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Multidentate Lewis Acids. Synthesis of an Organic Framework Designed To Hold Two Sites of Lewis Acidity in a Convergent Orientation

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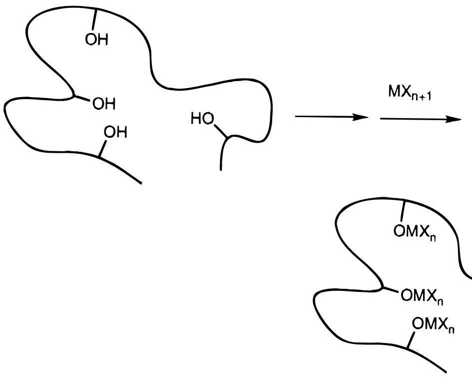
Treatment of 2,2′-(1,2-ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (**2**) with 2 equiv of $Al(i\text{-}Bu)_3$ converts the hydroxyl groups into potentially Lewis acidic $OAl(i\text{-}Bu)_2$ groups with a convergent orientation. Their intramolecular interaction produces the novel structure **11**, which incorporates an Al_2O_2 ring that is markedly distorted by constraints imposed by the diphenylacetylene framework. Unlike normal Al_2O_2 rings, which are planar and have trigonal planar oxygen atoms, the Al_2O_2 ring of compound **11** is puckered, and its oxygen atoms are distinctly pyramidalized. In addition, the average Al−O bond length in compound **11** (1.913(2) Å) is significantly longer than these found in related dimers of alkylaluminum alkoxides and aryloxides (1.840−1.895 Å).

Introduction

Multidentate Lewis acids interest chemists because they can be designed so that their multiple electrophilic sites are held in orientations favoring the recognition, binding, and chemical activation of molecules with complementary arrangements of basic sites.[2] We have shown that a convenient method for synthesizing multidentate Lewis acids is to add metal salts MX_{n+1} or related species to compounds containing hydroxyl groups or similar sites suitably oriented by an organic framework (eq 1).[3] This yields metal alkoxides **1** with multiple Lewis acidic sites OMX_n. In this paper, we show that 2,2′-(1,2-ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (**2**) provides a framework of potential value for the construction of bidentate Lewis acids with convergent electrophilic sites.[4,5]

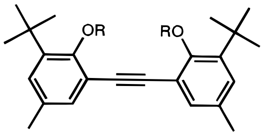


(1)

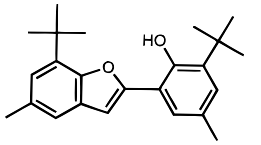
1

Results and Discussion

(1) Synthesis of Diphenol 2. Derivatives of 2-ethynylphenol are known to form benzofurans by rapid intramolecular addition of the hydroxyl group to the adjacent triple bond,[6] so we were not certain that diphenol **2** could be prepared and characterized. In fact, attempts to prepare compound **2** in a single step by Pd(0)/Cu(I)-catalyzed coupling of 2-(1,1-dimethylethyl)-6-iodo-4-methylphenol (**3**)[7] with acetylene were unsuccessful and led to the formation of benzofuran **4** in 80% yield. However, the less direct route summarized in Scheme 1 allowed us to synthesize diphenol **2** from iodophenol **3** in six steps in 62% overall yield. Compound **3** was first converted into 2-(1,1-dimethylethyl)-6-ethynyl-4-methylphenol (**5**) in 95% overall yield by direct Pd(0)/Cu(I)-catalyzed coupling with (trimethylsilyl)acetylene followed by treatment with methanolic KF.[8] It is noteworthy that OH stretching in ethynylphenol **5** occurs at 3509 cm^{-1} (0.2 M in CH_2Cl_2), whereas the corresponding vibration in 2,6-bis(1,1-dimethylethyl)-4-methylphenol appears at 3638 cm^{-1}.



2 (R = H)
8 (R = Ac)



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[2] For references, see: Vaugeois, J.; Simard, M.; Wuest, J. D. *Coord. Chem. Rev.* **1995**, *145*, 55.

[3] Bachand, B.; Wuest, J. D. *Organometallics* **1991**, *10*, 2015. Bélanger-Gariépy, F.; Hoogsteen, K.; Sharma, V.; Wuest, J. D. *Inorg. Chem.* **1991**, *30*, 4140. Phan Viet, M. T.; Sharma, V.; Wuest, J. D. *Inorg. Chem.* **1991**, *30*, 3026. Galeffi, B.; Simard, M.; Wuest, J. D. *Inorg. Chem.* **1990**, *29*, 955.

[4] For related studies of the use of *o,o′*-disubstituted diphenylacetylenes as frameworks able to hold groups in a prescribed orientation, see: Prince, P.; Evans, K. L.; Rosas-García, V. M.; Gandour, R. D.; Fronczek, F. R. *Tetrahedron Lett.* **1992**, *33*, 6431. Letsinger, R. L.; Nazy, J. R. *J. Am. Chem. Soc.* **1959**, *81*, 3013.

[5] For a discussion of convergent functional groups, see: Rebek, J., Jr.; Askew, B.; Killoran, M.; Nemeth, D.; Lin, F.-T. *J. Am. Chem. Soc.* **1987**, *109*, 2426. Rebek, J., Jr.; Marshall, L.; Wolak, R.; Parris, K.; Killoran, M.; Askew, B.; Nemeth, D.; Islam, N. *J. Am. Chem. Soc.* **1985**, *107*, 7476.

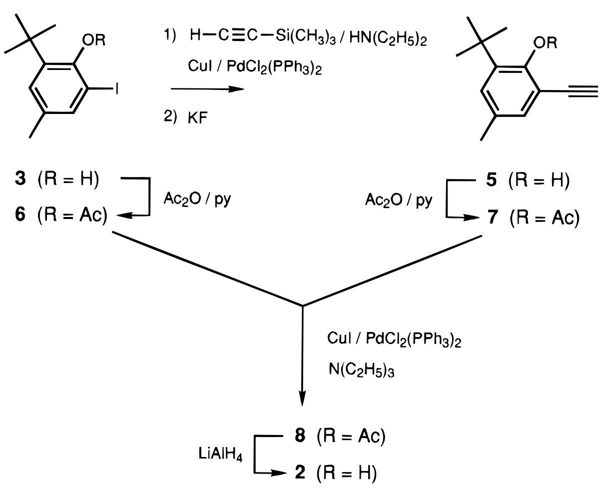
[6] Castro, C. E.; Gaughan, E. J.; Owsley, D. C. *J. Org. Chem.* **1966**, *31*, 4071.

[7] Tashiro, M.; Yoshiya, H. *Heterocycles* **1983**, *20*, 653.

[8] For related work, see: Arcadi, A.; Cacchi, S.; Marinelli, F. *Tetrahedron Lett.* **1989**, *30*, 2581.

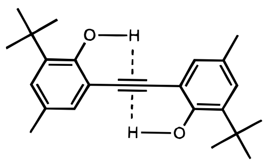
S0276-7333(95)00860-0 CCC: $12.00

Scheme 1



This large difference indicates that compound **5** must incorporate a hydroxyl group intramolecularly π-bonded to the triple bond.[9]

Phenols **3** and **5** were then converted in high yields into the corresponding acetates **6** and **7**, which were coupled by a standard procedure to give the diacetate **8** of required diphenol **2** in 86% yield. Initial attempts to prepare compound **2** by using conventional methods to deprotect diacetate **8** yielded only benzofuran **4**, suggesting that diphenol **2** might in fact be too reactive to isolate. Finally, however, we discovered that reductive deprotection could be effected with $LiAlH_4$ to give compound **2** in 90% yield. The OH region of its IR spectrum (0.2 M in CH_2Cl_2) contains a single sharp band at 3504 cm^{-1}, showing that both hydroxyl groups are equivalent and doubly π-bonded to the central triple bond in an approximately symmetric manner.[10] Both in the solid state and solution, structure **9** is more stable than the unsymmetrically hydrogen-bonded alternative **10**, presumably because even the closest approach of oxygen atoms held at the ortho positions of an undistorted diphenylacetylene framework leaves them much too far apart (~4.1 Å) to permit strong hydrogen bonding.



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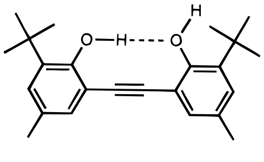

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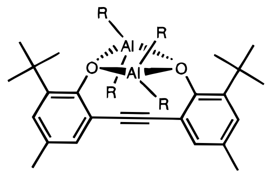
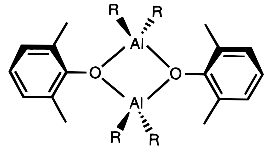
(2) Reaction of Diphenol 2 with Al(*i*-Bu)$_3$. Diphenol **2** was treated with 2 equiv of Al(i-Bu)$_3$ in pentane in order to convert the hydroxyl groups into convergent Lewis acidic OAl(i-Bu)$_2$ groups.[11] Slow evaporation of solvent gave a 93% yield of crystalline product. The simplicity of its ^1H and ^{13}C NMR spectra provided evidence of high symmetry, but two distinct types of i-Bu group were nevertheless present in a 1:1 ratio. These data are inconsistent with simple structures in which the OAl(i-Bu)$_2$ groups are unassociated; however, they are fully compatible with structure **11**, in which the two OAl(i-Bu)$_2$ groups interact intramolecularly to form a four-membered Al_2O_2 ring characteristic of dimers of related dialkylaluminum alkoxides and aryloxides.[12−14] This surprised us for two reasons: The OAl(i-Bu)$_2$ groups are constrained by the relatively rigid diphenylacetylene framework of compound **11** to be too far apart for normal bonding, and dialkylaluminum aryloxides derived from similarly hindered phenols are typically monomeric.[11]



11 (R = i-Bu)



12 (R = i-Bu)

An X-ray crystallographic study confirmed that structure **11** is adopted in the solid state. The results of this study, summarized in Figure 1 and Tables 1 and 2, show that structure **11** incorporates several unusual features. To minimize the O···O distance, the aromatic rings are essentially coplanar. In addition, the bond angles at the acetylenic carbon atoms are distinctly bent within the molecular plane in the direction of the Al_2O_2 ring, and the average C−C ≡ C angle is 167.0(2)°. This distortion further reduces the separation of the oxygen atoms to 2.542(2) Å, but they are still too far apart to allow the formation of an Al_2O_2 ring with normal geometric parameters, including an O···O distance no longer than 2.48 Å.[12−14] Previously observed Al_2O_2 rings are rigorously or approximately planar, and the oxygen atoms are normally trigonal planar.[12−14] In sharp contrast, the Al_2O_2 ring of structure **11** is conspicuously puckered, and the average Al−O−Al−O dihedral angle is 16.64(6)°; in addition, the oxygen atoms are distinctly pyramidalized, and the sum of their average bond angles is 347.44(12)°. These notable distortions arise because the oxygen atoms are joined by a diphenylacetylene framework, thereby placing the Al_2O_2 ring in a strained bicyclo[6.1.1] skeleton that incorporates a triple bond. Puckering permits the bridgehead oxygen atoms to approach trigonal planar coordination and decreases repulsive interactions of the aluminum atoms and their i-Bu substituents with the bridging diphenylacetylene unit.

The unique constraints imposed on structure **11** make its average Al−O bond length (1.913(2) Å) markedly longer than those observed in previously studied dimers of alkylaluminum alkoxides and aryloxides (1.840−

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[9] Visser, T.; van der Maas, J. H. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1649.

[10] The aromatic rings in doubly π-bonded structure **9** may adopt parallel, perpendicular, or intermediate orientations.

[11] For a review of the synthesis, structure, aggregation, and Lewis acidity of related monodentate alkylaluminum aryloxides, see: Healy, M. D.; Power, M. B.; Barron, A. R. *Coord. Chem. Rev.* **1994**, *130*, 63.

[12] For a review, see: Oliver, J. P.; Kumar, R. *Polyhedron* **1990**, *9*, 409.

[13] Ghazi, S. U.; Kumar, R.; Heeg, M. J.; Oliver, J. P. *Inorg. Chem.* **1994**, *33*, 411. Terry, K. W.; Ganzel, P. K.; Tilley, T. D. *Chem. Mater.* **1992**, *4*, 1290. Sierra, M. L.; Kumar, R.; de Mel, V. S. J.; Oliver, J. P. *Organometallics* **1992**, *11*, 206. Hendershot, D. G.; Kumar, R.; Barber, M.; Oliver, J. P. *Organometallics* **1991**, *10*, 1917. Benn, R.; Janssen, E.; Lehmkuhl, H.; Rufińska, A.; Angermund, K.; Betz, P.; Goddard, R.; Krüger, C. *J. Organomet. Chem.* **1991**, *411*, 37.

[14] Apblett, A. W.; Barron, A. R. *Organometallics* **1990**, *9*, 2137. Kumar, R.; Sierra, M. L.; de Mel, V. S. J.; Oliver, J. P. *Organometallics* **1990**, *9*, 484. Cetinkaya, B.; Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F.; Williams, H. D. *Polyhedron* **1990**, *9*, 239. Haaland, A.; Stokkeland, O. *J. Organomet. Chem.* **1975**, *94*, 345.

Table 1. Selected Bond Lengths and Angles for Aluminum Aryloxide 11

	Bond Lengths (Å)		
Al(1)−O(11)	1.915(2)	Al(2)−O(21)	1.909(2)
Al(1)−O(21)	1.917(2)	Al(2)−O(11)	1.912(2)
Al(1)−C(41)	1.955(2)	Al(2)−C(61)	1.958(2)
Al(1)−C(31)	1.977(2)	Al(2)−C(51)	1.983(2)
Al(1)−Al(2)	2.805(1)	O(11)−O(21)	2.542(2)
C(17)−C(27)	1.196(3)		
	Bond Angles (deg)		
O(11)−Al(1)−O(21)	83.13(6)	O(21)−Al(2)−O(11)	83.41(6)
O(11)−Al(1)−C(41)	126.31(9)	O(21)−Al(2)−C(61)	124.35(9)
O(21)−Al(1)−C(41)	109.84(8)	O(11)−Al(2)−C(61)	110.20(8)
O(11)−Al(1)−C(31)	101.11(8)	O(21)−Al(2)−C(51)	101.75(8)
O(21)−Al(1)−C(31)	110.83(8)	O(11)−Al(2)−C(51)	110.83(8)
C(41)−Al(1)−C(31)	119.69(10)	C(61)−Al(2)−C(51)	120.30(10)
C(11)−O(11)−Al(1)	129.69(12)	C(21)−O(21)−Al(2)	129.38(12)
C(11)−O(11)−Al(2)	123.48(12)	C(21)−O(21)−Al(1)	123.74(12)
Al(2)−O(11)−Al(1)	94.29(6)	Al(2)−O(21)−Al(1)	94.29(6)
O(21)−Al(1)−O(11)−Al(2)	−16.62(6)	O(11)−Al(2)−O(21)−Al(1)	−16.66(6)

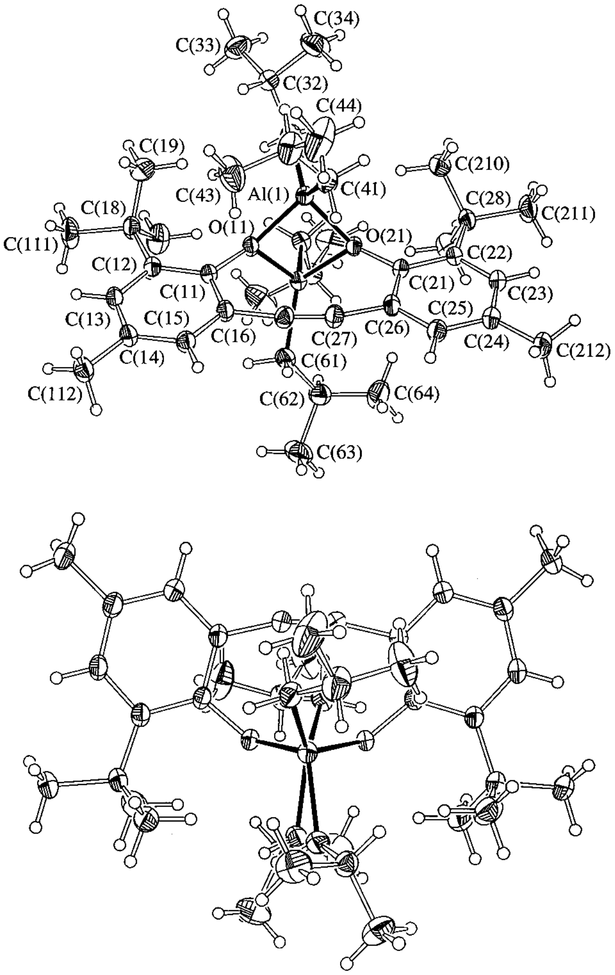

Figure 1. ORTEP drawings of two views of the structure of aluminum aryloxide **11**. Hydrogen atoms appear as spheres of arbitrary size, and other atoms are represented by ellipsoids corresponding to 40% probability. Bonds to aluminum are shown as solid lines. The top figure shows the Al_2O_2 ring and the atomic numbering, and the bottom figure highlights the puckering of the Al_2O_2 ring and the bending of angles at the acetylenic carbon atoms.

Table 2. Crystallographic Data for Aluminum Aryloxide 11

formula	$C_{40}H_{64}Al_2O_2$
fw	630.87
system	monoclinic
space group	$P2_1/n$
cell consts	
a, Å	10.645(3)
b, Å	17.975(5)
c, Å	20.812(5)
β, deg	98.88(2)
cell vol, Å^3	3935(2)
Z	4
T, K	220
D_{calcd}, g cm^{-3}	1.065
μ_{calcd}, mm^{-1}	0.86
radiation (λ, Å)	graphite-monochromated Cu Kα (1.540 56)
cryst dimens, mm	0.53 × 0.45 × 0.45
scan width	0.80 ± 0.14 tan θ
$2\theta_{max}$, deg	140
data collcn range	$\pm h, \pm k, \pm l$
no. of reflcns collcd	27 503
no. of reflcns retained	7461
no. of params refined	399
goodness-of-fit	0.940
R	0.056
R_w	0.077
$\Delta\rho_{max}$, e Å^{-3}	0.843
$\Delta\rho_{min}$, e Å^{-3}	−0.395

1.895 Å).[12−14] Distortions in structure **11** close the Al−O−Al angles to an average value of 94.29(6)° and open the O-Al−O angles to an average value of 83.27(6)°. Both values lie at or near the limits observed for comparable Al_2O_2 rings.[12−14] In particular, comparison of the average Al−O−Al and O−Al−O angles in structure **11** with those in the very closely related dimer **12** (101.5(1) and 78.5(1)°, respectively)[14] clearly reveals the striking geometric effect of constraints imposed by the diphenylacetylene framework. All of these deformations suggest that $-\Delta H$ for intramolecular association of the OAl(i-Bu)$_2$ groups in structure **11** must be smaller than that for intermolecular associations of related alkylaluminum alkoxides and aryloxides.

Other geometric features of structure **11** are unexceptional. For example, the average Al−C bond length (1.968(2) Å), nonbonded Al···Al distance (2.805(1) Å), length of the triple bond (1.196(3) Å), and exocyclic C−Al−C angle (120.00(10)°) resemble those found in related structures.[12−15] As expected, the aluminum atoms have highly distorted tetrahedral geometries, and the bond angles vary widely from 83.13(6) to 126.31(9)°.

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(15) Davis, D. S.; Fronczek, F. R.; Gandour, R. D. *Acta Crystallogr.* **1993**, *C49*, 1833.

Conclusions

Our observations suggest that derivatives of 2,2′-(1,2-ethynediyl)bis(phenol) can be used as frameworks for constructing bidentate Lewis acids with convergent electrophilic sites. In structure **11**, obtained by treating diphenol **2** with Al(*i*-Bu)$_3$, the convergence of two potentially Lewis acidic OAl(*i*-Bu)$_2$ groups permits their direct intramolecular association to form an Al_2O_2 ring. Constraints imposed by the diphenylacetylene framework cause novel geometric distortions of this ring, suggesting that $-\Delta H$ for intramolecular association is smaller than that for intermolecular associations of related alkylaluminum alkoxides and aryloxides. This may permit compound **11** or related derivatives to act as bidentate Lewis acids and to serve as effective receptors for bidentate Lewis bases with two complementary sites.

Experimental Section

Tetrahydrofuran (THF) was dried by distillation from the sodium ketyl of benzophenone, pentane was dried by distillation from CaH_2, acetic anhydride (Ac_2O) was purified by distillation from P_2O_5, pyridine was dried by distillation from NaOH, and dimethylformamide (DMF), $HN(C_2H_5)_2$, and $N(C_2H_5)_3$ were dried over anhydrous $MgSO_4$ and purified by distillation. Other commercial reagents were used without further purification. Flash chromatography was performed in the normal way.[16]

2-[7-(1,1-Dimethylethyl)-5-methylbenzofuran-2-yl]-6-(1,1-dimethylethyl)-4-methylphenol (4). A suspension of 2-(1,1-dimethylethyl)-6-iodo-4-methylphenol (**3**; 298 mg, 1.03 mmol),[7] $PdCl_2(PPh_3)_2$ (36 mg, 0.051 mmol), and CuI (19 mg, 0.10 mmol) in dry $HN(C_2H_5)_2$ (15 mL) was stirred at 25 °C under dry Ar, and a stream of acetylene was passed through the mixture for 6 h. After filtration and removal of volatiles from the filtrate by evaporation under reduced pressure, H_2O was added and the mixture was extracted with $CHCl_3$. The combined extracts were dried with anhydrous $MgSO_4$, and solvent was removed by evaporation under reduced pressure. Flash chromatography (silica, hexane (93%)/ethyl acetate (7%)) of the residue yielded 2-[7-(1,1-dimethylethyl)-5-methylbenzofuran-2-yl]-6-(1,1-dimethylethyl)-4-methylphenol (**4**; 290 mg, 0.827 mmol, 80%) as a colorless solid, which was further purified by recrystallization from hexane: mp 146−147 °C; IR (KBr) 3489 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.49 (s, 9H), 1.56 (s, 9H), 2.35 (s, 3H), 2.46 (s, 3H), 6.91 (s, 1H), 7.04 (m, 1H), 7.13 (m, 1H), 7.26 (m, 1H), 7.31 (m, 1H), 7.45 (s, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.8, 21.5, 29.6, 30.1, 34.1, 34.9, 102.8, 116.5, 118.6, 122.7, 125.6, 128.7, 128.8, 129.1, 132.7, 133.9, 137.3, 150.2, 150.7, 154.2; HRMS (FAB) calcd for $C_{24}H_{30}O_2$ *m*/*e* 350.2246, found *m*/*e* 350.2262.

2-(1,1-Dimethylethyl)-6-ethynyl-4-methylphenol (5). A suspension of 2-(1,1-dimethylethyl)-6-iodo-4-methylphenol (**3**; 4.32 g, 14.9 mmol),[7] $PdCl_2(PPh_3)_2$ (0.52 g, 0.74 mmol), and CuI (0.28 g, 1.5 mmol) in a mixture of dry $HN(C_2H_5)_2$ (16 mL) and dry DMF (4 mL) was stirred at 25 °C under dry N_2 and treated with (trimethylsilyl)acetylene (2.19 g, 22.3 mmol). The mixture was kept at 25 °C for 18 h, treated with 0.1 N aqueous HCl, and extracted with $CHCl_3$. The combined extracts were washed with saturated aqueous $NaHCO_3$ and H_2O, and then they were dried with anhydrous $MgSO_4$.

Evaporation of volatiles under reduced pressure left a residue that was treated with CH_3OH (60 mL) and $KF\cdot 2H_2O$ (4.21 g, 44.7 mmol). The resulting mixture was stirred at 25 °C for 7 h, diluted with H_2O, and extracted with $CHCl_3$. Evaporation of volatiles under reduced pressure left a residue that was purified by flash chromatography (silica, hexane (95%)/ethyl acetate (5%)) to provide 2-(1,1-dimethylethyl)-6-ethynyl-4-methylphenol (**5**; 2.66 g, 14.1 mmol, 95%) as a colorless solid, which was further purified by recrystallization from pentane: mp 31−32 °C; IR (CH_2Cl_2) 3509, 3299, 2099 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 9H), 2.25 (s, 3H), 3.45 (s, 1H), 6.00 (s, 1H), 7.06 (d, 1H, ^4J = 1.6 Hz), 7.07 (d, 1H, ^4J = 1.6 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.5, 29.3, 34.6, 79.0, 83.9, 108.4, 128.6, 129.2, 129.4, 135.4, 153.9; HRMS (EI) calcd for $C_{13}H_{16}O$ *m*/*e* 188.1201, found *m*/*e* 188.1201.

2-(1,1-Dimethylethyl)-6-iodo-4-methylphenol Acetate (6). A solution of 2-(1,1-dimethylethyl)-6-iodo-4-methylphenol (**3**; 3.33 g, 11.5 mmol)[7] in a mixture of dry pyridine (7 mL) and acetic anhydride (9 mL) was kept at 25° C for 36 h. Volatiles were then removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (80%)/ethyl acetate (20%)) to give pure 2-(1,1-dimethylethyl)-6-iodo-4-methylphenol acetate (**6**; 3.35 g, 10.1 mmol, 88%) as a colorless oil: bp 113 °C/0.3 Torr; IR (liquid film) 1767 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (s, 9H), 2.31 (s, 3H), 2.39 (s, 3H), 7.19 (d, 1H, ^4J = 1.3 Hz), 7.56 (d, 1H, ^4J = 1.3 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.7, 22.3, 30.4, 35.0, 94.0, 128.6, 137.1, 138.0, 142.9, 147.4, 168.9; HRMS (FAB) calcd for $C_{13}H_{17}IO_2$ + H *m*/*e* 333.0352, found *m*/*e* 333.0363.

2-(1,1-Dimethylethyl)-6-ethynyl-4-methylphenol Acetate (7). A solution of 2-(1,1-dimethylethyl)-6-ethynyl-4-methylphenol (**5**; 2.07 g, 11.0 mmol) in a mixture of dry pyridine (7 mL) and acetic anhydride (9 mL) was kept at 25 °C for 24 h. Volatiles were then removed under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (90%)/ethyl acetate (10%)) to give 2-(1,1-dimethylethyl)-6-ethynyl-4-methylphenol acetate (**7**; 2.43 g, 10.6 mmol, 96%) as a colorless solid. Recrystallization from hexane provided an analytically pure sample in the form of colorless needles: mp 68−70 °C; IR (melt) 2108, 1767 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (s, 9H), 2.31 (s, 3H), 2.36 (s, 3H), 3.19 (s, 1H), 7.20 (d, 1H, ^4J = 1.6 Hz), 7.22 (d, 1H, ^4J = 1.6 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.9, 21.5, 30.2, 34.4, 79.7, 81.0, 117.2, 129.0, 131.8, 135.0, 141.5, 148.8, 169.0; HRMS (FAB) calcd for $C_{15}H_{18}O_2$ + H *m*/*e* 231.1385, found *m*/*e* 231.1395. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.36; H, 8.14.

2,2′-(1,2-Ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] Diacetate (8). A suspension of 2-(1,1-dimethylethyl)-6-iodo-4-methylphenol acetate (**6**; 1.08 g, 3.25 mmol), $PdCl_2(PPh_3)_2$ (0.11 g, 0.16 mmol), and CuI (0.060 g, 0.32 mmol) in dry $N(C_2H_5)_3$ (5 mL) was stirred at 25 °C under dry Ar, and a solution of 2-(1,1-dimethylethyl)-6-ethynyl-4-methylphenol acetate (**7**; 1.12 g, 4.86 mmol) in dry $N(C_2H_5)_3$ (7 mL) was added dropwise. The resulting mixture was kept at 25 °C for 1 h, treated with 0.1 N aqueous HCl, and extracted with $CHCl_3$. The combined extracts were washed with water and dried with anhydrous $MgSO_4$, and volatiles were then removed by evaporation under reduced pressure. Purification of the residue by flash chromatography (silica, hexane (90%)/ethyl acetate (10%)) provided 2,2′-(1,2-ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] diacetate (**8**; 1.22 g, 2.81 mmol, 86%) as a colorless solid, which was further purified by recrystallization from $CHCl_3$: mp 158−161 °C; IR (KBr) 1763 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (s, 18H), 2.32 (s, 6H), 2.36 (s, 6H), 7.18 (d, 2H, ^4J = 1.6 Hz), 7.21 (d, 2H, ^4J = 1.6 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.9, 21.3, 30.2, 34.4, 89.0, 118.2, 128.6, 131.2, 134.9, 141.5, 148.2, 169.2; HRMS (FAB) calcd for $C_{28}H_{34}O_4$ + H *m*/*e* 435.2535, found *m*/*e* 435.2521.

2,2′-(1,2-Ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (2). A suspension of $LiAlH_4$ (0.23 g, 6.1 mmol) in dry THF (15 mL) was stirred at −78 °C under dry Ar and treated dropwise with a solution of 2,2′-(1,2-ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol diacetate (**8**; 1.08 g, 2.49 mmol) in dry THF (10 mL). The cooling bath was removed, and the mixture was kept at 25 °C for 12 h. The mixture was then cooled to 0 °C, treated dropwise with H_2O (10 mL), filtered

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[16] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

through Celite, and extracted with $CHCl_3$. The combined extracts were washed with H_2O and dried with anhydrous $MgSO_4$, and volatiles were removed by evaporation under reduced pressure. Flash chromatography (silica, hexane (93%)/ethyl acetate (7%)) of the residue provided 2,2′-(1,2-ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (**2**; 0.78 g, 2.23 mmol, 90%) as a colorless solid. Recrystallization from hexane provided an analytically pure sample: mp 138−140 °C; IR (CH_2Cl_2) 3504 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 18H), 2.30 (s, 6H), 6.00 (s, 2H), 7.14 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.6, 29.3, 34.6, 90.4, 109.1, 128.8, 129.2, 129.3, 135.5, 153.0; HRMS (FAB) calcd for $C_{24}H_{30}O_2 + H$ *m*/*e* 351.2324, found *m*/*e* 351.2311. Anal. Calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63. Found: C, 82.37; H, 9.14.

Reaction of Al(*i*-Bu)$_3$ with 2,2′-(1,2-Ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (2) and X-ray Crystallographic Study of the Product. A solution of 2,2′-(1,2-ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (**2**; 0.15 g, 0.43 mmol) in dry pentane (6 mL) was stirred at 25 °C under dry N_2 and treated dropwise with neat Al(*i*-Bu)$_3$ (0.17 g, 0.86 mmol). Slow evaporation of the solvent yielded colorless crystals of aluminum aryloxide **11** (0.25 g, 0.40 mmol, 93%): mp 192−194 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.04 (d, 4H, $^3J = 7.4$ Hz), 0.48 (d, 4H, $^3J = 7.4$ Hz), 0.49 (d, 12H, $^3J = 6.5$ Hz), 0.92 (d, 12H, $^3J = 6.5$ Hz), 1.50 (s, 18H), 1.58 (m, 2H), 1.83 (m, 2H), 2.33 (s, 6H), 7.11 (m, 2H), 7.19 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.7, 22.5, 24.9, 25.4, 25.9, 27.8, 27.9, 31.3, 34.8, 99.2, 118.1, 127.1, 129.3, 132.9, 140.9, 153.1. Anal. Calcd for $C_{40}H_{64}Al_2O_2$: C, 76.15; H, 10.23. Found: C, 74.77; H, 10.22.

Crystallographic data are summarized in Table 2. A single crystal of the aluminum aryloxide was mounted quickly in air and transferred under a stream of cold, dry N_2 to an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from 25 reflections in the range $20.0° \leq \theta \leq 22.5°$. No absorption correction was applied. The structure was solved by direct methods (SHELXS-86) and difference-Fourier calculations (SHELXL-93).[17] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated at idealized positions using a riding model with different C−H distances for different types of C−H bonds. Atomic scattering factors were taken from standard sources. Refinement converged to $R1 = 0.056$, $wR2 = 0.151$, and goodness-of-fit = 0.940 for 399 parameters refined.

Selected bond lengths and angles are listed in Table 1. Tables of atomic coordinates and isotropic thermal parameters, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates and thermal parameters, and distances to weighted least-squares planes are included as Supporting Information.

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Supporting Information Available: Tables of atomic coordinates and isotropic thermal parameters, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates and thermal parameters, and distances to weighted least-squares planes for aluminum aryloxide **11** (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any masthead page for ordering information.

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[17] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.