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Complexes of Strong Bidentate Lewis Acids Derived from 2,2′-(1,3-Butadiyne-1,4-diyl)bis[phenol]

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Treatment of 2,2′-(1,3-butadiyne-1,4-diyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (**1**) with 2 equiv of $Al(i\text{-}Bu)_3$ converts the two hydroxyl groups into $OAl(i\text{-}Bu)_2$ groups, thereby transforming diphenol **1** into the corresponding bis(di-*i*-butylaluminum phenoxide) **8**, which holds two strongly Lewis acidic atoms of aluminum in a potentially convergent orientation. Bidentate Lewis acid **8** forms a crystalline 1:1 adduct with 1,2-dimethoxyethane (DME). An X-ray crystallographic study revealed that the adduct is a linear oligomer in which the two Lewis acidic sites of reagent **8** each bind a basic oxygen atom from different molecules of DME. However, low-temperature NMR studies indicated that in solution a discrete 1:1 adduct **9** is favored, in which the two Lewis acidic sites of reagent **8** each bind one of the two basic sites in a single molecule of DME. Formation of adduct **9** provides an example of the recognition and binding of a multidentate Lewis base by a complementary multidentate Lewis acid. Addition of 2 equiv of $TiCl_4$ to diphenol **1** converts the hydroxyl groups into $OTiCl_3$ groups and produces the corresponding bis(trichlorotitanium phenoxide) **11**, which forms an unusual 1:2 complex with $CH_3COOC_2H_5$. An X-ray crystallographic study of this complex established that each Lewis acidic atom of titanium binds only 1 equiv of $CH_3COOC_2H_5$ to form an unprecedented pentacoordinate adduct with a square-pyramidal geometry. Formation of diverse reagents **8** and **11** from the same precursor demonstrates that the strategy of converting organic compounds with suitably oriented hydroxyl groups into the corresponding metal alkoxides is a versatile and effective way to make multidentate Lewis acids.

Introduction

The study of multidentate Lewis acids, which are complex reagents with multiple sites of Lewis acidity, is an increasingly active area of research.[2−5] Valuable applications of multidentate Lewis acids are likely to emerge as special features of their coordination chemistry become more fully understood and as effective methods for making them are developed. We have shown that a particularly convenient way to make multidentate Lewis acids is to convert organic compounds with suitably oriented hydroxyl groups or similar sites into metal alkoxides or related derivatives with strong Lewis acidity.[3,4] For example, appropriate diols can be treated with 2 equiv of $TiCl_4$ to produce the corresponding bis(trichlorotitanium alkoxides). By simple procedures of this type, hydroxyl groups can be transformed into various sites of strong Lewis acidity.

To allow useful multidentate Lewis acids to be created by this strategy, the hydroxyl groups must be held sufficiently close together that the resulting sites of Lewis acidity can operate in conjunction to recognize and bind basic substrates; however, the sites cannot be so close together that they interact directly in an

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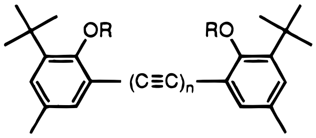
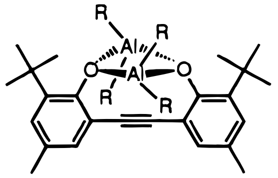
unproductive way. In this paper, we show that our strategy can be used successfully to convert 2,2′-(1,3-butadiyne-1,4-diyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (**1**) into reagents with two sites of strong Lewis acidity held in a potentially convergent orientation.[6]



1 (n = 2, R = H)
2 (n = 1, R = H)
3 (n = 1, R = Al(*i*-Bu)$_2$)
7 (n = 2, R = COCH$_3$)
8 (n = 2, R = Al(*i*-Bu)$_2$)
11 (n = 2, R = TiCl$_3$)

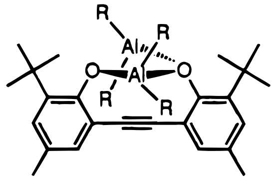


4 (R = *i*-Bu)

Results and Discussion

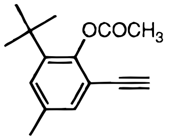
In earlier work,[4] we demonstrated that treatment of the closely analogous diphenol **2** with 2 equiv of Al(*i*-Bu)$_3$ did not yield the desired product **3**, with two OAl(*i*-Bu)$_2$ groups containing potentially convergent Lewis acidic atoms of aluminum. Instead, we obtained an isomer **4** in which the OAl(*i*-Bu)$_2$ groups associate intramolecularly to form a four-membered Al$_2$O$_2$ ring characteristic of dimers of similar dialkylaluminum alkoxides and aryloxides.[4] The sites of Lewis acidity in hypothetical structure **3** are therefore too close together to prevent their direct interaction. However, an X-ray crystallographic study showed that isomer **4** incorporates significant strain, which is revealed by abnormal bending of the triple bond and notable deformations of the Al$_2$O$_2$ ring.[4] These observations encouraged us to hope that structure **4** might be in rapid equilibrium in solution with significant amounts of the desired bidentate Lewis acid **3**.

To study this possibility, we recorded variable-temperature NMR spectra of compound **4**. At 25 °C, its ^{13}C NMR spectrum (100 MHz, toluene-d_8) showed separate peaks for all three different carbon atoms in the two pairs of nonequivalent *i*-Bu groups. In particular, signals assigned to the CH$_3$ groups appeared at δ 28.39 and 28.53. As the temperature was increased, these signals broadened and finally coalesced at $T_c = 55$ °C, enabling us to estimate that $\Delta G^{\ddagger} = 17.0 \pm 0.2$ kcal mol^{-1} for exchange of the *i*-Bu groups.[7] In principle, this exchange can occur by two distinct processes: (1) Breaking two Al−O bonds in compound **4** and cleaving the Al$_2$O$_2$ ring, thereby producing the desired bidentate Lewis acid **3**, or (2) breaking only one Al−O bond and opening the Al$_2$O$_2$ ring to generate intermediate **5**, followed by rapid rotation of the uncoordinated Al(*i*-Bu)$_2$ group around its single remaining Al−O bond. Breaking a single Al−O bond in the Al$_2$O$_2$ ring of [Al(*i*-OPr)$_3$]$_2$ is estimated to require at least 31.4 kcal mol^{-1}.[8] We suggest that exchange in compound **4** occurs by an analogous mechanism of single-bond cleavage and that opening of the ring is accelerated because Al−O bonds in the Al$_2$O$_2$ rings of dimeric dialkylaluminum phenoxides are intrinsically weaker than those of dimeric aluminum trialkoxides. In addition, relief of strain in the Al$_2$O$_2$ ring of compound **4** may help lower $\Delta G^{\ddagger}$. However, the observed value of $\Delta G^{\ddagger}$ is still too large to imply that the desired bidentate Lewis acid **3** is readily accessible from isomer **4**.



5 (R = *i*-Bu)

To prevent loss of full bidentate Lewis acidity by inadvertent intramolecular association, the two OAlR$_2$ groups must be attached to a framework that holds them farther apart. Such a framework is provided by diphenol **1**, which was prepared in 80% overall yield by standard oxidative coupling[9] of the known acetylene **6**,[4] followed by mild reductive deprotection of the resulting diester **7**. Treatment of diphenol **1** in pentane with 2 equiv of Al(*i*-Bu)$_3$ produced a homogeneous solution, and partial evaporation then gave crystals, presumably of the desired bidentate Lewis acid **8**. When the treatment of diphenol **1** with Al(*i*-Bu)$_3$ was followed by the addition of 1 equiv of 1,2-dimethoxyethane (DME), we obtained an 86% yield of crystals of a 1:1 complex of bidentate Lewis acid **8** with DME. Similarly, 1:1 complexes were also formed when bidentate Lewis acid **8** was treated with other bidentate bases such as dioxane and pyridazine; in contrast, a representative monodentate base, tetrahydrofuran, gave a 1:2 complex. The structure of the 1:1 complex of bidentate Lewis acid **8** with DME was determined by an X-ray crystallographic study. The results of this study, summarized in Figure 1 and in Tables 1 and 2, established that in the solid state the two OAl(*i*-Bu)$_2$ groups of compound **8** do not associate intramolecularly and are therefore fully available for binding Lewis bases. However, the two Lewis acidic atoms of aluminum do not bind the two complementary basic atoms of oxygen in a single molecule of DME, thereby forming the discrete 1:1 adduct **9**; instead, the Lewis acidic sites each bind a basic site in two different molecules of DME, creating an oligomeric complex of 1:1 stoichiometry. The observed bond lengths and angles are similar to those found in related structures.[4,10] In particular, normal values are observed for



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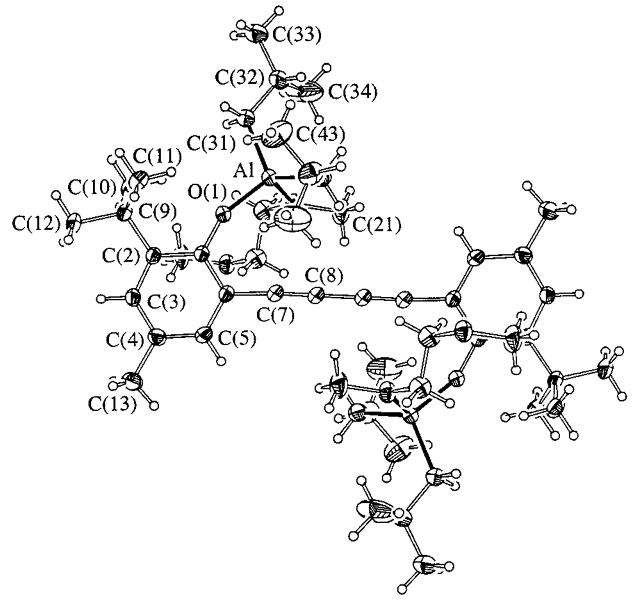
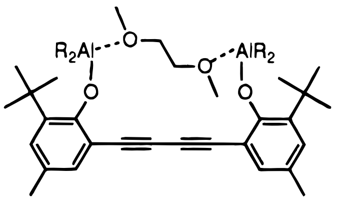
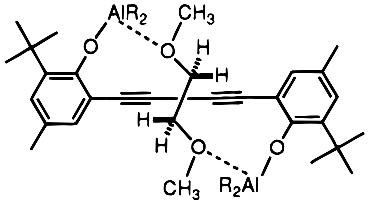


Figure 1. ORTEP view of the structure of the 1:1 complex of bidentate Lewis acid **8** with DME. Non-hydrogen atoms are represented by ellipsoids corresponding to 40% probability, hydrogen atoms are shown as spheres of arbitrary size, and bonds to aluminum are drawn using solid lines.



9 (R = *i*-Bu)



10 (R = *i*-Bu)

the lengths of the covalent Al−O(1) bond (1.734(1) Å) and the dative Al···O(22) bond (1.941(2) Å), as well as for the Al−O(1)−C(1) bond angle (156.6(1)°). Aluminum shows distorted tetrahedral coordination, and the bond angles at aluminum range from 99.0(1)° to 120.6(1)°. In addition, coordination of the bound oxygen atoms of DME is approximately trigonal planar, and the sum of the bond angles at O(22) is 359.3(1)°.

Even though the 1:1 adduct of bidentate Lewis acid **8** and DME proved to be a linear oligomer in the solid state, it is readily soluble in CH_2Cl_2. At 25 °C, the ^1H NMR spectrum of a 0.063 M solution prepared by dissolving the crystalline 1:1 adduct in CD_2Cl_2 showed two broad signals assigned to the CH_3 and CH_2 groups of DME at δ 3.75 (bs, 6H) and 4.28 (bs, 4H), respectively. The observed broadening indicates that DME must remain at least partly bound in solution. At the lowest accessible temperature (−100 °C), the signal corresponding to the CH_3 groups appeared as a sharp singlet at δ 3.66 (s, 6H), while the signal corresponding to the CH_2 groups had split into two widely separated and incompletely resolved multiplets ($\omega_{1/2} = 15$ Hz) at δ 3.76 (m, 2H) and 5.02 (m, 2H). These observations support the hypothesis that the predominant species in solution is not a linear oligomer but rather the discrete 1:1 adduct **9**, in which both Lewis acidic sites in bidentate Lewis acid **8** operate conjointly to bind the two basic sites in a single molecule of DME.[11] In particular, if DME is bound in its extended conformation in the manner suggested by structure **10**, then the CH_3 groups are equivalent by symmetry but the protons of each CH_2 group are diastereotopic and likely to have markedly different chemical shifts, as observed. In principle, exchange of the diastereotopic methylene protons can occur by (1) breaking a single dative Al···O bond or (2) interconverting doubly bonded structure **10** and its enantiomer by simple rotations, without cleaving dative Al···O bonds.

Our work establishes that diphenol **1** can be easily converted into bis(aluminum phenoxide) **8**, a strong multidentate Lewis acid; moreover, such reagents can recognize and bind complementary multidentate Lewis bases.[11] By similarly simple procedures, compound **1** can also be transformed into other strong bidentate Lewis acids with distinctly different properties. An important advantage of our basic strategy for making multidentate Lewis acids is that a wide variety can be made from a single organic precursor. For example, treatment of diphenol **1** with 2 equiv of $TiCl_4$, followed by the addition of 2 equiv of $CH_3COOC_2H_5$, produced red crystals of a 1:2 complex of bis(trichlorotitanium phenoxide) **11** with $CH_3COOC_2H_5$ in 63% yield. Because $TiCl_4$ and titanium(IV) chloroalkoxides normally form hexacoordinate octahedral 1:2 complexes with simple basic ligands,[12,13] the observed 1:2 stoichiometry of the complex of bidentate reagent **11** suggested that one Lewis acidic atom of titanium binds both equivalents of $CH_3COOC_2H_5$ while the other atom of titanium remains free, or that the two sites of Lewis acidity each bind 1 equiv of $CH_3COOC_2H_5$, and hexacoordination is then achieved by using chloride or $CH_3COOC_2H_5$ itself to doubly bridge the two atoms of titanium.

The structure of the complex was determined by X-ray crystallography, and the results are summarized in Figure 2 and in Tables 3 and 4. These data reveal that the complex incorporates several unusual features. In particular, the structure is symmetric, and the two atoms of titanium each bind a single molecule of $CH_3COOC_2H_5$ to form pentacoordinate adducts with ap-

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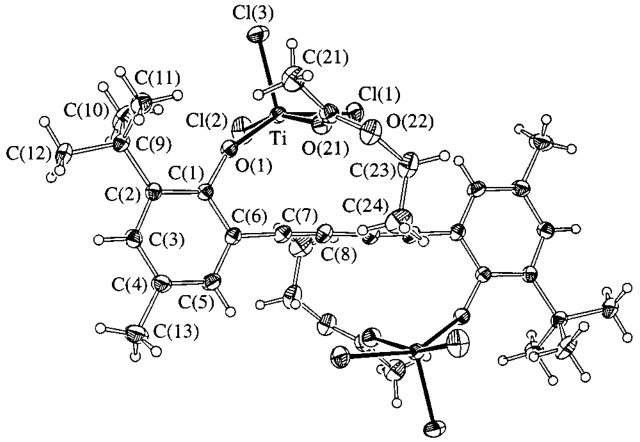

Figure 2. ORTEP view of the structure of the 1:2 complex of bidentate Lewis acid **11** with $CH_3COOC_2H_5$. Nonhydrogen atoms are represented by ellipsoids corresponding to 40% probability, hydrogen atoms are shown as spheres of arbitrary size, and bonds to titanium are drawn using solid lines.

Table 1. Selected Bond Lengths and Angles for the 1:1 Complex of Bidentate Lewis Acid 8 with DME

Bond Lengths (Å)			
Al−O(1)	1.734(1)	Al−C(41)	1.967(2)
Al−O(22)	1.941(2)	O(1)−C(1)	1.336(2)
Al−C(31)	1.971(2)	C(7)−C(8)	1.197(3)
Bond Angles (deg)			
O(1)−Al−O(22)	99.0(1)	C(1)−O(1)−Al	156.6(1)
O(1)−Al−C(31)	107.7(1)	C(6)−C(7)−C(8)	175.9(2)
O(1)−Al−C(41)	120.6(1)	Al−O(22)−C(21)	127.0(1)
O(22)−Al−C(31)	104.0(1)	Al−O(22)−C(23)	118.3(1)
O(22)−Al−C(41)	104.8(1)	C(21)−O(22)−C(23)	114.0(2)
C(31)−Al−C(41)	117.6(1)		

Table 2. Crystallographic Data for the 1:1 Complex of Bidentate Lewis Acid 8 with DME

formula	$C_{46}H_{74}Al_2O_4$
fw	745.01
cryst syst	triclinic
space group	$P\bar{1}$
cell constants	
a, Å	8.967(3)
b, Å	11.816(4)
c, Å	12.551(4)
α, deg	67.11(3)
β, deg	73.45(2)
γ, deg	78.23(2)
cell volume, $Å^3$	1167.8(7)
Z	1
T, K	210
D_{calcd}, g cm^{-3}	1.059
μ_{calcd}, mm^{-1}	0.843
radiation (λ, Å)	graphite-monochromated Cu Kα (1.540 56)
cryst dimens, mm	0.38 × 0.19 × 0.17
data collcn range	±*h*, ±*k*, ±*l*
no. of reflns collcd	29 061
no. of reflns refined	4418
goodness-of-fit	0.982
R1	0.0495
wR2	0.1364
$\Delta\rho_{max}$, e $Å^{-3}$	0.296
$\Delta\rho_{min}$, e $Å^{-3}$	−0.481

Table 3. Selected Bond Lengths and Angles for the 1:2 Complex of Bidentate Lewis Acid 11 with $CH_3COOC_2H_5$

Bond Lengths (Å)			
Ti−O(1)	1.782(2)	Ti−Cl(3)	2.204(1)
Ti−O(21)	2.078(2)	O(1)−C(1)	1.348(3)
Ti−Cl(1)	2.273(1)	O(21)−C(22)	1.222(4)
Ti−Cl(2)	2.264(1)	C(7)−C(8)	1.198(4)
Bond Angles (deg)			
O(1)−Ti−O(21)	86.2(1)	Cl(1)−Ti−Cl(2)	90.7(1)
O(1)−Ti−Cl(1)	150.3(1)	Cl(1)−Ti−Cl(3)	105.6(1)
O(1)−Ti−Cl(2)	91.2(1)	Cl(2)−Ti−Cl(3)	102.0(1)
O(1)−Ti−Cl(3)	103.0(1)	Ti−O(1)−C(1)	152.6(2)
O(21)−Ti−Cl(1)	82.8(1)	Ti−O(21)−C(22)	149.0(2)
O(21)−Ti−Cl(2)	161.5(1)	C(6)−C(7)−C(8)	178.1(3)
O(21)−Ti−Cl(3)	96.3(1)		

Table 4. Crystallographic Data for the 1:2 Complex of Bidentate Lewis Acid 11 with $CH_3COOC_2H_5$

formula	$C_{34}H_{44}Cl_6O_6Ti_2$
fw	857.19
cryst syst	triclinic
space group	$P\bar{1}$
cell constants	
a, Å	8.691(2)
b, Å	9.644(4)
c, Å	12.540(4)
α, deg	90.29(3)
β, deg	98.83(2)
γ, deg	105.68(3)
cell volume, $Å^3$	998.7(6)
Z	1
T, K	210
D_{calcd}, g cm^{-3}	1.425
μ_{calcd}, mm^{-1}	4.281
radiation (λ, Å)	graphite-monochromated Cu Kα (1.540 56)
cryst dimens, mm	0.40 × 0.30 × 0.06
data collcn range	±*h*, ±*k*, ±*l*
no. of reflns collcd	22 669
no. of reflns refined	3710
goodness-of-fit	0.986
R1	0.0473
wR2	0.1204
$\Delta\rho_{max}$, e $Å^{-3}$	0.724
$\Delta\rho_{min}$, e $Å^{-3}$	−0.762

proximate square-pyramidal geometries. Cl(3) is oriented apically, while Cl(1), Cl(2), O(1), and O(21) define the basal plane. Bond angles at Ti in the basal plane range from 82.8(1)° to 91.2(1)°, while those defined by apical Cl(3), Ti, and the basal ligands vary from 96.3(1)° to 105.6(1)°. The observed structure is noteworthy because (1) no other pentacoordinate 1:1 adducts of $TiCl_4$ or titanium(IV) chloroalkoxides with basic organic ligands are known and (2) calculations have predicted that the favored geometry of the hypothetical 1:1 complex of $TiCl_4$ with formaldehyde is trigonal bipyramidal, not square pyramidal.[12] The unusual preference of bis(trichlorotitanium phenoxide) **11** for pentacoordination is presumably due to steric hindrance created by substituents adjacent to the sites of Lewis acidity.

The C(7)−C(8) triple bond in the 1:2 complex of bis(trichlorotitanium phenoxide) **11** with $CH_3COOC_2H_5$ is oriented in such a way that its interaction with Ti trans to Cl(3) would produce a normal hexacoordinate complex with approximate octahedral geometry. However, complexes of Ti(IV) with olefins or acetylenes are very rare,[14] and the observed Ti···C(7) and Ti···C(8) distances (3.231(3) and 3.416(3) Å, respectively) are extremely long. We conclude that bis(trichlorotitanium phenoxide) **11** forms true pentacoordinate complexes.

When $TiCl_4$ reacts with 2 equiv of a simple carbonyl compound in a stepwise manner, binding of the first

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[14] For an example, see: Balaich, G. J.; Hill, J. E.; Waratuke, S. A.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1995**, *14*, 656.

equivalent to form a pentacoordinate 1:1 intermediate is normally calculated to be less exothermic than binding of the second equivalent to form the final hexacoordinate 1:2 adduct.[12] If so, binding of $CH_3COOC_2H_5$ in the novel pentacoordinate complex of bidentate Lewis acid **11** should be somewhat weaker than in related hexacoordinate complexes, and the dative Ti···O(21) bond length should be abnormally long. In fact, the observed distance (2.078(2) Å) is similar to those previously found in hexacoordinate complexes of esters with $TiCl_4$ and titanium trichloroalkoxides.[13] In addition, the average length of the two basal Ti−Cl bonds (2.268(1) Å) is normal, and the Ti−O(1) bond length (1.782(2) Å) is similar to those found in other titanium(IV) chlorophenoxides and their complexes,[15] which exhibit strong oxygen-p titanium-d π-bonding.[16] Further evidence of strong Ti−O(1) π-bonding in the 1:2 complex of bidentate Lewis acid **11** with $CH_3COOC_2H_5$ is the observed opening of the Ti−O(1)−C(1) bond angle to 152.6(2)°. Curiously, the Ti−O(1) bond shows normal strength even though O(1) is trans to Cl(1) rather than to the more weakly π-donating ester ligand. The only evidence that pentacoordination has any special effects on bond lengths is provided by unusual shortening of the apical Ti−Cl(3) bond (2.204(1) Å). Such shortening is typical of bonds to apical ligands in square-pyramidal complexes.[17] Although titanium has an unusual geometry and stoichiometry of coordination, $CH_3COOC_2H_5$ is bound in the normal $\eta^1(\sigma)$ manner,[18] with a Ti···O(21)−C(22) bond angle of 149.0(2)° and a Ti···O(21)−C(22)−C(21) dihedral angle of 1.9(6)°.

Conclusions

Our results show that the conversion of hydroxyl groups into metal alkoxides can serve as the basis of an effective strategy for constructing strong multidentate Lewis acids from simple organic precursors. Multidentate Lewis acids made by this strategy can be designed to have useful properties, such as the ability to recognize and bind complementary multidentate Lewis bases. Moreover, this strategy allows multidentate Lewis acids with markedly different properties to be made from the same precursor. We expect that our strategy for making multidentate Lewis acids will make them more readily available and will help promote further study of their unique coordination chemistry.

Experimental Section

Toluene and pentane were dried by distillation from sodium, and CH_2Cl_2 was dried by distillation from P_2O_5. $TiCl_4$ was purified by distillation; all other reagents were commercial products that were used without further purification. Flash chromatography was performed in the normal way.[19]

2,2′-(1,3-Butadiyne-1,4-diyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] Diacetate (7). A mixture of CuCl (0.845 g, 8.54 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.373 g, 3.21 mmol) in acetone (15 mL) was stirred at 25 °C for 1 h. The suspension was filtered, and the filtrate was added to a solution of 2-(1,1-dimethylethyl)-6-ethynyl-4-methylphenol acetate (**6**; 0.740 g, 3.21 mmol)[4] in acetone (30 mL). The resulting mixture was stirred at 60 °C for 2 h under an atmosphere of O_2. Then 2 N aqueous HCl was added, the mixture was extracted with $CHCl_3$, and the combined extracts were washed with H_2O and dried with anhydrous $MgSO_4$. Volatiles were removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (95%)/ethyl acetate (5%)) to give 2,2′-(1,3-butadiyne-1,4-diyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] diacetate (**7**; 0.717 g, 1.56 mmol, 97%) as a colorless solid. An analytically pure sample was prepared by recrystallization from $CHCl_3$: mp 126−128 °C; IR (melt) 1769 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 18H), 2.34 (s, 6H), 2.44 (s, 6H), 7.26 (s, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.7, 21.1, 30.0, 34.3, 77.2, 78.2, 116.7, 129.4, 131.6, 134.9, 141.6, 149.5, 168.7; HRMS (FAB) calcd for $C_{30}H_{34}O_4 + H$ *m*/*e* 459.2535, found *m*/*e* 459.2553.

2,2′-(1,3-Butadiyne-1,4-diyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (1). A solution of 2,2′-(1,3-butadiyne-1,4-diyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] diacetate (**7**; 4.51 g, 9.83 mmol) in toluene (60 mL) was stirred at −78 °C under dry Ar and was treated dropwise with a solution of $(i\text{-}Bu)_2AlH$ (52 mL, 1.5 M in toluene, 78 mmol). The cold mixture was treated with H_2O (80 mL), warmed to 25 °C, and filtered through Celite. The filtrate was extracted with $CHCl_3$, and the combined extracts were dried with anhydrous $MgSO_4$. Volatiles were removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (90%)/ethyl acetate (10%)) to give 2,2′-(1,3-butadiyne-1,4-diyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (**1**; 3.31 g, 8.84 mmol, 90%) as a colorless solid. An analytically pure sample was prepared by recrystallization from $CHCl_3$: mp 142−144 °C; IR (melt) 3517, 2128 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 18H), 2.26 (s, 6H), 5.91 (s, 2H), 7.09 (s, 2H), 7.11 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.3, 29.0, 34.4, 78.1, 79.7, 107.9, 128.8, 129.7, 129.9, 135.6, 154.6; HRMS (FAB) calcd for $C_{26}H_{30}O_2$ *m*/*e* 374.2246, found *m*/*e* 374.2230.

1:1 Adduct of Bidentate Lewis Acid 8 and DME. A solution of 2,2′-(1,3-butadiyne-1,4-diyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (**1**; 20.6 mg, 0.0550 mmol) in pentane (0.8 mL) was stirred at 25 °C under dry Ar and treated dropwise with neat $Al(i\text{-}Bu)_3$ (21.8 mg, 0.110 mmol). After 10 min, neat DME (5.0 mg, 0.055 mmol) was added. Partial evaporation of the solvent yielded colorless crystals of the 1:1 adduct of bidentate Lewis acid **8** and DME (35.4 mg, 0.0475 mmol, 86%): IR (Nujol) 2130 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.20 (d, 8H, $^3J = 6.4$ Hz), 0.90 (d, 24H, $^3J = 6.5$ Hz), 1.38 (s, 18H), 1.81 (m, 4H), 2.23 (s, 6H), 3.75 (bs, 6H), 4.28 (bs, 4H), 7.06 (s, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.6, 22.8, 25.7, 28.2, 29.6, 34.8, 59.7 (b), 69.0 (b), 78.0, 82.9, 112.6, 126.6, 129.5, 131.4, 139.1, 158.7.

1:2 Complex of Bidentate Lewis Acid 11 with $CH_3COOC_2H_5$. A solution of 2,2′-(1,3-butadiyne-1,4-diyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (**1**; 15.0 mg, 0.0400 mmol) in pentane (0.8 mL) was stirred at 25 °C under dry Ar and treated dropwise with neat $TiCl_4$ (15.6 mg, 0.0822 mmol). The resulting red suspension was then treated with $CH_3COOC_2H_5$ (7.2 mg, 0.082 mmol) and CH_2Cl_2 (0.4 mL). Partial evaporation of the solvent yielded red crystals of the 1:2 complex of bidentate Lewis acid **11** with $CH_3COOC_2H_5$ (21.6 mg, 0.0252 mmol, 63%): IR (Nujol) 1644 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$)

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[15] For previous structural studies of titanium trichlorophenoxides, see: Matilainen, L.; Klinga, M.; Leskelä, M. *Polyhedron* **1996**, *15*, 153. Troyanov, S.; Pisarevsky, A.; Struchkov, Yu. T. *J. Organomet. Chem.* **1995**, *494*, C4.

[16] For a discussion of metal−oxygen π-bonding, see: Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 2, Chapter 15.3.

[17] Kepert, D. L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 1, Chapter 2.

[18] Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 256.

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

δ 1.31 (t, 6H, ^3J = 7.2 Hz), 1.52 (s, 18H), 2.34 (s, 6H), 2.41 (s, 6H), 4.37 (q, 4H, ^3J = 7.2 Hz), 7.13 (m, 2H), 7.22 (m, 2H); ^{13}C NMR (75.4 MHz, CD_2Cl_2) δ 14.3, 21.3, 21.5, 30.3, 35.6, 63.4, 83.3, 83.4, 119.1, 129.6, 132.7, 135.7, 138.4, 170.7, 176.0.

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Supporting Information Available: Tables of atomic coordinates and isotropic thermal parameters, all bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates and thermal parameters, and distances to weighted least-squares planes for the 1:1 complex of bidentate Lewis acid **8** with DME and the 1:2 complex of bidentate Lewis acid **11** with $CH_3COOC_2H_5$ (27 pages). Ordering information is given on any current masthead page.

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