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Article

Half-Sandwich Titanium(IV) Complexes with Kläui's Tripod Ligand

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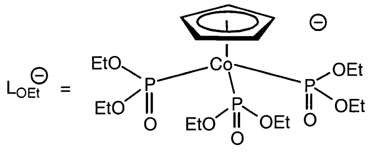
Treatment of [Ti(O-*i*-Pr)$_2$Cl$_2$] with NaL$_{OEt}$ (L$_{OEt}$$^-$ = [CpCo{P(O)(OEt)$_2$}$_3$]$^-$, Cp = η^5-C$_5$H$_5$) afforded [L$_{OEt}$Ti(O-*i*-Pr)$_2$Cl] that reacted with HCl in ether to give [L$_{OEt}$TiCl$_3$] (**1**). The average Ti–O and Ti–Cl distances in **1** are 1.975 and 2.293 Å, respectively. Reaction of titanyl sulfate with NaL$_{OEt}$ in water followed by addition of HBF$_4$ afforded [L$_{OEt}$TiF$_3$] (**2**), the Ti–O and Ti–F distances of which are 2.020(2) and 1.792(2) Å, respectively. The Zr(IV) analogue [L$_{OEt}$ZrF$_3$] (**3**) was prepared similarly from zirconyl nitrate, NaL$_{Oet}$, and HBF$_4$ in water. The Zr–O and average Zr–F distances in **3** are 2.139(2) and 1.938(2) Å, respectively. Treatment of **1** with tetrachlorocatechol (H$_2$Cl$_4$cat) afforded [L$_{OEt}$Ti(Cl$_4$cat)Cl] (**4**). The average Ti–O(P), Ti–O(C), and Ti–Cl distances in **4** are 1.972, 1.926, and 2.334 Å, respectively. Hydrolysis of **4** in the presence of Et$_3$N yielded the μ-oxo dimer [(L$_{OEt}$)$_2$Ti$_2$(Cl$_4$cat)$_2$(μ-O)] (**5**). The average Ti–O(P), Ti–O(C), and Ti–O(Ti) distances in **5** are 2.027, 1.926, and 1.7977(9) Å. Treatment of **1** with 1,1′-binaphthol (BINOLH$_2$) in the presence of Et$_3$N afforded [(L$_{OEt}$)$_2$Ti$_2$(μ-O)$_2$(μ-BINOL)]•2BINOLH$_2$ (**6**•2BINOLH$_2$). Complex **1** is capable of catalyzing ring opening of epoxides with Me$_3$SiN$_3$ under solvent-free conditions presumably via a Ti–azide intermediate.

Introduction

Chart 1



The anionic oxygen tripod ligands [CpCo{P(O)(OR)$_2$}$_3$]$^-$ (L$_{OR}$$^-$, R = alkyl group; Chart 1) developed by Kläui have been recognized as oxygen analogues of cyclopentadienyl.[1] Although the L$_{OR}$$^-$ ligands are known to have high affinity for d^0 metal ions, there are relatively few studies on their complexes with Ti,[2] particularly those of the type [L$_{OR}$TiX$_3$] (X = anionic ligand). This is in stark contrast with the well-explored [CpTiX$_3$] complexes, which are active catalysts for olefin polymerization.[3,4] Our interest in half-sandwich Ti−L$_{OR}$ complexes is stimulated by the fact that active sites of catalytically important Ti silicates and molecular sieves[5,6] contain Ti centers in oxygen-rich coordination environments. Therefore, the study of coordination chemistry of Ti−L$_{OEt}$ complexes may provide insights into the reaction mechanisms of these Ti-containing catalysts. Kläui and co-workers reported that the reaction of NaL$_{OEt}$ with Ti^{3+}(aq) afforded [(L$_{OEt}$)$_2$Ti]$^+$, which was air oxidized to [(L$_{OEt}$)$_2$Ti]$^{2+}$.[2] The strong tendency of formation of the Ti bis-tripod complexes is apparently due to the high affinity of Ti ions for the hard oxygen donor ligand. To avoid the formation of sandwich compounds, Ward and co-workers synthesized half-sandwich [L$_{OEt}$ZrCl$_3$] by the ligand exchange reaction between [CpZrCl$_3$] and NaL$_{OEt}$.[7] Recently, Koelle and co-workers reported that

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reaction of [$TiCl_4(THF)_2$] with a dianionic oxygen tripod ligand L^{2-} (H_2L = [$H_2(\eta^5$-$C_5Me_5)Ru\{P(O)Ph_2\}_3$]) afforded the chloro-bridged dimer [$LTiCl_2]_2$ that hydrolyzed to trinuclear [$\{LTiO\}_3(\mu_3$-O)H_2].[8] We herein report on the synthesis and crystal structures of half-sandwich Ti(IV)−L_{OEt} compounds and their catecholate and binaphtholate derivates. The catalytic activity of [$L_{OEt}TiCl_3$] toward ring opening of epoxides will be described.

Experimental Section

General Considerations. All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified, distilled, and degassed prior to use. NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300, 75, 282.5, and 121.5 MHz for ^1H, ^{13}C, ^{19}F, and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^1H and ^{13}C), $CF_3C_6H_5$ (^{19}F), and H_3PO_4 (^{31}P). Infrared spectra (Nujol) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Elemental analyses were performed by Medac Ltd., Surrey, U.K.

Materials. The ligand NaL_{OEt}[9] was prepared according to a literature method. [Ti(O-*i*-Pr)$_2Cl_2$] was prepared from [$TiCl_4$] with [Ti(O-*i*-Pr)$_4$] as described elsewhere.[10] Titanyl sulfate (15% in dilute sulfuric acid), zirconyl nitrate (35% in dilute nitric acid), and tetrachlorocatechol $H_2(Cl_4cat)$ were obtained from Aldrich and used as received.

Preparation of [$L_{OEt}TiCl_3$] (1). To a solution of [Ti(O-*i*-Pr)$_2Cl_2$] (66 mg, 0.278 mol) in ether (15 mL) at −78 °C was added NaL_{OEt} (155 mg, 0.277 mol) in diethyl ether (10 mL) dropwise. The solution immediately turned lemon yellow, and a white precipitate deposited. After the mixture was stirred for 1 h, HCl (1.5 mL of a 1 M solution in ether) was added via a syringe and the resulting new mixture was warmed to room temperature and filtered. The volatiles were pumped off, and the residue was washed with diethyl ether and hexane and dried in vacuo. X-ray-quality crystals were obtained upon recrystallization from toluene/hexane. Yield: 0.170 g, 89%. Anal. Calcd for $C_{17}H_{35}Cl_3CoO_9P_3Ti$: C, 29.61; H, 5.12. Found: C, 29.68; H, 5.14. ^1H NMR (C_6D_6): δ 1.34 (t, 18H, CH_3), 4.39 (m, 12H, OCH_2), 4.89 (s, 5H, C_5H_5). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 122.4 (m). MS (FAB): *m*/*z* 653 (M^+ − Cl).

Preparation of [$L_{OEt}TiF_3$] (2). To a solution of titanyl sulfate (0.062 mmol, 0.1 mL of 15% solution in dilute sulfuric acid) in water (10 mL) in air was added 1 equiv of NaL_{OEt} (31 mg, 0.056 mmol), and the mixture was stirred for 30 min at room temperature. Acidfication of the resulting solution with a few drops of HBF_4 (50% in water) resulted in formation of a pale yellow precipitate, which was collected, washed with water, and dried in air. Recrystallization from THF/hexane afforded yellow blocks that are suitable for X-ray diffraction. Yield: 27 mg, 76%. ^1H NMR (acetone-d_6): δ 1.45 (t, 18H, CH_3), 4.26 (m, 12H, OCH_2), 5.39 (s, 5H, Cp). ^{31}P $\{^1H\}$ NMR (acetone-d_6): δ 120 (s). ^{19}F NMR (acetone-d_6): −154.6. Anal. Calcd for $C_{17}H_{35}CoF_3O_9P_3Ti$: C, 31.9; H, 5.47. Found: C, 31.2; H, 5.5. MS (FAB): *m*/*z* 621 (M^+ − F).

Preparation of [$L_{OEt}ZrF_3$] (3). This was prepared similarly as for **2** using zirconyl nitrate (0.076 mmol, 0.1 mL of a 35% solution in dilute nitric acid) in place of titanyl sulfate. X-ray-quality crystals were obtained by recrystallization from THF/hexane. Yield: 33 mg, 71%. ^1H NMR (acetone-d_6): δ 1.29 (t, 18H, CH_3), 4.15 (m, 12H, OCH_2), 5.13 (s, 5H, Cp). ^{31}P $\{^1H\}$ NMR (acetone-d_6): δ 119 (s). ^{19}F NMR (acetone-d_6): −153.2. Anal. Calcd for $C_{17}H_{35}CoF_3O_9P_3Zr$: C, 29.8; H, 5.12. Found: C, 27.9; H, 5.25. MS (FAB): *m*/*z* 664 (M^+ − F).

Preparation of [$L_{OEt}Ti(Cl_4cat)Cl$] (4). To a mixture of **1** (119 mg, 0.172 mol) and THF (5 mL) was added tetrachlorocatechol monohydrate (45 mg, 0.174 mol), and the resulting red solution was stirred for 1 h. Upon addition of hexanes (20 mL) a red precipitate was formed and was collected and dried in vacuo. Recrystallization from toluene/hexane afforded deep red crystals that were suitable for X-ray diffraction study. Yield: 149 mg, 78%. Anal. Calcd for $C_{23}H_{35}Cl_5CoO_{11}P_3Ti$: C, 31.95; H, 4.08. Found: C 32.23; H, 4.25. ^1H NMR (C_6D_6): δ 1.33 (t, 18H, CH_3), 4.26−4.40 (m, 12H, OCH_2), 4.84 (s, 5H, C_5H_5). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 122.8 (m). MS (FAB): *m*/*z* 827 (M^+ − Cl).

Preparation of [$(L_{OEt})_2Ti_2(Cl_4cat)_2(\mu$-O)] (5). Method A. To a solution of **4** (100 mg, 0.116 mmol) in CH_2Cl_2 (10 mL) was added 1 equiv of $Ag(CF_3SO_3)$ (28 mg, 0.11 mmol), and the mixture was stirred for 30 min and filtered. The filtrate was evaporated to dryness and recrystallized from toluene/hexane to give red blocks. Yield: 77 mg, 79%. Anal. Calcd for $C_{46}H_{70}Cl_8Co_2O_{23}P_6Ti_2$: C, 32.97; H, 4.18. Found: C, 33.98; H, 4.31. ^1H NMR (C_6D_6): δ 1.18 (t, 12H, CH_3), 1.32 (t, 12H, CH_3), 1.44 (t, 12H, CH_3), 3.97−4.01 (m, 4H, OCH_2), 4.04−4.17 (m, 12H, OCH_2), 4.48−4.51 (m, 4H, OCH_2), 4.62−4.63 (m, 4H, OCH_2), 4.97 (s, 5H, C_5H_5). $^{31}P\{^1H\}$ NMR (C_6D_6): 123.1 (d), 113.3 (t). MS (FAB): *m*/*z* 1674 (M^+).

Method B. To a solution of **4** (100 mg, 0.116 mol) in toluene (10 mL) at −78 °C was added 2 equiv of PhLi or Ph_2Zn (0.22 mol). The color changed from red to orange and finally to red when the solution was warmed to room temperature. The volatiles were pumped off, and residue was washed with hexane. Recrystallization from toluene/hexane afforded red crystals. Yield: 70−82%.

Preparation of [$(L_{OEt})_2Ti_2(\mu$-O)$_2(\mu$-BINOL)]·2BINOLH$_2$ (6·2BINOLH$_2$). To a solution of **1** (91.4 mg, 0.164 mol) in CH_2Cl_2 (10 mL) was added racemic 1,1′-binaphthol (38 mg, 0.164 mol) in CH_2Cl_2 (5 mL), and the mixture was stirred at room-temperature overnight. The volatiles were pumped off, and the orange powder was extracted with hexane (20 mL). Cooling at −10 °C afforded yellow crystals. Yield: 72 mg, 53%. Anal. Calcd for $C_{54}H_{82}Co_2O_{22}P_6Ti_2\cdot 2C_{20}H_{14}O_2\cdot CH_2Cl_2$: C, 53.31; H, 5.27. Found: C, 52.72; H, 5.31. ^1H NMR (C_6D_6): δ 0.83 (t, 6H, CH_3), 1.10 (t, 6H, CH_3), 1.31 (t, 6H, CH_3), 1.35 (t, 6H, CH_3), 1.57 (t, 6H, CH_3), 1.65 (t, 6H, CH_3), 3.46−3.69 (m, 4H, OCH_2), 4.22−4.70 (m, 20H, OCH_2), 5.02 (s, 10H, C_5H_5), 7.58−7.84 (m, 8H, BINOL), 7.11−7.39 (27H, BINOL), 8.44 (d, 1H, BINLO). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 117.0 (d), 114.0 (t). MS (FAB): *m*/*z* 1482 (M^+ − 2BINOLH$_2$).

Ti-Catalyzed Solvent-Free Ring Opening of Epoxides. Typically, a solution of **1** (10 mg, 0.046 mmol) in epoxide (1.31 mmol) and Me_3SiN_3 (0.5 mL, 3.76 mmol) was stirred at room temperature under nitrogen for 12 h and filtered through a short column of silica gel to remove the catalyst. To the filtrate was added dilute H_2SO_4 (2 mL, 0.5 M), and the mixture was stirred for 5 h. The organic layer was collected, dried with anhydrous $MgSO_4$, and loaded onto a column of silica gel. The azidohydrin product was eluted with Et_2O/hexane and characterized by ^1H NMR spectroscopy and mass spectrometry.

Reaction between 1 and Me_3SiN_3. A mixture of **1** (100 mg, 0.179 mmol) and excess Me_3SiN_3 (0.2 mL) in toluene (2 mL) was heated at reflux overnight and evaporated to dryness. The yellow residue was washed with cold hexane and extracted with diethyl ether. The filtrate was concentrated, and hexane was added. Cooling at −20 °C afforded a yellow solid. Yield: 53 mg, 52%. ^1H NMR ($CDCl_3$): δ 1.28 (t, 18H, CH_3), 4.20 (m, 12H, OCH_2), 5.05 (s, 5H,

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Table 1. Crystallographic Data and Experimental Details for [$L_{OEt}TiCl_3$] (**1**), [$L_{OEt}TiF_3$] (**2**), [$L_{OEt}ZrF_3$] (**3**), [$L_{OEt}Ti(Cl_4cat)Cl$] (**4**), and [$(L_{OEt})_2Ti_2(Cl_4cat)_2(\mu\text{-}O)$] (**5**)

	1	**2**	**3**	**4**	**5**
formula	$C_{17}H_{35}Cl_3CoO_9P_3Ti$	$C_{17}H_{35}CoF_3O_9P_3Ti$	$C_{17}H_{35}CoF_3O_9P_3Zr$	$C_{23}H_{35}Cl_5CoO_{11}P_3Ti$	$C_{46}H_{70}Cl_8CoO_{23}P_6Ti_2$
fw	689.54	640.19	683.51	864.50	1674.10
a, Å	9.0570(13)	12.888(2)	12.9896(4)	27.9482(12)	10.2230(17)
b, Å	15.289(2)	12.888(2)	12.9896(4)	14.2362(6)	13.316(2)
c, Å	10.8523(16)	9.743(3)	9.8982(7)	16.9517(7)	14.789(5)
α, deg	90	90	90	90	69.219(3)
β, deg	100.158(3)	90	90	90	72.545(3)
γ, deg	90	120	120	90	70.702(3)
V, Å^3	1479.2(4)	1401.4(5)	1446.37(12)	6744.7(5)	1738.0(5)
Z	2	2	2	8	1
cryst system	monoclinic	trigonal	trigonal	orthrorhombic	triclinic
space group	$P2_1$	$P\bar{3}$	$P\bar{3}$	$Pca2_1$	$P\bar{1}$
ρ_{calc}, g cm^{-3}	1.548	1.517	1.569	1.703	1.599
T, K	293(2)	293(2)	293(2)	100(2)	293(2)
μ, mm^{-1}	1.304	1.108	1.158	1.321	1.205
F(000)	708	660	696	3520	854
no. of reflcns	7446	7961	8531	76 567	8763
no. of indep reflcns	4112	2107	2178	16 192	5992
R_{int}	0.0558	0.0286	0.0210	0.0448	0.0222
R1, wR2 ($I > 2.0\sigma(I)$)	0.0567, 0.1049	0.0470, 0.1220	0.0410, 0.1065	0.0439, 0.0964	0.0611, 0.1515
R1, wR2 (all data)	0.1045, 0.1223	0.0688, 0.1352	0.0487, 0.1118	0.0473, 0.0980	0.1002, 0.1773
GoF[a]	0.985	1.030	1.039	1.104	1.008

[a] $GoF = [(\Sigma w|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

C_5H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 116.6 (m). IR (Nujol, cm^{-1}): 2071 [$\nu(N_3)$].

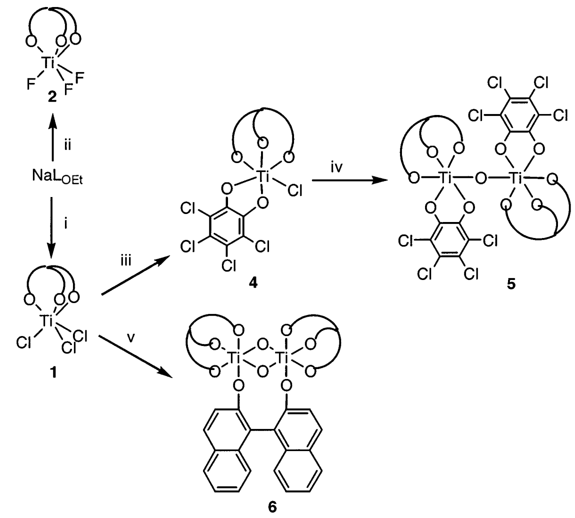
X-ray Diffraction Measurements. A summary of crystallographic data and experimental details for complexes **1**−**5** is listed in Table 1. Intensity data were collected on a Bruker SMART-APEX diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.701\ 73$ Å). The data were corrected for absorption by empirical methods. The structures were solved by direct methods and refined by full-matrix least-squares analyses on F^2. Some ethyl groups in L_{OEt}^- in these complexes were found to be disordered, and thus, large thermal parameters were observed. For **2** and **3**, the Cp ring is disordered over three sets of positions with an occupancy ratio of 67:33. For **4**, the asymmetric unit consists of two molecules that are not related by inversion symmetry, as the ethyl groups in the L_{OEt}^- of each molecule were found to flip in different direction. For **5**, the ethyl groups [C(21)−C(22) and C(23)−C(24)] in the L_{OEt}^- ligand are disordered over two sets of positions with 50:50 occupancy ratio. Calculations were performed using the SHELXTL[11] crystallographic software package. Selected bond lengths and angles for **1**−**5** are listed in Tables 2−6, respectively.

Results and Discussion

Preparation of [$L_{OEt}TiCl_3$]. The preparations of half-sandwich Ti−L_{OEt} complexes are summarized in Scheme 1.

[$L_{OEt}ZrCl_3$] was previously synthesized by the ligand exchange reaction of [$CpZrCl_3$] with NaL_{OEt}.[7] However, we found that reaction of [$CpTiCl_3$] with NaL_{OEt} afforded [$(L_{OEt})_2Ti$]$^{2+}$ instead of [$L_{OEt}TiCl_3$] apparently due to the high affinity of Ti(IV) for the oxygen tripod. Reaction of $TiCl_4$ with 1 equiv of NaL_{OEt} resulted in a mixture of products including [$\{(L_{OEt})_2Ti\}Cl_2$]. The half-sandwich complex [$L_{OEt}TiCl_3$] (**1**) could be synthesized in good yield by chlorination of [$L_{OEt}Ti(O\text{-}i\text{-}Pr)_2Cl$], which was prepared in situ from [$Ti(O\text{-}i\text{-}Pr)_2Cl_2$][10] with NaL_{OEt}, with HCl in ether. The structure of **1** has been established by X-ray crystallography. Figure 1 shows a view of the molecule; selected bond lengths and angles are listed in Table 2. The geometry around Ti in **1** is pseudooctahedral with a facially coordinated L_{OEt}^-. The average Ti−O distance of 1.975 Å is slightly shorter than the Ti−O(P) distances in the Ti phosphate complex [$Ti(O\text{-}i\text{-}Pr)_3\{O_2P(O\text{-}t\text{-}Bu)_2\}]_2$ (average 2.0225 Å).[12] The average Ti−Cl distance of 2.293 Å is similar to those in [$CpTiCl_3$] (2.201(5)−2.248(5) Å)[13] and [$\{HB(3,5\text{-}Me_2py)TiCl_3\}$] (average 2.262 Å).[14] Complex **1** is soluble in most common organic solvents except hexane. It is air stable in the solid state but is somewhat moisture sensitive in solution, especially in the presence of a base. Attempts to alkylate **1** with

Scheme 1 [a]



[a] Reagents and conditions: (i) [$Ti(O\text{-}i\text{-}Pr)_2Cl_2$], HCl; (ii) titanyl sulfate, HBF_4; (iii) H_2Cl_4cat; (iv) $Ag(CF_3SO_3)$ or Ph_2Zn; (v) H_2BINOL, Et_3N.

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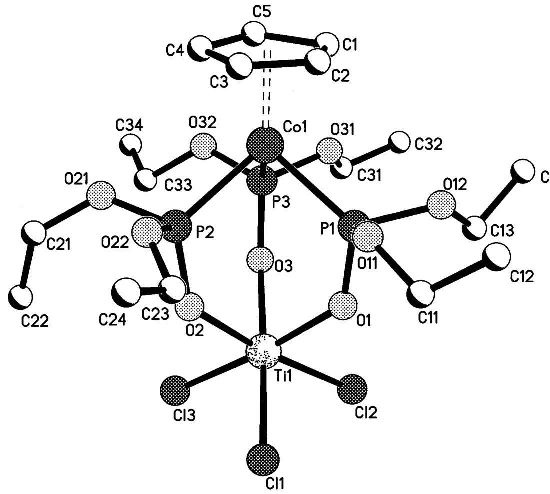

Figure 1. Perspective view of $[L_{OEt}TiCl_3]$ (**1**). Hydrogen atoms are not shown for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[L_{OEt}TiCl_3]$ (**1**)

Ti(1)−O(2)	1.970(6)	Ti(1)−O(3)	1.977(6)
Ti(1)−O(1)	1.978(6)	Ti(1)−Cl(1)	2.288(3)
Ti(1)−Cl(2)	2.290(3)	Ti(1)−Cl(3)	2.302(3)
O(2)−Ti(1)−O(3)	86.5(2)	O(2)−Ti(1)−O(1)	86.1(2)
O(3)−Ti(1)−O(1)	87.0(2)	O(2)−Ti(1)−Cl(1)	88.10(19)
O(3)−Ti(1)−Cl(1)	174.26(19)	O(1)−Ti(1)−Cl(1)	90.75(19)
O(2)−Ti(1)−Cl(2)	173.08(19)	O(3)−Ti(1)−Cl(2)	90.67(18)
O(1)−Ti(1)−Cl(2)	87.43(18)	Cl(1)−Ti(1)−Cl(2)	94.49(12)
O(2)−Ti(1)−Cl(3)	91.9(2)	O(3)−Ti(1)−Cl(3)	88.17(18)
O(1)−Ti(1)−Cl(3)	174.9(2)	Cl(1)−Ti(1)−Cl(3)	93.95(11)
Cl(2)−Ti(1)−Cl(3)	94.28(11)		

various alkylating agents, such as alkyllithium, Grignard, and dialkyl zinc reagents, were unsuccessful. Metathesis of **1** with silver triflate in CH_2Cl_2 afforded AgCl precipitate and an air-sensitive oily species, presumably the triflato complex $[L_{OEt}Ti(CF_3SO_3)_3]$, which hydrolyzed readily in solution to give dinuclear Ti(μ-O_2)Ti species.[15]

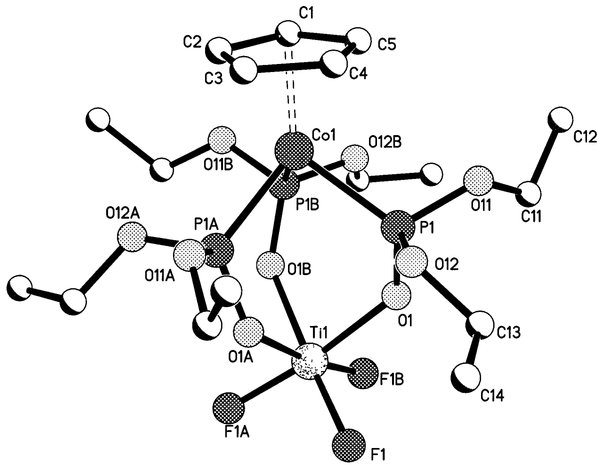

Figure 2. Perspective view of $[L_{OEt}TiF_3]$ (**2**). Hydrogen atoms are not shown for clarity.

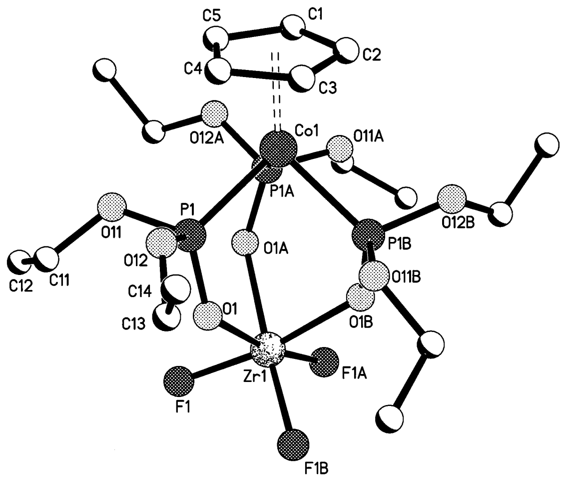

Figure 3. Perspective view of $[L_{OEt}ZrF_3]$ (**3**). Hydrogen atoms are not shown for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[L_{OEt}TiF_3]$ (**2**)

Ti(1)−F(1)	1.792(2)	Ti(1)−O(1)	2.020(2)
F(1A)−Ti(1)−F(1)	95.16(8)	F(1)−Ti(1)−O(1)	89.82(8)
F(1A)−Ti(1)−O(1)	172.92(9)	F(1B)−Ti(1)−O(1)	89.40(9)
O(1A)−Ti(1)−O(1)	85.18(8)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[L_{OEt}ZrF_3]$ (**3**)

Zr(1)−F(1)	1.938(2)	Zr(1)−O(1)	2.139(2)
F(1)−Zr(1)−F(1A)	96.18(8)	F(1)−Zr(1)−O(1)	90.29(9)
F(1A)−Zr(1)−O(1)	170.42(9)	F(1B)−Zr(1)−O(1)	90.13(9)
O(1A)−Zr(1)−O(1)	82.61(9)		

Preparation of $[L_{OEt}MF_3]$ (M = Ti, Zr). Treatment of NaL_{OEt} with titanyl sulfate in water followed by addition of HBF_4 resulted in the formation of the trifluoride compound $[L_{OEt}TiF_3]$ (**2**). It seems likely that titanyl suflate reacted with L_{OEt}^- to give initially a water-soluble Ti(IV) oxo or hydroxo species, which abstracted fluoride from BF_4^- to give **2**. Unlike **1**, **2** is air stable both in the solid state and solution apparently due to the strong Ti−F bonds that resist hydrolysis. The ^{19}F NMR spectrum of **2** shows a singlet at δ −154.6 assignable to the coordinated fluoride ligands. Similarly, the zirconium analogue was prepared from NaL_{OEt}, zirconyl nitrate, and HBF_4 in water and isolated as air-stable yellow crystals. The ^{19}F resonant signal for **3** was observed at δ −153.2. The solid-state structures of isostructural complexes **2** and **3** have been established by X-ray crystallography. It may be noted that although Ti and Zr fluorides are well documented, crystal structures of half-sandwich Ti and Zr trifluoride compounds have not been reported. The molecular structures of **2** and **3** are shown in Figures 2 and 3, respectively; the corresponding bond lengths and angles are listed in Tables 3 and 4. Both compounds have pseudooctahedral geometry. The Ti−O distances (2.020(2) Å) are slightly longer than those in **1** due to the strong Ti−F π bonding. The Ti−F distances in **2** (1.792(2) Å) are similar to those in $[(TiF_4)_2(\mu\text{-}C_2O_4)]^{2-}$ (1.770 Å).[16] The Zr−O distances (2.139(2) Å) in **3** are longer to those in $[L_{OEt}ZrCl_3]$ (average 2.093 Å), indicative of Zr−F π bonding. The Zr−F distances in **3** (1.938(2) Å) are similar to those in $[ZrF_4(Me_2SO)(H_2O)_2]$ (average 2.031 Å).[17]

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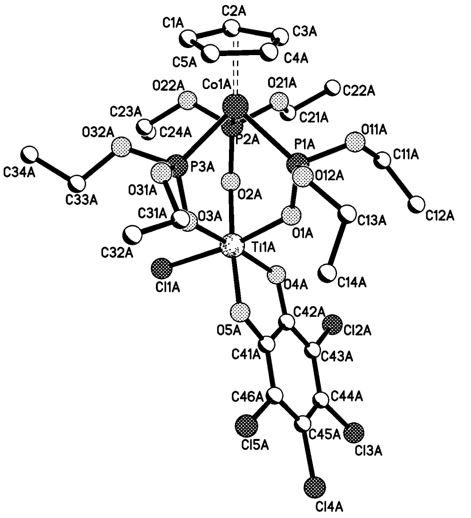

Figure 4. Perspective view of [L_{OEt}Ti(Cl_4cat)Cl] (**4**). Hydrogen atoms are not shown for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for [L_{OEt}Ti(Cl_4cat)Cl] (**4**)

Ti(1A)−O(1A)	1.996(3)	Ti(1B)−O(1B)	1.952(3)
Ti(1A)−O(2A)	1.963(2)	Ti(1B)−O(2B)	1.994(3)
Ti(1A)−O(3A)	1.957(2)	Ti(1B)−O(3B)	1.975(2)
Ti(1A)−O(4A)	1.924(2)	Ti(1B)−O(4B)	1.923(2)
Ti(1A)−O(5A)	1.935(3)	Ti(1B)−O(5B)	1.922(2)
Ti(1A)−Cl(1A)	2.3371(11)	Ti(1B)−Cl(1B)	2.3306(12)
O(4A)−C(42A)	1.325(4)	O(4B)−C(41B)	1.330(4)
O(5A)−C(41A)	1.321(4)	O(5B)−C(42B)	1.318(4)
O(4A)−Ti(1A)−O(5A)	81.35(10)	O(5B)−Ti(1B)−O(4B)	81.13(11)
O(4A)−Ti(1A)−O(3A)	171.88(10)	O(5B)−Ti(1B)−O(1B)	169.67(11)
O(5A)−Ti(1A)−O(3A)	91.05(10)	O(4B)−Ti(1B)−O(1B)	90.40(10)
O(4A)−Ti(1A)−O(2A)	94.01(10)	O(5B)−Ti(1B)−O(3B)	94.47(10)
O(5A)−Ti(1A)−O(2A)	174.80(10)	O(4B)−Ti(1B)−O(3B)	175.54(10)
O(3A)−Ti(1A)−O(2A)	93.46(10)	O(1B)−Ti(1B)−O(3B)	93.89(11)
O(4A)−Ti(1A)−O(1A)	92.09(11)	O(5B)−Ti(1B)−O(2B)	89.28(11)
O(5A)−Ti(1A)−O(1A)	92.53(11)	O(4B)−Ti(1B)−O(2B)	93.74(11)
O(3A)−Ti(1A)−O(1A)	85.35(10)	O(1B)−Ti(1B)−O(2B)	85.36(11)
O(2A)−Ti(1A)−O(1A)	85.26(11)	O(3B)−Ti(1B)−O(2B)	85.43(10)
O(4A)−Ti(1A)−Cl(1A)	93.26(9)	O(5B)−Ti(1B)−Cl(1B)	95.04(9)
O(5A)−Ti(1A)−Cl(1A)	93.92(8)	O(4B)−Ti(1B)−Cl(1B)	94.19(9)
O(3A)−Ti(1A)−Cl(1A)	90.10(8)	O(1B)−Ti(1B)−Cl(1B)	91.45(9)
O(2A)−Ti(1A)−Cl(1A)	88.66(8)	O(3B)−Ti(1B)−Cl(1B)	86.90(8)
O(1A)−Ti(1A)−Cl(1A)	172.17(9)	O(2B)−Ti(1B)−Cl(1B)	171.47(9)

Catecholate Complexes. Ti catecholate complexes are of special interest due to their catalytic activity toward olefin polymerization.[18] Treatment of **1** with tetrachlorocatechol (Cl_4catH_2) afforded red [L_{OEt}Ti(Cl_4cat)Cl] (**4**), which is stable in the solid state but moisture sensitive in solution, especially after the chloride ligand has been displaced (vide infra). The solid-state structure of **4** has been determined. Two independent molecules were found in the asymmetric unit of **4**. Figure 4 shows a perspective view of one of the two molecules; selected bond lengths and angles are listed in Table 5. The average Ti−O(P) (1.972 Å) and Ti−Cl (2.334 Å) distances are similar to those in **1**. The average Ti−O(Cl_4-cat) (1.926 Å) and C−O (1.324 Å) distances are similar to those in $[Et_3NH]_2[Ti(cat)_3]$ (average 1.966 and 1.345 Å, respectively)[19] and are consistent with the formulation of Cl_4-cat as a catecholate(2−).

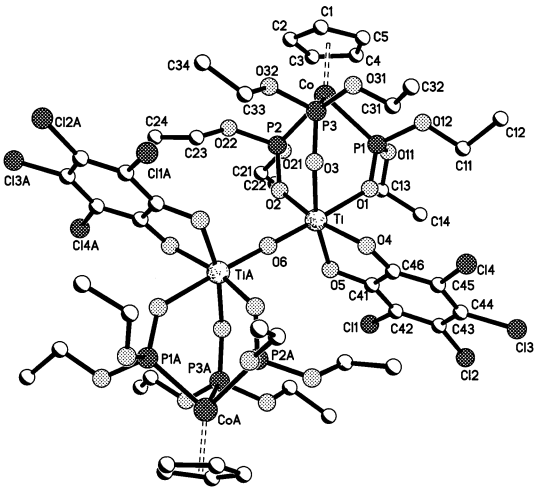

Figure 5. Perspective view of [$(L_{OEt})_2Ti_2(Cl_4cat)_2(\mu\text{-}O)$] (**5**). Hydrogen atoms are not shown for clarity.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for [$(L_{OEt})_2Ti_2(Cl_4cat)_2(\mu\text{-}O)$] (**5**)

Ti−O(1)	2.106(3)	Ti−O(2)	1.993(4)
Ti−O(3)	1.982(4)	Ti−O(4)	1.923(4)
Ti−O(5)	1.929(4)	Ti−O(6)	1.7977(9)
O(6)−Ti−O(4)	98.87(12)	O(6)−Ti−O(5)	98.45(12)
O(4)−Ti−O(5)	81.67(17)	O(6)−Ti−O(3)	93.71(11)
O(4)−Ti−O(3)	93.17(16)	O(5)−Ti−O(3)	167.38(16)
O(6)−Ti−O(2)	96.41(12)	O(4)−Ti−O(2)	164.40(16)
O(5)−Ti−O(2)	93.07(16)	O(3)−Ti−O(2)	88.90(15)
O(6)−Ti−O(1)	177.62(12)	O(4)−Ti−O(1)	81.71(15)
O(5)−Ti−O(1)	83.91(15)	O(3)−Ti−O(1)	83.95(15)
O(2)−Ti−O(1)	83.15(15)		

Treatment of **4** with alkyllithium and Grignard reagents resulted in dark materials, which did not crystallize. Reaction of **4** with Ph_2Zn gave an orange solution from which the μ-oxo dimer [$(L_{OEt})_2Ti_2(Cl_4cat)_2(\mu\text{-}O)$] (**5**) was produced presumably via the hydrolysis of a Ti phenyl intermediate. Metathesis of **4** with Ag(CF_3SO_3) afforded AgCl and moisture-sensitive [L_{OEt}Ti(Cl_4cat)(CF_3SO_3)] that hydrolyzed readily to **5** upon recrystallization. The structure of **5** has been established by X-ray crystallography. Figure 5 shows a perspective view of the molecule; selected bond lengths and angles are listed in Table 6. The molecule consists of two symmetric [L_{OEt}Ti(Cl_4cat)] units with the bridging oxo group at the inversion center. The geometry around each Ti is distorted octahedral. The average Ti−O(P) (2.027 Å) and Ti−O(Cl_4cat) (1.926 Å) distances are similar to those in **4**. The Ti−O(Ti) distance (1.7977(9) Å) is short and similar to that in [$CpTiCl_2$](μ-O) (1.777(1) Å),[20] indicative of strong π interaction between Ti and the oxo group. Accordingly, the Ti−O(1) bond that is trans to the μ-oxo group is longer than the Ti−O(2) and Ti−O(3) bonds.

Binaphtholate Complex. 1,1′-Binaphthol ($BINOLH_2$) in combination with various Ti precursors such as Ti alkoxides comprises an important class of enantioselective catalysts for asymmetric organic transformations.[21,22] It is therefore

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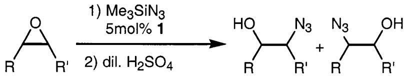
of interest to prepare half-sandwich Ti binaphtholate complexes containing the bulky L_{OEt}^- tripod ligand. Treatment of **1** with BINOLH$_2$ in the presence of Et$_3$N gave dinuclear [(L_{OEt})$_2$Ti$_2$(μ-BINOL)(μ-O)$_2$]$\cdot$2BINOLH$_2$ (**6**$\cdot$2BINOLH$_2$). A preliminary X-ray diffraction study[23] showed that complex **6** contains a {Ti$_2$(μ-O)$_2$} core with a μ-BINOL ligand bridging the two Ti centers. Complexes containing {Ti$_2$(μ-O)$_2$} titanoxane cores are well documented, e.g. K$_4$[Ti$_2$(cat)$_4$(μ-O)$_2$][19] and [Ti$_2$(acac)$_4$(μ-O)$_2$] (acac = acetylacetonate).[24] The μ-O,O′ binding mode for BINOL ligand has been previously observed for [{(*t*-BuMe$_2$Si)$_2$BINO}Ti$_2$(O-*i*-Pr)$_6$][25] and [(HYDBINO)$_2$Ti$_2$Cl$_4$] (HYBINO = 5,5′,6,6′,7,7′,8,8′-octahydronaphtholate).[26] It seems likely that the initial product of the reaction is a Ti chloride species that hydrolyzed to the μ-oxo-bridged dimer by the moisture of solvent in the presence of Et$_3$N. Mononuclear L_{OEt}Ti complex with a chelating BINOL ligand was not produced possibly because of steric reasons.

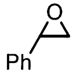
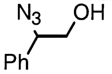
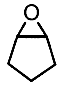
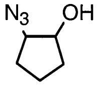
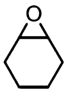
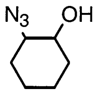
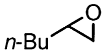
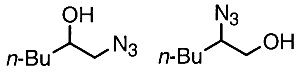
Ti-Catalyzed Solvent-Free Ring Opening of Epoxides. Lewis acid-catalyzed ring opening of epoxides by azide has become a versatile synthetic route to vicinal azidohydrins that are precursors to biologically important β-amino alcohols.[27] To this end, the catalytic activity of Ti−L_{OEt} complexes toward epoxide ring opening was examined. The use of Ti−L_{OEt} complexes as Lewis acid catalysts is of interest because they are soluble in epoxide substrates so that the ring opening reaction can be carried under solvent-free conditions. Complex **1** was found to be active catalysts for ring opening of epoxides with Me$_3$SiN$_3$ (eq 1), and the results are summarized in Table 7.



(1)

Thus, reaction of epoxides with Me$_3$SiN$_3$ in the presence of 5 mol % **1** followed by hydrolysis with dilute H$_2$SO$_4$ afforded the corresponding azidohydrins in 28−72% yield. Azidolysis of styrene oxide was regioselective, and the 2-azidohydrin was isolated exclusively. The regioselectivity of the ring opening of styrene oxide can be attributed to the stability of incipient benyzlic carbocation intermediate. For the ring opening of 1,2-epoxyhexane, a 3:2 mixture of 1-azido and 2-azido products was obtained, indicating that there is competition between steric and electronic factors in the nucleophilic attack on the epoxide by azide. It is believed that the active intermediates of metal-mediated azidolysis of epoxides are metal azide species that act as nucleophiles to attack epoxides.[28] Indeed, reaction of **1** with excess Me$_3$SiN$_3$ afforded a Ti−azido species characterized by IR spectroscopy (ν(N$_3$) = 2071 cm^{-1}). Unfortunately, we have not been able to crystallize this Ti azide complex, which was found to hydrolyze easily upon recrystallization.

Table 7. Ti-Catalyzed Solvent-Free Ring Opening of Epoxides with Me$_3$SiN$_3$[a]

epoxide	product	% yield[b]
		52
		28
		72
	 1.5 : 1[c]	70

[a] Experimental conditions: Epoxide (1.31 mmol), Me$_3$SiN$_3$ (3.76 mmol), and **1** (0.046 mmol) were stirred at room temperature for 12 h. [b] Isolated yield. [c] Regioselectivity determined by ^{1}H NMR spectroscopy.

Conclusions

In summary, we have developed convenient syntheses of half-sandwich Ti(IV) trichloride and trifluoride complexes containing the oxygen tripod ligand L_{OEt}^-. The Ti trichloride compound was found to be a good starting material for preparations of Ti catecholate and binaphtholate complexes. The Ti chloride compounds hydrolyzed readily to give monooxo- or dioxo-bridged dinuclear complexes. Ti−L_{OEt} complexes have potential applications as Lewis acid catalysts for organic transformations, e.g. ring opening of epoxides with azide.

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Supporting Information Available: Tables of crystal data, final atomic coordinates, anisotropic thermal parameters, and complete bond lengths and angles for complexes **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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