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Conformation of Heterocycles Controlled by the Existence of Unusual C−H···X Hydrogen Bonds: Syntheses and Structure Determination of Aluminum Aryloxides

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The reactions of $AlMe_3$ in diethyl ether with 1 molar equiv of 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol) (MMBP-H_2), 2,2′-methylenebis(4,6-di-*tert*-butylphenol) (MDBP-H_2), and 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (EDBP-H_2) afford series of four-coordinate monomeric aluminum aryloxides, MeAl(O∼O)(OEt_2), **1**−**3** (**1**, (O∼O) = MMBP; **2**, (O∼O) = MDBP; **3**, (O∼O) = EDBP). In THF, 1 molar equiv of EDBP-H_2 reacts with $AlMe_3$ to provide the THF-coordinated complex MeAl(EDBP)(THF) **4**. However, in the absence of a coordinating solvent, the reaction of EDBP-H_2 with $AlMe_3$ yields the dimeric complex $[MeAl(\mu\text{-EDBP})]_2$ (**5**). Complex **5** further reacts with Et_4NCl, Et_4NBr, and Ph_3PO to afford the corresponding monomeric ionic complex $[Et_4N][MeAl(EDBP)(X)]$ (**6**, X = Cl; **7**, X = Br) and the neutral complex $[MeAl(EDBP)(O{=}PPh_3)]$ (**8**), respectively. Complexes **1**, **2**, **4** and **6**−**8** are subjected to X-ray structure analyses, and the solid state structures reveal that the conformations of the eight-membered heterocycles are governed by the formation of the unusual C−H···X hydrogen bonds.

Introduction

Since the discovery of the C−H···O hydrogen bond by Sutor in 1963,[1] C−H···X hydrogen bonds have been postulated to stabilize the geometries of many organic and inorganic compounds in the solid state.[2] For example, the importance of C−H···O hydrogen bond interactions in aligning molecules of 1,3,5-trinitrobenzene has been examined by Desiraju et al.[3] Compounds 2,2′-methylenebis(4,6-di-*tert*-butylphenol) (MDBP-H_2), 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol (MMBP-H_2), and 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (EDBP-H_2) have the potential to form eight-membered heterocycles in which the phosphorus derivatives of MDBP and EDBP have been reported extensively in the literature as stabilizers for polymeric substances.[4] Our recent interest has been directed toward the preparation and use of aluminum derivatives as Lewis acids for various reactions such as Diels−Alder reactions, ring-opening polymerization, etc.[5] The existence of the C−H···O hydrogen bond in [Al(MMBP)X(S)] and [Al(MDBP)X(S)] systems has been observed.[6] Study about the factors governing the geometry of aluminum in the heterocycles still remains interesting, though the conformations of eight-membered heterocycles have been extensively reviewed by Moore and Anet[7] in which the boat-chair (BC) conformation has been found in the phosphocin ring system.[8]

In order to further explore the geometries and reactivities of aluminum aryloxides, we report herein our results on the syntheses of a series of four-coordinate monomeric or dimeric aluminum aryloxides from the reactions of diaryl alcohol, such as MMBP-H_2, MDBP-H_2, or EDBP-H_2, with aluminum alkyls. In this study, it is interesting to note that the conformations of eight-membered heterocycles as well as the geometries of the aluminum center are controlled by the existence of the unusual C−H···X hydrogen bond.

Results and Discussion

Synthesis and Spectroscopic Studies. The reactions of $AlMe_3$ with 1 equivalent of 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol) (MMBP-H_2) or 2,2′-methylenebis(4,6-di-*tert*-butylphenol) (MDBP-H_2) in diethyl ether afford monomeric four-coordinated compounds **1** and **2** in moderate to high yield as shown in Scheme 1. For compound **1**, the ^1H NMR spectrum shows one set of resonances for the methyl and *tert*-butyl substituents on the phenyl rings at δ 2.25 and 1.37 ppm, respectively. Similarly, one set of two resonances for the two hydrogens on both aryl moieties was observed at δ 7.06 and 6.91 ppm. These observations suggest that these two aryl moieties are equivalent. However, the two hydrogens in the bridging methylene (C-7) are observed to be magneticaly nonequivalent with the ^1H chemical shifts at δ 4.05 and 3.37 ppm, and the $^2J_{HH}$ value of 13.6 Hz is similar to the one reported for the trivalent phosphorus compounds of MDBP. To account for this observation, among the five different conformations as shown in Figure 1, only the BC conformation results with the nonequivalence of the two methylene hydrogens. Nonequivalent

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10.1021/ic9909835 CCC: $19.00

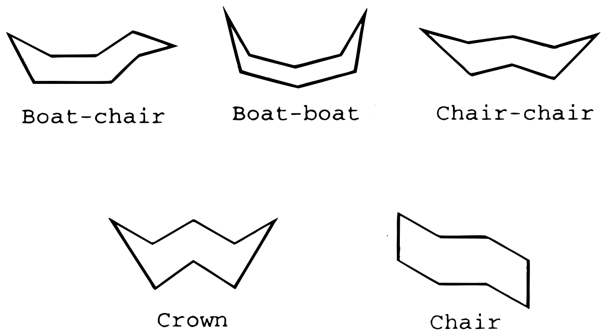
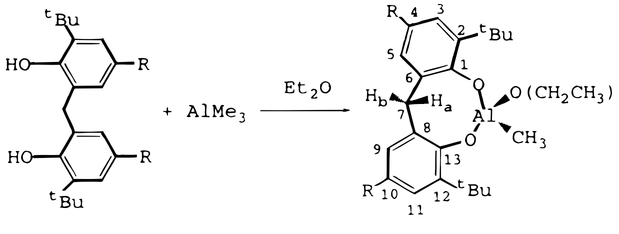


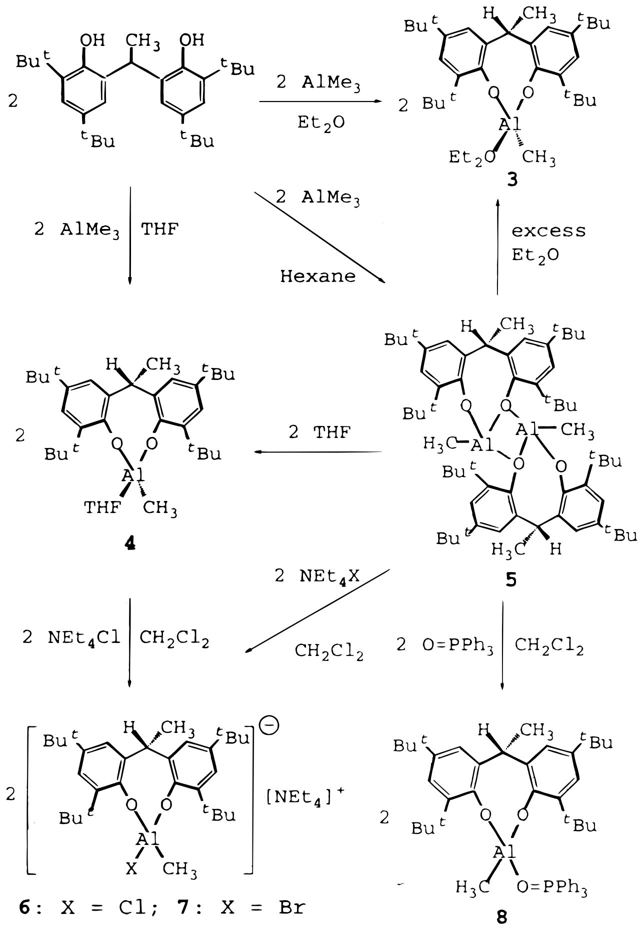
Figure 1. Five possible conformations of eight-membered rings.

Scheme 1



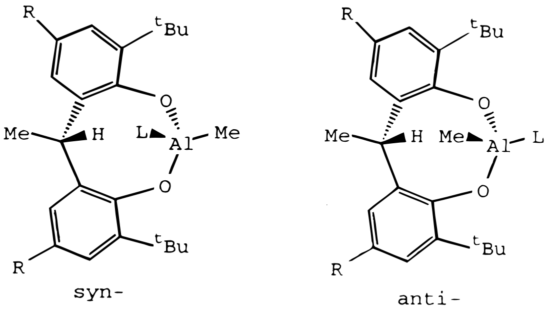
1: R = CH_3
2: R = Bu^t

Scheme 2



6: X = Cl; **7**: X = Br

Chart 1



methylene hydrogens are observed also for compound **2** with the ^1H NMR chemical shifts at δ 4.08 and 3.43 ppm. In order to distinguish the two methylene hydrogens and the two aryl hydrogens (H(3) and H(5)) spectroscopically, a nuclear Overhauser effect difference spectroscopy experiment was performed on compound **2** by irradiating the 3.43 ppm resonance. The NOE spectrum does show positive hydrogen signals at δ 7.28 and 4.08 ppm indicating that the hydrogens with the chemical shift at δ 7.28 ppm are located in closer proximity to the hydrogen atom with the chemical shift at δ 3.43 ppm. On the basis of the labeled structure (Scheme 1), the peak at δ 3.43 is assigned to the methylene hydrogen H_b which is distanced away from the metal center but is close to H(5) and H(9) with the resonance at δ 7.28 ppm. Accordingly, the peak at δ 4.08 ppm is assigned to H_a and the peak at δ 7.13 ppm to H(3) and H(11).

2,2′-Ethylidenebis(4,6-di-*tert*-butylphenol) (EDBP-H_2) reacts with $AlMe_3$ in coordinating solvent such as Et_2O or THF to afford a solvent-coordinated monomeric compound [Al(EDBP)(Me)(Et_2O)] (**3**) or [Al(EDBP)(Me)(THF)] (**4**) (Scheme 2). However, the reactions of EDBP-H_2 with $AlMe_3$ in noncoordinating solvents like hexane give the dimeric complex [Al(μ-EDBP)(Me)]$_2$ (**5**). It is found that compound **5** is slowly dissolved in Et_2O to give compound **3**, whereas **5** reacts rapidly with 2 molar equiv of THF to yield the monomeric compound **4**. On treatment of compound **5** with 2 molar equiv of Et_4NCl, Et_4NBr, or Ph_3PO in CH_2Cl_2, the corresponding monomeric ionic compound [Et_4N][Al(EDBP)(Me)X] (**6**, X = Cl; **7**, X = Br) or the neutral compound [Al(EDBP)(Me)($OPPh_3$)] (**8**) is obtained. Compounds **3**−**8** are moisture sensitive, and their ^1H NMR data are listed in Table 1. The ^1H NMR data of **3**−**5** reveal only one set of peaks. However, two sets of resonances are observed for compounds **6**, **7**, and **8** with a relative ratio of 2:1 for **6** and 3:1 for **7** and **8**, indicating the presence of two geometric isomers for compounds **6**, **7**, and **8** (shown in Chart 1).

Molecular Structures of 1 and 2. The molecular structures of **1** and **2** are shown in Figure 2. The selected bond distances and bond angles of **1** and **2** are summarized in Table 2. Compound **1** crystallizes in the space group *Pbca*, and it is found that each asymmetric unit contains two independent molecules. The geometry around Al for compound **1** is distorted tetrahedral with the averaged bond distances of Al−O(1) (phenoxy) at 1.708(5) Å, Al−O(2) (phenoxy) at 1.701(5) Å, Al−O(3) (ethereal) at 1.882(5) Å, and Al−C(31) at 1.926(7) Å, which are all compatible with the bond lengths observed for four-coordinate aluminum steric bulky phenoxide derivatives.[9] The ether molecule coordinated on Al is disordered with two positions for each carbon atom. The site occupancy is refined as a fraction of 0.5 for each position.

It is worth noting that one of the methylene hydrogens H(7A), which is located from the successive Fourier calculations, is

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(9) (a) Shreve, A. P.; Mulhaupt, R.; Fultz, W.; Calabrese, J.; Robbins, W.; Ittel, S. D. *Organometallics* **1988**, *7*, 409. (b) Healy, W. D.; Wierda, D. A.; Barron, A. R. *Organometallics* **1988**, *7*, 2543. (c) Healy, M. D.; Ziller, J. W.; Barron, A. R. *J. Am. Chem. Soc.* **1990**, *112*, 2949. (d) Schulz, S.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *J. Chem. Soc., Dalton Trans.* **1995**, 177.

Table 1. ^{1}H NMR Data (ppm) for **3**−**8**

	3	**4**	**5**	**6**	**7**	**8**
Ph*H*	7.09 (d)	7.10 (d)	7.12−7.42 (m)	6.99 (d)	7.00 (d)	7.05 (d)
				7.02 (d)	7.03 (d)	7.00 (d)
	7.37 (d)	7.37 (d)		7.23 (d)	7.25 (d)	7.28 (d)
				7.28 (d)	7.29 (d)	7.35 (d)
H (bridging)	4.61 (q)	4.56 (q)	4.79 (q)	4.63 (q)	4.62 (q)	4.92 (q)
				5.10 (q)	5.24 (q)	4.54 (q)
CH_3 (bridging)	1.64 (d)	1.64 (d)	1.73 (d)	1.54 (d)	1.56 (d)	1.43 (d)
				1.57 (d)	1.58 (d)	1.67 (d)
CH_3 (Bu^t)	1.29 (s)	1.30 (s)	1.23 (s)	1.26 (s)	1.27 (s)	1.20 (s)
			1.26 (s)	1.27 (s)	1.28 (s)	1.28 (s)
	1.37 (s)	1.38 (s)	1.34 (s)	1.36 (s)	1.37 (s)	1.37 (s)
			1.43 (s)	1.42 (s)	1.44 (s)	
CH_3 (AlMe)	−0.59 (s)	−0.61 (s)	−0.27 (s)	−0.66 (s)	−0.54 (s)	−0.87 (s)
				−0.63 (s)	−0.51 (s)	−0.82 (s)

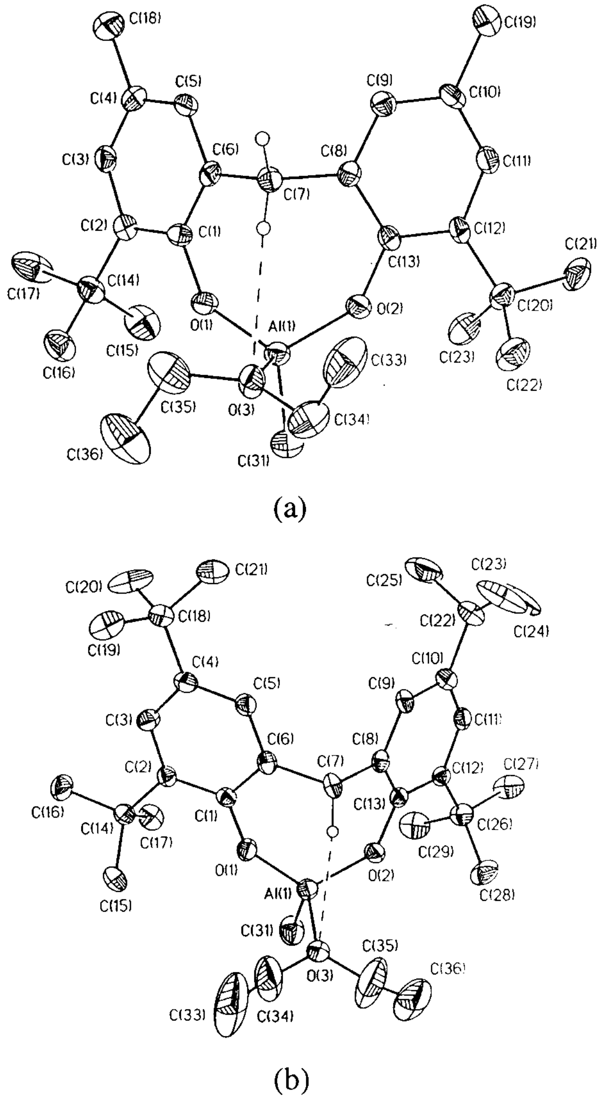

Figure 2. Molecular structures of (a) [AlMe(MMBP)(Et_2O)] **1** and (b) [AlMe(MDBP)(Et_2O)] **2**. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for **1** and **2**

	1	**2**
Al(1)−O(1)	1.708(5)	1.701(5)
Al(1)−O(2)	1.701(5)	1.714(5)
Al(1)−O(3)	1.882(5)	1.888(6)
Al(1)−C(31)	1.926(7)	1.933(8)
Al(2)−O(4)	1.705(4)	1.712(6)
Al(2)−O(5)	1.706(5)	1.706(5)
Al(2)−O(6)	1.892(5)	1.880(7)
Al(2)−C(71)	1.930(7)	1.924(8)
O(1)−Al(1)−O(2)	117.0(2)	116.4(3)
O(1)−Al(1)−O(3)	101.4(2)	102.3(3)
O(2)−Al(1)−O(3)	102.9(2)	101.5(3)
O(1)−Al(1)−C(31)	114.3(3)	113.8(3)
O(2)−Al(1)−C(31)	112.4(3)	114.8(3)
O(3)−Al(1)−C(31)	106.9(3)	105.6(3)
Al(1)−O(1)−C(1)	144.3(4)	146.4(5)
Al(1)−O(2)−C(13)	144.0(4)	140.4(4)
Al(1)−O(3)−C(34)	121.7(4)	124.3(7)
Al(1)−O(3)−C(35)	121.7(5)	123.0(9)
O(4)−Al(2)−O(5)	114.7(2)	116.8(3)
O(4)−Al(2)−O(6)	103.5(2)	104.0(3)
O(5)−Al(2)−O(6)	104.1(2)	100.6(3)
O(4)−Al(2)−C(71)	112.9(3)	112.8(3)
O(5)−Al(2)−C(71)	114.5(3)	114.6(3)
O(6)−Al(2)−C(71)	105.6(3)	105.9(4)
Al(2)−O(4)−C(41)	144.9(4)	141.6(4)
Al(2)−O(5)−C(53)	139.7(4)	144.8(5)

bending toward the ethereal oxygen atom with a relatively short H(7A)···O(3) distance of 2.419 Å, and H(47A)···O(6) at 2.359 Å for another molecule. These distances are substantially shorter than the van der Waals distance of 2.77 Å for the O and H distance.[10] The unusually short H···O distance along with the nearly linear C(7)−H(7A)···O(3) angle at 167.8° and the C(47)−H(47A)···O(6) angle at 165.1° led to the proposal for the existence of a C−H···O hydrogen bond. In addition, the Al(1), O(3), C(31), C(7), H(7A), and H(7B) atoms are nearly coplanar with a deviation from the plane at 0.031 Å. This coplanarity is indicative of the equivalence of two aryl moieties, which is consistent with the observation based on the ^{1}H NMR studies.

For compound **2**, which differs from compound **1** by replacing the methyl substituents at the 4-positions on both aryl rings with the *tert*-butyl substituents, each asymmetric unit contains two independent molecules and also a solvated diethyl ether molecule. The geometry around Al is nearly identical to that for **1** with the averaged Al(1)−O(1) distance of 1.701(5) Å, the averaged Al(1)−O(2) distance of 1.714(5) Å, the averaged Al(1)−O(3) distance of 1.888(6) Å, and the averaged Al(1)−C(31) distance of 1.933(8) Å similar to the values for compound **1**.

Molecular Structures of 4, 6, 7, and 8. The molecular structures of compounds **4**, **6**, **7**, and **8** are shown in Figure 3, and selected bond distances and bond angles are listed in Table 3. All of these compounds are four-coordinate monomeric

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(10) (a) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960. (b) Emsley, J. *The Elements*; Oxford University Press: Oxford, 1989.

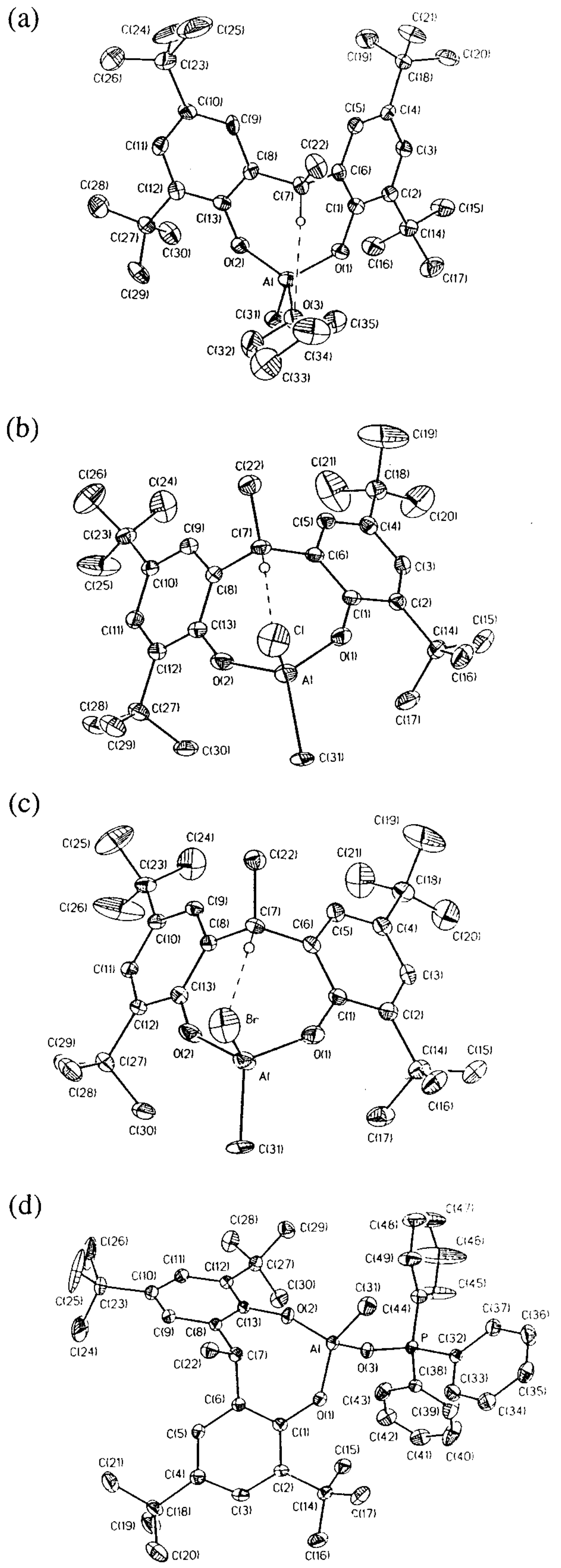

Figure 3. ORTEP representations of (a) [AlMe(EDBP)(THF)] **4**, (b) [AlMe(EDBP)Cl]$^-$ **6**, (c) [AlMe(EDBP)Br]$^-$ **7**, and (d) [AlMe(EDBP)(OPPh$_3$)] **8**.

species that differ only with the attached Lewis bases L (L = THF (**4**), Cl$^-$ (**6**), Br$^-$ (**7**), or OPPh$_3$ (**8**)). As illustrated in Chart 1, there are two possible geometric isomers for these compounds. Both the steric and electronic effects of the substituents on Al may affect the existence of geometric isomers. The observation of the syn form only for **4** both in solution and in the solid state suggests that the syn form is more stable due to the steric hindrance of *tert*-butyl groups of phenyl rings or the existence of a C−H···O hydrogen bond in which the H(7A)−O distance of 2.344 Å and C(7)−H(7A)−O(3) angle of 176.6° are observed. Though both syn and anti isomers are detected in the NMR spectroscopic studies for **6**, **7**, and **8**, only the syn form for **6** and **7**[11] but the anti form for **8** are observed in the solid state. The observation of the anti form for **8** in the solid state illustrates that the steric effect does not play the major role. Therefore, the observation of the syn form for **6** and **7** in the solid state can only be explained by the existence of a C−H···X hydrogen bond. In **6**, an H(7a)−Cl distance of 2.735 Å and a C(7)−H(7a)−Cl angle of 177.8° are observed. A H(7a)−Br distance of 2.925 Å and a C(7)−H(7a)−Br angle of 171.6° suggest the existence of a C−H···Br hydrogen bond in **7**.[12] Among the five different conformations of eight-membered heterocycles reported, the BC conformation is considered to be the most stable form in cyclooctane. The observation of a distorted BC conformation (shown in Figure 4) in which Al is coplanar with C(1)C(13)O(1)O(2) in **4**, **6**, and **7** may also result from the existence of a C−H···X hydrogen bond. In compound **7**, it has been found that the methyl position attached on Al is

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for **4** and **6**−**8**

	4	**6**	**7**	**8**
Al−O(1)	1.715(6)	1.723(4)	1.721(5)	1.737(4)
Al−O(2)	1.713(5)	1.734(5)	1.729(5)	1.721(4)
Al−X[a]	1.864(6)	2.158(3)	2.350(2)	1.818(4)
Al−C(31)	1.924(8)	1.978(7)	1.893(32)	1.938(7)
P−O(3)				1.513(4)
O(1)−Al−O(2)	116.5(3)	111.3(2)	112.2(3)	113.2(2)
O(1)−Al−X[a]	99.6(3)	109.2(2)	109.0(2)	103.1(2)
O(2)−Al−X[a]	103.8(3)	106.7(2)	106.7(2)	101.4(2)
O(1)−Al−C(31)	117.2(3)	111.0(2)	112.1(9)	113.7(2)
O(2)−Al−C(31)	111.1(3)	110.2(3)	111.0(9)	114.5(2)
X−Al−C(31)	106.4(3)	108.3(2)	105.5(9)	109.4(2)
Al−O(1)−C(1)	136.5(5)	143.7(4)	143.0(5)	134.3(3)
Al−O(2)−C(13)	148.3(5)	145.5(4)	145.0(5)	146.8(4)
Al−O(3)−P				146.9(3)

[a] X = O(3) for **4**, Cl for **6**, Br for **7**, and O(3) for **8**.

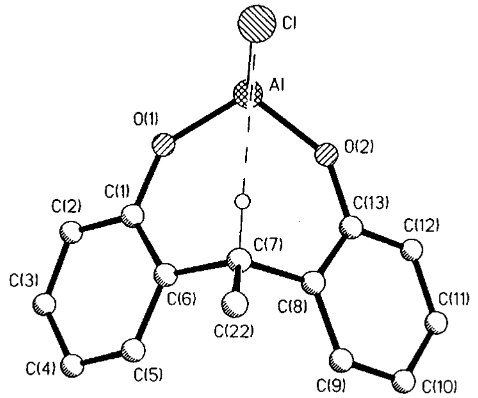

Figure 4. Coplanarity of AlO(1)O(2)C(13)C(1) in **6** results from the C−H···Cl interaction. The mean deviation for plane AlO(1)O(2)C(13)C(1) is only 0.0364 Å.

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(11) The crystal structure of **7** shows that it is a mixture of 90% [Et$_4$N][Al(EDBP)(Me)Br] and 10% [Et$_4$N][Al(EDBP)Br$_2$].

(12) The summation of van der Waals radiis for H and Cl and for H and Br is 3.01 and 3.15 Å respectively.

disordered with respect to methyl/bromide occupancy and the site occupancy is refined as a fraction of 0.9 for Me and 0.1 for Br. However, this does not affect the C−H···Br distance.

Conclusion

Series of sterically hindered aluminum bis-aryloxides are synthesized in which the bis-aryloxides form eight-membered heterocycles of distorted BC conformation with an aluminum metal center. The solid state structures show that one of the bridging methylene hydrogens in the MMBP ligand or the bridging ethylidene hydrogen in the EDBP ligand directs geometrically toward the coordinated ligand X with the formation of C−H···X hydrogen bonding.

Experimental Section

General. All experiments were carried out under a dry nitrogen atmosphere. Solvents were dried by refluxing for at least 24 h over sodium/benzophenone (toluene, hexane, diethyl ether, tetrahydrofuran) or phosphorus pentoxide (CH_2Cl_2) and freshly distilled prior to use. Deuterated solvents (Aldrich) were dried over molecular sieves. Ph_3PO, $AlMe_3$ (2.0 M in toluene), Et_4NCl, Et_4NBr, 2,4-di-*tert*-butylphenol, 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol), and 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol) were purchased from Aldrich and used without further purification. 2,2′-Methylenebis(4,6-di-*tert*-butylphenol) was prepared according to literature procedure.[13] Melting points were determined with a Buchi 535 digital melting point apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300 (300 MHz) or a Gemini-200 (200 MHz) spectrometer with chemical shifts given in parts per million with TMS as the internal standard. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. Infrared spectra were obtained from a Bruker Equinox 55 spectrometer.

(Diethyl ether)methyl{2,2′-methylenebis(4-methyl-6-*tert*-butylphenato)} aluminum(III) (1). To an ice cold solution (0 °C) of 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol) (0.340 g, 1.0 mmol) in diethyl ether (10 mL) was added slowly an $AlMe_3$ (0.60 mL, 2.0 M in toluene, 1.2 mmol) solution. After all of the solution was added, the mixture was stirred for 2.5 h and then dried in vacuo. The residue was extracted with 15 mL of Et_2O. The extract was then concentrated to ca. 5 mL and cooled to −20 °C to furnish colorless crystals. Yield: 0.35 g (78%). Anal. Calcd for $C_{28}H_{43}AlO_3$: C, 73.97; H, 9.53. Found: C, 74.02; H, 9.47. ^1H NMR ($CDCl_3$, ppm): δ 7.06 (d, 2H, Ph, $J_{H-H} = 2.2$ Hz), 6.91 (d, 2H, Ph, $J_{H-H} = 2.2$ Hz), 4.32 (br, 4H, $OC\mathit{H}_2CH_3$), 4.05 (d, 1H, CH_2, $J_{H-H} = 13.6$ Hz), 3.37 (d, 2H, CH_2, $J_{H-H} = 13.6$ Hz), 2.25 (s, 6H, CH_3), 1.40 (t, 6H, $OCH_2C\mathit{H}_3$), 1.37 (s, 18H, $C(CH_3)_3$), −0.56 (s, 3H, $AlCH_3$). IR (KBr, cm^{-1}): 2951.1 (s), 2915.9 (s), 2868.3 (m), 1478.0 (s), 1440.9 (s), 1388.6 (m), 1309.1 (s), 1291.6 (m), 1280.6 (s), 1252.4 (m), 1197.5 (m), 1020.3 (m), 928.0 (m).

(Diethyl ether)methyl{2,2′-methylenebis(4,6-di-*tert*-butylphenato)}-aluminum(III) (2). To an ice cold solution (0 °C) of 2,2′-methylenebis-(4,6-di-*tert*-butylphenol) (0.424 g, 1.0 mmol) in diethyl ether (10 mL) was added slowly an $AlMe_3$ (0.60 mL, 2.0 M in toluene, 1.2 mmol) solutions. The mixture was stirred for 2.5 h and then dried in vacuo. The residue was extracted with 15 mL of Et_2O and filtered. The filtrate was then concentrated to ca. 5 mL and cooled to −20 °C to furnish colorless crystals. Yield: 0.51 g (88%). Anal. Calcd for $C_{34}H_{55}AlO_3\cdot{}^1/_2(C_4H_{10}O)$: C, 75.09; H, 10.50. Found: C, 74.43; H, 10.34. ^1H NMR ($CDCl_3$, ppm): δ 7.28 (d, 2H, Ph, $J_{H-H} = 2.6$ Hz), 7.13 (d, 2H, Ph, $J_{H-H} = 2.6$ Hz), 4.30 (br, 4H, $OC\mathit{H}_2CH_3$), 4.08 (d, 1H, CH_2, $J_{H-H} = 13.6$ Hz), 3.43 (d, 1H, CH_2, $J_{H-H} = 13.6$ Hz), 1.40 (br, 6H,$OCH_2C\mathit{H}_3$), 1.38 (s, 18H, $C(CH_3)_3$), 1.30 (s, 18H, $C(CH_3)_3$), −0.58 (s, 3H, $AlCH_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 152.44, 139.81, 137.45, 130.04, 124.94, 121.84 (Ph), 67.21($O\mathit{C}H_2CH_3$), 33.52 ($\mathit{C}H_2$), 35.07, 34.06, 31.73, 29.98 (*t*-Bu), 14.0 ($OCH_2\mathit{C}H_3$), −12,48 ($Al\mathit{C}H_3$). IR (KBr, cm^{-1}): 2945.9 (s), 2870.5 (s), 1476.2 (s), 1414.4 (s), 1389.7 (m), 1361.4 (s), 1308.2 (s), 1239.1 (s), 1203.2 (m), 1176.5 (m), 1151.6 (m), 1136.9 (m), 1093.8 (m), 1021.3 (m), 928.0 (m).

Table 4. Crystallographic Data for **1** and **2**

	1	**2**·0.5Et_2O
formula	$C_{28}H_{43}AlO_3$	$C_{36}H_{60}AlO_{3.5}$
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/n$
a (Å)	24.657(2)	15.948(1)
b (Å)	14.180(1)	19.184(2)
c (Å)	32.540(3)	25.268(2)
α (deg)	90	90
β (deg)	90	100.69(2)
γ (deg)	90	90
V (Å^3)	11377(2)	7596.5(11)
Z	16	8
D_{calcd}, $Mg\cdot m^{-3}$	1.062	1.007
λ (Mo Kα) (Å)	0.71073	0.71073
abs coeff (mm^{-1})	0.095	0.084
2θ range (deg)	4−48°	3.5−48°
scan type	$\theta-2\theta$	$\theta-2\theta$
rflns collected	8804	12215
obsd rflns	3581 ($F > 4.0\sigma(F)$)	4398 ($F > 5.0\sigma(F)$)
no. of refined params	573	730
R^a for signif rflns	0.0683	0.0747
$R_w{}^b$ for signif rflns	0.0594	0.0753
GOF^c	1.80	2.09

[a] $R = |\Sigma(|F_o - F_c|)/\Sigma|F_o||$. [b] $R_w = \Sigma\sqrt{w}(|F_o - F_c|)/\Sigma\sqrt{w}|F_o||$; $w = 1/[\sigma^2(F) + c(F^2)]$; $c = 0.002$ for **1**; $c = 0.0005$ for **2**. [c] GOF = $[\Sigma w(|F_o| - |F_c|)^2/(N_{rflns} - N_{params})]^{1/2}$.

(Diethyl ether)methyl{2,2′-ethylidenebis(4,6-di-*tert*-butylphenato)}-aluminum(III) (3). To an ice cold solution (0 °C) of 2,2′-ethylidenebis-(4,6-di-*tert*-butylphenol) (0.876 g, 2.0 mmol) in diethyl ether (30 mL) was added slowly an $AlMe_3$ (1.2 mL, 2.0 M in toluene, 2.4 mmol) solution. The mixture was stirred for 2.5 h and then dried in vacuo. The residue was extracted with 25 mL of diethyl ether and filtered. The filtrate was then concentrated to ca. 10 mL and cooled to −20 °C to furnish colorless crystals. Yield: 1.03 g (84%). Anal. Calcd for $C_{39}H_{67}AlO_3\cdot{}^1/_2(C_4H_{10}O)$: C, 75.99, H, 9.82. Found: C, 74.52; H, 10.54. ^1H NMR ($CDCl_3$, ppm): δ 7.37 (d, 2H, Ph, $J = 2.4$ Hz), 7.09 (d, 2H, Ph, $J = 2.4$ Hz); 4.61 (q, 1H, $C\mathit{H}(CH_3)$, $J = 7.4$ Hz); 4.28 (m, 4H, $OC\mathit{H}_2CH_3$); 1.64 (d, 3H, $CH(C\mathit{H}_3)$, $J = 7.4$ Hz); 1.20 (m, 6H, $OCH_2C\mathit{H}_3$); 1.37 (s, 18H, $C(CH_3)_3$); 1.29 (s, 18H, $C(CH_3)_3$); −0.59 (s, 3H, $AlCH_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 152.15, 139.72, 137.08, 134.30, 121.23, 121.04 (Ph); 66.96 ($O\mathit{C}H_2CH_3$); 35.07, 34.23, 31.69, 29.93 (*t*-Bu); 29.79 ($\mathit{C}H(CH_3)$); 21.97 ($CH(\mathit{C}H_3)$); 13.92 ($OCH_2\mathit{C}H_3$); −12.79 ($AlCH_3$). IR (KBr, cm^{-1}): 2963.4 (s), 2904.7 (m), 2870.2 (m), 1477.7 (s), 1443.2 (s), 1389.4 (m), 1361.0 (m), 1347.7 (m), 1303.8 (s), 1269.0 (m), 1238.5 (m), 1202.4 (m), 1019.2 (m), 909.4 (m), 879.0 (s).

(Tetrahydrofuran)methyl{2,2′-ethylidenebis(4,6-di-*tert*-butylphenato)}aluminum (III) (4). To an ice cold solution (0 °C) of 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (0.876 g, 2.0 mmol) in THF (30 mL) was slowly added an $AlMe_3$ (1.2 mL, 2.0 M in toluene, 2.4 mmol) solution. The mixture was stirred for 2.5 h and then dried in vacuo. The residue was extracted with 20 mL of toluene and filtered. The filtrate was then concentrated to ca. 10 mL and cooled to −20 °C to furnish colorless crystals. Yield: 0.89 g (81%). Anal. Calcd for $C_{35}H_{55}AlO_3$: C, 76.32; H, 10.06. Found: C, 75.89; H, 9.50. ^1H NMR ($CDCl_3$, ppm): δ 7.30 (d, 2H, Ph, $J = 2.6$ Hz), 7.10 (d, 2H, Ph, $J = 2.6$ Hz); 4.56 (q, 1H, $C\mathit{H}(CH_3)$, $J = 7.2$ Hz); 4.36 (m, 4H, $OC\mathit{H}_2CH_2$); 2.13 (m, 4H, $OCH_2C\mathit{H}_2$); 1.64 (d, 3H, $CH(C\mathit{H}_3)$, $J = 7.2$ Hz); 1.38 (s, 18H, $C(CH_3)_3$); 1.30 (s, 18H, $C(CH_3)_3$); −0.61 (s, 3H, $AlCH_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 152.17, 139.45, 136.79, 134.03, 121.12, 120.87 (aromatics), 71.63 ($O\mathit{C}H_2CH_2$), 30.20 (CH_2), 35.28, 34.40, 31.87, 30.11 (*t*-Bu), 30.20 ($\mathit{C}H(CH_3)$), 25.43 ($OCH_2\mathit{C}H_2$), 22.38 ($CH(\mathit{C}H_3)$), −13.69 ($AlCH_3$). IR (KBr, cm^{-1}): 2963.7 (br, s), 2871.8 (m), 1474.3 (s), 1443.5 (s), 1361.2 (m), 1348.1 (m), 1303.8 (s), 1271.0 (m), 1239.4 (m), 1199.0 (m), 927.3 (m), 909.1 (m).

Bis[methyl{2,2′-ethylidenebis(4,6-di-*tert*-butylphenato)}aluminum-(III)] (5). To an ice cold solution (0 °C) of 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) (0.876 g, 2.0 mmol) in hexane (30 mL) was slowly

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(13) Odorisio, P. A.; Pastor, S. D.; Spivack, J. D.; Bini, D.; Rodebaugh, R. K. *Phosphorus Sulfur Relat. Elem.* **1984**, *19*, 285.

Table 5. Crystallographic Data for **4** and **6**−**8**

	4$\cdot$0.5C_7H_8	**6**	**7**	**8**
formula	$C_{38.5}H_{59}AlO_3$	$C_{39}H_{67}AlClNO_2$	$C_{38.9}H_{66.7}AlBr_{1.1}NO_2$	$C_{56}H_{70}AlO_3P$
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	9.912(2)	10.163(2)	10.153(2)	14.275(2)
b (Å)	24.680(3)	22.164(2)	22.052(3)	16.756(2)
c (Å)	16.168(2)	18.283(2)	18.543(2)	21.909(3)
α (deg)	90	90	90	90
β (deg)	103.80 (2)	97.00(2)	96.72(1)	97.79(2)
γ (deg)	90	90	90	90
V (Å^3)	3841.0(10)	4087.4(10)	4123.1(10)	5192.1(12)
Z	4	4	4	4
D_{calcd}, Mg$\cdot$m^{-3}	1.032	1.047	1.120	1.086
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
abs coeff (mm^{-1})	0.084	0.145	1.145	0.110
2θ range (deg)	4.0−48°	3.5−48.0°	2.0−50.0°	3.5−45.0°
scan type	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$
rflns collected	6339	6696	7583	7010
obsd rflns	2055 ($F > 4.0\sigma(F)$)	2779 ($F > 4.0\sigma(F)$)	2575 ($F > 5.0\sigma(F)$)	3589 ($F > 4.0\sigma(F)$)
no. of refined params	380	397	406	550
R^a for signif rflns	0.0744	0.0709	0.0583	0.0617
$R_w{}^b$ for signif rflns	0.0620	0.0700	0.0582	0.0653
GOF^c	1.73	1.77	1.63	1.23

^{a} $R = |\Sigma(|F_o - F_c|)/\Sigma|F_o||$. ^{b} $R_w = \Sigma\sqrt{w}(|F_o - F_c|)/\Sigma\sqrt{w}|F_o||$; $w = 1/[\sigma^2(F) + c(F^2)]$; $c = 0.002$ for **4**; $c = 0.0006$ for **6**; $c = 0.0005$ for **7**; $c = 0.002$ for **8**. ^{c} GOF $= [\Sigma w(|F_o| - |F_c|)^2/(N_{rflns} - N_{params})]^{1/2}$.

added an $AlMe_3$ (1.2 mL, 2.0 M in toluene, 2.4 mmol) solution. The mixture was stirred for 2.5 h and then dried in vacuo. The residue was dissolved in hot toluene (20 mL, 85 °C). The hot toluene solution was allowed to cool to ambient temperature, affording a colorless crystal product. Yield: 0.80 g (84%). Anal. Calcd for $C_{31}H_{47}AlO_2$: C,77.78; H, 9.90. Found: C, 77.44; H, 10.02. ^{1}H NMR ($CDCl_3$, ppm): δ 7.12−7.42 (m, 4H, Ph); 4.79 (q, 1H, C*H*(CH_3), $J = 6.8$ Hz), 1.73 (d, 3H, CH(C*H*$_3$), $J = 6.8$ Hz), 1.43, 1.34, 1.26, 1.23 (s, 36H, C(CH_3)$_3$), −0.27 (s, 3H, $AlCH_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 150.88, 146.97, 143.44, 140.36, 139.95, 138.07, 136.59, 133.94, 124.43, 124.10, 121.61, 119.93 (Ph), 35.98, 34.86, 34.43, 34.37, 32.75, 31.77, 31.18, 30.49 (*t*-Bu), 32.37 (*C*H(CH_3)), 22.09 (CH(*C*H$_3$)), −9.77 ($AlCH_3$). IR (KBr, cm^{-1}): 2960.7 (br, s), 2905.9 (m), 2870.8 (m), 1476.2 (s), 1443.5 (s), 1361.9 (m), 1321.6 (m), 1309.7 (s), 1280.7 (m), 1239.4 (m), 1203.9 (m), 1098.9 (m), 904.5 (m).

Tetraethylammonium chloromethyl{2,2′-ethylidenebis(4,6-di-*tert*-butylphenato)}aluminum(III) (6). To a rapidly stirred solution of **5** (0.96 g, 1.0 mmol) in CH_2Cl_2 (20 mL) was added a solution of tetraethylammonium chloride (0.33 g, 2.0 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred at 27 °C for 12 h, and the volatile materials were removed under vacuum to produce a white powder. The residue was extracted with THF (20 mL), and hexane (20 mL) was added slowly. Colorless crystals were obtained after 24 h. Yield: 1.17 g (91%). Mp: 209−212 °C dec. Anal. Calcd for $C_{39}H_{67}AlClNO_2$: N, 2.17; C, 72.69; H, 10.48. Found: N, 2.09; C, 72.13; H, 10.32. ^{1}H NMR ($CDCl_3$, ppm): δ 7.28, 7.23, 7.02, 6.99 (d, 4H, Ph); 5.10, 4.63 (q, 1H, C*H*(CH_3), $J = 7.2$ Hz); 2.86 (q, 8H, NC*H*$_2$CH$_3$, $J = 7.2$ Hz); 1.57, 1.54 (d, 3H, CH(C*H*$_3$), $J = 7.2$ Hz); 1.42, 1.36, 1.27, 1.26 (s, 36H, C(CH_3)$_3$); 1.06 (t, 12H, NCH$_2$C*H*$_3$, $J = 7.2$ Hz); −0.63, −0.66 (s, 3H, $AlCH_3$). IR (KBr, cm^{-1}): 2958.6 (s), 2905.5 (m), 2867.3 (m), 1480.3 (s), 1441.9 (s), 1415.8 (m), 1391.1 (m), 1357.5 (m), 1308.4 (s), 1279.3 (m), 1237.1 (m), 1173.8 (m), 999.4 (m), 926.8 (m).

Tetraethylammonium bromomethyl{2,2′-ethylidenebis(4,6-di-*tert*-butylphenato)}aluminum(III) (7). To a rapidly stirred solution of **3** (1.66 g, 3.0 mmol) in CH_2Cl_2 (20 mL) was added a solution of tetraethylammonium bromide (0.63 g, 3.0 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred at 27 °C for 24 h, and the volatile materials were removed under vacuum to produce a white powder. The residue was extracted with CH_2Cl_2 (20 mL), and hexane (40 mL) was added slowly. Colorless crystals were obtained after 24 h. Yield: 1.80 g (86%). Mp: 178 °C dec. Anal. Calcd for $C_{39}H_{67}AlBrNO_2$: N, 2.03; C, 68.00; H, 9.80. Found: N, 2.02; C, 68.83; H, 9.64. ^{1}H NMR ($CDCl_3$, ppm): δ 7.29, 7.25, 7.03, 7.00 (d, 4H, Ph); 5.24, 4.62 (q, 1H, C*H*(CH_3), $J = 7.2$ Hz); 3.16 (q, 8H, NC*H*$_2$CH$_3$, $J = 7.2$ Hz); 1.58, 1.56 (d, 3H, CH(C*H*$_3$), $J = 7.2$ Hz); 1.44, 1.37, 1.28, 1.27 (s, 36H, C(CH_3)$_3$); 1.23 (t, 12H, NCH$_2$C*H*$_3$, $J = 7.2$ Hz); −0.51, −0.54 (s, 3H, $AlCH_3$). IR (KBr, cm^{-1}): 2962 (s), 2862 (m), 1474 (s), 1438 (s), 1295 (s), 880 (m), 643 (m).

(Triphenylphosphine oxide)methyl{2,2′-ethylidenebis(4,6-di-*tert*-butylphenato)}aluminum(III) (8). A solution of triphenylphosphine oxide (0.56 g, 2.0 mmol) in CH_2Cl_2 (20 mL) was added to a rapidly stirred solution of **5** (0.96 g, 1.0 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at 27 °C for 2 h, and the volatile materials were removed under vacuum. The residue was extracted with hot toluene (40 mL, 85 °C), and the filtrate was allowed to cool to 27 °C, affording colorless crystals. Yield: 1.36 g (84%). Anal. Calcd for $C_{49}H_{62}AlO_3P\cdot{}^1/_2C_7H_8$; C, 78.52; H, 8.28. Found: C, 78.42; H, 8.29. ^{1}H NMR ($CDCl_3$, ppm): δ 7.73−7.49 (m, 15H, Ph), 7.35, 7.28, 7.05, 7.00 (d, 4H, Ph), 4.92, 4.54 (q, 1H, C*H*(CH_3), $J = 7.2$ Hz), 1.67, 1.43 (d, 3H, CH(C*H*$_3$), $J = 7.2$ Hz), 1.37, 1.28, 1.20 (s, 36H, C(CH_3)$_3$), −0.82, −0.87 (s, 3H, $AlCH_3$). IR (KBr, cm^{-1}): 2953 (s), 2899.1 (m), 2864.5 (m), 1589.7 (m), 1474.2 (s), 1457.9 (m), 1439.0 (s), 1352.0 (m), 1312.3 (m), 1153.7 (s), 1124.0 (m), 1093.9 (s), 879.1 (s), 864.3 (s).

X-ray Crystallographic Studies. Suitable crystals of **1**, **2**, **4**, and **6**−**8** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Siemens P4 diffractometer. The crystallographic data were collected using a $\theta-2\theta$ scan mode with Mo Kα radiation. Cell constants were obtained by least-squares analysis on positions of at least 25 randomly selected reflections in the 2θ range of 4−28°. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct methods using a Siemens SHELXTL PLUS package.[14] All non-H atoms and hydrogen atoms attaching to the carbon atom bridging two phenyl rings were located from successive Fourier maps. Other H atoms were refined using a riding model.[15] Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. The crystallographic data of **1** and **2** and of **4** and **6**−**8** are listed in Table 4 and Table 5, respectively.

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(14) Sheldrick, G. M. *SHELXTL PLUS User's Manual*, revision 4.1; Nicolet XRD Corporation: Madison, WI, 1991.

(15) Hydrogen atoms were allowed to ride on carbons or oxygens in their idealized positions and held fixed with the C−H distances of 0.96 Å.

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Supporting Information Available: Tables furnishing full details of the crystal data, data collection, structure solution parameters, atomic coordinates of all atoms, bond distances, bond angles, anisotropic thermal parameters of non-hydrogen atoms, and isotropic thermal parameters of hydrogen atoms for **1**, **2**, and **4**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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