), relative to "free" benzophenone (1650 cm^{-1} and 195.6 ppm). We have previously shown that these results are typical of the coordination of ketones to aluminum Lewis acids.[4,6]

Thermolysis of a benzene solution of either **2** in the absence of excess benzophenone or a mixture of **1** and $AlEt(BHT)_2$ yields the alkoxide bis(aryloxide) complex $Al(BHT)_2(OCHPh_2)$ (**3**) as the only product (Scheme I, paths iv and v). Compound **3** could only be isolated as an oil, but in solution it reacts readily with Et_2O, THF, or $O{=}CPh_2$ to give the respective Lewis acid–base complexes $Al(BHT)_2(OCHPh_2)(L)$ (L = Et_2O (**4**), THF (**5**), $O{=}CPh_2$ (**1**)). The Et_2O ligand in **4** may be displaced by either THF or $O{=}CPh_2$, giving **5** and **1**, respectively, while THF displaces the coordinated $O{=}CPh_2$ in **1** to yield **5** (Scheme I, paths vi–viii). This ordering of affinities is consistent with the relative bond dissociation energies for the methyl $AlMe(BHT)_2L$ complexes, i.e., $OEt_2 < O{=}CPh_2 <$ THF (see below).

There is no evidence from ^1H NMR spectroscopy, even at elevated temperatures, for the presence of a Meerwein–Ponndorf type degenerate hydrogen transfer between the diphenylmethoxide and coordinated benzophenone (i.e., eq 21).

$$Al(BHT)_2(OC^*HPh_2)(O{=}CPh_2) \rightleftharpoons Al(BHT)_2(OCHPh_2)(O{=}C^*Ph_2) \quad (21)$$

Reaction of Benzophenone with $AlEt_2(BHT)$ (Scheme II). The reaction of $AlEt_2(BHT)(OEt_2)$ with benzophenone in pentane yields the expected Lewis acid–base complex $AlEt_2(BHT)(O{=}CPh_2)$ (**6**) (Scheme II, path ii). The IR and NMR spectra of **6** (see Experimental Section) are consistent with the presence of a coordinated benzophenone.

Although the isolation of **6** is enabled in part by the existence of solution equilibria analogous to those discussed for the bis(aryloxide) compound **2** (see eqs 9–14), the lower concentrations of Et_2O present, i.e., 1 molar equiv, would not be expected to have such a drastic effect on the rate of benzophenone reduction. However, the insolubility of **6** in pentane results in its precipitation from the reaction mixture, and further reaction occurs only over several hours at ambient temperature.

Compound **6** can be thermolyzed in the solid state to liberate ethylene and give the monomeric compound $AlEt(BHT)(OCHPh_2)$ (**7**) (Scheme II, path iii). Compound **7** is indefinitely stable in the solid phase and can be characterized by its melting point (135 °C) and IR spectrum but rapidly dimerizes in solution (Et_2O, THF, benzene, or pentane) to give a product identified as $[AlEt(BHT)(\mu\text{-}OCHPh_2)]_2$ (**8**; mp 173–174 °C; Scheme II, path iv). Likewise, the isolated acid–base complex $AlEt_2(BHT)(O{=}CPh_2)$, when suspended in benzene at room temperature, dissolves slowly with concomitant reduction of the benzophenone and subsequently dimerizes to give **8**. This reaction contrasts with the behavior of the proposed intermediate "$Al(BHT)_2(OCHPh_2)$" (Scheme I, path v), which is prevented from dimerizing by the BHT ligands' steric bulk, and in which reduction of benzophenone is followed by complexation with another Lewis base, i.e., a second ketone (Scheme I, paths vi–viii) or solvent molecule.

In the presence of excess benzophenone, **6** undergoes reduction of the coordinated ketone, losing ethylene, and subsequent coordination of a second molecule of benzophenone to give the monomeric complex $[AlEt(BHT)(OCHPh_2)(O{=}CPh_2)]$ (**9**; (Scheme II, path vi). Compound **9** may also be prepared directly by the interaction of excess benzophenone with a previously prepared equimolar mixture of AlR_3 and BHT–H (Scheme II, path vii).

Thermolysis of **9** in hexane does not result in the reduction of the second benzophenone but in disproportionation to give a moderate yield of the asymmetric dimer $Et(BHT)Al(\mu\text{-}OCHPh_2)_2AlEt(OCHPh_2)$ (**10**; Scheme II, path viii), which contains both bridging and terminal diphenylmethoxy groups. In contrast, the thermolysis of **9** in the presence of excess benzophenone does result in the reduction of a second equivalent of benzophenone and the formation of the monomeric $Al(BHT)(OCHPh_2)_2(O{=}CPh_2)$ (**11**; Scheme II, path ix).

Reaction of Acetophenone with $AlEt_x(BHT)_{3-x}$ (x = 1, 2). $AlEt(BHT)_2[O{=}C(Me)Ph]$ (**12**) and $AlEt_2(BHT)[O{=}C(Me)Ph]$ (**13**). Both complexes show a decrease in the carbonyl stretching frequency in the IR spectrum and a downfield shift in the ^{13}C NMR signal for the carbonyl α-carbon, when compared to that of the "free" ketone, consistent with coordination of the ketone to aluminum. It is worth noting that the magnitudes of these effects are nearly identical with those for the methyl analogues, for example $\nu(C{=}O)$: $AlMe_2(BHT)[O{=}C(Me)Ph]$, 1625 cm^{-1};[4] $AlEt_2(BHT)[O{=}C(Me)Ph]$, 1625 cm^{-1}. This would suggest that the replacement of methyl with ethyl on the aluminum has little effect on its Lewis acidity and/or the aluminum–ketone interaction.

Unlike other ketone complexes of either $AlEt(BHT)_2$ or $AlEt_2(BHT)$, compounds **12** and **13** show no propensity to undergo further reaction of the ketone. Extended thermolysis in refluxing toluene results in their decomposition to a multitude of uncharacterized products.

Bond Dissociation Energies for $AlMe(BHT)_2L$. Given the common occurrence of Lewis acid–base complexes for the group 13 elements, it is perhaps surprising that reports of thermodynamic data such as bond dissociation energies (BDE's) are sparse. The majority of studies have been carried out on the complexes of $AlMe_3$, $AlEt_3$, and $AlPh_3$.[16] Unfortunately, the dissociation process for the complex is complicated by the dimerization

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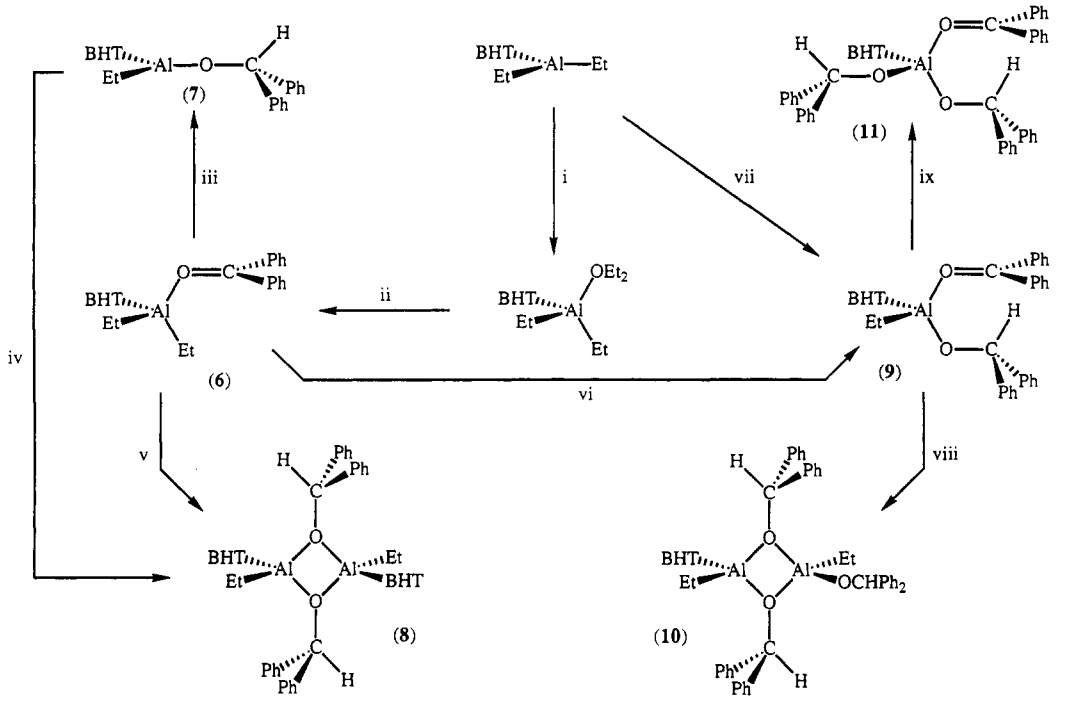
Scheme II[a]



[a] Reagents and conditions: (i) Et_2O; (ii) $O{=}CPh_2$; (iii) 90 °C, no solvent; (iv) Et_2O or benzene; (v) 80 °C, benzene; (vi) $O{=}CPh_2$, benzene; (vii) 2 $O{=}CPh_2$, benzene; (viii) hexane reflux; (ix) >35 °C, $O{=}CPh_2$, toluene.

of AlR_3.[17] The measurement of any solution equilibrium process would, therefore, be greatly simplified for monomeric three-coordinate compounds whose steric bulk precludes dimerization. Thus, the bis-BHT compounds $AlR(BHT)_2$ make ideal subjects for study.

As part of our present work, it would be desirable to determine the BDE's for $AlEt(BHT)_2(O{=}CPh_2)$, $AlEt(BHT)_2(OEt_2)$, and $Al(BHT)(OCHPh_2)(O{=}CPh_2)$, but the reaction of the first compound precludes direct measurement. However, given the apparent similarity of the Lewis acidity of the methyl and ethyl homologues, to coordination of O=C(Me)Ph (see above), we have instead determined the BDE values for $AlMe(BHT)_2L$ (L = Et_2O,[14] THF,[14] py,[14] $O{=}CPh_2$,[4] O_2N-C_6H_4-*p*-Me[6]). The relative BDE's for a series of complexes may be derived from the temperature dependence of the equilibrium constant, K_{eq} (eq 22)

$$AlMe(BHT)_2L \overset{K_{eq}}{\rightleftharpoons} AlMe(BHT)_2 + L \qquad (22)$$

where

$$\ln K_{eq} = \frac{-\Delta H_D}{R}\left(\frac{1}{T}\right) + \frac{\Delta S_D}{R} \qquad (23)$$

For the equilibrium between the complexes $AlMe(BHT)_2L$ and their constituents (eq 22), the equilibrium constant, K_{eq}, may be derived in terms of the mole fractions of aluminum present as free $AlMe(BHT)_2$, χ_{free}, and the total initial concentration, [total]:

$$K_{eq} = \frac{[\text{total}](\chi_{free})^2}{(1 - \chi_{free})} \qquad (24)$$

The ^1H NMR spectra of the complexes $AlMe(BHT)_2L$ show a single resonance due to the $Al{-}CH_3$ group over the temperature ranges measured, indicating that the equilibria are rapid on the NMR time scale. Assuming the ^1H NMR shift of the $Al{-}CH_3$ group is directly proportional to the mole fraction of the total species present as uncomplexed or "free" $AlMe(BHT)_2$, χ_{free}, the ^1H NMR chemical shift of $Al{-}CH_3$, at a given temperature, may be used to calculate χ_{free} (eq 25).

$$\chi_{free} = \frac{\delta_{sample} - \delta_{coord}}{\delta_{free} - \delta_{coord}} \qquad (25)$$

The δ_{sample} value is measured directly from the sample under investigation, while δ_{free} is the ^1H NMR chemical shift of $AlMe(BHT)_2$. Although the latter was found to be independent of concentration (consistent with the compound's monomeric formulation[18]), some dependence on temperature was observed (see Table I). The temperature-corrected shifts were subsequently employed for all calculations. The chemical shift for the fully coordinated species $AlMe(BHT)_2L$ was determined by addition of an excess of the Lewis base and the measurement of the ^1H NMR spectrum at low temperature, where the degenerate exchange (eq 26) had ceased.[19] A data set for the

$$AlMe(BHT)_2L + L^* \rightleftharpoons AlMe(BHT)_2L^* + L \qquad (26)$$

Table I. Determination of K_{eq} for the Ligand Dissociation of $AlMe(BHT)_2(O{=}CPh_2)$ from the ^1H NMR Chemical Shift of the $Al{-}CH_3$ Group[a]

temp	δ_{sample}	δ_{free}[b]	χ_{free}[c]	K_{eq}[d]
308	−0.105	−0.274	0.238	2.62×10^{-2}
318	−0.125	−0.276	0.325	5.53×10^{-1}
323	−0.139	−0.277	0.387	8.61×10^{-1}
328	−0.152	−0.277	0.444	1.25×10^{-1}
333	−0.166	−0.277	0.506	1.83×10^{-1}

[a] Temperature in K. [b] Corrected for temperature. [c] $\chi_{free} = (\delta_{sample} - \delta_{coord})/(\delta_{free} - \delta_{coord})$; $\delta_{coord} = -0.052$. [d] $K_{eq} = [\text{total}]\chi_{free}/(1 - \chi_{free})$; [total] = 0.0745 M.

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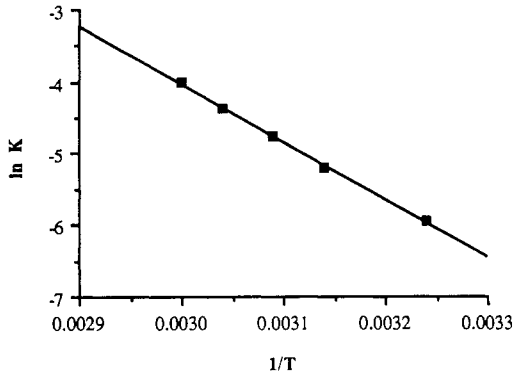

Figure 1. Temperature dependence of the equilibrium constant, K_{eq}, for the dissociation of $AlMe(BHT)_2(O{=}CPh_2)$ (R = 0.998).

Table II. Selected Equilibrium and Thermodynamic Data for Lewis Base Complexes of $AlMe_3$, $AlMe(BHT)_2$, and $Al(BHT)_2(OCHPh_2)$[a]

compd	ΔH, kJ mol^{-1}	ΔS, J K^{-1} mol^{-1}
$AlMe_3(OEt_2)$[b]	84.6	
$AlMe(BHT)_2(OEt_2)$	63.8 (5)	179 (8)
$AlMe_3(THF)$[b]	95.8	
$AlMe(BHT)_2(THF)$	76.8 (3)	181 (6)
$AlMe_3(py)$[b]	115.3	
$AlMe(BHT)_2(py)$	76.9 (5)	179 (9)
$AlMe(BHT)_2(O_2N\text{-}C_6H_4\text{-}p\text{-}Me)$	69.3 (5)	211 (9)
$AlMe(BHT)_2(O{=}CPh_2)$	67.1 (3)	167 (5)
$Al(BHT)_2(OCHPh_2)(O{=}CPh_2)$	92.5 (4)	237 (9)

[a] Error given in parentheses. [b] Henrickson, C. H.; Duffy, D.; Eyman, D. P. *Inorg. Chem.* **1968**, *7*, 1047.

representative benzophenone complex is given in Table I. The associated ln K_{eq} versus $1/T$ plot, from which the enthalpy (ΔH) and entropy (ΔS) were calculated, is shown in Figure 1. All calculated ΔH and ΔS values are given in Table II. Also listed are the ΔH_D values determined for the corresponding $AlMe_3$ complexes.

From the NMR data the following decreasing order of bond strength (ΔH_D) of ligand L, to $AlMe(BHT)_2$, has been determined: py ≈ THF > $O_2N\text{-}C_6H_4\text{-}p\text{-}Me$ > $O{=}CPh_2$ > Et_2O. Although the overall order is similar to that observed for $AlMe_3$, i.e., py > THF > Et_2O, the absolute values are significantly lower. This difference is consistent with not only increased steric repulsion due to the steric bulk of the BHT ligand but also our previous experimental and theoretical studies. Gas-phase photoelectron spectral measurements[20] of the aluminum–ligand bonding energies in aluminum aryloxide complexes and ab initio calculations[21] have both indicated that the R_3Al–L bond is significantly weakened with the replacement of alkyl with alkoxide or aryloxide ligands. We have assigned this weakening to a σ-type interaction between the aryloxide oxygen lone-pair p orbital and the aluminum ligand σ^* orbital.

The larger ΔH_D for compound **11** compared to that for $AlMe(BHT)_2(O{=}CPh_2)$ is consistent with the observed reactivity (see above) and the increased Lewis acidity of a *tris*- over a *bis*(alkoxide). For all the compounds, ΔS_D is large and positive, as would be expected for a dissociative process.

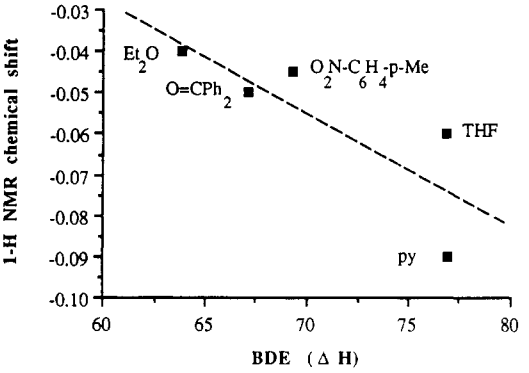

Figure 2. Aluminum methyl ^1H NMR shift (δ) as a function of the calculated bond dissociation energy (ΔH_D) for Lewis base complexes of $AlMe(BHT)_2$.

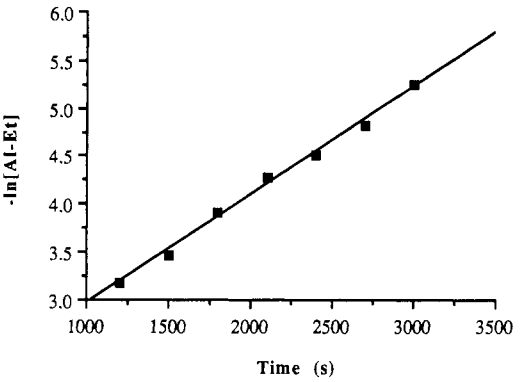

Figure 3. Representative first-order rate plot for the reduction of $O{=}CPh_2$ by $AlEt(BHT)_2$ at 316 K (R = 0.996).

As is shown in Figure 2, there is a general trend observed for the ^1H NMR chemical shift and the heat of dissociation, ΔH_D. The trend is that the more stable adducts have a greater upfield shift of the Al–CH_3 resonance. This is the opposite of the trend reported for $GaMe_3(L)$[22] and, therefore, confirms our previous NMR[23] and X-ray crystallographic studies[24] that aluminum–ligand energies cannot be calculated directly from ^1H NMR chemical shift data as has been suggested.[22]

Kinetic Studies of Benzophenone Reduction by $AlEt(BHT)_2$ and $AlEt(BHT)(OCHPh_2)$. The reduction reactions are conveniently studied by ^1H NMR spectroscopy, since the chemical shifts for the BHT *tert*-butyl groups for the equilibrium mixture of the aluminum ethyl containing compounds are quite distinct from those of the products. The reduction reactions were studied under pseudo-first-order conditions at aluminum–ketone ratios ranging from 1:2 to 1:4. This was the widest range allowed by the solubility of the reactants and products in toluene-d_8. The rate data were recorded for each aluminum–ketone ratio over a range of temperatures ($AlEt(BHT)_2$, 292, 300, 308, and 316 K; $AlEt(BHT)(OCHPh_2)$, 308, 318, and 328 K).

$AlEt(BHT)_2$. As we have indicated in the Introduction, the presence of single reaction pathways for the reaction of organic carbonyls with the sterically hindered aryloxides of aluminum would make these suitable systems for mechanistic investigation. Unfortunately, the reduction

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of coordinated benzophenone in compound **2** is complicated by the competition between product and reactant for benzophenone coordination (see eq 13 above). However, if the reaction is carried out under pseudo-first-order conditions, i.e., in the presence of a large excess of O=CPh_2, then the resulting overall reaction (Scheme I, path i) is applicable for kinetic study.

When **2** was allowed to react in the presence of an excess of O=CPh_2, the ^1H NMR signal due to the BHT *tert*-butyl groups of the aluminum ethyl compound disappeared in a first-order fashion (i.e., eq 27). First-order observed rate

$$-\delta[\text{Al-Et}]/\delta t = k_{obs}[\text{Al-Et}] \quad (27)$$

constants, k_{obs}, were calculated from the corresponding plot of −ln [Al-Et] versus time (e.g., Figure 3). A plot of k_{obs} versus [O=CPh_2] indicates that the reaction is independent of the benzophenone concentration under the conditions of the experiment.

If the reduction of benzophenone by $AlEt(BHT)_2$ occurs by a mechanism analogous to that proposed by Ashby[12] and others,[25,26] then the reaction can be represented by the mechanism given by eqs 28–30. If it is assumed that k_1

$$AlEt(BHT)_2 + O{=}CPh_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AlEt(BHT)_2(O{=}CPh_2) \text{ (rapid)} \quad (28)$$

$$AlEt(BHT)_2(O{=}CPh_2) \xrightarrow{k_2} Al(BHT)_2(OCHPh_2) + C_2H_4 \text{ (rate controlling)} \quad (29)$$

$$Al(BHT)_2(OCHPh_2) + O{=}CPh_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Al(BHT)_2(OCHPh_2)(O{=}CPh_2) \text{ (rapid)} \quad (30)$$

and k_3 are both much larger than k_2 and that the concentration of reactants as determined from the ^1H NMR spectra, [Al-Et], can be expressed as

$$[\text{Al-Et}] = [AlEt(BHT)_2] + [AlEt(BHT)_2(O{=}CPh_2)] \quad (31)$$

then the rate of reduction of benzophenone is given by

$$\text{rate} = \frac{k_2K_1[O{=}CPh_2][\text{Al-Et}]}{1 + K_1[O{=}CPh_2]} \quad (32)$$

For this rate law the dependence on O=CPh_2 varies between 0 and 1, depending on the relative magnitude of the two terms in the denominator.

The observed first-order dependence of the reduction of coordinated benzophenone on the concentration of the aluminum ethyl groups is consistent with the proposed mechanism (eqs 28–30). The observed zero-order dependence on benzophenone concentration is consistent with saturation kinetics.

The enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) were obtained from the appropriate Eyring plot (Figure 4), from which the values of 87.0 kJ mol^{-1} and −27.7 J K^{-1} mol^{-1} were obtained. The enthalpy of activation (ΔH^*) is, as would be expected, large and positive. However, ΔH^* is also larger than our estimated enthalpy of benzophenone dissociation (ΔH = 67.1 kJ mol^{-1}), suggesting that if eqs 28–30 hold true, $k_{-1} \leq k_2$; i.e., the lifetime of the complexed species is sufficient to allow for reduction of the coordinated ketone to occur.

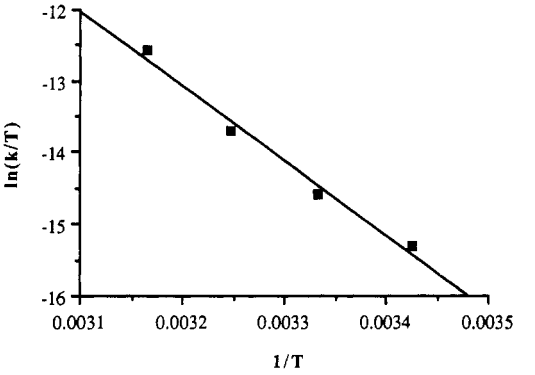

Figure 4. Eyring plot for the determination of ΔH^* (87.0 kJ mol^{-1}) and ΔS^* (−27.7 J K^{-1} mol^{-1}) for the reduction of O=CPh_2 by $AlEt(BHT)_2$ (R = 0.983).

Although the small negative value for ΔS^* is difficult to interpret, it is consistent with the highly ordered six-membered cyclic transition state previously proposed.[25-27]

AlEt(BHT)(OCHPh$_2$). While the reduction of the coordinated benzophenone in **2** occurs rapidly on mild heating in the absence of an excess of benzophenone, the reduction of the coordinated benzophenone in **9** does not occur *at any temperature* unless in the presence of an excess of benzophenone (see above). This apparent dissimilarity in the reduction reactions has prompted us to undertake a kinetic study, for comparison of the latter with the former.

When **9** is heated in the presence of an excess of O=CPh_2, the ^1H NMR signal due to the BHT *tert*-butyl groups of the aluminum ethyl compound disappeared with first-order kinetics. First-order observed rate constants, k_{obs}, were calculated from the plot of −ln [Al-Et] versus time. A plot of k_{obs} versus [O=CPh_2] indicates that under the experimental conditions the reaction is independent of excess benzophenone. The experimental rate law for the reduction of benzophenone by $AlEt(BHT)(OCHPh_2)$ is analogous to that for $AlEt(BHT)_2$ (eqs 28–30), a result not unexpected due to the similarity of the reactants: i.e. $AlEt(OR)_2$ versus AlEt(OR)(OR′).

The enthalpy (ΔH^*) and entropy (ΔS^*) of activation were obtained from the appropriate Eyring plot. The value of ΔH^* (102.8 kJ mol^{-1}) is much larger than that determined for the reduction of benzophenone by $AlEt(BHT)_2$. If we assume that ΔH_D for $AlEt(BHT)(OCHPh_2)$ is comparable to that for $AlMe(BHT)_2(O{=}CPh_2)$, i.e., *ca.* 67.1 kJ mol^{-1}, then this result suggests that the rate of benzophenone reduction is slower than that for ligand dissociation. Thus, as is indeed observed, ketone reduction will only occur in the presence of excess ketone, resulting in a shift of the equilibrium toward complexation.

ΔS^* (−0.2 J K^{-1} mol^{-1}) is close to zero, suggesting that little rearrangement of the ligands occurs in reaching the cyclic transition state I.[12]

The enthalpy of activation for the reduction of benzophenone by both $AlEt(BHT)_2$ and $AlEt(BHT)(OCHPh_2)$ is larger than that determined for the analogous reduction by $Al(^iBu)_3$, i.e., 66.1 kJ mol^{-1}.[12] Thus, although it is clear that the presence of aryloxide and/or alkoxide ligands has a considerable effect on the energetics of the reduction reaction, we are unable to determine whether this is steric,

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Table III. Product Distribution from the Reaction of O=CPh$_2$ with [R$_2$Al(DPP)]$_2$

compd	amt of O=CPh$_2$,[a] molar equiv	T, °C	product ratio O=CPh$_2$: HOCPh$_2$[b]	O=CPh$_2$ reduced per Al
Me$_2$Al(DPP)	1	25	100:0	0
Et$_2$Al(DPP)	1	25	36:64	0.64
Et$_2$Al(DPP)	2	25	52:48	0.97
Et$_2$Al(DPP)	3	25	70:30	0.89
Et$_2$Al(DPP)	3	80	69:31	0.95

[a] Molar equivalent of O=CPh$_2$ per aluminum. [b] As determined from ^{1}H NMR spectroscopy after hydrolysis.

electronic, or both in origin.

Reaction of Benzophenone with [AlR$_2$(μ-DPP)]$_2$ (R = Me, Et). While it is clear that, on the basis of the results presented above and elsewhere,[5,6,8] the aluminum BHT compounds do react with organic carbonyls in a controlled manner, a question of importance remains: *is the reactivity due to the steric bulk of the BHT ligand or the monomeric nature of the aluminum BHT compounds*? In an effort to address this question we have investigated the reactivity of O=CPh$_2$ with the dimeric aryloxide compounds derived from 2,6-diphenylphenol, DPP-H.[28]

Reaction of AlR$_3$ with DPP-H yields the appropriate mono(aryloxide) compound [R$_2$Al(μ-DPP)]$_2$ (R = Me (**14**), Et (**15**)). The ^{1}H and ^{13}C NMR spectral shifts of the aluminum alkyl groups are consistent with a dimeric structure in which the alkyls are terminal. This formulation is confirmed by solution molecular weights.

Interaction of [Me$_2$Al(μ-DPP)]$_2$ with excess O=CPh$_2$, in pentane, results in the formation of a deep orange color consistent with complexation. However, unlike the case for the BHT analogue, no complex, i.e. AlMe$_2$(DPP)(O=CPh$_2$), could be isolated. Analysis of the product from the hydrolysis of the reaction mixture indicated that no alkylation or reduction of the benzophenone had occurred.

As with the methyl compound of [Et$_2$Al(μ-DPP)]$_2$, the reaction with O=CPh$_2$ does not allow for isolation of either a complex or a reduced product analogous to **1**. However, analysis of the hydrolysis product indicates that some of the benzophenone is reduced. The results from the reaction of **15** with varying molar equivalents of O=CPh$_2$ are given in Table III, from which it can be clearly seen that only one of the two possible aluminum ethyl groups available for reaction has reacted, even at elevated temperatures. Although we have been unable to isolate a single product from these experiments, we propose, on the basis of ^{1}H NMR data, that the reduction of benzophenone by **15** occurs in a manner similar to that of O=C(H)Ph by AlEt$_2$(BHT).

On the basis of these results we propose that the "clean" reactivity observed for the aluminum BHT compounds with O=CPh$_2$ is a result of the monomeric nature of the compounds and not per se the presence of a bulky aryloxide ligand. Conversely, since the reduction of organic carbonyls with aluminum alkyls requires the formation of the coordination complex prior to reduction (see above), and the presence of strongly bridging aryloxide ligands inhibits such a complexation (e.g. eq 33), the subsequent reduction is also inhibited.

$$^1/_2[R_2Al(\mu\text{-}OR)]_2 + O{=}CR_2 \rightleftharpoons AlR_2(OR)(O{=}CR_2) \quad (33)$$

Attempted formation of the bis-DPP compounds AlR(DPP)$_2$ (R = Me, Et) by the reaction of AlR$_3$ with 2 equiv of DPP-H was unsuccessful. The ^{1}H NMR spectra of the reaction mixtures showed the presence of several species, which eluded further characterization.

Experimental Section

Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY. Melting points were determined in sealed capillaries and are uncorrected. Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) were recorded on a Seiko SS-200 instrument under an atmosphere of dry nitrogen. IR spectra (4000–700 cm^{-1}) were recorded on a Nicolet 5ZDX FT-IR spectrometer as Nujol mulls (NaCl). ^{1}H and ^{13}C NMR spectra, in C$_6$D$_6$ unless otherwise stated, were recorded on a Bruker AM-500 instrument (δ in parts per million relative to SiMe$_4$). Molecular weight measurements were made in benzene with the use of an instrument similar to that described by Clark.[29] All manipulations were carried out under nitrogen. Solvents were dried, distilled, and degassed before use. AlEt(BHT)$_2$, AlMe(BHT)$_2$, and AlEt$_2$(BHT)(OEt$_2$) were prepared as described previously.

Al(BHT)$_2$(OCHPh$_2$)(O=CPh$_2$) (1). To AlEt(BHT)$_2$ (1.0 g, 2.0 mmol) in pentane (30 mL) was added dropwise benzophenone (0.736 g, 4.0 mmol) in pentane solution (30 mL). As the addition proceeded, a deep red color formed, and toward the end an orange precipitate was evident. The resulting mixture was stirred for 1 h, after which the precipitate was filtered and dried under vacuum. The filtrate was reduced in volume to ca. 30 mL and set aside in the freezer (−20 °C) overnight, to yield further crystalline red product. The combined products were recrystallized from hexane: yield ca. 80%; mp 100–102 °C. Anal. Calcd for C$_{56}$H$_{67}$AlO$_4$: C, 80.73; H, 8.10. Found C, 80.30; H, 8.01. IR (cm^{-1}): 1615 (m), 1585 (m), 1565 (m), 1330 (m), 1295 (m), 1255 (m), 1235 (s), 1215 (sh), 1185 (w), 1165 (w), 1100 (m), 1090 (m), 1065 (m), 1020 (w), 880 (s), 855 (m), 790 (m), 770 (m), 740 (w), 700 (s). NMR (δ, C$_6$D$_6$): ^{1}H, 7.46 [8 H, app t, two overlapping doublets, J(H–H) = 7.5 Hz, *o*-C*H*, O=CPh$_2$, and OCHPh$_2$], 7.18 (4 H, s, C$_6$*H*$_2$, BHT), 7.08 [4 H, t, J(H–H) = 7.5 Hz, *m*-C*H*, OCHPh$_2$], 7.04 [2 H, t, J(H–H) = 7.5 Hz, *p*-CH, O=CPh$_2$], 6.95 [2 H, t, J(H–H) = 7.5 Hz, *p*-C*H*, O=CPh$_2$], 6.84 [4 H, t, J(H–H) = 7.5 Hz, *m*-C*H*, O=CPh$_2$], 6.15 (1 H, s, OC*H*Ph$_2$), 2.33 (6 H, s, C*H*$_3$, BHT), 1.53 [36 H, s, C(C*H*$_3$)$_3$, BHT]; ^{13}C, 206.97 (O=*C*), 155.50 (O*C*, BHT), 148.72 [OC(H)—*C*, OCHPh$_2$], 139.33 (*o*-*C*, BHT), 136.10 (O=C—*C*, O=CPh$_2$), 135.05 (O—*C*, O=CPh$_2$), 133.98 (*m*-*C*, O=CPh$_2$), 128.44 (*p*-*C*, O=CPh$_2$), 127.09 (*o*-*C*, OCHPh$_2$), 126.42 (*m*-*C*, OCHPh$_2$), 126.36 (*m*-*C*, BHT), 125.91 (*p*-*C*, OCHPh$_2$), 125.80 (*p*-*C*, BHT), 78.57 (O*C*, OCHPh$_2$), 35.60 [*C*(CH$_3$)$_3$, BHT], 32.14 [C(*C*H$_3$)$_3$, BHT], 21.37 (*C*H$_3$, BHT).

AlEt(BHT)$_2$(O=CPh$_2$) (2). To a suspension of AlEt(BHT)$_2$ (5.0 g, 10.0 mmol) in ether (30 mL) was added an ether solution (30 mL) of benzophenone (1.84 g, 10.0 mmol). An orange-red color formed immediately. The resulting clear solution was stirred for $^1/_2$ h. The ether solution was then reduced in volume under vacuum to ca. 20 mL, and 50 mL of pentane was added. The resulting solution was again reduced in volume by half. A large quantity of orange precipitate resulted, which was filtered and dried under vacuum: yield ca. 85–90%; mp 107–108 °C. Anal. Calcd for C$_{45}$H$_{61}$AlO$_3$: C, 79.84; H, 9.08. Found: C, 79.66; H, 8.49. IR (cm^{-1}): 1589 (s), 1570 (s), 1389 (m), 1377 (m), 1359 (m), 1334 (s), 1293 (m), 1243 (s), 1203 (m), 1179 (w), 1171 (w), 1161 (w), 1120 (w), 1075 (w), 1028 (w), 998 (w), 986 (w), 977 (w), 969 (w), 947 (w), 924 (w), 887 (w), 866 (s), 808 (w), 776 (s), 710 (s), 691 (w), 635 (s), 620 (w), 607 (m), 577 (w), 548 (m). NMR (δ, C$_6$D$_6$): ^{1}H, 7.55 [4 H, d, J(H–H) = 7.79 Hz, *o*-C*H*, O=CPh$_2$], 7.21 (4 H, s, C$_6$*H*$_2$, BHT), 7.04 [2 H, t, J(H–H) = 7.8 Hz, *p*-C*H*, O=CPh$_2$], 6.86 [4 H, t, J(H–H) = 7.8 Hz, *m*-C*H*, O=CPh$_2$], 2.32 (6 H, s, C*H*$_3$, BHT), 1.57 [36 H, s, C(C*H*$_3$)$_3$, BHT], 1.29 [3 H,t, J(H–H) = 8.18 Hz, Al—CH$_2$C*H*$_3$], 0.549 [2 H, q, J(H–H) = 8.0 Hz, Al—C*H*$_2$]; ^{13}C 206.03 (O=*C*), 155.59 (O*C*, BHT), 138.78 (*o*-*C*, BHT), 135.96 (O=C—*C*, O=CPh$_2$), 135.16 (*o*-*C*, O=CPh$_2$), 133.26 (*m*-*C*, O=CPh$_2$), 128.61 (*p*-*C*, O=CPh$_2$), 126.35 (*m*-*C*, BHT), 125.66 (*p*-*C*,

(28) We note that Rothwell and co-workers have demonstrated that niobium and tantalium compounds of DPP have significantly different reactivities of their BHT analogues. See: (a) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1991**, *10*, 15. (b) Hill, J. H.; Balaich, G. J.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1991**, *10*, 3428 and references therein.

(29) Clark, E. P. *Ind. Eng. Chem., Anal. Ed.* **1941**, *13*, 820.

BHT), 35.50 [$C(CH_3)_3$, BHT], 32.08 [$C(CH_3)_3$, BHT], 21.39 (CH_3, BHT), 9.97 (Al–CH_2CH_3), 5.51 (Al—CH_2).

Al(BHT)$_2$(OCHPh$_2$) (3). Method 1. Equimolar quantities of AlEt(BHT)$_2$ (1.18 g, 2.38 mmol) and Al(BHT)$_2$(OCHPh$_2$)(O=CPh$_2$) (2.0 g, 2.40 mmol) were heated to reflux in hexane (50 mL) overnight. Attempts to isolate solid material by removal of solvent under vacuum proved fruitless, yielding an impure oil. However, addition of Et$_2$O resulted in the formation of the complex Al(BHT)$_2$(OCHPh$_2$)(OEt$_2$) (see below).

Method 2. AlEt(BHT)$_2$(O=CPh$_2$) (5.0 g, 7.38 mmol) was refluxed in hexane (100 mL) overnight. The deep orange color disappeared to leave a clear solution. Attempts to isolate any solid material failed. However, the adduct Al(BHT)$_2$(OCHPh$_2$)(OEt$_2$) was isolated upon addition of Et$_2$O (see below).

Al(BHT)$_2$(OCHPh$_2$)(OEt$_2$) (4). The adduct AlEt(BHT)$_2$(O=CPh$_2$) (3.0 g, 4.43 mmol) was dissolved in a mixture of benzene (50 mL) and Et$_2$O (2 mL). The resulting solution was warmed to reflux for 4–5 h and then cooled. The solvent was then removed under vacuum to leave an orange oily residue, which after washing with pentane (ca. 30 mL) yielded a white precipitate. This was filtered and dried under vacuum: yield ca. 60%; mp 120–123 °C. Anal. Calcd for $C_{47}H_{67}AlO_4$: C, 78.07; H, 9.33. Found C, 78.42; H, 9.19. IR (cm^{-1}): 1598 (w), 1388 (s), 1377 (s), 1360 (s), 1333 (w), 1289 (m), 1262 (s), 1233 (s), 1202 (m), 1188 (s), 1154 (w), 1144 (w), 1121 (m), 1094 (s), 1068 (s), 1015 (s), 991 (m), 953 (w), 923 (m), 896 (s), 878 (m), 859 (s), 836 (w), 813 (sh), 800 (s) 774 (s), 768 (m), 743 (s), 722 (w), 705 (s), 650 (m), 644 (m), 602 (s), 591 (w), 575 (w), 531 (m), 521 (m), 484 (w), 452 (w). NMR (δ, C_6D_6): ^{1}H, 7.46 [4 H, d, J(H–H) = 7.52 Hz, *o*-C*H*, OCHPh$_2$], 7.20 (4 H, s, C_6H_2, BHT), 7.12 [4 H, t, J(H–H) = 7.52 Hz, *m*-C*H*, OCHPh$_2$], 6.98 [2 H, t, J(H–H) = 7.5 Hz, *p*-C*H*, OCHPh$_2$], 6.02 (1 H, s, OC*H*Ph$_2$), 3.61 [4 H, q, J(H–H) = 6.84 Hz, OCH_2, Et$_2$O], 2.32 (6 H, s, CH_3, BHT), 1.55 [36 H, s, C(CH_3)$_3$, BHT], 0.38 [6 H, t, J(H–H) = 6.8 Hz, OCH$_2$$CH_3$, Et$_2$O); ^{13}C, 155.12 (*O*C, BHT), 147.61 [OC—*C*, OCHPh$_2$], 139.16 (*o*-*C*, BHT), 128.14 (*o*-*C*, OCHPh$_2$), 127.39 (*m*-*C*, OCHPh$_2$), 126.70 (*p*-*C*, OCHPh$_2$), 126.62 (*m*-*C*, BHT), 126.41 (*p*-*C*, BHT), 78.64 (O—C, OCHPh$_2$), 66.62 (CH_2, Et$_2$O), 35.72 [*C*(CH_3)$_3$, BHT], 32.36 [C(*C*H$_3$)$_3$, BHT], 21.28 (CH_3, BHT), 11.41 (CH_3, Et$_2$O).

Al(BHT)$_2$(OCHPh$_2$)(THF) (5). Method 1. THF (20 mL) was added via syringe to 4 (1.5 g, 2.07 mmol) and the resulting clear solution stirred for 5 min. The solvent was then removed under vacuum, leaving a white residue, which was recrystallized from pentane (10 mL, –20 °C): yield *ca.* 90%.

Method 2. Compound **7** may similarly be synthesized by the reaction of **1** with THF: yield *ca.* 90%; mp 162–166 °C. Anal. Calcd for $C_{47}H_{65}AlO_4$: C, 78.29; H, 9.08. Found: C, 77.73; H, 8.64. IR (cm^{-1}): 1730 (w), 1598 (w), 1387 (s), 1377 (s), 1358 (s), 1324 (w), 1299 (sh), 1291 (m), 1268 (s), 1258 (s), 1238 (s), 1220 (sh), 1205 (s), 1187 (s), 1175 (sh), 1153 (w), 1121 (m), 1094 (s), 1068 (s), 1037 (sh), 1027 (m), 995 (s), 958 (m), 922 (m), 914 (sh), 891 (s), 842 (s), 803 (s), 774 (s), 745 (s), 722 (w), 705 (s), 654 (m), 618 (w), 595 (s), 575 (w), 523 (m), 484 (m), 413 (m). NMR (δ, C_6D_6): ^{1}H, 7.49 [4 H, d, J(H–H) = 7.27 Hz, *o*-C*H*, OCHPh$_2$], 7.20 (4 H, s, C_6H_2, BHT), 7.15 [4 H, t, J(H–H) = 7.53 Hz, *m*-C*H*, OCHPh$_2$], 6.98 [2 H, t, J(H–H) = 7.5 Hz, *p*-C*H*, OCHPh$_2$], 5.93 (1 H, s, OC*H*, OCHPh$_2$), 3.62 (4 H, m, O—CH_2, THF), 2.33 (6 H, s, CH_3, BHT), 1.57 [36 H, s, C(CH_3)$_3$, BHT], 0.847 (4 H, m, OCH$_2$$CH_2$, THF); ^{13}C 155.29 (*O*C, BHT), 148.16 [OC(H)*C*, Ph], 139.18 (*o*-*C*, BHT), 128.18 (*o*-*C*, OCHPh$_2$), 127.11 (*m*-*C*, OCHPh$_2$), 126.65 (*p*-*C*, OCHPh$_2$), 126.54 (*m*-*C*, BHT), 126.30 (*p*-*C*, BHT), 78.56 (*O*C, OCHPh$_2$), 74.17 [OCH_2, THF], 35.63 [*C*(CH_3)$_3$, BHT], 32.13 [C-(*C*H$_3$)$_3$, BHT], 24.23 [OCH$_2$$CH_2$, THF], 21.28 ($CH_3$, BHT).

AlEt$_2$(BHT)(O=CPh$_2$) (6). Benzophenone (1.2 g, 6.58 mmol) was dissolved in 20 mL of ether and this solution then added dropwise quickly to a solution of [(BHT)AlEt$_2$(Et$_2$O)] (2.5 g, 6.60 mmol) in ether (30 mL). An orange-red color formed. The resulting solution was stirred for $^1/_2$ h and then reduced in volume to ca. 20 mL under vacuum. Degassed pentane (40 mL) was added, and a further ca. 30 mL of solvent from the resulting solution was removed under vacuum. As the cooled solution was warmed to room temperature, the product precipitated as an orange solid. This was filtered and dried under vacuum: yield ca. 80–85%; mp 90 °C. Anal. Calcd for $C_{32}H_{43}O_2Al$: C, 78.97; H, 8.90. Found: C, 78.18; H, 8.18. IR (cm^{-1}): 1606 (s), 1590 (s), 1585 (s), 1378 (s), 1358 (sh), 1331 (s), 1281 (s), 1261 (s), 1232 (sh), 1201 (w), 1182 (m), 1162 (w), 1122 (w), 1073 (w), 1026 (w), 996 (w), 977 (m), 949 (m), 925 (w), 875 (s), 863 (sh), 845 (w), 809 (w), 769 (s), 705 (s), 639 (s), 628 (s), 591 (m), 455 (w). NMR (δ, C_6D_6): ^{1}H, 7.70 [4 H, d, J(H–H) = 7.73 Hz, *o*-C*H*, O=CPh$_2$], 7.26 (2 H, s, C_6H_2, BHT), 7.08 [2 H, t, J(H–H) = 7.7 Hz, *p*-C*H*, O=CPh$_2$], 6.92 [4 H, t, J(H–H) = 7.7 Hz, *m*-C*H*, O=CPh$_2$], 2.36 (3 H, s, CH_3, BHT), 1.61 [18 H, s, C(CH_3)$_3$, BHT], 1.30 [6 H, t, J(H–H) = 8.13 Hz, AlCH$_2$$CH_3$], 0.537 [4 H, q, J(H–H) = 8.1 Hz, Al—CH_2]; ^{13}C, 204.78 (O=*C*), 156.07 (O*C*, BHT), 138.73 (*o*-*C*, BHT), 136.05 (O=C—*C*, O=CPh$_2$), 135.03 (*p*-*C*, Ph$_2$CO), 133.09 (*o*-*C*, Ph$_2$CO), 128.82 (*m*-*C*, O=CPh$_2$), 126.15 (*m*-*C*, BHT), 125.13 (*p*-C, BHT), 35.14 [*C*(CH_3)$_3$, BHT], 31.35 [C(*C*H$_3$)$_3$, BHT], 21.54 (*C*H$_3$, BHT), 10.17 (Al—$CH_2$$CH_3$), 3.65 (Al—*C*H$_2$).

AlEt(BHT)(OCHPh$_2$) (7). AlEt$_2$(BHT)(O=CPh$_2$) (2.0 g, 4.10 mmol) may be heated slowly as a solid under nitrogen. At ca. 90 °C (oil bath temperature) the orange solid melts and forms a white solid by 135 °C. Thermogravimetric analysis indicates loss of ethylene to yield monomeric white AlEt(BHT)(OCHPh$_2$). This white solid melts at 134–135 °C. It is soluble in THF and benzene but quickly forms the dimer [AlEt(BHT)(μ-CHPh$_2$)]$_2$, which is insoluble (mp 173–174 °C). Anal. Calcd for $C_{30}H_{39}AlO_2$: C, 78.56; H, 8.57. Found: C, 78.52; H, 8.32. IR (cm^{-1}): 1388 (m), 1376 (m), 1362 (m), 1335 (w), 1290 (sh), 1260 (s), 1235 (s), 1198 (m), 1191 (m), 1157 (w), 1121 (m), 1083 (w), 1071 (w), 1029 (w), 1001 (sh), 967 (s), 937 (sh), 915 (m), 888 (sh), 874 (s), 767 (s), 743 (m), 696 (s), 682 (s), 654 (s), 618 (m), 576 (w), 560 (m), 532 (w), 479 (s).

[AlEt(BHT)(μ-OCHPh$_2$)]$_2$ (8). AlEt$_2$(BHT)(O=CPh$_2$) (2.0 g, 4.10 mmol) was dissolved in toluene or benzene and heated to ca. 80 °C for 1 h. The color lightened from deep orange to give a pink tinge to the solution. When the mixture was cooled to room temperature, a white precipitate formed, which was filtered, washed once with pentane, and finally dried under vacuum: yield ca. 75%; mp 173–174 °C. Anal. Calcd for the dimer $C_{60}H_{78}Al_2O_4$: C, 78.56; H, 8.57. Found: C, 78.45; H, 8.47. Molecular weight (benzene): calcd 917.23, found 908. IR (cm^{-1}): 1393 (m), 1377 (s), 1363 (m), 1258 (s), 1244 (s), 1208 (m), 1194 (m), 1182 (sh), 1118 (w), 983 (s), 922 (m), 888 (w), 872 (s), 859 (m), 784 (s), 744 (m), 705 (s), 695 (s), 683 (s), 655 (s), 619 (m), 589 (w), 570 (w), 534 (w), 487 (m). NMR (δ, $CDCl_3$): ^{1}H, 7.31 [4 H, d, J(H–H) = 7.81 Hz, *o*-C*H*, OCHPh$_2$], 7.26 [4 H, d, J(H–H) = 6.72 Hz, *o*-C*H*, OCHPh$_2$], 7.09–7.02 [8 H, m, *m*-C*H*, OCHPh$_2$], 7.01 (4 H, s, C_6H_2, BHT), 6.82 [4 H, t, J(H–H) = 7.67 Hz, *p*-C*H*, OCHPh$_2$], 6.46 (2 H, s, OC*H*, OCHPh$_2$), 2.30 (6 H, s, CH_3, BHT), 1.29 [36 H, s, C(CH_3)$_3$, BHT], 0.417 [6 H, t, J(H–H) = 7.85 Hz, Al—$CH_2$$CH_3$], –0.21 [4 H, q, J(H–H) = 7.85 Hz, AlCH_2]; ^{13}C, 154.39 (O*C*, BHT), 141.08, 140.42 (OC—*C*, OCHPh$_2$), 139.09 (*o*-*C*, BHT), 129.00, 128.69 (*o*-*C*, OCHPh$_2$), 128.29, 128.16 (*p*-*C*, OCHPh$_2$), 128.06, 126.18 (*m*-*C*, μ-Ph$_2$CHO), 126.75 (*m*-*C*, BHT), 126.29 (*p*-*C*, BHT), 81.28 (O*C*, OCHPh$_2$), 35.44 [*C*(CH_3)$_3$, BHT], 32.32 [C(*C*H$_3$)$_3$, BHT], 20.80 (CH_3, BHT), 8.70 (Al—$CH_2$$CH_3$), 4.47 (Al—*C*H$_2$).

AlEt(BHT)(OCHPh$_2$)(O=CPh$_2$) (9). Method 1. BHT-H (2.2 g, 10.0 mmol) was dissolved in 20 mL of pentane. To this was added AlEt$_3$ (10.0 mL of a 1.0 M solution in hexanes, 10.0 mmol) via syringe. The resulting solution was stirred for $^1/_2$ h. Then, benzophenone (3.64 g, 20.0 mmol) in 40 mL of pentane was added slowly dropwise. After completion of the addition and when the mixture was stirred for 1 h, an orange precipitate formed. This was filtered, washed with pentane, and dried under vacuum: yield ca. 75%. Minor quantities of Al(BHT)$_2$(OCHPh$_2$)(O=CPh$_2$) were isolated from the filtrate.

Method 2. If 2 equiv of benzophenone is added to 1 equiv of AlEt$_2$(BHT)(OEt$_2$) in pentane, initially the adduct AlEt$_2$(BHT)(O=CPh$_2$) precipitates, and then the second equivalent reacts to form AlEt(BHT)(OCHPh$_2$)(O=CPh$_2$): yield ca. 90%; mp 104–105 °C. Anal. Calcd for $C_{46}H_{49}AlO_3$: C, 80.59; H, 7.70. Found: C, 79.77; H, 7.59. IR (cm^{-1}): 1610 (s), 1590 (s), 1565 (m), 1370 (s), 1330 (s), 1290 (s), 1275 (s), 1260 (sh), 1190 (w), 1165 (w), 1115 (m), 1065 (w), 1025 (w), 995 (w), 980 (w), 950 (w), 920 (w), 890 (m), 860 (w), 780 (m), 770 (m), 735 (m), 700 (s). NMR (δ, C_6D_6): ^{1}H, 7.67 [4 H, d, J(H–H) = 7.4 Hz, *o*-C*H*, O=CPh$_2$], 7.47 [4 H, d, J(H–H) = 6.5 Hz, *o*-C*H*, OCHPh$_2$], 7.27 (2 H, s, C_6H_2, BHT), 7.15–6.96 (8 H, m, *m*-C*H*, O=CPh$_2$ and OCHPh$_2$], 6.87 [4 H, t, J(H–H) = 7.5 Hz, *p*-C*H*, O=CPh$_2$ + OCHPh$_2$], 6.19 (1 H, s, OC*H*Ph$_2$), 2.37 (3 H, CH_3, BHT), 1.59 [18 H, s, C(CH_3)$_3$, BHT], 1.26 (3 H, t, J(H–H) = 8.0 Hz, Al—$CH_2$$CH_3$), 0.53 (2 H,

q, Al—CH_2); ^{13}C, 204.62 (O=*C*), 155.48 (O*C*, BHT), 149.13 (OCH—*C*, Ph), 138.92 (*o*-*C*, BHT), 136.11 (O=C—*C*, Ph), 134.49 (*o*-*C*, O=CPh_2), 133.61 (*m*-*C*, O=CPh_2), 128.74 (*p*-*C*, O=CPh_2), 128.07 (*o*-*C*, $OCHPh_2$), 126.99 (*m*-*C*, BHT), 126.23 (*m*-*C*, $OCHPh_2$), 126.13 (*p*-*C*, $OCHPh_2$), 125.54 (*p*-*C*, BHT), 77.25 ($OCHPh_2$), 35.13 [*C*(CH_3)$_3$, BHT], 31.28 [C(*C*H_3)$_3$, BHT], 21.54 (*C*H_3, BHT), 10.02 (Al—CH_2*C*H_3), 1.34 (Al—*C*H_2).

(BHT)(Et)Al(μ-OCHPh$_2$)$_2$Al(OCHPh$_2$)(Et) (10). Al(Et)(BHT)($OCHPh_2$)(O=CPh_2) (2.0 g, 3.12 mmol) was refluxed for 4 h in hexane (60 mL). The orange suspension dissolved to give a deep orange solution, which lightened in color somewhat to leave a clear red solution after 4 h. The solution was cooled and then set aside in the freezer (−20 °C) overnight. Both starting material (orange) and product (white) precipitated: isolated yield of product ca. 50–55%; mp 173–174 °C. Anal. Calcd for $C_{58}H_{66}O_4Al_2$: C, 79.06; H, 7.54. Found: C, 79.37; H, 7.38. Molecular weight (benzene): calcd for $C_{58}H_{66}Al_2O_4$ 881.121, found 888. IR (cm^{-1}): 1377 (s), 1366 (sh), 1266 (s), 1231 (w), 1223 (w), 1205 (m), 1188 (m), 1155 (w), 1113 (m), 1070 (m), 1028 (w), 1001 (w), 965 (s), 928 (m), 918 (m), 886 (s), 861 (w), 804 (m), 775 (m), 764 (s), 747 (m), 739 (s), 711 (s), 702 (s), 672 (s), 657 (s), 631 (s), 622 (sh), 548 (m), 486 (m), 471 (m), 461 (w). NMR (δ): ^1H (C_6D_6), 7.71 [4 H, d, *J*(H–H) = 7.5 Hz, *o*-C*H*, $OCHPh_2$], 7.43 [8 H, d, *J*(H–H) = 6.8 Hz, *o*-C*H*, μ-$OCHPh_2$], 7.30 (2 H, s, C_6H_2, BHT), 7.26 [4 H, t, *J*(H–H) = 7.7 Hz, *m*-C*H*, $OCHPh_2$], 7.08 [2 H, t, *J*(H–H) = 7.3 Hz, *m*-C*H*, μ-$OCHPh_2$], 7.03 [4 H, t, *J*(H–H) = 7.7 Hz, *m*-C*H*, $OCHPh_2$], 6.95 [2 H, t, *J*(H–H) = 7.5 Hz, *m*-C*H*, μ-$OCHPh_2$], 6.87 (3 H, t, *p*-C*H*, $OCHPh_2$ and μ-$OCHPh_2$), 6.40 (2 H, s, μ-OC*H*Ph_2), 5.90 (1 H, s, OC*H*Ph_2), 2.36 (3 H, s, CH_3, BHT), 1.56 [18 H, s, C(CH_3)$_3$, BHT), 1.30 [3 H, t, *J*(H–H) = 8.0 Hz, Al—CH_2CH_3], 0.57 [3 H, t, *J*(H–H) = 8.3 Hz, Al—CH_2CH_3], −0.08 [2 H, q, *J*(H–H) = 8.0 Hz, Al—CH_2], 0.64 [2 H, q, *J*(H–H) = 8.3 Hz, Al—CH_2]; ^{13}C ($CDCl_3$), 153.83 (O*C*, BHT), 147.79 (OCH—*C*, $OCHPh_2$), 140.48 (OCH—*C*, μ-$OCHPh_2$), 138.75 (*o*-*C*, BHT), 129.02, 128.28, 128.15, 127.55, 127.08, 126.74, 126.40 (Ph, $OCHPh_2$), 126.47 (*m*-*C*, BHT), 125.99 (*p*-*C*, BHT), 80.64 (μ-$OCHPh_2$), 77.51 ($OCHPh_2$), 34.99 [*C*(CH_3)$_3$, BHT], 31.64 [C(*C*H_3)$_3$, BHT], 21.04 (*C*H_3, BHT), 8.66, 7.73 (Al—CH_2*C*H_3), 3.34, −0.44 (Al—*C*H_2).

Al(BHT)(OCHPh$_2$)$_2$(O=CPh$_2$) (11). AlEt(BHT)($OCHPh_2$)(O=CPh_2) (0.05 g, 0.078 mmol) and excess (2 equiv) benzophenone (0.028 g, 0.156 mmol) were mixed in C_6D_6, and the reaction was monitored by ^1H NMR spectroscopy at room temperature. After $^3/_4$ h the peaks due to the starting material were replaced essentially quantitatively with a peak at δ 5.25 (C_2H_4) and the following NMR spectrum consistent with the species "Al(BHT)($OCHPh_2$)$_2$": δ 7.66–6.92 (22 H, m, C_6H_5 Ph and C_6H_2 BHT), 6.06 (2 H, s, OC*H*Ph_2), 2.31 (3 H, s, CH_3, BHT), 1.46 [18 H, s, C(CH_3)$_3$, BHT]. If the sample is then warmed gently (60–70 °C), further reaction occurs, yielding the species Al(BHT)($OCHPh_2$)$_2$(O=CPh_2): δ 7.63–6.96 (32 H, m, C_6H_5 Ph and C_6H_2 BHT), 6.08 (2 H, s, OC*H*Ph_2), 2.36 (3 H, s, CH_3, BHT), 1.50 [18 H, s, C(CH_3)$_3$, BHT]. Attempted isolation of these species proved unsuccessful, owing to the presence of excess benzophenone.

AlEt(BHT)$_2$[O=C(Me)Ph] (12). Acetophenone (0.635 mL, 5.45 mmol) in pentane (40 mL) was added dropwise to AlEt(BHT)$_2$ (2.70 g, 5.45 mmol), also in pentane (30 mL). An orange precipitate formed. This was filtered immediately and dried under vacuum: yield 86%; mp 110–112 °C. Anal. Calcd for $C_{40}H_{59}AlO_3$: C, 78.13; H, 9.67. Found: C, 78.06; H, 9.58. IR (cm^{-1}): 1620 (s), 1590 (m), 1570 (m), 1310 (sh), 1290 (sh), 1278 (s), 1260 (s), 1225 (sh), 1200 (w), 1180 (w), 1160 (w), 1120 (w), 1100 (w), 1090 (w), 1070 (w), 1020 (w), 970 (w), 955 (w), 925 (w), 890 (s), 880 (s), 855 (m), 840 (w), 800 (w), 770 (m), 760 (m), 720 (w), 690 (m). NMR (δ, C_6D_6): ^1H, 7.71 [2 H, d, *J*(H–H) = 7.5 Hz, *o*-C*H*, O=C(Me)Ph], 7.21 (4 H, s, C_6H_2, BHT), 7.01 [1 H, t, *J*(H–H) = 7.47 Hz, *p*-C*H*, O=C(Me)Ph], 6.83 [2 H, t, *J*(H–H) = 7.5 Hz, *m*-C*H*, O=C(Me)Ph], 2.31 (6 H, s, CH_3, BHT), 2.17 (3 H, s, CH_3, O=C(Me)Ph), 1.62 [36 H, s, C(CH_3)$_3$, BHT], 1.29 [3 H, t, *J*(H–H) = 7.9 Hz, Al—CH_2CH_3], 0.67 [2 H, q, *J*(H–H) = 8.0 Hz, Al—CH_2]; ^{13}C, 212.44 (O=*C*), 155.18 (O*C*, BHT), 138.82 (*o*-*C*, BHT), 137.63 (O=C—*C*), 134.40 [*p*-*C*, O=C(Me)Ph], 131.65 [*m*-*C*, O=C(Me)Ph], 128.95 [*o*-*C*, O=C(Me)Ph], 126.45 (*m*-*C*, BHT), 125.85 (*p*-*C*, BHT), 35.50 [*C*(CH_3)$_3$, BHT], 32.01 [C(*C*H_3)$_3$, BHT], 26.66 [CH_3, O=C(Me)Ph], 21.35 (*C*H_3, BHT), 10.19 (Al—CH_2*C*H_3), 5.7 (Al—*C*H_2).

AlEt$_2$(BHT)[O=C(Me)Ph] (13). An excess of acetophenone (1.38 mL, 11.88 mmol) was added via syringe to a solution of $AlEt_2$(BHT)(OEt_2) (3.0 g, 7.92 mmol) in pentane (40 mL). Immediately a large amount of yellow precipitate formed; this was filtered and dried under vacuum: yield 83%; mp 96 °C. Anal. Calcd for $C_{27}H_{41}AlO_2$: C, 76.37; H, 9.73. Found: C, 76.14; H, 9.51. IR (cm^{-1}): 1625 (s), 1595 (s), 1575 (s), 1370 (m), 1300 (sh), 1290 (sh), 1280 (s), 1270 (sh), 1220 (w), 1185 (m), 1165 (w), 1125 (w), 1100 (w), 1070 (w), 1025 (m), 990 (w), 975 (m), 955 (m), 925 (w), 870 (s), 840 (w), 805 (w), 780 (m), 760 (m), 750 (w), 725 (w), 680 (m), 630 (s), 600 (s), 585 (w), 570 (w), 540 (m). NMR (δ, C_6D_6): ^1H, 7.62 [2 H, d, *J*(H–H) = 7.1 Hz, *o*-C*H*, O=C(Me)Ph], 7.25 (2 H, s, C_6H_2, BHT), 7.02 [1 H, t, *J*(H–H) = 7.6 Hz, *p*-C*H*, O=C(Me)Ph], 6.82 [2 H, t, *J*(H–H) = 7.7 Hz, *m*-C*H*, O=C(Me)Ph], 2.35 (3 H, s, CH_3, BHT), 2.25 (3 H, s, CH_3, O=C(Me)Ph), 1.60 [18 H, s, C(CH_3)$_3$, BHT], 1.39 [6 H, t, *J*(H–H) = 8.18 Hz, Al—CH_2CH_3], 0.58 [4 H, q, *J*(H–H) = 8 Hz, Al—CH_2]; ^{13}C, 210.49 (O=*C*), 155.96 (O*C*, BHT), 138.54 (*o*-*C*, BHT), 137.36 (O=C—*C*, Ph), 134.29 [*p*-*C*, O=C(Me)Ph], 131.04 [*m*-*C*, O=C(Me)Ph], 129.15 [*o*-*C*, O=C(Me)Ph], 126.11 (*m*-*C*, BHT), 125.20 (*p*-*C*, BHT), 35.11 [*C*(CH_3)$_3$, BHT], 31.35 [C(*C*H_3)$_3$, BHT], 26.20 [CH_3, O=C(Me)Ph], 21.51 (*C*H_3, BHT), 10.17 (Al—CH_2*C*H_3), 3.33 (Al—*C*H_2).

[Me$_2$Al(μ-DPP)]$_2$ (14). To a pentane (30 mL) solution of DPP-H (1.00 g, 4.07 mmol) at room temperature was added $AlMe_3$ (2.0 M, hexane, 2.04 mL). Gas evolution was observed as addition proceeded. The reaction mixture was stirred for 12 h, during which time a white precipitate was formed. Removal of the solvent allowed for the isolation of the crude product. Purification was accomplished by crystallization from toluene: yield ca. 90%; mp >270 °C. Anal. Calcd for $C_{20}H_{19}AlO$: C, 79.44; H, 6.33. Found: C, 78.87; H, 6.28. MS (*m*/*z*, 100%): 302 (M^+, 3%), 287 (M^+ − Me, 10%). IR (cm^{-1}): 1306 (w), 1261 (w), 1197 (m), 1188 (m), 1091 (m), 1071 (m), 1029 (w), 1013 (w), 839 (m), 814 (w), 801 (w), 761 (m), 721 (m), 700 (s), 680 (m). NMR (δ, C_6D_6): ^1H, 7.40–6.72 (13 H, m, C_6H_3 and C_6H_5), −1.38 (6 H, s, Al—CH_3); ^{13}C, 146.28 (OC, DPP), 139.09 (*o*-*C*, DPP), 134.73, 132.99, 131.06, 129.28, 123.17 (C_6H_5, *m*-*C* and *p*-*C*, DPP), −9.18 (Al—*C*H_3).

[Et$_2$Al(μ-DPP)]$_2$ (15) was prepared in a manner analagous to that for **13**: yield ca. 80%; mp 215–219 °C. Anal. Calcd for $C_{22}H_{23}AlO$: C, 79.97; H, 7.02. Found: C, 79.94; H, 7.04. Molecular weight (benzene): 624 (2M = 656). IR (cm^{-1}): 1297 (m), 1263 (s), 1245 (s), 1216 (s), 1158 (m), 1121 (m), 1038 (w), 1026 (w), 1000 (m), 964 (m), 957 (m), 919 (s), 892 (s), 857 (s), 773 (m), 722 (w), 671 (s), 605 (w). NMR (δ, C_6D_6): ^1H, 7.47–6.65 (13 H, m, C_6H_3 and C_6H_5), 0.81 [6 H, t, *J*(H–H) = 8.2 Hz, Al—CH_2CH_3], −0.72 [4 H, q, *J*(H–H) = 8.2 Hz, Al—CH_2]; ^{13}C, 147.37 (O*C*, DPP), 139.41 (*o*-*C*, DPP), 134.55, 133.56, 130.93, 129.23, 128.37, 123.45 (C_6H_5, *m*-*C* and *p*-*C*, DPP), 9.43 (Al—CH_2*C*H_3), −4.84 (Al—*C*H_2).

Reaction of O=CPh$_2$ with [R$_2$Al(μ-DPP)]$_2$ (R = Me, Et). In a typical reaction AlR_2(DPP) (6.06 mmol) and benzophenone were placed in a Schlenk flask, to which pentane (40 mL) was added. If precipitation occurred, further solvent was added, and the reaction mixture was stirred for 12 h. The resulting solution was hydrolyzed with aqueous HCl and extracted with diethyl ether. Analyses of the reaction mixtures using various amounts of O=CPh_2 were carried out by ^1H NMR spectroscopy; the results are summarized in Table III.

Equilibrium Studies. A solution of each Lewis acid–base complex AlMe(BHT)$_2$L (L = Et_2O, THF, py, O=CPh_2, O_2N-C_6H_4-*p*-Me, O=C(NMe_2)Ph) and Al(BHT)$_2$($OCHPh_2$)(O=CPh_2) was prepared gravimetrically in toluene-d_8 (for which a density of 0.94 g mL^{-1} was assumed). The sample was heated and the NMR spectrum obtained until no change was observed. Constancy of the spectrum was taken as evidence for the attainment of equilibrium. Alternative points on the ln K_{eq} versus $1/T$ plot were obtained during the upward and downward passages over the temperature range spanned. Because both sets of points fell on the same line, we consider that equilibration was achieved. Since the Al—CH_3 peak is well separated from the others in the ^1H NMR spectra, its shift was used to determine the relative amount of each species for the complexes of AlMe(BHT)$_2$. Since Al(BHT)$_2$($OCHPh_2$)(O=CPh_2) contains no aluminum methyl groups, the ^1H NMR *o*-C*H* protons were used to calculate the chemical shift for the K_{eq} values in a manner analogous to that for AlMe(BHT)$_2$L.

Kinetic Studies. A mixture of benzophenone and either **2**

or **9** was accurately weighed (ca. 0.05 g) into a series of 5-mm NMR tubes. Toluene-d_8 (ca. 0.25 mL) was added. The samples were heated to appropriate temperatures within the NMR spectrometer, and a series of ^1H NMR spectra were collected every 5–6 min for approximately 2–3 h. The integrations of the *tert*-butyl proton resonances were used to determine the relative quantity of each species. Rate constants were calculated from plots of ln [Al-Et] versus time and k_{obs} versus [O=CPh$_2$], while $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were calculated from the appropriate Eyring plots.

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Scope and Diastereoselectivity of Intramolecular [4 + 2] Diels–Alder Cycloadditions within the Coordination Sphere of $[(\eta^5\text{-}C_5H_5)Ru(DMPP)_{3-n}(dienophile)_n]PF_6$

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The complex $[(\eta^5\text{-}C_5H_5)Ru(DMPP)_2(CH_3CN)]PF_6$ (**1**; DMPP = 1-phenyl-3,4-dimethylphosphole) reacts with the dieneophiles $Ph_2PCH{=}CH_2$ (DPVP), $PhP(CH{=}CH_2)_2$ (DVPP), $PhP(CH_2CH{=}CH_2)_2$ (DAPP), $PhS(O)CH{=}CH_2$, $PhSCH{=}CH_2$, and 2-vinylpyridine to produce one (**10**, **12**), two (**4**, **11**), or three (**5**, **9**) diastereomers of (η^5-cyclopentadienyl)(1-phenyl-3,4-dimethylphosphole)[*syn-exo*-2-(diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]ruthenium(II) hexafluorophosphate (**4a,b**), (η^5-cyclopentadienyl)(1-phenyl-3,4-dimethylphosphole)[*syn-exo*-2-(phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]ruthenium(II) hexafluorophosphate (**5a,b**), (η^5-cyclopentadienyl){*syn-exo-meso*-phenylbis[5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-en-2-yl]phosphine}ruthenium(II) hexafluorophosphate (**5c**), (η^5-cyclopentadienyl)(1-phenyl-3,4-dimethylphosphole)[*syn-exo*-2-((allylphenylphosphino)methyl)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]-hept-5-ene]ruthenium(II) hexafluorophosphate (**9a,b**), (η^5-cyclopentadienyl){*syn*-exo-*dl*-phenylbis[(5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene-2-yl]phosphine}ruthenium(II) hexafluorophosphate (**9c**), (η^5-cyclopentadienyl)(1-phenyl-3,4-dimethylphosphole)[*syn-exo*-2-(phenylsulfinyl)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]ruthenium(II) hexafluorophosphate (**10**), (η^5-cyclopentadienyl)(1-phenyl-3,4-dimethylphosphole)[*syn-exo*-2-(phenylthio)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]ruthenium(II) hexafluorophosphate (**11**), (η^5-cyclopentadienyl)[*syn-exo*-2-(2-pyridyl)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene]ruthenium(II) hexafluorophosphate (**12**), respectively, by intramolecular [4 + 2] Diels–Alder cycloadditions in high yields. Similar Diels–Alder cycloadditions occur with $[(\eta^5\text{-}C_5H_5)Ru(DPVP)_2(CH_3CN)]PF_6$ (**2**) and $[(\eta^5\text{-}C_5H_5)Ru(DVPP)_2(CH_3CN)]PF_6$ (**3**) and DMPP to form **6a,b** and **7a,b**, respectively. Reactions of **1** with the potential dienophilic ligands L = $Me_2NC(O)CH{=}CH_2$, $PhS(O)_2CH{=}CH_2$, $P(OCH_2CH{=}CH_2)_3$, $P(C{\equiv}CPh)_3$, $H_2NCH_2CH{=}CH_2$, $N{\equiv}C{-}CH{=}CH_2$, $N(CH_2C(CH_3){=}CH_2)_3$, and $C_2H_5OCH{=}CH_2$ produced the $[(\eta^5\text{-}C_5H_5)Ru(DMPP)_2L)]PF_6$ complexes **14–21**, which could not be induced to undergo subsequent [4 + 2] Diels–Alder cycloadditions. New complexes were characterized by elemental analyses, physical properties, cyclic voltammetry, infrared spectroscopy, and ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and in some cases by $^1H\{^{31}P\}$ nuclear magnetic resonance spectroscopy. Complex **11** is stereochemically nonrigid with sulfur inversion occurring rapidly at room temperature; $\Delta G^\ddagger$ = 59.8 kJ mol^{-1}. The structures of **4b**, **5c**, and **11** were confirmed by X-ray crystallography. They crystallize in the $P2_1/c$, $P2_1/m$, and $C2/c$ space groups, respectively, in unit cells of the following dimensions: **4b**, a = 20.965 (9) Å, b = 11.125 (4) Å, c = 21.678 (9) Å, β = 118.26 (2)°, ρ(calcd) = 1.438 g cm^{-3}, Z = 4; **5c**, a = 11.137 (3) Å, b = 19.124 (5) Å, c = 8.686 (3) Å, β = 102.93 (2)°, ρ(calcd) = 1.564 g cm^{-3}, Z = 2; **11**, a = 11.392 (2) Å, b = 19.018 (5) Å, c = 35.610 (8) Å, β = 96.40 (2)°, ρ(calcd) = 1.429 g cm^{-3}, Z = 8. Refinements converged to $R(F)$ = 0.051, 0.042, and 0.048 for 4842, 1975, and 3178 independent observed ($I \geq 3\sigma(I)$) reflections, respectively.

Introduction

We have recently shown that a series of new conformationally rigid chelating ligands could be readily obtained by metal-promoted intramolecular [4 + 2] Diels–Alder cycloadditions of 1-phenyl-3,4-dimethylphosphole (DMPP) and various dienophiles.[2-8]

The DMPP ligand shows distinct chemistry from other phosphorus ligands.[9-13] Its facile reaction with good

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