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Articles

Complexes of Strong Bidentate Lewis Acids Derived from 2,7-Bis(1,1-dimethylethyl)fluorene-1,8-diol

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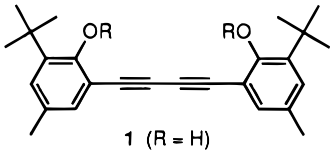
Treatment of 2,7-bis(1,1-dimethylethyl)fluorene-1,8-diol (**3**) with 2 equiv of $TiCl_4$ converts the two OH groups into $OTiCl_3$ groups and thereby yields bis(trichlorotitanium phenoxide) **7**, a structurally well-defined reagent that holds two sites of strong Lewis acidity in close proximity. Bidentate Lewis acid **7** forms a crystalline 1:2 complex with 4,4′-dimethylbenzophenone. An X-ray crystallographic study revealed that each atom of titanium binds only one molecule of ketone to form an unusual pentacoordinate adduct with an approximately trigonal bipyramidal geometry. Treatment of fluorenediol **3** with 2 equiv of $Al(CH_2CH_3)_3$ does not yield the expected bis(diethylaluminum phenoxide) **8**, but rather its dimer **9**. Formation of diverse reagents **7** and **9** from the same precursor demonstrates that the strategy of converting organic compounds with suitably oriented hydroxyl groups into the corresponding metal alkoxides is a particularly versatile and effective way to make strong, structurally well-defined multidentate Lewis acids.

Introduction

An increasingly active area of research in coordination chemistry is the study of multidentate Lewis acids, which are reagents with multiple sites of Lewis acidity available for the complexation of complementary Lewis bases.[2−7] Complexes of multidentate Lewis acids are chemically important because they promise to be more highly associated than analogous complexes of simple monodentate Lewis acids.[7] In addition, the recognition of bases by multidentate Lewis acids should be more selective, and the reactivity of bound substrates should be modified more dramatically.[7] As a result, multidentate Lewis acids are likely to become increasingly useful to chemists as the special features of their coordination chemistry are revealed, and as simple ways to make them are devised.

Our earlier work has shown that a particularly convenient strategy for making strong multidentate Lewis acids is to convert organic compounds with multiple hydroxyl groups or similar sites into the corresponding metal alkoxides or related derivatives.[3−5] For example, treatment of diphenol **1** with 2 equiv of $TiCl_4$ can be used to make complexes of bis(trichlorotitanium phenoxide) **2**, which is a strong bidentate Lewis acid.[5] Unfortunately, rotation of the aryl groups around the diyne linker in compound **2** is expected to occur readily, and no conformational constraints ensure that the two sites of Lewis acidity are held in the closest possible proximity in a potentially convergent manner.[8] As a result, they are free to operate independently.



1 (R = H)
2 (R = $TiCl_3$)

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(2) Vaugeois, J.; Simard, M.; Wuest, J. D. *Organometallics* **1998**, *17*, 1215. (b) Vaugeois, J.; Simard, M.; Wuest, J. D. *Coord. Chem. Rev.* **1995**, *145*, 55. (c) Simard, M.; Vaugeois, J.; Wuest, J. D. *J. Am. Chem. Soc.* **1993**, *115*, 370. (d) Nadeau, F.; Simard, M.; Wuest, J. D. *Organometallics* **1990**, *9*, 1311.

(3) Saied, O.; Simard, M.; Wuest, J. D. *Organometallics* **1996**, *15*, 2345.

(4) (a) Sharma, V.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1992**, *114*, 7931. (b) Bachand, B.; Wuest, J. D. *Organometallics* **1991**, *10*, 2015. (c) Bélanger-Gariépy, F.; Hoogsteen, K.; Sharma, V.; Wuest, J. D. *Inorg. Chem.* **1991**, *30*, 4140. (d) Phan Viet, M. T.; Sharma, V.; Wuest, J. D. *Inorg. Chem.* **1991**, *30*, 3026. (e) Galeffi, B.; Simard, M.; Wuest, J. D. *Inorg. Chem.* **1990**, *29*, 955.

(5) Saied, O.; Simard, M.; Wuest, J. D. *Organometallics* **1998**, *17*, 1128.

(6) For other recent studies of multidentate Lewis acids, see: (a) Hawthorne, M. F.; Zheng, Z. *Acc. Chem. Res.* **1997**, *30*, 267. (b) Ooi, T.; Takahashi, M.; Maruoka, K. *J. Am. Chem. Soc.* **1996**, *118*, 11307. (c) Holman, K. T.; Halihan, M. M.; Jurisson, S. S.; Atwood, J. L.; Burkhalter, R. S.; Mitchell, A. R.; Steed, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 8, 9567. (d) Gabbaï, F. P.; Schier, A.; Riede, J.; Schichl, D. *Organometallics* **1996**, *15*, 4119. (e) Scheerder, J.; Engbersen, J. F. J.; Reinhoudt, D. N. *Recl. Trav. Chim. Pays-Bas* **1996**, *115*, 307. (f) Nozaki, K.; Yoshida, M.; Takaya, H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2043. (g) Grdenić, D.; Korpar-Čolig, B.; Matković-Čalogović, D. *J. Organomet. Chem.* **1996**, *522*, 297. (h) Tikhonova, I. A.; Dolgushin, F. M.; Yanovsky, A. I.; Struchkov, Yu. T.; Gavrilova, A. N.; Saitkulova, L. N.; Shubina, E. S.; Epstein, L. M.; Furin, G. G.; Shur, V. B. *J. Organomet. Chem.* **1996**, *508*, 271. (i) Tamao, K.; Hayashi, T.; Ito, Y. *J. Organomet. Chem.* **1996**, *506*, 85. (j) Chapman, W. H., Jr.; Breslow, R. *J. Am. Chem. Soc.* **1995**, *117*, 5462. (k) Spaether, W.; Erker, G.; Rump, M.; Krüger, C.; Kuhnigk, J. *Organometallics* **1995**, *14*, 2621. (l) Dakternieks, D.; Jurkschat, K.; Zhu, H.; Tiekink, E. R. T. *Organometallics* **1995**, *14*, 2512. (m) Stemmler, A. J.; Kampf, J. W.; Pecoraro, V. L. *Inorg. Chem.* **1995**, *34*, 2271. (n) Reilly, M.; Oh, T. *Tetrahedron Lett.* **1995**, *36*, 217. (o) Nguyen, P.; Dai, C.; Taylor, N. J.; Power, W. P.; Marder, T. B.; Pickett, N. L.; Norman, N. C. *Inorg. Chem.* **1995**, *34*, 4290. (p) Anderson, H. L.; Bashall, A.; Henrick, K.; McPartlin, M.; Sanders, J. K. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 429. (q) Zheng, B.; Srebnik, M. *J. Organomet. Chem.* **1994**, *474*, 49. (r) Balch, A. L. *Prog. Inorg. Chem.* **1994**, *41*, 239. (s)

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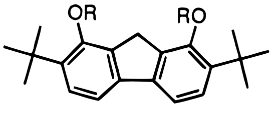
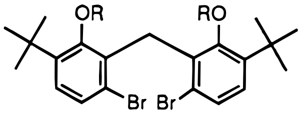
To allow structurally well-defined multidentate Lewis acids to be created by our strategy, the hydroxyl groups should be oriented more rigidly, in positions close enough together to ensure that the resulting sites of Lewis acidity can act in conjunction but far enough apart to prevent the sites from interacting directly in unproductive ways. In this paper, we show that our strategy can be used successfully to convert 2,7-bis(1,1-dimethylethyl)fluorene-1,8-diol (**3**) into reagents with well-defined structures that hold two sites of strong Lewis acidity in close proximity.



3 (R = H)
4 (R = CH_3)
7 (R = $TiCl_3$)
8 (R = $Al(CH_2CH_3)_2$)



5 (R = H)
6 (R = CH_3)

Results and Discussion

Fluorenediol **3** was prepared in 86% yield from the known dimethyl ether **4**[9] by adding BBr_3 and then water. Dimethyl ether **4** was synthesized in four steps by a modification of the published method, which requires six steps.[9] The modification involves direct *tert*-butylation of 3-bromophenol, condensation of the resulting 5-bromo-2-(1,1-dimethylethyl)phenol[9] with formaldehyde to produce diphenol **5**,[9] methylation to give protected intermediate **6**,[9] and subsequent Ni(0)-catalyzed intramolecular aryl−aryl coupling. Our modifications increased the overall yield of dimethyl ether **4** from 3-bromophenol from 11% to 28%. Moreover, we found that fluorenediol **3** could be made from 3-bromophenol in only three steps by direct aryl−aryl coupling of unprotected diphenol **5**, but the overall yield was somewhat lower.

To test our general strategy for making multidentate Lewis acids from organic compounds with suitably oriented hydroxyl groups, we attempted to convert fluorenediol **3** into the corresponding bis(trichlorotitanium phenoxide) **7**, a strong bidentate Lewis acid, by adding 2 equivalents of $TiCl_4$ to a solution of compound **3** in CH_2Cl_2. Slow evaporation then provided a 90% yield of red crystals of a compound assigned structure **7**. This assignment was confirmed by X-ray crystallography, which provided the structural data summarized in Figure 1 and in Tables 1and 2. These data reveal that compound **7** is a true bidentate Lewis acid, with two free $OTiCl_3$ groups held in close proximity. The average lengths of the Ti−Cl bonds (2.174(2) Å) and the Ti−O bonds (1.727(3) Å) are similar to those found in other uncomplexed titanium trichlorophenoxides.[10] In addition, the average Ti−O−C bond angle has a large value (163.6(3)°) that is close to those found in related compounds with strong oxygen-p titanium-*d* π-bonding.[10,11] As expected, each atom of titanium adopts an approximately tetrahedral geometry, and the bond angles at titanium vary only from 107.9(1) to 111.0(1)°.

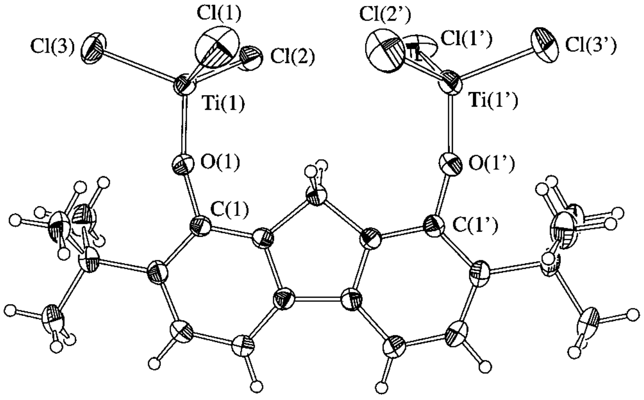


Figure 1. ORTEP view of the structure of bis(trichlorotitanium phenoxide) **7**. Non-hydrogen atoms are represented by ellipsoids corresponding to 40% probability, and hydrogen atoms are shown as spheres of arbitrary size.

Treatment of a solution of bis(trichlorotitanium phenoxide) **7** in CH_2Cl_2 with 2 equiv of 4,4′-dimethylbenzophenone, followed by partial evaporation of the solvent, provided red crystals of a 1:2 complex, which was isolated as a CH_2Cl_2 solvate in 81% yield. Because $TiCl_4$ and titanium(IV) chloroalkoxides normally form hexacoordinate octahedral 1:2 complexes with simple basic ligands,[12] the observed 1:2 stoichiometry of the complex of bidentate reagent **7** was unexpected. It suggested that one Lewis acidic atom of titanium binds both equivalents of ketone while the other atom of titanium remains free, or that the two sites of Lewis acidity each bind 1 equiv of ketone, and hexacoordination is then achieved by using chloride or the carbonyl oxygen atoms of the ketones to doubly bridge the two atoms of titanium.

The structure of the solvated 1:2 complex of bis(trichlorotitanium phenoxide) **7** with 4,4′-dimethylbenzophenone was determined by X-ray crystallography, and the results are summarized in Figure 2 and in Tables 1 and 3. These data reveal that the complex incorporates several unusual features. In particular, the two atoms of titanium each bind a single molecule of 4,4′-dimethylbenzophenone to form pentacoordinate adducts with approximately trigonal bipyramidal geometries. All Ti−O bonds are oriented apically, and all Ti−Cl bonds are equatorial. The Cl−Ti−Cl bond angles range from 111.4(1) to 133.8(1)° and average 119.5(1)°, the Cl−Ti−O bond angles involving the phenoxide oxygen atoms range from 87.8(1) to 99.9(1)° and average 94.4(1)°, the Cl−Ti−O bond angles involving the carbonyl oxygen atoms of the bound ketones range from 82.6(1) to 91.2(1)° and average 86.1(1)°, and the O−Ti−O bond angles average 170.8(1)°. The observed structure is noteworthy because the 1:2 adduct of bis(trichlorotitanium

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Rothmaier, M.; Simon, W. *Anal. Chim. Acta* **1993**, *271*, 135. (t) Köster, R.; Seidel, G.; Wagner, K.; Wrackmeyer, B. *Chem. Ber.* **1993**, *126*, 305. (u) Jacobson, S.; Pizer, R. *J. Am. Chem. Soc.* **1993**, *115*, 11216. (v) Fields, L. B.; Jacobsen, E. N. *Tetrahedron: Asymmetry* **1993**, *4*, 2229.

(7) For a discussion of the special thermodynamic and kinetic effects of the multiple binding of bases by multidentate Lewis acids, see: Vaugeois, J.; Wuest, J. D. *J. Am. Chem. Soc.* **1998**, submittted for publication.

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

(9) Sharma, V.; Bachand, B.; Simard, M.; Wuest, J. D. *J. Org. Chem.* **1994**, *59*, 7785.

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

(11) 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.

(12) (a) Branchadell, V.; Oliva, A. *Inorg. Chem.* **1995**, *34*, 3433. (b) Branchadell, V.; Oliva, A. *J. Am. Chem. Soc.* **1992**, *114*, 4357.

Table 1. Crystallographic Data for Bis(trichlorotitanium phenoxide) **7** (Column A), the CH_2Cl_2 Solvate of the 1:2 Complex of Bis(trichlorotitanium phenoxide) **7** with 4,4′-Dimethylbenzophenone (Column B), and the Dimer **9** of Bis(diethylaluminum phenoxide) **8** (Column C)[a]

	column A	column B	column C
empirical formula	$C_{21}H_{24}Cl_6O_2Ti_2$	$C_{51}H_{52}Cl_6O_4Ti_2\cdot CH_2Cl_2$	$C_{58}H_{88}Al_4O_4$
fw	616.90	1122.35	957.264
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
cell constants			
a, Å	15.551(6)	12.756(3)	12.330(3)
b, Å	9.988(5)	21.458(13)	14.588(3)
c, Å	19.842(10)	20.047(7)	16.638(9)
α, deg	90	90	73.95(3)
β, deg	113.96(4)	101.28(2)	84.88(4)
γ, deg	90	90	79.97(2)
cell volume, Å^3	2816(2)	5381(4)	2829(2)
Z	4	4	2
T, K	225	210	225
D_{calcd}, g cm^{-3}	1.455	1.385	1.135
μ_{calcd}, mm^{-1}	10.39	4.181	1.186
cryst dimens, mm	0.64 × 0.28 × 0.18	0.70 × 0.43 × 0.11	0.58 × 0.46 × 0.38
data collcn range	$\pm h, +k, +l$	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$
no. of reflcns collcd	19488	38277	45681
no. of reflcns refined	5338	10208	10709
goodness-of-fit	0.920	0.981	1.031
*R*1	0.0608	0.0598	0.0581
w*R*2	0.1512	0.1715	0.1662
$\Delta\rho_{max}$, e Å^{-3}	0.974	0.639	0.686
$\Delta\rho_{min}$, e Å^{-3}	−0.743	−1.164	−0.407

[a] Radiation used was graphite-monochromated Cu Kα (λ = 1.540 56 Å).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Bis(trichlorotitanium phenoxide) **7**

Ti(1)−O(1)	1.723(3)	Ti(1)−Cl(2)	2.179(2)
Ti(1′)−O(1′)	1.731(3)	Ti(1′)−Cl(2′)	2.159(2)
Ti(1)−Cl(1)	2.157(2)	Ti(1)−Cl(3)	2.185(2)
Ti(1′)−Cl(1′)	2.192(2)	Ti(1′)−Cl(3′)	2.170(2)
Cl(1)−Ti(1)−O(1)	109.6(1)	Cl(1′)−Ti(1′)−Cl(2′)	108.6(1)
Cl(1′)−Ti(1′)−O(1′)	108.4(1)	Cl(1)−Ti(1)−Cl(3)	109.9(1)
Cl(2)−Ti(1)−O(1)	107.9(1)	Cl(1′)−Ti(1′)−Cl(3′)	109.6(1)
Cl(2′)−Ti(1′)−O(1′)	109.7(1)	Cl(2)−Ti(1)−Cl(3)	109.8(1)
Cl(3)−Ti(1)−O(1)	110.1(1)	Cl(2′)−Ti(1′)−Cl(3′)	109.6(1)
Cl(3′)−Ti(1′)−O(1′)	111.0(1)	C(1)−O(1)−Ti(1)	162.7(3)
Cl(1)−Ti(1)−Cl(2)	109.5(1)	C(1′)−O(1′)−Ti(1′)	164.6(3)

phenoxide) **2** with $CH_3COOCH_2CH_3$ is the only other related complex known to incorporate pentacoordinate Ti(IV), and in this case an approximately square pyramidal geometry is favored.[5] Calculations have predicted that the preferred geometry of the hypothetical 1:1 complex of $TiCl_4$ with formaldehyde is trigonal bipyramidal, not square pyramidal,[12] but our observations suggest that both structures are accessible. The unusual preferences of bis(trichlorotitanium phenoxides) **2** and **7** for pentacoordination are presumably due to steric hindrance created by substituents adjacent to the sites of Lewis acidity.

Other geometric parameters in the structure of the 1:2 complex of bis(trichlorotitanium phenoxide) **7** with 4,4′-dimethylbenzophenone have normal values. For example, the average dative Ti···O bond length involving the carbonyl oxygen atoms (2.062(3) Å) and the average Ti−O bond length involving the phenoxide oxygen atoms (1.770(3) Å) are closely similar to those found in the related 1:2 complex of bis(trichlorotitanium phenoxide) **2** with $CH_3COOCH_2CH_3$.[5] The Ti−Cl bond lengths also have a normal average value (2.248(2) Å), and the average phenoxy Ti−O−C bond angles are expectedly large (155.3(2)°), which confirms the presence of strong Ti−O *π*-bonding. Although $CH_3COOCH_2CH_3$ is bound by bis(trichlorotitanium phenoxide) **2** in the normal $\eta^1(\sigma)$ manner,[13] with Ti close to the carbonyl plane, 4,4′-dimethylbenzophenone is bound by bis(trichlorotitanium phenoxide) **7** with an average Ti···O═C bond angle of 161.7(3)° and an average Ti···O═C−C dihedral angle of 33.0(10)°. This reveals that Ti lies far from the carbonyl plane and that the interaction must therefore have important *π* character.

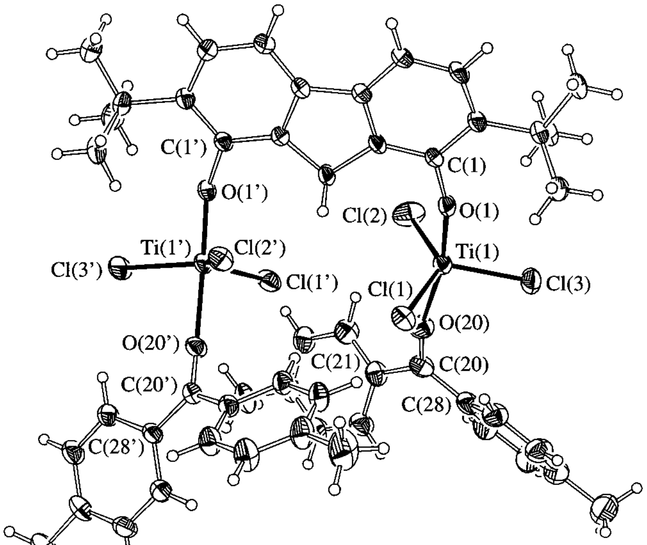

Figure 2. ORTEP view of the structure of the CH_2Cl_2 solvate of the 1:2 complex of bis(trichlorotitanium phenoxide) **7** with 4,4′-dimethylbenzophenone. Non-hydrogen atoms are represented by ellipsoids corresponding to 40% probability, hydrogen atoms are shown as spheres of arbitrary size, bonds to titanium are drawn using solid lines, and CH_2Cl_2 is omitted for clarity.

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(13) For a recent discussion of the *σ* and *π* complexation of carbonyl compounds by $TiCl_4$, see: Singh, D. K.; Springer, J. B.; Goodson, P. A.; Corcoran, R. C. *J. Org. Chem.* **1996**, *61*, 1436.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for the CH_2Cl_2 Solvate of the 1:2 Complex of Bis(trichlorotitanium phenoxide) **7** with 4,4′-Dimethylbenzophenone

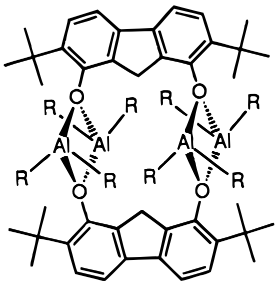
Ti(1)−O(1)	1.764(3)	Ti(1)−Cl(2)	2.265(2)
Ti(1′)−O(1′)	1.776(3)	Ti(1′)−Cl(2′)	2.271(2)
Ti(1)−O(20)	2.066(3)	Ti(1)−Cl(3)	2.223(1)
Ti(1′)−O(20′)	2.058(3)	Ti(1′)−Cl(3′)	2.234(1)
Ti(1)−Cl(1)	2.257(2)	O(20)−C(20)	1.248(5)
Ti(1′)−Cl(1′)	2.236(2)	O(20′)−C(20′)	1.269(4)

O(1)−Ti(1)−O(20)	168.8(1)	O(20′)−Ti(1′)−Cl(2′)	85.6(1)
O(1′)−Ti(1′)−O(20′)	172.8(1)	O(20′)−Ti(1′)−Cl(3′)	86.4(1)
O(1)−Ti(1)−Cl(1)	94.1(1)	Cl(1)−Ti(1)−Cl(2)	133.8(1)
O(1)−Ti(1)−Cl(2)	91.6(1)	Cl(1)−Ti(1)−Cl(3)	112.6(1)
O(1)−Ti(1)−Cl(3)	99.9(1)	Cl(2)−Ti(1)−Cl(3)	111.4(1)
O(1′)−Ti(1′)−Cl(1′)	98.1(1)	Cl(1′)−Ti(1′)−Cl(2′)	121.3(1)
O(1′)−Ti(1′)−Cl(2′)	87.8(1)	Cl(1′)−Ti(1′)−Cl(3′)	112.4(1)
O(1′)−Ti(1′)−Cl(3′)	95.1(1)	Cl(2′)−Ti(1′)−Cl(3′)	125.2(1)
O(20)−Ti(1)−Cl(1)	82.6(1)	Ti(1)−O(1)−C(1)	162.9(2)
O(20)−Ti(1)−Cl(2)	83.0(1)	Ti(1′)−O(1′)−C(1′)	147.6(2)
O(20)−Ti(1)−Cl(3)	91.2(1)	Ti(1)−O(20)−C(20)	165.0(3)
O(20′)−Ti(1′)−Cl(1′)	87.8(1)	Ti(1′)−O(20′)−C(20′)	158.4(3)

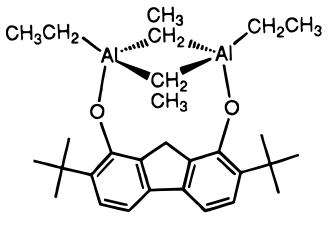
Ti(1)−O(20)−C(20)−C(21)	−158.5(10)
Ti(1)−O(20)−C(20)−C(28)	21.8(15)
Ti(1′)−O(20′)−C(20′)−C(21′)	−44.9(9)
Ti(1′)−O(20′)−C(20′)−C(28′)	136.4(6)

Our work establishes that fluorenediol **3** can easily be converted into bis(trichlorotitanium phenoxide) **7**, a bidentate Lewis acid that is strong and structurally well-defined. In principle, equally simple procedures should transform compound **3** into many other bidentate Lewis acids. This versatility is an important advantage of our basic strategy for making multidentate Lewis acids because it allows a wide variety of reagents to be made from a single organic precursor. To test the generality of our strategy, we attempted to make a new bidentate Lewis acid **8** by treating a solution of fluorenediol **3** in toluene with 2 equivalents of $Al(CH_2CH_3)_3$. Partial evaporation of solvent yielded colorless crystals of a bis(diethylaluminum phenoxide) in 62% yield. The aromatic region of its ^{1}H NMR spectrum, recorded at 25 °C, showed that the fluorene ring was symmetrically substituted but that two different ethyl groups were present, thereby excluding the expected structure **8**.

Two closely related alternative structures that are consistent with the observed NMR spectrum are the dimer **9** and the ethyl-bridged monomer **10**. To distinguish these alternatives, we recorded variable-temperature ^{1}H NMR spectra (400 MHz, toluene-d_8) and analyzed the exchange of the nonequivalent ethyl groups. At 25 °C, the spectrum showed separate ethyl quartets centered at δ 0.51 and 0.62. As the temperature was increased, these signals broadened and finally coalesced at $T_c = 92$ °C, enabling us to estimate that $\Delta G^{\ddagger} = 18.2 \pm 0.2$ kcal mol^{-1} for exchange of the ethyl groups.[14] In principle, this exchange can occur in hypothetical dimer **9** by breaking individual Al−O bonds and opening the Al_2O_2 rings, or simply by rotating the rings around axes defined by their O···O diagonals. Exchange can occur in hypothetical ethyl-bridged structure **10** by breaking at least one three-center two-electron bond and opening the Al_2C_2 ring. The observed $\Delta G^{\ddagger}$ is similar to those measured for processes in which analogous Al_2O_2 rings are opened,[5] and it is much larger than the $\Delta G^{\ddagger}$ observed for exchange of the terminal and bridging ethyl groups in $[Al(CH_2CH_3)_3]_2$, which is only 10.2 ± 0.3 kcal mol^{-1} in toluene at 25 °C.[15] As a result, we conclude that the structure favored in solution must be dimer **9** or a higher cyclic oligomer, and we suggest that exchange occurs by breaking individual Al−O bonds and opening the Al_2O_2 rings.



9 (R = CH_2CH_3)



10

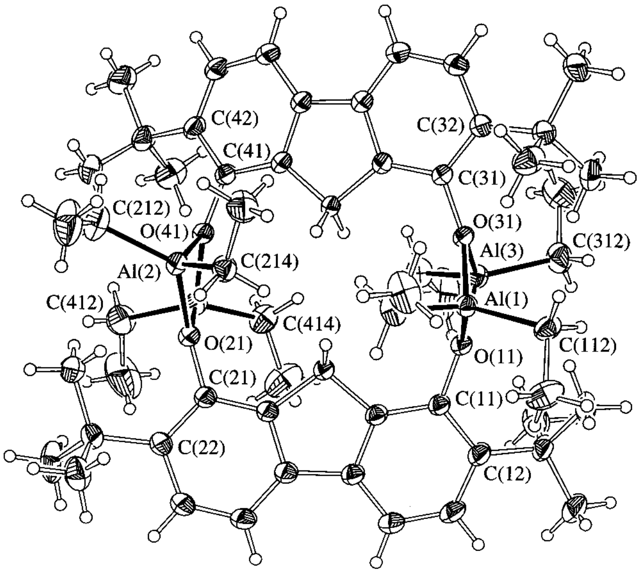


Figure 3. ORTEP view of the structure of the dimer **9** of bis(diethylaluminum phenoxide) **8**. Non-hydrogen atoms are represented by ellipsoids corresponding to 40% probability, hydrogen atoms are shown as spheres of arbitrary size, and bonds to aluminum are drawn using solid lines.

An X-ray crystallographic study subsequently confirmed that dimer **9** is formed in the solid state. The results of this study, summarized in Figure 3 and in Tables 1 and 4, show that dimer **9** incorporates several interesting features. Normal Al_2O_2 rings are rigorously or approximately planar,[3] but those of dimer **9** are distinctly puckered, and the average of the absolute values of the Al−O−Al−O dihedral angles is 12.8(1)°. However, the oxygen atoms are nearly trigonal planar, and the average value of the sums of their bond angles is 358.8(1)°, so the amount of strain is small. This is confirmed by the average Al−O bond length (1.884(2) Å), which is rather long but still within the range of distances normally observed in the Al_2O_2 rings of dimeric alkylaluminum alkoxides and aryloxides (1.840−1.895 Å).[3] In addition, the average values of the Al−O−Al angles (99.1(1)°), O−Al−O angles (79.6(1)°), Al−C bond lengths (1.956(3) Å), nonbonded Al···Al distances (2.866(2) Å), nonbonded O···O distances (2.411(2) Å), and C−Al−C angles (112.0(1)°) are similar to those found in other Al_2O_2 rings.[3]

The Al_2O_2 rings of dimer **9** are approximately orthogonal to the aryl groups to which they are connected, and the average

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[14] Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982; p 96.

[15] Yamamoto, O.; Hayamizu, K.; Yanagisawa, M. *J. Organomet. Chem.* **1974**, *73*, 17.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for the Dimer **9** of Bis(diethylaluminum phenoxide) **8**

Al(1)−O(11)	1.894(2)	Al(4)−O(21)	1.889(2)
Al(1)−O(31)	1.865(2)	Al(4)−O(41)	1.870(2)
Al(1)−C(112)	1.963(2)	Al(4)−C(412)	1.969(3)
Al(1)−C(114)	1.943(3)	Al(4)−C(414)	1.947(3)
Al(3)−O(11)	1.882(2)	Al(1)···Al(3)	2.862(1)
Al(3)−O(31)	1.904(2)	Al(2)···Al(4)	2.871(2)
Al(3)−C(312)	1.960(3)	O(11)···O(31)	2.424(2)
Al(3)−C(314)	1.951(3)	O(21)···O(41)	2.398(2)
Al(2)−O(21)	1.868(2)	O(11)−C(11)	1.415(2)
Al(2)−O(41)	1.903(2)	O(31)−C(31)	1.417(2)
Al(2)−C(212)	1.966(3)	O(21)−C(21)	1.409(2)
Al(2)−C(214)	1.953(2)	O(41)−C(41)	1.410(2)

O(11)−Al(1)−O(31)	80.3(1)	O(21)−Al(4)−O(41)	79.3(1)
O(11)−Al(1)−C(112)	109.3(1)	O(21)−Al(4)−C(412)	107.6(1)
O(11)−Al(1)−C(114)	119.0(1)	O(21)−Al(4)−C(414)	121.8(1)
C(112)−Al(1)−C(114)	113.7(1)	C(412)−Al(4)−C(414)	112.1(1)
O(31)−Al(1)−C(112)	118.9(1)	O(41)−Al(4)−C(412)	119.0(1)
O(31)−Al(1)−C(114)	111.8(1)	O(41)−Al(4)−C(414)	113.7(1)
O(11)−Al(3)−O(31)	79.6(1)	C(11)−O(11)−Al(1)	124.8(1)
O(11)−Al(3)−C(312)	120.6(1)	C(11)−O(11)−Al(3)	135.4(1)
O(11)−Al(3)−C(314)	110.8(1)	Al(1)−O(11)−Al(3)	98.6(1)
C(312)−Al(3)−C(314)	112.6(1)	C(31)−O(31)−Al(1)	134.1(1)
O(31)−Al(3)−C(312)	108.1(1)	C(31)−O(31)−Al(3)	125.4(1)
O(31)−Al(3)−C(314)	121.9(1)	Al(1)−O(31)−Al(3)	98.8(1)
O(21)−Al(2)−O(41)	79.0(1)	C(21)−O(21)−Al(2)	136.9(1)
O(21)−Al(2)−C(212)	126.2(1)	C(21)−O(21)−Al(4)	121.7(1)
O(21)−Al(2)−C(214)	108.0(1)	Al(2)−O(21)−Al(4)	99.7(1)
C(212)−Al(2)−C(214)	109.8(1)	C(41)−O(41)−Al(2)	119.0(1)
O(41)−Al(2)−C(212)	104.6(1)	C(41)−O(41)−Al(4)	141.5(1)
O(41)−Al(2)−C(214)	128.4(1)	Al(2)−O(41)−Al(4)	99.1(1)

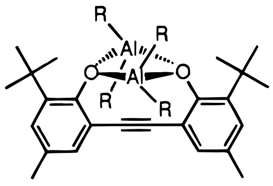
O(11)−Al(1)−O(31)−Al(3)	−12.4(1)
O(11)−Al(3)−O(31)−Al(1)	12.5(1)
O(31)−Al(1)−O(11)−Al(3)	12.5(1)
O(31)−Al(3)−O(11)−Al(1)	−12.3(1)
O(21)−Al(2)−O(41)−Al(4)	13.3(1)
O(21)−Al(4)−O(41)−Al(2)	−13.1(1)
O(41)−Al(2)−O(21)−Al(4)	−13.2(1)
O(41)−Al(4)−O(21)−Al(2)	13.4(1)
C(12)−C(11)−O(11)−Al(1)	−104.8(2)
C(12)−C(11)−O(11)−Al(3)	90.9(2)
C(32)−C(31)−O(31)−Al(1)	87.6(2)
C(32)−C(31)−O(31)−Al(3)	−110.8(2)
C(22)−C(21)−O(21)−Al(2)	94.5(2)
C(22)−C(21)−O(21)−Al(4)	−103.6(2)
C(42)−C(41)−O(41)−Al(2)	−110.3(2)
C(42)−C(41)−O(41)−Al(4)	80.2(3)

of the absolute values of the C(*t*-Bu)−C−O−Al dihedral angles is 97.8(3)°. This conformational preference separates the ethyl groups in dimer **9** into two diastereotopic sets, one oriented toward the interior of the dimer and the other toward the exterior, and each aluminum atom is bonded to one ethyl group of each type. Exchange of the ethyl groups by simple rotations of intact Al_2O_2 rings around axes defined by their O···O diagonals is presumably disfavored because this would create highly unfavorable interactions with adjacent substituents on the aryl rings.

It is instructive to compare $\Delta G^{\ddagger}$ for exchange in dimer **9** (18.2 ± 0.2 kcal mol^{-1} at 92 °C) with that observed for the closely related exchange of *i*-butyl groups in structure **11** (17.0 ± 0.2 kcal mol^{-1} at 55 °C).[5] Even though the Al_2O_2 ring of structure **11** is much more highly distorted than that of dimer **9**, its opening is only slightly faster. This suggests that the observed deformations are not enthalpically costly.

Conclusions

Our results confirm 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. Precursors with rigidly oriented hydroxyl groups give rise to multidentate Lewis acids that are structurally well-defined, in which the sites of Lewis acidity are held close enough together to be able to act in conjunction but far enough apart to avoid interacting directly in unproductive ways. In principle, multidentate Lewis acids made by this strategy can be designed to have useful properties, such as the ability to recognize and bind complementary 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 synthesizing structurally well-defined multidentate Lewis acids will make them more readily available and will help promote further study of their unique coordination chemistry.



11 (R = *i*-Bu)

Experimental Section

Pentane was dried by distillation from sodium, CH_2Cl_2 was dried by distillation from P_2O_5, and $TiCl_4$ was purified by distillation. All other reagents were commercial products that were used without further purification. Flash chromatography was performed in the normal way.[16]

5-Bromo-2-(1,1-dimethylethyl)phenol.[9,17] A suspension prepared by adding SiO_2 (14.4 g, 240 mmol)[18] and Na_2CO_3 (5.05 g, 47.6 mmol) to 3-bromophenol (5.00 g, 28.9 mmol) in CCl_4 (40 mL) was stirred at 25 °C and treated dropwise with 2-bromo-2-methylpropane (4.76 g, 34.7 mmol). The mixture was then heated at reflux for 18 h, cooled to 25 °C, and filtered. The filtered solid was washed with $CHCl_3$, and the washings were added to the original filtrate. The combined organic phases were washed with H_2O and saturated aqueous NaCl, and then they were dried with anhydrous $MgSO_4$. Volatiles were removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (93%)/ethyl acetate (7%)) to give 5-bromo-2-(1,1-dimethylethyl)phenol (5.75 g, 25.1 mmol, 87%) as a colorless oil.[9]

2,2′-Methylenebis[3-bromo-6-(1,1-dimethylethyl)phenol] (5).[9] Diphenol **5** was prepared from 5-bromo-2-(1,1-dimethylethyl)phenol by the published method.[9]

1,1′-Methylenebis[6-bromo-3-(1,1-dimethylethyl)-2-methoxybenzene] (6).[9] A suspension prepared by adding K_2CO_3 (2.70 g, 19.5 mmol) to 2,2′-methylenebis[3-bromo-6-(1,1-dimethylethyl)phenol] (**5**; 0.917 g, 1.95 mmol) in acetone (20 mL) was stirred at 25 °C and treated with iodomethane (5.70 g, 40.2 mmol). The mixture was then heated at reflux for 36 h, cooled to 25 °C, and filtered. The filtered solid was washed with $CHCl_3$, and the washings were added to the original filtrate. Volatiles were removed by evaporation under reduced pressure, the residue was treated with saturated aqueous NH_4Cl, and the resulting mixture was extracted with $CHCl_3$. The combined extracts were washed with saturated aqueous NaCl and dried with anhydrous $MgSO_4$. Volatiles were removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (100%)) to give 1,1′-methylenebis[6-bromo-3-(1,1-dimethylethyl)-2-methoxybenzene] (**6**; 0.923 g, 1.85 mmol, 95%) as a colorless solid. An analytically pure sample was prepared by recrystallization from hexane: mp 165−167 °C (lit.[9] 164−166 °C).

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

(17) For a similar *tert*-butylation procedure, see: Kamitori, Y.; Hojo, M.; Masuda, R.; Izumi, T.; Tsukamoto, S. *J. Org. Chem.* **1984**, *49*, 4161.

(18) Although the *tert*-butylation procedure of Hojo and co-workers specifies the use of SiO_2 that has been dried by heating under vacuum,[17] we found that SiO_2 of the type normally employed for flash chromatography[16] could be used directly without special treatment.

2,7-Bis(1,1-dimethylethyl)-1,8-dimethoxy-9*H*-fluorene (4).[9] Dimethyl ether **4** was prepared from 1,1′-methylenebis[6-bromo-3-(1,1-dimethylethyl)-2-methoxybenzene] (**6**) by the published procedure.[9]

2,7-Bis(1,1-dimethylethyl)-9*H*-fluorene-1,8-diol (3). A solution of 2,7-bis(1,1-dimethylethyl)-1,8-dimethoxy-9*H*-fluorene (**4**; 225 mg, 0.665 mmol) in CH_2Cl_2 (10 mL) was stirred at −78 °C under dry Ar and treated dropwise with a solution of BBr_3 (666 mg, 2.66 mmol) in CH_2Cl_2 (2.6 mL). The cooling bath was removed, and the temperature was allowed to rise to 25 °C. After 18 h, the resulting mixture was recooled to 0 °C, treated with H_2O (15 mL), and extracted with $CHCl_3$. The combined extracts were washed with saturated aqueous NaCl and dried with anhydrous $MgSO_4$. Volatiles were removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, hexane (93%)/ethyl acetate (7%)) to give 2,7-bis-(1,1-dimethylethyl)-9*H*-fluorene-1,8-diol (**3**; 178 mg, 0.573 mmol, 86%) as a colorless solid. An analytically pure sample was prepared by recrystallization from $CHCl_3$: mp 176−178 °C; IR (melt) 3548 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.48 (s, 18H), 3.64 (s, 2H), 4.80 (s, 2H), 7.27 (d, 2H, $^3J = 8.0$ Hz), 7.32 (d, 2H, $^3J = 8.0$ Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.5, 30.0, 34.5, 112.4, 126.3, 128.1, 134.4, 141.4, 150.8; HRMS (EI) calcd for $C_{21}H_{26}O_2$ m/e 310.1933, found m/e 310.1925.

Bis(trichlorotitanium phenoxide) 7. A solution of 2,7-bis(1,1-dimethylethyl)-9*H*-fluorene-1,8-diol (**3**; 10.6 mg, 0.0341 mmol) in CH_2Cl_2 (0.5 mL) was stirred at 25 °C under dry Ar and treated dropwise with neat $TiCl_4$ (13.8 mg, 0.0727 mmol). After the addition was complete, the resulting red mixture was kept at 25 °C for 20 min. Partial evaporation of solvent then yielded red crystals of bis(trichlorotitanium phenoxide) **7** (19.0 mg, 0.0308 mmol, 90%): mp 172−176 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.59 (s, 18H), 4.60 (s, 2H), 7.42 (d, 2H, $^3J = 8.0$ Hz), 7.53 (d, 2H, $^3J = 8.0$ Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 30.5, 33.6, 35.2, 118.2, 126.4, 135.7, 137.0, 140.9, 168.9.

1:2 Complex of Bis(trichlorotitanium phenoxide) 7 with 4,4′-Dimethylbenzophenone. A solution of 2,7-bis(1,1-dimethylethyl)-9*H*-fluorene-1,8-diol (**3**; 27.0 mg, 0.0870 mmol) in CH_2Cl_2 (1.2 mL) was stirred at 25 °C under dry Ar and treated dropwise with neat $TiCl_4$ (32.9 mg, 0.173 mmol). After the addition was complete, the resulting red mixture was kept at 25 °C for 15 min and was then treated with a solution of 4,4′-dimethylbenzophenone (37.0 mg, 0.176 mmol) in CH_2Cl_2 (1.2 mL). Partial evaporation of solvent then yielded red crystals of the 1:2 complex of bis(trichlorotitanium phenoxide) **7** with 4,4′-dimethylbenzophenone as a solvate containing an equimolar amount of CH_2Cl_2 (79.0 mg, 0.0704 mmol, 81%): mp 102−110 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.60 (s, 18H), 2.45 (s, 12H), 4.77 (s, 2H), 5.30 (s, 2H), 7.31 (d, 8H, $^3J = 8.0$ Hz), 7.39 (d, 2H, $^3J = 8.0$ Hz), 7.48 (d, 2H, $^3J = 8.0$ Hz), 7.90 (d, 8H, $^3J = 8.0$ Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.8, 30.6, 35.0, 35.2, 53.3, 117.2, 125.6, 129.1, 132.5, 133.4, 137.4, 141.2, 145.7, 145.7, 168.2, 201.4.

Dimer 9 of Bis(diethylaluminum phenoxide) 8. A solution of 2,7-bis(1,1-dimethylethyl)-9*H*-fluorene-1,8-diol (**3**; 14.8 mg, 0.0477 mmol) in a mixture of pentane (0.6 mL) and CH_2Cl_2 (0.2 mL) was stirred at 25 °C under dry Ar and treated dropwise with neat $Al(CH_2CH_3)_3$ (10.9 mg, 0.0955 mmol). After the addition was complete, the resulting brown mixture was kept at 25 °C for 20 min. Partial evaporation of solvent then yielded brown crystals of the dimer **9** of bis(diethylaluminum phenoxide) **8** (14.6 mg, 0.0153 mmol, 62%): ^1H NMR (400 MHz, $CDCl_3$) δ 0.28 (q, 8H, $^3J = 8.1$ Hz), 0.35 (q, 8H, $^3J = 8.1$ Hz), 0.65 (t, 12H, $^3J = 8.1$ Hz), 0.87 (t, 12H, $^3J = 8.1$ Hz), 1.55 (s, 36H), 4.75 (s, 4H), 7.52 (d, 4H, $^3J = 8.0$ Hz), 7.55 (d, 4H, $^3J = 8.0$ Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 2.1, 5.2, 8.1, 8.7, 33.1, 36.4, 36.9, 115.7, 128.9, 134.5, 139.6, 141.7, 148.8.

X-ray Crystallographic Studies of Bis(trichlorotitanium phenoxide) 7, the 1:2 Complex of Bis(trichlorotitanium phenoxide) 7 with 4,4′-Dimethylbenzophenone, and the Dimer 9 of Bis(diethylaluminum phenoxide) 8. Data were collected on an Enraf-Nonius CAD-4 diffractometer. Cell constants were obtained using 25 well-centered reflections. Five standard reflections were measured every 1 h of exposure time and showed only small fluctuations. The data were corrected for absorption by Gaussian integration. The structures were solved by direct methods using either SHELXS-85[19] or SHELXS-96.[20] Full-matrix least-squares refinements on F^2 were carried out with SHELXL-93.[21] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in ideal positions and refined using a riding model with isotropic thermal parameters 1.2 times those of their carrier atoms (1.5 times for methyl groups).

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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 bis(trichlorotitanium phenoxide) **7**, the CH_2Cl_2 solvate of its 1:2 complex with 4,4′-dimethylbenzophenone, and the dimer **9** of bis(diethylaluminum phenoxide) **8** (70 pages). Ordering information is given on any current masthead page.

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(19) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(20) Sheldrick, G. M. *SHELXS-96*; University of Göttingen: Göttingen, Germany, 1996.

(21) Sheldrick, G. M. *SHELXL-93*; University of Göttingen: Göttingen, Germany, 1993.