Synthesis and Reactivity of Titanium(IV)−Salen Complexes Containing Oxygen and Chloride Ligands

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The reaction of in situ-generated $Ti(O^iPr)_2(X)_2$ (X = OAr, OTf) with H_2salen or H_2salen* yields the stable, well-characterized Ti(salen)X_2 series of complexes. Ti(salen*)$(OTf)_2$ could also be synthesized by reacting the previously unknown Ti(salen*)Cl_2 with TMSOTf or AgOTf. The ditriflates could be converted back to the aryloxides upon reaction with 2 equiv of NaOAr. Ti(salen)(4-*tert*-butyphenoxy)$_2$ was characterized by X-ray crystallography and found to contain a pseudoplanar salen ligand with two axially coordinated aryloxide ligands. H_2salen and H_2salen* were also found to cleanly react with in situ-generated $Ti(O^iPr)_3(X)$ (X = OC(O)R, OTf) to yield the unsymmetrically substituted Ti(salen)$(O^iPr)(X)$ and Ti(salen*)-$(O^iPr)(X)$ complexes, respectively. In the case of X = OTf, the isopropoxide ligand could be cleanly protonated with 4-*tert*-butylphenol to yield Ti(salen)(OAr)(OTf) in high yield. This complex could also be accessed by the comproportionation reaction of Ti(salen)$(OAr)_2$ and Ti(salen)$(OTf)_2$.

Introduction

N,*N*′-Ethylenebis(salicylideneiminate) dianion (salen) is a well-known tetradentate Schiff base ligand which normally provides a rigid, planar coordination environment for a metal.[1] The synthesis and reactivity of numerous metal complexes containing various salen derivatives have been extensively studied. Most studies to date have focused on salen complexes of the middle and late d-block metals due to their use as asymmetric catalysts for olefin epoxidation,[2] cyclopropanation,[3] and aziridination,[4] sulfide[5] oxidation, the Diels−Alder reaction,[6] C−H activation,[7] and the asymmetric ring-opening of epoxides.[8]

Literature references on metal−salen complexes of the group 4 elements are, unexpectedly, rather sparse.[9] The best known group 4 metal−salen complexes are (salen)$TiCl_2$ complexes with achiral or chiral salen derivatives.[10] The chemical reactivity of these complexes has been limited to alkylations or arylations of the apical chloride ligands and reduction (Ti(IV) to Ti(III)).[11] Recently, a structurally characterized chiral titanium salen complex containing two axial chloride ligands was shown to be an active catalyst for the asymmetric addition of TMSCN to benzaldehyde.[12] This study was an extension of earlier studies wherein two groups independently reported the use of in situ-generated chiral "(salen)$Ti(O^iPr)_2$" complexes (from $Ti(O^iPr)_4$) as catalysts for this reaction, each group proposing that the reaction proceeds by a different mechanism.[13,14] Contributing to the uncertainty in this mechanistic debate is the lack of structural models for reasonable catalyst intermediates.

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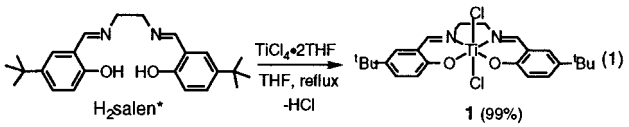
Our interest in titanium salen complexes stems from the rapid development of titanium reagents or catalysts in asymmetric synthesis[15] and the power of chiral salen derivatives in asymmetric catalysis. The expansion of Ti−salen-based catalytic methods, however, is hindered by the lack of synthetic routes to well-characterized complexes. To begin filling this void, we present herein our efforts to discover new syntheses of symmetric and asymmetrically disubstituted titanium(IV)−salen complexes possessing oxygen-donor ligands. We have examined methods for their synthesis, explored their substitution reactivity, and characterized a homobisadduct by X-ray crystallography.

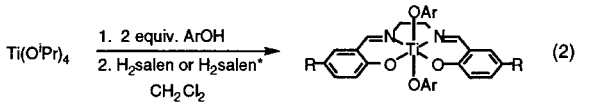
Results

Synthesis of Symmetrically Disubstituted Titanium(IV) Salen Complexes. Symmetrically disubstituted six-coordinate titanium(IV) salen complexes can be synthesized through two independent routes: direct addition of H_2salen to a suitable Ti-precursor or ligand substitution at a Ti−salen complex. Analogous to the method reported for the synthesis of Ti(salen)Cl_2,[8a,b] direct reaction of H_2salen* (*N*,*N*′-ethylenebis(5-*tert*-butylsalicylideneimine)) with $TiCl_4$ or $TiCl_4$·2THF in methylene chloride or THF solvent cleanly produces Ti(salen*)Cl_2 (**1**) (eq 1). Unlike Ti(salen)Cl_2, however, **1** has good solubility in organic solvents (e.g., CH_2Cl_2, CH_3CN, and THF), allowing for full characterization by ^{1}H and ^{13}C NMR spectroscopy.



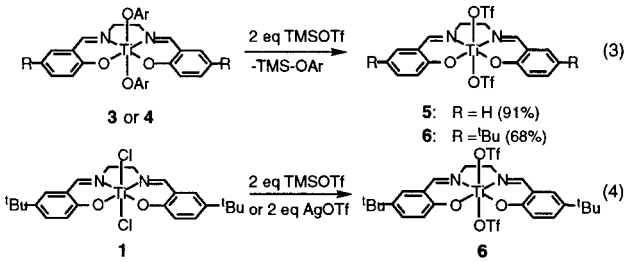
When Ti(O^{i}Pr)$_4$ in CH_2Cl_2 or CH_3CN is similarly treated with H_2salen* (1 equiv) at ambient temperature, an uncharacterizable yellow insoluble solid precipitates from even dilute solutions. In situ monitoring of this reaction by ^{1}H NMR (CD_2Cl_2) indicates that the starting materials are initially converted into a pair of titanium salen products in a 2:1 ratio. The spectrum of the major product is consistent with the expected Ti(salen*)-(O^{i}Pr)$_2$ product,[16] but over the course of several minutes, this mixture leads to the insoluble yellow material described above. The instability of the expected product at least suggests that chiral versions of the diisopropoxide may also be prone to ligand distribution processes under catalytic conditions, further clouding the mechanistic issues in the Belekon/Jiang debate.[13,14]

In contrast to the reaction of H_2salen* with Ti(O^{i}Pr)$_4$, the reaction of in situ-generated Ti(O^{i}Pr)$_2$(OAr)$_2$ with either H_2salen or H_2salen* produces a single titanium complex. Thus, a CH_2Cl_2 solution of Ti(O^{i}Pr)$_4$, when sequentially treated with phenol (2 equiv) and H_2salen (1 equiv), selectively eliminates 2-propanol to yield Ti(salen)(OPh)$_2$ (**2**), (eq 2). Using this method, Ti(salen)-(4-*tert*-butylphenolate)$_2$ (**3**) and Ti(salen*)(4-*tert*-butylphenolate)$_2$ (**4**) were similarly prepared from the reactions of Ti(O^{i}Pr)$_4$, 4-*tert*-butylphenol (2 equiv), and the corresponding salen ligands. The bulky *tert*-butyl groups in **3** and **4** make them significantly more soluble than **2** in CH_2Cl_2 and CH_3CN.



2: R= H; Ar= Ph (89%)
3: R =H; Ar= 4-^{t}Bu-Ph (92%)
4: R =^{t}Bu; Ar= 4-^{t}Bu-Ph (89%)

An alternative method for preparing symmetrically disubstituted titanium salen complexes is through ligand substitution. For example, when **3** was treated with TMSOTf (2 equiv), the two aryloxide ligands were each silylated and replaced by OTf (eq 3).[17] The ^{1}H NMR spectrum of the product Ti(salen)(OTf)$_2$ (**5**) in CD_3-CN indicates a single set of salen resonances shifted downfield from H_2salen, **2** and **3**. The singlet at −77.3 ppm in the ^{19}F NMR is assigned to a coordinated OTf ligand (vide infra), shifted slightly downfield of TMSOTf (−78.2 ppm). In addition to silyl ether elimination, TMS−Cl elimination was also found to be facile, as the dichloride **1** could be cleanly converted to **6** upon treatment with TMSOTf (eq 4). Although slightly less convenient, the elimination of AgCl from the reaction of **1** with AgOTf (2 equiv) also gives **6**.



In comparison to the known (salen)$TiCl_2$ derivatives, the spectral properties of **1**−**6** are also consistent with six-coordinate monomeric structures containing a pseudoplanar salen and apical aryloxide, chloro, or OTf ligands.[8] The X-ray crystallographic analysis of **3** (vide infra) also confirms this structural assignment. In the ^{1}H NMR spectra of these homobisadducts the imine and aryl proton resonances are shifted downfield by 0.1−0.5 ppm compared to those of H_2salen or H_2salen*.

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(16) ^{1}H NMR of Ti(salen*)(O^{i}Pr)$_2$ (CD_2Cl_2): δ 8.32 (s, 2H, H−C=N), 7.45 (dd, J = 8.8, 2.5 Hz, 2H, Ar), 7.30 (d, J = 2.5 Hz, 2H, Ar), 6.67 (d, J = 8.8 Hz, 2H, Ar), 3.99 (septet, J = 6.3 Hz, 2H, CH), 3.96 (s, 4H, CH_2), 1.30 (s, 18H, CH_3), 0.69 (d, J = 6.3 Hz, 12H, CH_3).

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Table 1. Selected NMR Data for Titanium Salen Complexes[a]

	δ ppm (^{1}H)		δ ppm (^{13}C)		δ ppm (^{19}F)
compound	N=C−H	CH_2−CH_2	N=C	CH_2−CH_2	$(CF_3SO_3)^-$
H_2salen	8.26 s	3.80 s	166.8	60.0	
H_2salen*	8.38 s	3.93 s	164.1	59.2	
1	8.41 s	4.21 s	164.1	59.2	
2	8.29 s	3.69 s	163.3	58.8	
3	8.32 s	3.71 s	163.3	58.9	
4	8.36 s	3.74 s	163.6	58.9	
5[b]	8.75 s	4.20 s	167.8	60.0	−77.3
6[b]	8.68 s	4.20 s	166.8	59.3	−80.0
7[b]	8.67 s	4.05 m	167.1	59.7	−78.0
8	8.50 s	4.20/3.92 m	165.8	59.2	−76.0
9	8.36 s	4.20/3.85 m	164.1	59.0	
10	8.47 s	4.15 m	165.7	59.2	−78.1[b]
11	8.39 s	4.33/4.00 m	163.7	59.2	
12	8.41 s	4.36/4.04 m	164.4	59.2	
13	8.39 s	4.30/3.82 m	163.7	59.0	
14	8.39 s	4.31/3.83 m	163.8	59.2	
15	8.35 s	3.68 t	164.4	59.2	

[a] Obtained in CD_2Cl_2 unless otherwise noted. [b] acetonitrile-d_3.

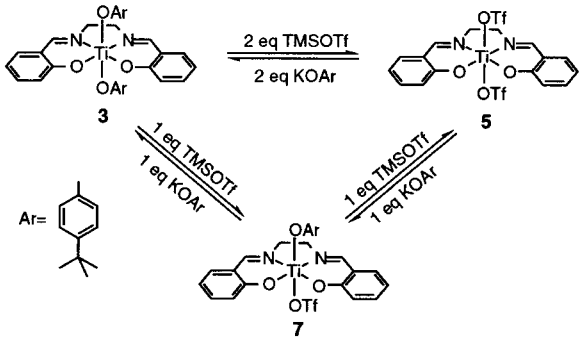
Especially diagnostic of the symmetric structure is a methylene singlet in the 3.6−4.2 ppm region, assigned to the four equivalent bridging methylene protons (Table 1). Although the point group symmetry of these structures requires unique pseudoaxial and -equatorial positions in the ethylene bridge, a net C_{2v} symmetry is observed due to a rapid interconversion of the accessible conformers.

Complexes **1** and **2** are relatively resistant to air hydrolysis in the solid state, but are water sensitive in solution and form μ-oxo-bridged dinuclear complexes that usually precipitate.[18] The ditriflates (**5** and **6**) are highly sensitive to moisture both in solution and in the solid state, yielding a relatively insoluble material which is consistent with the μ-oxo-dimeric structure [Ti(salen)(OTf)]$_2$(μ^2-O).[19] Fortunately, treatment of the crude mixture containing [Ti(salen)(OTf)]$_2$(μ^2-O) with Ti(O^{i}Pr)$_4$ breaks up the oxo-bridge and regenerates **5** as the sole Ti−salen product. In suitable cases, a small amount of Ti(O^{i}Pr)$_4$ in the solvents used for the precipitation and washing process helps to reduce μ-oxo dimer formation (see Experimental Section).

Synthesis of Unsymmetrically Disubstituted Titanium(IV) Salen Complexes. The above symmetrically disubstituted titanium(IV) salen complexes are useful precursors for the synthesis of new heterosubstituted products through ligand substitution and comproportionation. They may also be prepared by direct reaction of H_2salen with appropriate XTi(O^{i}Pr)$_3$ precursors.

The diaryloxides **3** and **4** readily react with 1 equiv of TMSOTf to selectively produce monosubstitution products. For example, when **3** was treated with 1 equiv of TMSOTf in CH_2Cl_2, the monotriflate **7** was obtained

Scheme 1



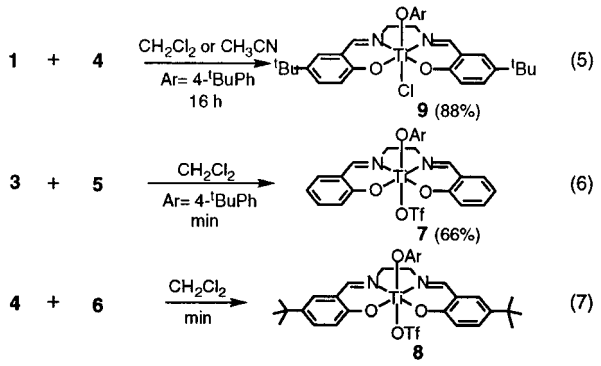
(Scheme 1). The product **7** was isolated by solvent removal in vacuo followed by washing with a hexane solution containing Ti(O^{i}Pr)$_4$. The presence of Ti(O^{i}Pr)$_4$ effectively removed traces of water and allowed for the isolation of product free of the μ-oxo dimer hydrolysis product. The ^{1}H NMR spectra of hetero bis-substituted compounds such as **7** are diagnostic in that the bridging methylene resonances are transformed from the singlet observed in the symmetric complexes to a set of AA′BB′ multiplets. Consistent with a stepwise conversion of **3**/**4** to **5**/**6**, the addition of a second equivalent of TMSOTf to **7** cleanly produces **5**. The ditriflate complex **5** also proved to be synthetically useful, as reaction with 1 or 2 equiv of potassium 4-*tert*-butylphenolate gives **7** and **3**, respectively. The ability to interconvert between **3**, **5**, and **7** is highlighted in Scheme 1. The complex **4** undergoes similar reactions with 1 and 2 equiv of TMSOTf to produce Ti(salen*)(4-*tert*-butylphenolate)(OTf) (**8**) and **6**, respectively.

The comproportionation reaction of symmetrically disubstituted titanium(IV) salen complexes was also found to be useful for the synthesis of heterosubstituted complexes, as complete conversion to clean products was generally obtained. For example, a combination of **1** and **4** in acetonitrile at room temperature produces Ti(salen*)(4-*tert*-butylphenolate)Cl (**9**) exclusively over the course of 16 h (eq 5). The reactions between diaryloxides and ditriflates at room temperature (**3** and **5** (eq 6) or **4** and **6** (eq 7)) also result in complete conversion to the expected comproportionation products, Ti(salen)(4-*tert*-butylphenolate)(OTf) (**7**) and Ti(salen*)(4-*tert*-butylphenolate)(OTf) (**8**), although much quicker (min). To the extent that ^{1}H NMR is sensitive to exchange, a mixture of **2** and **4** (1:1, CD_2Cl_2), on the other hand, did not react over the course of 2 days. It appears that maximization of electronic asymmetry (i.e., basicity) in the axial ligands is the driving force for these reactions. These observations are consistent with previous octahedral Ti(IV) porphyrin comproportionation studies[20] and a series of mononuclear octahedral Ti(IV) complexes,[21] where the weakest ligands are found to always coordinate trans to the strongest.

In addition to ligand substitution reactions on preformed Ti(IV)−salen precursors, a variety of heterobisadducts could be synthesized from the reaction of in situ-derived XTi(O^{i}Pr)$_3$ precursors with H_2salen and H_2salen*. For example, when Ti(O^{i}Pr)$_4$ was pretreated with 1 equiv of TMSOTf in CH_2Cl_2 followed by H_2salen (1 equiv, eq 8), a clear yellow solution was obtained. Solvent removal in vacuo cleanly yielded complex **10**, the ^{1}H NMR of which features two bridging methylene

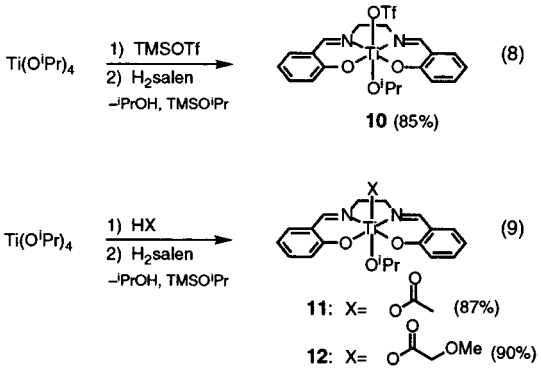
(18) The synthesis and characterization of oxo-bridged titanium salen complexes have been reported: (a) Franceschi, F.; Gallo, E.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C.; Re, N.; Sgamellotti, A. *Chem. Eur. J.* **1996**, *2*, 1466−1476. (b) Sasaki, C.; Nakajima, K.; Kojima, M.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1318−1324. ^{1}H NMR of [Ti(salen*)Cl]$_2$(μ^2−O), (CD_2Cl_2): δ 7.87 (s, 4H, H−C=N), 7.36 (dd, J = 8.3, 2.0 Hz, 4H, Ar), 7.27 (d, J = 2.0 Hz, 4H, Ar), 7.02 (d, J = 8.3 Hz, 4H, Ar), 3.88 (m, 8H, CH_2), 1.37 (s, 36H, CH_3).

(19) ^{1}H NMR of [Ti(salen)(OTf)]$_2$(μ^2−O), (CD_3CN/CD_2Cl_2 (1:1)): δ 8.18 (s, 4H, H−C=N), 7.46 (ddd, J = 11.2, 9.2, 2.0 Hz, 4H, Ar), 7.22 (dd, J = 9.5, 2.0 Hz, 4H, Ar), 6.91 (dd, J = 9.2, 1.5 Hz, 4H, Ar), 6.79 (dd, J = 10.5, 1.5 Hz, 4H, Ar), 4.00 (brs, 8H, CH_2).



(5) (6) (7)

multiplets at 4.27 and 4.02 ppm, characteristic of an unsymmetrical axial substitution pattern. In an operationally similar synthetic method, Ti(salen)(O^iPr)($OC(O)CH_3$) (**11**) and Ti(salen)(O^iPr)($OC(O)CH_2OCH_3$) (**12**) were prepared in analytically pure form by treating $Ti(O^iPr)_4$ with the corresponding carboxylic acid, followed by H_2salen (eq 9). These heterobisadducts are extremely moisture sensitive, and so dilute $Ti(O^iPr)_4$ solutions were used to inhibit product hydrolysis (**7**, **10**−**12**) in the workup. In addition to sequestering H_2O, $Ti(O^iPr)_4$ was also found to selectively convert any bridging oxo-dimers present back to the mixed carboxylate/isopropoxide bisadducts.



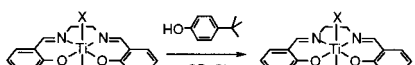
(8) (9)

The limitation of this experimental protocol was revealed by the reaction of H_2salen with in situ-derived $Ti(O^iPr)_3(OPh^tBu)$. In a variety of solvents and temperatures, the reaction leads to a complex mixture containing the putative Ti(salen)(O^iPr)(4-*tert*-butylphenolate)[22] and **4** as the major products. Optimized conditions for the synthesis of the mixed isopropoxide/phenoxide require a mixture of $Ti(O^iPr)_4$ and 4-*tert*-butylphenol (0.25 equiv) in diethyl ether to be treated with H_2salen. From the resulting clear orange solution, yellow crystals gradually precipitate. The ^{1}H NMR of these isolated yellow crystals (CD_2Cl_2) show that they are primarily a mixture of Ti(salen)(O^iPr)(4-*tert*-butylphenolate) and **4** (combined yield is > 90%). However, continued monitoring of this sample indicates that the mixture is unstable since after 8 h the initial product:**4** ratio (7:1) decreases to 2.5:1. This observation suggests that the initially formed Ti(salen)(O^iPr)(4-*tert*-butylphenolate) disproportionates to **4** and unstable Ti(salen)$(O^iPr)_2$ (vide supra).

The coordination geometry of titanium in these heterobisadducts (**7**−**12**) is undoubtedly similar to the homobisadducts. ^{1}H NMR spectra of those complexes that have C_s symmetry feature two multiplets for the two sets of chemically inequivalent bridging methylene protons, diagnostic signatures for asymmetric apical ligation. The ^{1}H NMR spectra of the Ti(salen)(O^iPr)X (X = OTf, carboxylate, and aryloxide) series of complexes show that electron-deficient trans ligands shift the salen and isopropoxide resonances downfield, indicating that there is electronic communication between the ligands on the metal (e.g., compare **1**, **2**, **5**, **7**, and **11**; Table 1).

Substitution Reactivity of Titanium(IV) Salen Complexes. When the titanium diaryloxide complex **3** is treated with acetic acid, a rapid equilibrium is established with a new titanium complex **13** and 4-*tert*-butylphenol. The ^{1}H NMR spectrum of the reaction mixture clearly shows the free 4-*tert*-butylphenol and new methyl/*tert*-butyl resonances at 1.53 and 1.17 ppm, respectively, with a carbonyl resonance at 175.8 ppm in the ^{13}C NMR. The combined spectroscopic analysis suggests that **13** is the monosubstitution product Ti(salen)(4-*tert*-butylphenolate)($OC(O)CH_3$). More than 4 equiv of acetic acid is required for a >90% conversion of **3** to **13**. In situ monitoring of the reaction between **3** and methoxyacetic acid (1.1 equiv) in CD_2Cl_2 shows that an equilibrium between the expected product Ti(salen)(4-*tert*-butylphenolate)($OC(O)CH_2OCH_3$) (**14**), **3**, and a third titanium complex (presumably the disubstitution product) is quickly established (10:1:1 respectively). The more extensive conversion for the latter acid likely reflects its enhanced pK_a relative to acetic acid.[23] Attempts to isolate **13** by the above synthetic method were unsuccessful, as solvent removal under vacuum selectively removed acetic acid from the system and regenerated **3**. Attempts to isolate an analytically pure sample of **14** were frustrated by the formation of μ-oxo dimeric complexes during workup. Unfortunately, $Ti(O^iPr)_4$ was found to react with **14** in a complicated fashion.

The titanium salen complexes **10**−**12** were used to react with 1 equiv of 4-*tert*-butylphenol. While **10** reacts with 4-*tert*-butylphenol to exclusively produce **7**, the reactions of **11** and **12** with 4-*tert*-butylphenol proceed with poor chemoselectivity to ultimately yield a mixture of the starting material, **3**, and the corresponding heterobisadducts **13** and **14**. The product ratios from these reactions are summarized in eq 10.



(10)

X	Starting Material	Hetero-bisadduct	Hetero-bisadduct	S. M.	3
OTf	10	7	> 95%		
O(C=O)Me	11	13	3	2.5	1
O(C=O)CH$_2$OMe	12	14	5	1	1

Ti(salen)(4-*tert*-butylphenolate)(OTf) (**7**) reacts with sodium acetate to produce **13** as the major species and

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(22) ^{1}H NMR of Ti(salen)(O^iPr)(4−*tert*−butylphenolate) (CD_2Cl_2): δ 8.33 (s, 2H, H−C=N), 7.46 (m, 4H, Ar), 6.91 (m, 4H, Ar), 6.86 (d, J = 8.8 Hz, 2H, Ar), 5.99 (d, J = 8.8 Hz, 2H, Ar), 4.23 (septet, J = 6.3 Hz, 1H, CH), 3.90 (m, 2H, CH_2), 3.77 (m, 2H, CH_2), 1.14 (s, 9H, CH_3), 0.81 (d, J = 6.3 Hz, 6H, CH_3).

(23) Bordwell F. G. *Acc. Chem. Res.* **1988**, *21*, 456−463.

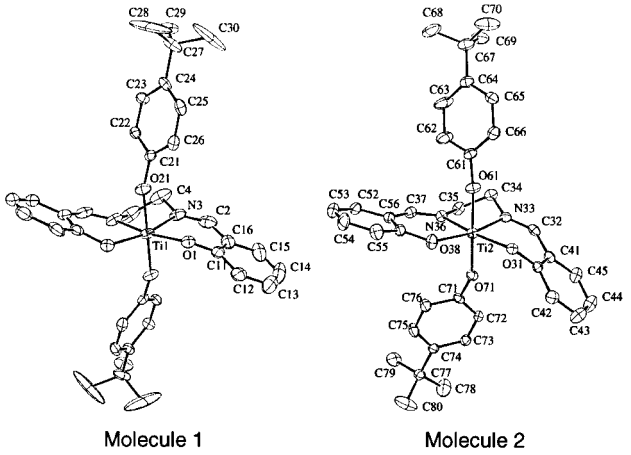

Figure 1. ORTEP drawings and atom-numbering scheme for **3**.

several unidentified byproducts. In contrast, reactions with sodium or potassium aryloxide salts cleanly produce the monosubstitution products by elimination of NaOTf or KOTf (Scheme 1). For example, **7** reacts with sodium 3,5-dimethylphenoxide to give a new titanium complex Ti(salen)(4-*tert*-butylphenolate)(3,5-dimethylphenolate) (**15**). The ^{1}H NMR of this complex (CD_2Cl_2) surprisingly shows a singlet (albeit broadened) for the methylene bridge, indicating that although heterodisubstituted, the two faces are chemically similar.

When the neutral nucleophiles pyridine and SMe_2 were combined with **7**, no triflate displacement reactions were observed. The ^{1}H NMR spectrum of a mixture of **7** and PPh_3 does show broadened phenyl and bridging methylene resonances; however, starting material is recovered upon precipitation with hexanes. A comparison of the ^{19}F NMR spectra of **7** in the presence and absence of PPh_3 shows no observable shift in the fluorine resonance, suggesting weak binding at best.

Crystal and Molecular Structure of Ti(salen)(4-*tert*-butylphenolate)$_2$ (3). Orange-red crystals of **3** suitable for X-ray diffraction studies were grown at room temperature under N_2 from a saturated solution of CH_2Cl_2/Et_2O (1:1) with slow diffusion of hexanes. Two independent molecules of **3** were found in the orthorhombic unit cell. ORTEP drawings and the numbering schemes for the two molecules are shown in Figure 1. Structure acquisition data and selected bond distances and angles are listed in Tables 2 and 3, respectively. The two structures are rather similar, with the main distinction being that molecule 1 has crystallographic C_2 symmetry[24] while molecule 2 is asymmetric. A ^{1}H NMR spectrum of the orange-red crystals indicates a single species with C_{2v} symmetry, suggesting that molecules 1 and 2 simply represent accessible, dynamic conformers of **3**.

In both molecules, the coordination around titanium is best described as a distorted octahedron with the titanium atom lying in the plane of the N_2O_2 core with short Ti−O bond lengths (∼1.89 Å) and longer Ti−N bonds (∼2.16 Å), Table 3. The two aryloxide ligands are bound to the Ti(salen) moiety in a trans arrangement (O(21)−Ti(1)−O′(21) = 174.74(8)°), with the two axial Ti−O bonds not quite orthogonal to the N_2O_2 plane and slightly bent toward the imine nitrogens. A comparison of the metrical parameters for the two molecules indicates that aside from conformation, molecules 1 and 2 have similar bond lengths. In both molecules the aromatic portion of the salen ligand is canted above and below the TiO_2N_2 square plane, symmetrically (necessarily) for molecule 1 and asymmetrically for molecule 2.

Table 2. Crystallographic Data and Collection Parameters for 3

compound	Ti(salen)(4-*tert*-butylphenolate)$_2$
formula	$C_{36}H_{40}N_2O_4Ti$
molecular weight, g/mmol	612.62
color, habit	orange red, crystal
cryst size, mm	0.40 × 0.30 × 0.20
cryst system	orthorhombic
space group	*Fd*2*d*
a, Å	15.5667(7)
b, Å	17.8314(8)
c, Å	69.531(3)
V, Å^3	19300.1(15)
Z	24
$D_{c,\ g/cm^3}$	1.265
diffractometer	Siemens SMART
F(000)	7786.93
radiation	MoKα (0.710 73)
μ, mm-1	0.31
T, °C	−100
scan mode	Ω
data collected	$\pm h, \pm k, \pm l$
$2\theta_{max}$, deg	50.0
total no. of rflns	39 580
no. of unique reflns	8537
no. of rflns with $I > 3.0\sigma(I)$	7852
R_{merge}	0.034
no. of variables	582
R_f[a]	0.045
R_w[b]	0.049
GoF[c]	2.75
max Δ/σ	0.001
residual density, e/Å^3	−0.340, 0.510

[a] $R_f = \sum(F_o-F_c)/\sum F_o$. [b] $R_f = [\sum w(F_o-F_c)2/\sum wF_o^2]^{1/2}$. [c] GoF = $[\sum w(F_o-F_c)^2/(n-p)]^{1/2}$, where n = number of reflections and p = number of parameters.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 3[a]

		Molecule 1[b]	
Ti(1)−O(1)	1.899(2)	O(1)−Ti(1)-O′(21)	94.07(9)
Ti(1)−N(3)	2.159(2)	N(3)−Ti(1)-N′(3)	75.30(11)
Ti(1)−O(21)	1.862(2)	N(3)−Ti(1)-O(21)	87.30(9)
O(1)−Ti(1)-O′(1)	114.94(9)	N(3)−Ti(1)-O′(21)	88.54(9)
O(1)−Ti(1)-N(3)	84.90(10)	N(3)′-Ti(1)-O(21)	88.54(9)
O(1)−Ti(1)-N′(3)	160.12(10)	O(21)−Ti(1)-O′(21)	174.74(8)
O(1)−Ti(1)-O(21)	88.76(8)	Ti(1)−O(21)-C(21)	156.8(2)
		Molecule 2	
Ti(2)−O(31)	1.889(2)	O(31)−Ti(2)-O(71)	87.26(8)
Ti(2)−N(33)	2.147(2)	N(33)−Ti(2)-N(36)	75.27(8)
Ti(2)−N(36)	2.168(2)	N(33)−Ti(2)-O(38)	161.14(8)
Ti(2)−O(38)	1.884(2)	N(33)−Ti(2)-O(61)	87.24(8)
Ti(2)−O(61)	1.867(2)	N(33)−Ti(2)-O(71)	86.59(8)
Ti(2)−O(71)	1.870(2)	O(38)−Ti(2)-O(71)	93.29(9)
O(31)−Ti(2)-N(33)	84.71(8)	O(61)−Ti(2)-O(71)	172.44(9)
O(31)−Ti(2)-N(36)	159.12(8)	Ti(2)−O(61)-C(61)	159.6(2)
O(31)−Ti(2)-O(38)	114.13(8)	Ti(2)−O(71)-C(71)	153.9(2)
O(31)−Ti(2)-O(61)	96.51(8)		

[a] The number in parentheses is the standard deviation and refers to the last significant digit. [b] The ′ symbol refers to the symmetry equivalent atom related by a crystallographic 2-fold.

(24) As indicated by several large thermal parameters in the *tert*-butyl groups of this molecule, disorder was observed in these positions. Attempts to resolve the disorder using isotropic partially occupied carbon atoms did not give rise to fits that were chemically any more reasonable than the anisotropic model.

Discussion

Salen ligands have been a source of interest for inorganic and organic chemists due to their ability to support catalytically active metal complexes while providing electronically and sterically tunable structural features.[1−8,25] Despite the potential utility of these ligands for modifying the reactivity and selectivity of titanium Lewis acid catalysts, little work has appeared regarding the synthesis and structure of Ti−salen coordination complexes. In the present study, $Ti(O^iPr)_4$ and several mixed titanium isopropoxides have been used as precursors for the synthesis of a family of new six-coordinate Ti(IV)(salen) complexes.

The in situ generation of functional equivalents of $Ti(O^iPr)_2(OAr)_2$ and $Ti(O^iPr)_2(OTf)_2$ from $Ti(O^iPr)_4$ plus HOAr and TMSOTf, respectively, followed by reaction with H_2salen(*), offers a convenient and high yielding route to symmetrically disubstituted Ti(IV)salen complexes (**2**−**6**). It is known that the reaction of phenols with $Ti(O^iPr)_4$ requires azeotropic removal of 2-propanol for the synthesis of $(ArO)_2Ti(O^iPr)_2$-type complexes.[26] This suggests that $Ti(O^iPr)_4$ reacts first with H_2salen(*) to access (salen)$Ti(O^iPr)_2$ and that this intermediate gets trapped with ArOH. For the synthesis of mixed acetoxy/isopropoxy complexes (**11**, **12**) from in situ-generated $Ti(O^iPr)_3OC(O)R$, a similar mechanistic picture unfolds, as the reported syntheses of the titanium carboxylates (e.g., $Ti(O^iPr)_3(OAc)$),[27] require reflux conditions for the azeotropic removal of 2-propanol.

The stepwise addition of TMSOTf and H_2salen(*), on the other hand, is on slightly better mechanistic footing, as in situ monitoring of the addition of 1 equiv of TMSOTf to $Ti(O^iPr)_4$ (CD_3CN) quickly generates 1 equiv of $TMSO^iPr$ and a new Ti−isopropoxide whose methine resonance shifts downfield by 0.55 ppm relative to $Ti(O^iPr)_4$. This observation suggests that the TMSOTf initially reacts with the starting material to form a species with the composition $Ti(O^iPr)_3OTf$, and it is this species that reacts with H_2salen(*) to yield **10**. Similarly, the reaction of $Ti(O^iPr)_4$ and 2 equiv of TMSOTf results in the rapid formation of 2 equiv of $TMSO^iPr$ and a new Ti−isopropoxide. The methine resonance of this new species shifts 0.65 ppm downfield of $Ti(O^iPr)_4$, consistent with a substantial net reduction in electron density at the Ti center. The direct reaction of this ditriflate complex with H_2salen(*) is the most likely pathway to compounds **5** and **6**. The driving force for formation of a Ti−OTf bond is noteworthy in these complexes, as the ditriflates are also accessible from the reaction of the diaryloxides with TMSOTf, or dichlorides with TMSOTf or AgOTf.

The comproportionation reactivity noted herein (eqs 5−7) has also been observed in several TiX_4 (X = OAr, O^iPr, NR_2, and Cl)[28] and six-coordinate titanium porphyrin complexes ((tetraphenylporphyrin)TiX_2; X = Cl, NPh_2, OPh, OMe, O^tBu).[20] In general, this reactivity is restricted to systems that can readily associate to facilitate ligand exchange (e.g., four-coordinate) or that can dissociate a ligand to open up a coordination site on the metal for facilitating the transfer. The rapidity with which complexes **5** and **6** comproportionate suggests that dissociation of the OTf ligand is possible,[29] as the formation of bridged intermediates is not likely given the steric saturation of each Ti center. An example of a Ti−OTf complex that does not dissociate OTf was found to also not participate in comproportionation reactions.[17a] The inability of neutral ligands such as phosphines and pyridines to coordinate to **5** and **6** suggests that if the triflate does dissociate, the ion pair is not especially stable. Since comproportionation activity was also found to occur with dichlorides and diaryloxides, but not with two sets of diaryloxides, suggests that chloride ligands may also access ion-paired intermediates (albeit slowly), but that aryloxide ligands cannot.

The facility of axial ligand substitution in the described Ti−salen complexes is primarily dictated by the acidity of the incoming ligand relative to the outgoing ligand, with isopropoxide being the easiest to remove and triflate being the easiest to add (O^iPr < OAr < OC(O)R < OTf). For nonoxygenated ligands the substitution potential is more complex since, for example, **3** does not react with *N*-benzyltriflamide ($PhCH_2NH-SO_2CF_3$) even though the sulfonamide is more acidic than phenol by 7 orders of magnitude ($pK_a = \sim 11$ and $pK_a = 18.4$ in DMSO, respectively).[23] The attenuated π-basicity of this nitrogen ligand almost certainly contributes to its low stability.

To our knowledge, **3** represents the first structurally characterized transition metal salen complex containing two trans aryloxide ligands. Five-coordinate monoaryloxide metal salen complexes are known for Al(III) and Fe(III), with these complexes adopting a square-pyramidal geometry with the metal residing above the N_2O_2 plane and with an axial aryloxide.[30] Titanium(IV) complexes prefer to adopt the more rigid octahedral geometry, and thus the bond angles around titanium and the four coordinating atoms in the salen ligand are in good agreement with (salen)$TiCl_2$[10a] and (salen)$TiMe_2$.[11b] A comparison of the Ti−O and Ti−N bond lengths in the salen ligands of the three compounds highlighted in Table 4 clearly shows that the axial ligands have a significant effect on the Ti−O bond lengths and a moderate effect on the Ti−N bond lengths. The enhanced σ- and π-donating ability of the aryloxy ligands in **3**, and to a lesser extent the chloride ligands in (salen)$TiCl_2$, accounts for the lengthened Ti−O and Ti−N bonds.[31,32] In addition to trends in the bond

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(29) The availability of a coordinatively unsaturated cationic Ti center suggests that these complexes might act as efficient Lewis acid catalysts in organic synthesis. Experiments to address this issue are currently under way.

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(31) For the effect of $d_\pi-p_\pi$ bonding in Ti−aryloxide complexes, see: (a) Latesky, S. L.; Keddington, J.; McMullen, A. K.; Rothwell, I. P. *Inorg. Chem.* **1985**, *24*, 995−1001. (b) Durfee, L. D.; Latesky, S. L.; Rothwell, I. P.; Huffman, J. C.; Folting, K. *Inorg. Chem.* **1985**, *24*, 45669−4573.

Table 4. Metrical Parameters for the Three Known Ti(salen) Symmetrically Disubstituted Complexes

	Ti(salen)Me_2[a]	Ti(salen)Cl_2[b]	**3**, molecule 1	**3**, molecule 2
		Distances (Å)		
Ti−O	1.829(11)	1.835(5)	1.899(2)	1.889(2)
Ti−O′	1.864(10)	1.835(5)	1.899(2)	1.884(2)
Ti−N	2.142(14)	2.141(5)	2.159(2)	2.147(2)
Ti−N′	2.153(15)	2.141(5)	2.159(2)	2.168(2)
		Angles (deg)		
O−Ti−O′	110.9(4)	113.2(2)	114.94(9)	114.13(8)
O−Ti−N	86.5(5)	85.4(2)	84.9(1)	84.7(2)
N−Ti−N′	76.5(6)	76.1(2)	75.3(1)	75.27(8)
O′−Ti−N′	86.1(5)	85.4(2)	84.9(1)	85.9(2)

[a] Reference 10b. [b] Reference 9a.

lengths, the axial ligands in each of the compounds are distorted toward the nitrogen ligands with the C−Ti−C (154.9°), Cl−Ti−Cl (168.7°), and O−Ti−O angles (174.7° and 172.4°) tracking with both π-basicity and size of the axial ligands. Although the in-plane Ti−N bond lengths are substantially longer than the Ti−O bond lengths of the salen, the cause of the axial distortion is not completely obvious.

Summary

In this study we have demonstrated that a variety of six-coordinate Ti−salen complexes can be synthesized by (1) direct reaction of H_2salen with several Ti(O^iPr)$_2X_2$ and Ti(O^iPr)$_3$X functional equivalents, (2) ligand substitution on preformed Ti(salen)X_2 complexes, and (3) comproportionation reaction of two homobis-substituted Ti(salen)X_2 complexes. These products were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, and each was consistent with an octahedral titanium center containing a pseudoplanar four-coordinate salen ligand and two axially coordinated ligands. The X-ray structure of **3** confirmed this assignment. The reactivity of several symmetrically and unsymmetrically disubstituted complexes toward axial substitution was found to be primarily dominated by the acidity of the involved oxygen ligands, but that non-oxygen ligands did not necessarily follow this trend. These results underpin future studies utilizing chiral Ti(IV)−salen complexes as chiral Lewis acid catalysts for a variety of organic transformations.

Experimental Section

Abbreviations. Salen = *N*,*N*′-ethylenebis(salicylideneiminate); salen* = *N*,*N*′-ethylenebis(5-*tert*-butylsalicylideneiminate); OTf = $CF_3SO_3^-$.

General Procedures. All reactions were conducted under an atmosphere of dry, oxygen-free nitrogen or argon using standard Schlenk techniques or in a Vacuum Atmospheres Co. glovebox. All solvents except THF (CH_2Cl_2, hexanes, diethyl ether, and pentane) were dried by running through a column of activated alumina.[33] THF was refluxed for at least 8 h over sodium/benzophenone and freshly distilled. The dry solvents were freeze−pump−thaw degassed and stored in the glovebox. Deuterated solvents (CD_2Cl_2 and CD_3CN) were vacuum transferred from CaH_2 and degassed via several freeze−pump−thaw cycles prior to use. Air and moisture sensitive reagents were handled using standard syringe techniques or in the glovebox. *N*,*N*′-Ethylenebis(5-*tert*-butylsalicylideneimine) was prepared according to a literature procedure.[34] Triethylamine was distilled from CaH_2, while all the other reagents were used as received except that they were deoxygenated prior to use. Sodium acetate was dried under high vacuum at 100 °C for 10 h prior to use.

Routine ^{1}H NMR spectra were recorded at ambient temperature on a Brucker AC200 spectrometer (200 MHz, ^{1}H NMR) or a Brucker MW250 spectrometer (250 MHz, ^{1}H NMR) unless otherwise noted. Routine ^{13}C NMR spectra were recorded at ambient temperature on a Brucker AC200 spectrometer (50 MHz, ^{13}C NMR) or a Varian Gemini 2000 spectrometer (75 MHz, ^{13}C NMR) unless otherwise noted. Chemical shifts are recorded in ppm and are referenced to residual solvent peaks. All ^{19}F NMR spectra were recorded on a Varian Gemini 2000 spectrometer (288 MHz, ^{19}F NMR) with either C_6F_6 as external reference in CD_2Cl_2 or $CFCl_3$ as external reference in CD_3CN. E+R Microanalytical Laboratory Inc., Corona, New York, performed elemental analyses.

For completeness, the ^{1}H NMR data for Ti(salen)Cl_2 are presented here.[10a,b] ^{1}H NMR (CD_2Cl_2): δ 8.42 (s, 2H, H−C=N), 7.63 (m, 2H, Ar), 7.60 (m, 2H, Ar), 7.14 (dd, 2H, Ar), 6.84 (dd, 2H, Ar), 4.22 (s, 4H, CH_2).

Ti(salen*)Cl_2 (1). A solution of $TiCl_4$·2THF (605 mg, 1.81 mmol) in THF (8 mL) was added slowly to a solution of H_2-salen* (695 mg, 1.83 mmol) in THF (7 mL), resulting in a red solution. The reaction mixture was stirred and refluxed at 70 °C for 1 h, then cooled to ambient temperature, and concentrated in vacuo to dryness. The orange-brown solid was slurried with Et_2O (20 mL), filtered through a fine-fritted funnel, washed with additional Et_2O, and dried under high vacuum at 80 °C for 2 h. Yield of orange-brown solid: 897 mg (1.80 mmol, 99%). ^{1}H NMR (CD_2Cl_2): δ 8.41 (s, 2H, H−C=N), 7.64 (dd, J = 9.0, 2.5 Hz, 2H, Ar), 7.54 (d, J = 2.5 Hz, 2H, Ar), 6.76 (d, J = 9.0 Hz, 2H, Ar), 4.21 (s, 4H, CH_2), 1.35 (s, 18H, CH_3). ^{13}C NMR (CD_2Cl_2): δ 164.1 (C=N), 160.8, 146.4, 134.4, 131.8, 125.0, 115.9, 59.2 (CH_2), 34.7 ($C(CH_3)_3$), 31.4 (CH_3). Anal. Calcd for $C_{24}H_{30}Cl_2N_2O_2Ti$: C, 57.96; H, 6.08; N, 5.63. Found: C, 57.74; H, 6.30; N, 5.44.

Ti(salen)$(OPh)_2$ (2). A CH_2Cl_2 solution (1 mL) of Ti(O^i-Pr)$_4$ (60.7 mg, 0.203 mmol) was combined with a CH_2Cl_2 solution (1 mL) of PhOH (38.0 mg, 0.404 mmol), resulting in a yellow solution. To this reaction mixture was added H_2salen (54.8 mg, 0.204 mmol) in CH_2Cl_2 (1.5 mL), producing an orange-yellow solution. After 5 min, the reaction mixture was concentrated in vacuo to dryness. The solid was slurried with hexanes (10 mL), filtered through a fine-fritted funnel, washed with additional hexanes, and dried under high vacuum at 80 °C for 1 h. Yield of orange-yellow solid: 90.2 mg (0.180 mmol, 89%). ^{1}H NMR (CD_2Cl_2): δ 8.29 (s, 2H, H−C=N), 7.52 (m, 4H, Ar), 6.92 (m, 8H, Ar), 6.59 (t, J = 7.0 Hz, 2H, Ar), 6.23 (d, J = 7.5 Hz, 4H, Ar), 3.69 (s, 4H, CH_2). ^{13}C NMR (CD_2Cl_2): δ 165.9, 164.6, 163.3 (C=N), 136.4, 134.5, 129.1, 123.7, 119.6, 119.5, 118.6, 118.0, 58.8 (CH_2). Anal. Calcd for $C_{28}H_{24}N_2O_4$-Ti: C, 67.21; H, 4.83; N, 5.60. Found: C, 67.41; H, 4.86; N, 5.59.

Ti(salen)(4-*tert*-butylphenolate)$_2$ (3). A CH_2Cl_2 solution (1 mL) of Ti(O^iPr)$_4$ (563 mg, 1.98 mmol) was combined with a CH_2Cl_2 solution (3 mL) of 4-*tert*-butyl-PhOH (636 mg, 4.23 mmol), resulting in a yellow solution. To this reaction mixture was added H_2salen (509 mg, 1.90 mmol) in CH_2Cl_2 (3.5 mL), producing an orange solution. After 10 min, the contents were concentrated in vacuo to dryness. The solid was slurried with hexanes (10 mL), filtered through a medium-fritted funnel,

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washed with additional hexanes (3 × 5 mL), and dried under high vacuum at 100 °C for 3 h. Yield of orange solid: 1.113 g (1.82 mmol, 92%). ^{1}H NMR (CD_2Cl_2): δ 8.32 (s, 2H, H−C═N), 7.53 (m, 4H, Ar), 6.98 (m, 4H, Ar), 6.94 (m, 4H, Ar), 6.15 (m, 4H, Ar), 3.71 (s, 4H, CH_2), 1.16 (s, 18H, CH_3). ^{13}C NMR (CD_2Cl_2): δ 165.0, 164.0, 163.3 (C═N), 142.2, 136.3, 134.5, 125.9, 123.8, 119.4, 118.2, 118.0, 58.9 (CH_2), 34.3 ($C(CH_3)_3$), 31.8 (CH_3). Anal. Calcd for $C_{36}H_{40}N_2O_4Ti$: C, 70.58; H, 6.58; N, 4.57. Found: C, 70.60; H, 6.57; N, 4.61.

Ti(salen*)(4-*tert*-butylphenolate)$_2$ (4). A CH_2Cl_2 solution (2.5 mL) of Ti(O^{i}Pr)$_4$ (204 mg, 0.682 mmol) was combined with a CH_2Cl_2 solution (3 mL) of 4-*tert*-butyl-PhOH (206 mg, 1.372 mmol) to yield a clear yellow solution. To this was added H_2salen* (259 mg, 0.681 mmol) in CH_2Cl_2 (4.5 mL), producing an orange-red solution, which after 10 min was concentrated in vacuo to dryness. The solids were slurried with hexanes (10 mL), filtered through a fine-fritted funnel, washed with additional hexanes (3 × 5 mL), and dried under high vacuum at 100 °C for 3 h. Yield of orange solid: 439 mg (0.605 mmol, 89%). ^{1}H NMR (CD_2Cl_2): δ 8.36 (s, 2H, H−C═N), 7.63 (dd, J = 8.8, 2.4 Hz, 2H, Ar), 7.50 (d, J = 2.4 Hz, 2H, Ar), 6.98 (dd, J = 6.8, 2.0 Hz, 4H, Ar), 6.87 (d, J = 8.8 Hz, 2H, Ar), 6.20 (dd, J = 6.8, 2.0 Hz, 4H, Ar), 3.74 (s, 4H, CH_2), 1.41 (s, 18H, CH_3), 1.22 (s, 18H, CH_3). ^{13}C NMR (CD_2Cl_2): δ 164.0, 163.6 (C═N), 162.9, 142.2, 141.9, 133.9, 130.7, 125.7, 123.1, 117.9, 117.5, 58.9 (CH_2), 34.4 ($C(CH_3)_3$), 34.2 ($C(CH_3)_3$), 31.8 (CH_3), 31.6 (CH_3). Anal. Calcd for $C_{44}H_{56}N_2O_4Ti$: C, 72.91; H, 7.79; N, 3.86. Found: C, 72.65; H, 7.93; N, 4.01.

Ti(salen)(OTf)$_2$ (5). Upon the addition of TMSOTf (125.3 mg, 0.564 mmol) to a concentrated solution of **3** (164.0 mg, 0.268 mmol) in CH_2Cl_2 (3 mL) a black-brown solid precipitated from the solution. The resulting slurry was filtered through a fine-fritted funnel, washed with CH_2Cl_2, and dried in vacuo. Yield of black-brown solid: 149.0 mg (0.243 mmol, 91%). ^{1}H NMR (CD_3CN): δ 8.75 (s, 2H, H−C═N), 7.71 (m, 4H, Ar), 7.25 (t, J = 7.5 Hz, 2H, Ar), 6.80 (d, J = 8.0 Hz, 2H, Ar), 4.20 (s, 4H, CH_2). ^{13}C NMR (CD_3CN): δ 167.8 (C═N), 162.5, 138.6, 136.7, 125.8, ∼118 (aryl carbon resonance overlap with the solvent peak), 60.0 (CH_2), the CF_3 quartet was not observed due to the product's low solubility in CD_3CN. ^{19}F NMR (282.88 MHz, CD_3CN): δ −77.3 (s). Anal. Calcd for $C_{18}H_{14}F_6N_2O_8S_2$-Ti: C, 35.31; H, 2.30; N, 4.57. Found: C, 35.42; H, 2.27; N, 4.43.

Ti(salen*)(OTf)$_2$ (6). To a solution of **1** (83.4 mg, 0.168 mmol) in CH_2Cl_2 (1.5 mL) was added an acetonitrile solution (7 mL) of AgOTf (89.4 mg, 0.0506 mL), producing a pale white precipitate. The dark red slurry was filtered through a fine fritted funnel, and the filtrate was concentrated to dryness. The solid was triturated with CH_2Cl_2 to remove acetonitrile, and the resulting solid isolated. Yield of black-brown solid: 82.5 mg (0.114 mmol, 68%). ^{1}H NMR (CD_3CN): δ 8.68 (s, 2H, H−C═N), 7.74 (dd, J = 9.0, 2.4 Hz, 2H, Ar), 7.69 (d, J = 2.4 Hz, 2H, Ar), 6.70 (d, J = 9.0 Hz, 2H, Ar), 4.20 (s, 4H, CH_2), 1.33 (s, 18H, CH_3). ^{13}C NMR (75 MHz, CD_3CN): δ 166.8 (2C═N), 160.6, 148.3, 135.6, 132.3, 124.6, 115.2, 59.3 (CH_2), 34.8 ($C(CH_3)_3$), 31.2 (CH_3), the CF_3 quartet was not observed due to the product's low solubility in CD_3CN. ^{19}F NMR (282.88 MHz, CD_3CN): δ −80.0 (s). Anal. Calcd for $C_{26}H_{30}F_6N_2O_8S_2$-Ti: C, 43.10; H, 4.17; N, 3.87. Found: C 42.99; H, 4.17; N, 3.93.

Ti(salen)(4-*tert*-butylphenolate)(OTf) (7). The titanium complex **3** (57.6 mg, 0.0940 mol) was dissolved in CH_2Cl_2 (1.1 mL), and to it was added a solution of **5** (57.9 mg, 0.0945 mmol) in acetonitrile (0.8 mL). After stirring for 5 min, the solution was concentrated in vacuo to dryness. The resulting red oil was triturated with CH_2Cl_2, to yield 76.6 mg (0.125 mmol, 66%) of a crystalline golden solid. ^{1}H NMR (CD_3CN, 400 MHz): δ 8.67 (s, 2H, H−C═N), 7.66 (dd, J = 7.6, 1.6 Hz, 2H, Ar), 7.62 (td, J = 7.6, 1.6 Hz, 2H, Ar), 7.11 (d, J = 6.8 Hz, 2H, Ar), 7.09 (d, J = 8.8 Hz, 2H, Ar), 6.84 (d, J = 6.8 Hz, 2H, Ar), 6.44 (d, J = 8.8 Hz, 2H, Ar), 4.05 (m, 4H, CH_2), 1.16 (s, 9H, CH_3). ^{13}C NMR (CD_3CN, 100 MHz): δ 167.1 (2C═N), 166.0, 163.5, 147.2, 137.8, 136.0, 126.9, 124.4, 122.5, 117.5, 117.1, 59.7 (CH_2), 34.9 ($C(CH_3)_3$), 31.6 (CH_3), the CF_3 quartet was not observed due to the product's low solubility in CD_3CN. ^{19}F NMR (282.88 MHz, CD_3CN): δ −78.0 (s). Anal. Calcd for $C_{27}H_{27}F_3N_2O_6$-STi: C, 52.95; H, 4.44; N, 4.57. Found: C, 52.96; H, 4.58; N, 4.44.

Ti(salen*)(4-*tert*-butylphenolate)(OTf) (8). The titanium complex **9** (122 mg, 0.199 mmol) was dissolved in CH_2Cl_2 (2 mL), and to it was added an acetonitrile (1.5 mL) solution of AgOTf (52.2 mg, 0.203 mmol), causing a pale white solid to precipitate. The resulting slurry was filtered through a fine-fritted funnel, and the orange-red filtrate concentrated in vacuo to dryness. Yield of red-brown solid: 95.3 mg (0.132 mmol, 66%). ^{1}H NMR (CD_2Cl_2): δ 8.50 (s, 2H, H−C═N), 7.66 (dd, J = 8.6, 2.4 Hz, 2H, Ar), 7.54 (d, J = 2.4 Hz, 2H, Ar), 7.07 (d, J = 8.6 Hz, 2H, Ar), 6.84 (d, J = 8.6 Hz, 2H, Ar), 6.43 (d, J = 8.6 Hz, 2H, Ar), 4.20 (m, 2H, CH_2), 3.92 (m, 2H, CH_2), 1.37 (s, 18H, CH_3), 1.20 (s, 9H, CH_3). ^{13}C NMR (CD_2Cl_2): δ 165.8 (2C═N), 165.0, 161.7, 146.2, 144.5, 134.8, 131.2, 126.1, 123.1, 117.0, 116.4, 59.2 (CH_2), 34.5 ($C(CH_3)_3$), 31.5 (CH_3), 31.4 (CH_3), the CF_3 quartet was not observed due to the product's low solubility in CD_2Cl_2. ^{19}F NMR (282.88 MHz, CD_2Cl_2): δ −76.0 (s). Anal. Calcd for $C_{35}H_{43}F_3N_2O_6STi$: C, 58.01; H, 5.98; N, 3.87. Found: C, 57.81; H, 5.85; N, 3.88. **8** can also be prepared cleanly by the comproportionation of **4** and **6**.

Ti(salen*)(4-*tert*-butylphenolate)Cl (9). A Schlenk flask was charged with **1** (166 mg, 0.333 mol) and **4** (241 mg, 0.332 mmol). Dichloromethane (4 mL) was added, producing an intense orange-red solution that was stirred for 16 h at ambient temperature and then concentrated in vacuo to dryness. The solid was slurried with hexanes (2 mL × 5), filtered through a fine-fritted funnel, washed, and dried in vacuo. Yield of dark tan solid: 358 mg (0.587 mmol, 88%). ^{1}H NMR (CD_2Cl_2): δ 8.36 (s, 2H, H−C═N), 7.63 (dd, J = 8.7, 2.6 Hz, 2H, Ar), 7.49 (d, J = 2.6 Hz, 2H, Ar), 7.02 (d, J = 8.7 Hz, 2H, Ar), 6.81 (d, J = 8.7 Hz, 2H, Ar), 6.32 (d, J = 8.7 Hz, 2H, Ar), 4.20 (m, 2H, CH_2), 3.85 (m, 2H, CH_2), 1.36 (s, 18H, CH_3), 1.18 (s, 9H, CH_3). ^{13}C NMR (CD_2Cl_2): δ 164.8, 164.1 (2C═N), 161.9, 144.6, 143.9, 134.2, 131.1, 126.0, 123.6 117.5, 116.7, 59.0 (CH_2), 34.5 ($C(CH_3)_3$), 34.4 ($C(CH_3)_3$), 31.6 (CH_3), 31.5 (CH_3). Anal. Calcd for $C_{34}H_{43}ClN_2O_3Ti$: C, 66.83; H, 7.09; N, 4.58. Found: C, 66.77; H, 7.08; N, 4.38.

Ti(salen)(O^{i}Pr)(OTf) (10). A solution of Ti(O^{i}Pr)$_4$ (239.7 mg, 0.818 mmol) in CH_2Cl_2 (0.9 mL) was combined with a solution of TMSOTf (176.4 mg, 0.794 mmol) in CH_2Cl_2 (0.9 mL). To this mixture was added H_2salen (218 mg, 0.813 mmol) in CH_2Cl_2 (0.6 mL), producing a clear yellow solution which after 2 min, was concentrated in vacuo to dryness. The resulting solid was slurried with a solution of Ti(O^{i}Pr)$_4$ (209 mg) in hexanes (6 mL), filtered through a fine-fritted funnel, washed with a diethyl ether solution of Ti(O^{i}Pr)$_4$, and dried under high vacuum at 80 °C for 10 h. Yield of yellow solid: 372.4 mg (0.674 mmol, 85%). ^{1}H NMR (CD_2Cl_2): δ 8.47 (s, 2H, H−C═N), 7.56 (m, 4H, Ar), 7.01 (td, J = 7.0, 1.2 Hz, 2H, Ar), 6.86 (dd, J = 8.2, 1.2 Hz, 2H, Ar), 4.66 (septet, J = 6.4 Hz, 1H, CH), 4.15 (m, 4H, CH_2), 1.01 (d, J = 6.4 Hz, 6H, CH_3). ^{13}C NMR (CD_2Cl_2): δ 165.7 (C═N), 163.8, 137.0, 134.8, 123.1, 120.6, 119.8 (q, J_{CF} = 319 Hz), 117.2, 85.5 (CH), 59.2 (CH_2), 24.8 (CH_3). ^{19}F NMR (282.88 MHz, CD_3CN): δ −78.1 (s). Anal. Calcd for $C_{22}H_{21}F_3N_2O_6STi$: C, 45.99; H, 4.05; N, 5.36. Found: C, 46.08; H, 4.04; N, 5.47.

Ti(salen)(O^{i}Pr)(OC(O)CH$_3$) (11). A solution of Ti(O^{i}Pr)$_4$ (117 mg, 0.385 mmol) in CH_2Cl_2 (0.5 mL) was combined with a solution of acetic acid (35.7 mg, 0.595 mmol) in CH_2Cl_2 (0.6 mL). To this mixture was added H_2salen (82.4 mg, 0.307 mmol) in CH_2Cl_2 (0.4 mL) and after 2 min was concentrated in vacuo to dryness. The solid was slurried first by a solution of Ti(O^{i}Pr)$_4$ (280 mg) in Et_2O (3 mL) and then by a hexanes solution (5 mL) of Ti(O^{i}Pr)$_4$, filtered through a fine-fritted

funnel, washed with a hexanes solution of $Ti(O^iPr)_4$, and dried in vacuo for 2 h. Yield of yellow solid: 116 mg (0.268 mmol, 87%). ^1H NMR (CD_2Cl_2): δ 8.39 (s, 2H, H−C═N), 7.50 (m, 4H, Ar), 6.91 (td, J = 7.4, 1.0 Hz, 2H, Ar), 6.83 (d, J = 8.2 Hz, 2H, Ar), 4.36 (septet, J = 6.4 Hz, 1H, CH), 4.33 (m, 2H, CH_2), 4.00 (m, 2H, CH_2), 1.41 (s, 3H, CH_3), 0.87 (d, J = 6.4 Hz, 6H, CH_3). ^{13}C NMR (CD_2Cl_2): δ 174.6 (C═O), 164.6, 163.7 (2C═N), 136.1, 134.4, 123.1, 119.3, 117.7, 80.2 (CH), 59.2 (CH_2), 25.1 (CH_3), 24.4 (CH_3). Anal. Calcd for $C_{21}H_{24}N_2O_5Ti$: C, 58.34; H, 5.60; N, 6.48. Found: C, 58.33; H, 5.60; N, 6.37.

Ti(salen)(O^iPr)($OC(O)CH_2OCH_3$) (12). A solution of $Ti(O^iPr)_4$ (332 mg, 1.102 mmol) in CH_2Cl_2 (0.9 mL) was combined with a solution of methoxyacetic acid (115.8 mg, 1.260 mmol) in CH_2Cl_2 (1.0 mL). To this mixture was added H_2salen (267 mg, 0.993 mmol) in CH_2Cl_2 (0.7 mL), which after 2 min was concentrated in vacuo to dryness. The resulting solid was slurried with a solution of $Ti(O^iPr)_4$ (300 mg) in Et_2O (4 mL), followed by the addition of $Ti(O^iPr)_4$ (256 mg) in hexanes (4 mL). The final slurry was filtered through a fine-fritted funnel, washed with a $Ti(O^iPr)_4$ solution in hexanes, and dried in vacuo for 2 h. Yield of yellow solid: 415 mg (0.898 mmol, 90%). ^1H NMR (CD_2Cl_2): δ 8.41 (s, 2H, H−C═N), 7.50 (m, 4H, Ar), 6.91 (td, J = 7.6, 1.0 Hz, 2H, Ar), 6.83 (d, J = 8.4 Hz, 2H, Ar), 4.39 (septet, J = 6.4 Hz, 1H, CH), 4.36 (m, 2H, CH_2), 4.04 (m, 2H, CH_2), 3.30 (s, 2H, CH_2), 2.95 (s, 3H, OCH_3), 0.89 (d, J = 6.4 Hz, 6H, CH_3). ^{13}C NMR (CH_2Cl_2): δ 173.2 (C═O), 164.4, 163.9 (C═N), 136.1, 134.4, 123.1, 119.4, 117.6, 80.6 (CH), 71.5 (OCH_2), 59.2 (CH_2), 58.3 (OCH_3), 25.0 (CH_3). Anal. Calcd for $C_{22}H_{26}N_2O_6Ti$: C, 57.15; H, 5.67; N, 6.06. Found: C, 57.22; H, 5.80; N, 6.05.

Ti(salen)(4-*tert*-butylphenolate)($OC(O)CH_3$) (13). A solution of the titanium complex **7** (0.180 mmol) was prepared by the combination of a CH_2Cl_2 solution (1.0 mL) of **3** (55.2 mg, 0.090 mmol) and an acetonitrile solution (1.0 mL) of **5** (55.3 mg, 0.090 mmol). To the orange-red solution was added an acetonitrile solution of dry sodium acetate (15.7 mg, 0.191 mmol). The slurry was stirred at ambient temperature for 6 h and then concentrated in vacuo to dryness. The solid was dissolved with CH_2Cl_2 (3 mL) and filtered through a fine-fritted funnel, and the solvent was removed in vacuo to yield 69.8 mg of orange-red solid. ^1H NMR of the solid indicates a mixture of **13** (∼80%), starting material, and oxo-bridged dimer. ^1H NMR (CD_2Cl_2): δ 8.38 (s, 2H, H−C═N), 7.53 (m, 4H, Ar), 6.99 (m, 4H, Ar), 6.88 (d, J = 8.6 Hz, 2H, Ar), 6.23 (d, J = 8.6 Hz, 2H, Ar), 4.30 (m, 2H, CH_2), 3.82 (m, 2H, CH_2), 1.53 (s, 3H, CH_3), 1.17 (s, 9H, CH_3). ^{13}C NMR (CD_2Cl_2): δ 173.2 (C═O), 164.7, 164.3, 163.7 (C═N), 144.4, 136.3, 134.7, 126.0, 123.6, 120.4, 117.5, 117.2, 59.0 (CH_2), 34.4, 31.5 (CH_3), 23.7 (CH_3).

Ti(salen)(4-*tert*-butylphenolate)($OC(O)CH_2OCH_3$) (14). A red solution of **3** (110 mg, 0.179 mmol) in CH_2Cl_2 (0.6 mL) was combined with a solution of methoxyacetic acid (17.6 mg, 0.195 mmol) in CH_2Cl_2 (0.3 mL) to give a cherry red solution. After 5 min, the solution was diluted with dry *tert*-butyl methyl ether (22 mL), and with stirring, hexanes (50 mL) was slowly added to precipitate out an orange solid. The slurry was filtered through 15/M fritted funnel, washed with hexanes, and dried in vacuo. Yield of orange solid: 58.9 mg. By ^1H NMR, the product was a mixture of **14** (∼80%), starting material, and oxo-bridged dimeric complexes. ^1H NMR (CD_2Cl_2): δ 8.39 (s, 2H, H−C═N), 7.53 (m, 4H, Ar), 6.99 (m, 6H, Ar), 6.26 (d, J = 8.6 Hz, 2H, Ar), 4.31 (m, 2H, CH_2), 3.83 (m, 2H, CH_2), 3.43 (s, 2H, OCH_2), 3.01 (s, 3H, OCH_3), 1.19 (s, 9H, CH_3). ^{13}C NMR (CD_2Cl_2): δ 173.2 (C═O), 164.3, 162.9 (3q), 163.8 (C═N), 144.4, 136.5, 134.7, 126.1, 123.8, 120.5, 117.7, 117.4, 71.4 (OCH_2), 59.2, 58.6, 34.5 ($C(CH_3)_3$), 31.7 (CH_3).

Ti(salen)(4-*tert*-butylphenolate)(3,5-dimethylphenolate) (15). The titanium complex **7** (95.5 mg, 0.156 mmol) was dissolved in acetonitrile (1.5 mL), and the mixture was added to a suspension of sodium 3,5-dimethylphenoxide (22.2 mg, 0.154 mmol) in acetonitrile (1.5 mL). After stirring for 20 min, the red slurry cleared to a homogeneous orange solution and was concentrated in vacuo to dryness. The oily solid was triturated with a 1:1 mixture of CH_2Cl_2 and hexanes. The resulting orange solid was redissolved in CH_2Cl_2, filtered through a fine fritted funnel, and dried in vacuo. Yield of orange solid: 81.3 mg (0.139 mmol, 90%). ^1H NMR (CD_3CN): δ 8.35 (s, 2H, C═N), 7.49 (m, 4H, Ar), 6.93 (m, 4H, Ar), 6.83 (m, 2H, Ar), 6.23 (s, 1H, Ar), 6.11 (m, 2H, Ar), 5.84 (s, 2H, Ar), 3.68 (br t, J = 4.0 Hz, 4H, CH_2), 1.94 (s, 6H, CH_3), 1.12 (s, 9H, CH_3). ^{13}C NMR (CD_3CN): δ 166.6, 164.9, 164.5, 164.4 (C═N), 142.5, 139.0, 136.6, 135.5, 126.4, 124.6, 121.8, 120.1, 118.4, 118.0, 116.9, 59.2 (CH_2), 34.5 ($C(CH_3)_3$), 31.8 (CH_3), 21.3 (CH_3). Anal. Calcd for $C_{34}H_{36}N_2O_4Ti$: C, 69.86; H, 6.21; N, 4.79. Found: C, 69.85; H, 6.27; N, 4.95.

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