Synthesis, Characterization, and Metal Complexes of a Salen Ligand Containing a Quinoline Base

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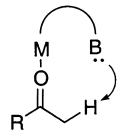
Metal salen complexes containing intramolecular bases have been designed for use as bifunctional catalysts. A ligand containing a quinoline base and the salen core has been synthesized for this purpose. Ruthenium, chromium, titanium, and zinc complexes of the salen have been formed and characterized. A crystal structure of a μ-oxo−titanium dimer incorporating the bifunctional ligand shows a typical salen coordination pattern *and* illustrates that the nitrogens of the quinoline groups participate in neither intra- nor intermolecular coordination. In addition, the quinoline groups orient in an appropriate manner to act as bases toward substrates coordinated at the apical positions of these complexes. As an indication that the quinoline bases can alter the activity of salen metal complexes, the addition of dialkylzincs to aldehydes was shown to be accelerated by the quinoline salen ligand relative to a salen lacking the quinoline groups.

Introduction

Investigation into the mechanism of carboxypeptidase A[1] and aldolase[2] has revealed that a Lewis acid acting in concert with a Brønsted base will effect the intramolecular enolization of ketones as shown in **1**. An exciting



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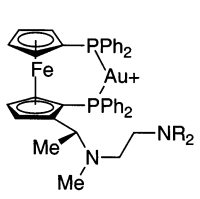
area of research is the design of bifunctional ligands[3,4] with noncoordinating basic groups. When these ligands are bound to a metal, the complexes behave like enzymes, combining molecular recognition with catalysis.

There are a number of notable applications of bifunctional Lewis acid−Brønsted base complexes toward ketone enolization. Ito and Hayashi[5] developed complex **2** to catalyze the aldol reaction of isocyanates and aldehydes. In 1987, Aoyama and Ogoshi[6] made an important contribution with rigid porphyrin ligand **3**, which incorporates a weakly basic quinoline that is



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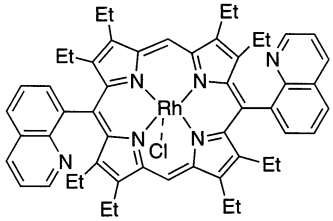

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sufficiently separated from the Lewis acid to avoid complexation. While enolization of acetone was accomplished under mild, neutral conditions to generate the carbon-bound Rh enolate, the presumed lack of reactivity of the Rh enolate has prevented the development of a general catalytic system with this complex. Shibasaki and co-workers have recently described heterobimetallic lithium−lanthanum BINOL complexes which catalyze the direct aldol, nitro-aldol, and Michael reactions with good yields and enantioselectivities.[4]

The goal of this research effort is to design and prepare Lewis acid−base complexes that incorporate the structural rigidity of **3** but possess greater reactivity. Two architectures (**4** and **5**) were examined as starting points (Scheme 1). With the aid of vector placement and a CAVEAT structural database search[7] several potential scaffolds were identified which fulfilled our structural criteria. Not surprisingly, a porphyrin architecture (CSD structure YIYPIF, **7**)[8] similar to that used by Aoyama and Ogoshi was one of the best leads found. We used compound **7** as the starting point for the design of the salen species **8**. Due to the structural rigidity combined with the ease of preparation and derivatization of salens, this ligand type is a an attractive scaffold for the development of bifunctional complexes.

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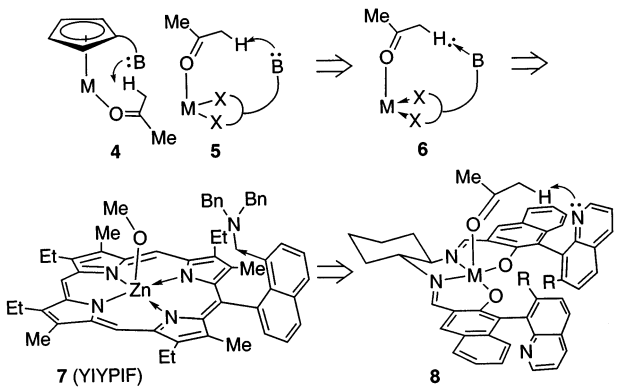
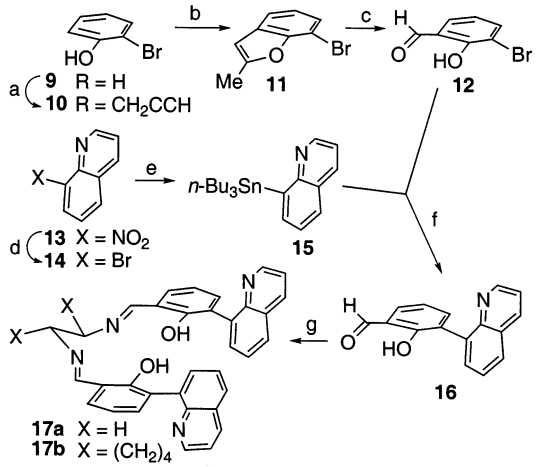
Scheme 1



Scheme 2 [a]



[a] Legend: (a) propargyl bromide, Et_3N; (b) CsF, Et_2NPh; (c) (i) O_3, (ii) DMS, (iii) K_2CO_3; (d) (i) H_2, PtO_2, (ii) $NaNO_2$, HBr, CuBr; (e) *n*-BuLi, *n*-Bu_3SnCl; (f) $Pd(PPh_3)_4$, CuBr; (g) (*S*,*S*)-*trans*-cyclohexane-1,2-diamine, $-H_2O$.

Modeling complex **8** using semiempirical level (PM3-tm) calculations[9] indicates that the quinoline nitrogen lone pair is disposed at the correct distance and trajectory to deprotonate a bound ketone. In addition, the quinoline nitrogen is out of reach for direct coordination of the metal center. Such an intramolecular coordination would cause deactivation by sequestering both the Lewis acid and Brønsted base. The steric environment provided by C1 of the quinoline also prevents intermolecular aggregation. As such, compound **8** was expected to provide a mild enolization pathway, as illustrated by **6**.

Results and Discussion

Synthesis of the Salen Ligand. Initial synthetic efforts focused on the slightly simpler quinoline salen derivative **17** (Scheme 2). The synthesis of this compound utilizes a Stille coupling to unite fragments **12** and **15**, thereby establishing the biaryl bond. With commercially available 2-bromophenol **9** as the starting material, benzofuran **11** was prepared via Claisen rearrangement of the intermediate propargyl ether **10**. Ozonolysis of benzofuran **11** then afforded bromoaldehyde **12**.[10] The tin coupling partner was generated from 2-bromoquinoline (**14**), which is readily prepared by reduction and diazotization of commercial 2-nitroquinoline (**13**).[11] Careful control of temperature (<−78 °C) and the rate of addition was required in the lithium−halogen exchange of **14** with *n*-BuLi in order to prevent addition of the *n*-butyl anion to the highly electrophilic quinoline nucleus. When these precautions were exercised, high yields (83−97%) of the desired tri-*n*-butyltin quinoline **15** could be obtained.

Before embarking on the Stille coupling to produce **16**, the compatibility of the aldehyde **12** toward Stille reaction conditions was examined. When aldehyde **12** and commercially available phenyltri-*n*-butyltin were treated under standard conditions ($Pd(PPh_3)_4$ in toluene at reflux), a 74% yield of the coupled product was observed. This encouraging result prompted us to undertake the coupling between **12** and **15**. In the first trials, only the transfer of an *n*-butyl group to aldehyde **12** was observed, due to the presence of contaminating $(n\text{-Bu})_4Sn$ from the preparation of **15**. However, after careful removal of this contaminant, standard Stille cross-coupling conditions resulted only in degradation of the starting components. Reasoning that the hindered tin species **15** transfers the quinoline moiety slowly (which is consistent with the competitive *n*-butyl transfer described above) and that aldehyde compatibility is not the issue, a copper(I) bromide cocatalyst was examined, since such species are reported to increase the reaction rate.[12] To our delight, this procedure produced the coupled material **16** in 57−64% yield. Salen species **17a** and **17b** were readily produced as yellow crystalline solids by treating aldehyde **16** with ethylenediamine and (*R*,*R*)-*trans*-cylcohexane-1,2-diamine, respectively, under dehydrating conditions. Due to the higher solubility of **17b** relative to **17a**, **17b** was used to generate the salen metal complexes described below.

Formation of Metal Complexes. A number of factors were considered in the selection of a metal center to employ with ligand **17**. In particular, the metal center must be sufficiently Lewis acidic so that ketones with pK_a values near 20 are viable substrates. Since related ruthenium, chromium, and titanium complexes have been shown to be good Lewis acids, these metals were selected for further examination.

Air-stable ruthenium−salen complexes such as **18**[13] and **19**[14] have recently emerged as a powerful class of Lewis acid catalysts. The nitrosyl ligand at the axial position in **18** is a strong π-acceptor and enhances the Lewis acidity of the cationic ruthenium while labilizing water via a strong trans influence. Activation of **19** is accomplished by irradiation with incandescent light,

(9) SPARTAN version 5.1.2; Wavefunction, Inc., 18401 Von Karman Ave., Suite 370, Irvine, CA 92612.

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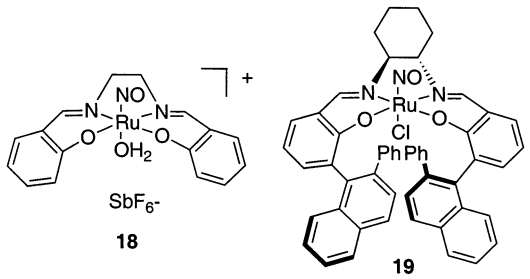
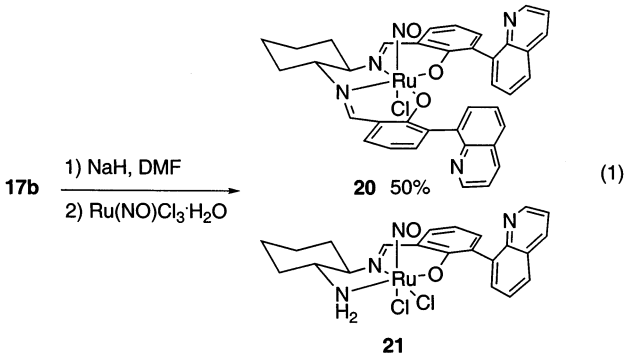


which promotes dissociation of the nitrosyl ligand to provide a vacant coordination site. On the basis of these precedents, a ruthenium salen complex would allow two alternative modes of activation: reaction with a silver salt to precipitate AgCl or light-induced cleavage of the nitrosyl ligand. A ketone deprotonation cycle would involve ruthenium−enolate intermediates, which are stable compounds[15] that have also been proposed as intermediates in catalytic cycles.[16] The most notable report of these compounds is found in the catalytic Michael and Knoevenagel reactions that proceed by oxidative (α-CH) addition of ruthenium(0) complexes to active methylene compounds, providing a reactive ruthenium−enolate intermediate.[17]

The air-stable ruthenium-salen complex **20** was prepared in 50% yield, as shown in eq 1. The major



byproduct in this reaction is a dark green solid, for which structure **21** has been proposed on the basis of NMR and mass spectral data. Complex **20** is only soluble in polar solvents and tends to decompose to a dark green compound, presumably **21**, when left in solution for an extended period of time.

Both modes of activation of the ruthenium complex **20** were attempted (eqs 2 and 3). In an effort to avoid any potential problems that might be associated with

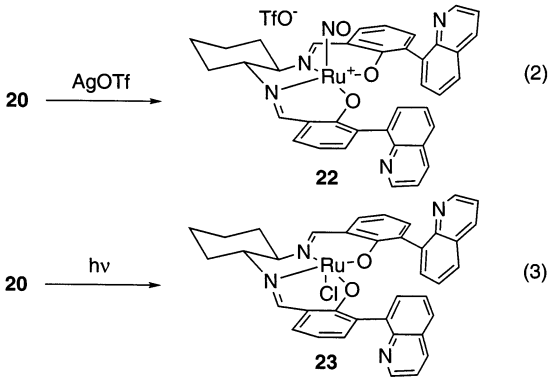
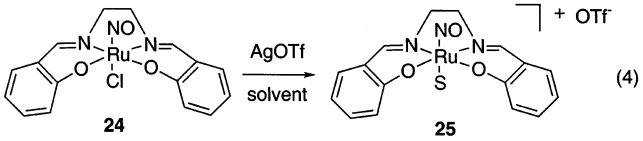


Table 1. ^{1}H NMR Studies of the in Situ Activation of 24 (Eq 4)

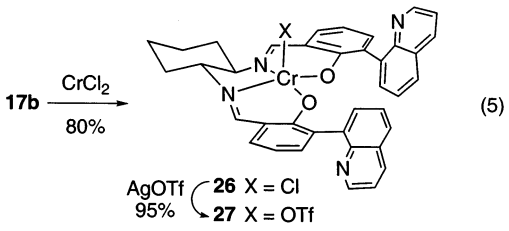
entry	solvent	conversn, %	time	solubility	dec
1	CD_2Cl_2	79	6 h	moderate	none
		79	20 h	poor	yes
2	2:1 CD_2Cl_2/ acetone-d_6	86	44 h	good	none
		100	7 days	good	none

the presence of a coordinated water molecule as in **18**, the cationic ruthenium complex **22** was prepared in solution by reaction with a silver salt and filtration of the silver chloride precipitate under anhydrous conditions. When this activation was attempted, the resultant complex was unstable and poorly soluble. To determine if a complex such as **22** with an empty coordination site was viable, the in situ activation of model system **25** was examined (eq 4).



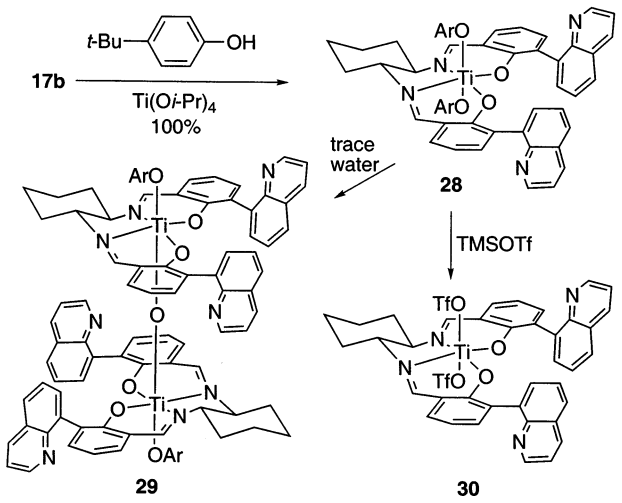
The reaction of **24** with AgOTf to provide the cationic complex **25**[13] was monitored by ^{1}H NMR (Table 1). Initially, CD_2Cl_2 was chosen as a solvent, since **24** is stable for at least 1 day in CD_2Cl_2 and is moderately soluble; however, product solubility and substrate decomposition problems were encountered in CD_2Cl_2. As such, a more polar solvent system, CD_2Cl_2−acetone-d_6 (2:1), was examined. In this system, acetone would presumably occupy the vacant coordination site in **25**, thereby stabilizing the complex. As expected, no product solubility or substrate decomposition problems arose in this solvent system with **22** (eq 2). A photolysis activation pathway (eq 3) was also examined. While **23** could be generated, this compound was relatively unstable.

Chromium complexes of **17b** were also considered, in light of the success of chromium−salen complexes as Lewis acids in asymmetric catalysis. Jacobsen and coworkers have used Cr(II)−salen complexes to catalyze hetero-Diels−Alder reactions[18] and epoxide ring opening with $TMSN_3$.[19] This complex was also later used to promote epoxide opening with lithium enolates.[20] The chromium(III) neutral and cationic complexes **26** and **27**, incorporating the quinoline salen species, were prepared as shown in eq 5.



Titanium derivatives of quinoline salen **17b** were also examined (Scheme 3), since titanium salen complexes are well-known to act as effective Lewis acid catalysts[21] and titanium enolates can be formed in situ by deprotonation with amine bases.[22] The titanium complex **28** was readily prepared following the method of Gagne et al. by treatment of salen **17b** with Ti(Oi-Pr)$_4$ and 2 equiv

Scheme 3



of 4-*tert*-butylphenol.[23] This protocol was employed, since the aryloxy titanium salen complexes are more stable than their alkoxy counterparts. Unfortunately, complex **28** was not exceptionally stable; while complex **28** formed cleanly, over time the complex slowly converted to a μ-oxo species (**29**), as observed by ^{1}H NMR spectroscopy.

Indeed, under the <5 ppm water levels in a nitrogen glovebox only complex **29** crystallized. Even so, the crystal structure of dimer **29** provided concrete structural data, confirming that the designed complexes were forming as initially intended (Figure 1). While there are crystal structures of 35 titanium salen complexes in the Cambridge Structural Database, none of these complexes contain an ancillary amine base as in **28**−**30**. In particular, the salen ligand of **29** adopts a *mer*, pseudoplanar coordination around the titanium center and the ligand does not deform to allow coordination of the quinoline moieties.[24] Furthermore, the quinoline nitrogens are not engaged in intermolecular coordination to other titanium centers. Surprisingly, the quinoline groups of each salen are oriented in the same direction (toward the μ-oxo bridge). Since significant π-stacking does not appear to be occurring, this result may be a result of the crystal packing to give the densest lattice, which is affirmed by examination of the crystal-packing diagram. Regardless, the quinolines are oriented toward the titanium centers such that replacement of the μ-oxo ligand with a ketone ligand places the quinoline nitrogens close to the ketone α-proton, as would be required for the quinoline to mediate deprotonation.

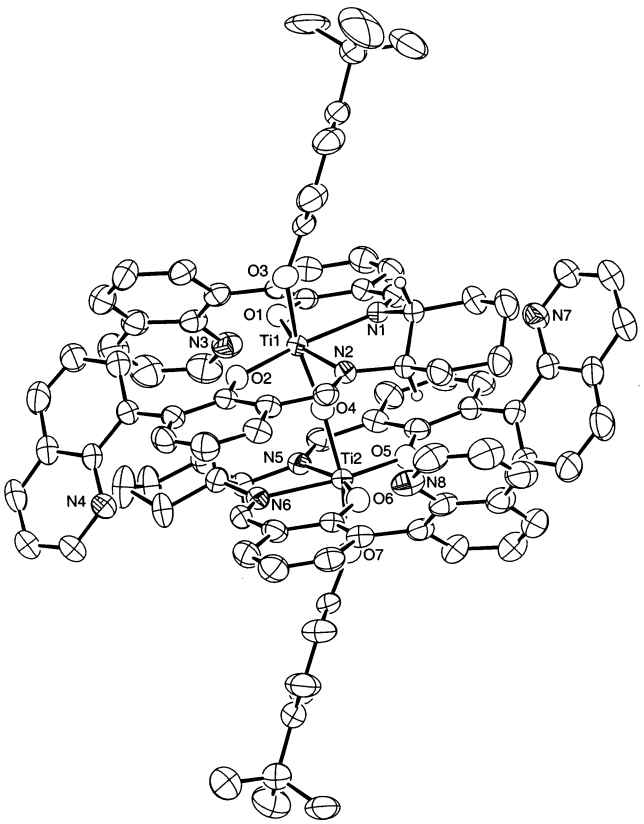
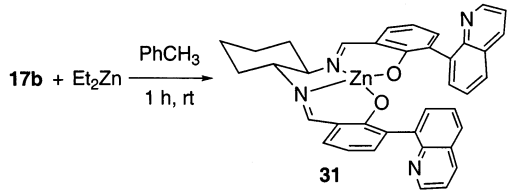
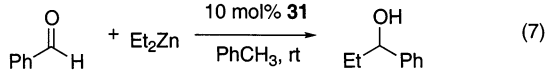


Figure 1. ORTEP drawing of **29** with thermal ellipsoids at the 30% probability level.

The zinc complex **31**[25,26] of the quinoline salen (eq 6) could also be formed, although its solubility was poor.





In a preliminary result, **31** did prove to be a very reactive catalyst in the addition of diethylzinc to benzaldehyde (eq 7; 10 mol % 31, 89% conversion, 2 h at room temperature).[27]

Concluding Remarks

The bifunctional salen ligands **17a** and **17b**, containing a quinoline base, have been synthesized. Importantly, conditions have been identified to form the

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(25) For examples of salen−Zn complexes, see: (a) Morris, G. A.; Zhou, H.; Stern, C. L.; Nguyen, S. T. *Inorg. Chem.* **2001**, *40*, 3222−3227. (b) Singer, A. L.; Atwood, D. A. *Inorg. Chim. Acta* ***1998***, 277, 157−162.
(26) The zinc complexes were prepared in situ by stirring the ligand with an equivalent amount of Et_2Zn for 1 h at room temperature prior to the addition of substrates.
(27) Control reactions in related systems have established that the quinoline base is key to the high reactivity of catalyst **31**: DiMauro, E. F.; Kozlowski, M. C. *Org. Lett.* **2001**, *3*, 3053−3056.

ruthenium, chromium, titanium, and zinc complexes of salen **17b** without generating salts (i.e. HCl adducts) of the quinoline. These complexes are stable and have been characterized. A crystal structure of titanium complex **29** shows a typical salen coordination pattern, with the nitrogens of the quinoline groups undergoing neither intra- or intermolecular coordination. In addition, the structure of **29** illustrates that the quinoline groups are properly oriented to act as bases toward substrates coordinated at the apical positions of these complexes. With this result, we have established that the salen architecture is appropriate for the development of bifunctional catalysts. Given the modular nature of the salen structure, we anticipate that a large number of different bifunctional complexes can be prepared rapidly. Preliminary results indicate that zinc complex **31** significantly accelerates the addition of diethylzinc to benzaldehyde and the quinoline base plays a pivotal role in this reactivity. Future efforts are directed toward the synthesis of further bifunctional salen complexes and investigating the catalytic activity of this class of compounds.

Experimental Section

General Considerations. Unless otherwise stated, all nonaqueous reactions and distillations were carried out under an atmosphere of dry nitrogen in glassware that had been either flame-dried under a stream of nitrogen or dried in an oven (90 °C) for at least 12 h. All manipulations involving Et_2Zn were carried out using standard Schlenk techniques. When necessary, solvents and reagents were dried prior to use. Et_2O and CH_2Cl_2 were deoxygenated by purging with Ar and then dried by passing through activated alumina. THF was distilled from Na/benzophenone ketyl. Toluene and dioxane were distilled from Na and MeCN from CaH_2. DMF was distilled from CaH_2 under reduced pressure. Et_2Zn was used as a freshly prepared 1.0 M solution in toluene. (−)-(1*R*,2*R*)-1,2-Cyclohexanediamine was prepared as previously described.[28] Benzaldehyde was distilled prior to use.

Analytical thin-layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica gel 60-F plates. Preparative thin-layer chromatography was performed on EM Reagents 1.00 mm silica gel plates. Visualization was accomplished with UV light. Chromatography on silica gel was performed using a forced flow of the indicated solvent system on EM Reagents silica gel 60 (230−400 mesh). Melting points were obtained on a Thomas Scientific Unimelt apparatus and are uncorrected. Conversions in the aldehyde alkylation were measured using a Hewlett-Packard 5890 gas chromatograph (GC) with a Supelco β-DEX 120 column (12 m × 0.25 mm). Optical rotations were measured on a Perkin-Elmer polarimeter, Model 341, with a sodium lamp and are reported as follows: $[\alpha]^T_\lambda$ (*c*, g/100 mL of solvent).

^{1}H NMR spectra were recorded on Bruker AM-500 (500 MHz), AM-250 (250 MHz), and AM-200 (200 MHz) spectrometers. ^{13}C NMR spectra were recorded on a Bruker AM-500 (125 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane (0 ppm) or with the solvent resonance as the internal standard ($CDCl_3$, 7.26 ppm; DMSO-d_6, 2.49 ppm; D_2O, 4.80 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants, and number of protons. IR spectra were taken on a Perkin-Elmer FT-IR spectrometer using thin films. Mass spectra were obtained on a low-resonance Micromass Platform LC in electrospray mode. High-resolution mass spectra were recorded on a VG Autospec instrument with an ionization mode of either CI or ES. Elemental analysis was done with a Perkin-Elmer CHN Analyzer, Model 2400.

8-(Tri-*n*-butylstannyl)quinoline (15). A solution of *n*-BuLi in hexanes (20.3 mL, 50.8 mmol) was dissolved in Et_2O (40 mL) and cooled to −78 °C. A cooled solution (−40 °C) of the 8-bromoquinoline **14**[11] (4.80 g, 23.1 mmol) in Et_2O (20 mL) was added dropwise to the mixture via a cannula (it is very important that the temperature remains below −70 °C). After this mixture was stirred for 30 min, a cooled solution (−40 °C) of tri-*n*-butyltin chloride (18.0 g, 53.0 mmol) in Et_2O (15 mL) was slowly added. The solution was stirred for 1 h at −78 °C and was quenched with a saturated solution of $NaHCO_3$. The aqueous layer was extracted with EtOAc. The organic layers were washed twice with a saturated solution of KF and then dried over $MgSO_4$. After the removal of the solvent in vacuo, the crude product was purified by two consecutive chromatographic purifications (hexanes) to afford stannane **15** as a colorless oil (8.0 g, 83%). When this reaction was carried out on a smaller scale (0.314 g of **14**), **15** was obtained in 97% yield: R_f 0.34 (100% hexanes); ^{1}H NMR ($CDCl_3$) δ 8.86 (d, 1H, J = 4.2 Hz), 8.10 (d, 1H, J = 8.1 Hz), 7.89 (d, 1H, J = 6.5 Hz), 7.76 (d, 1H, J = 7.8 Hz), 7.51 (m, 1H), 7.31 (m, 1H), 1.60 (m, 6H), 1.37 (m, 6H), 1.19 (t, 6H, J = 9.1 Hz), 0.88 (t, 9H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 149.1, 148.1, 137.3, 135.9, 127.7, 127.5, 126.1, 120.6, 117.2, 29.2, 27.3, 13.7, 10.5; IR (film) 1487, 1454, 1374, 1296 cm^{-1}; HRMS (CI) *m*/*z* 420.1713 [MH$^+$], found *m*/*z* 420.1715.

Aldehyde 16. To a solution of stannane **15** (2.77 g, 6.62 mmol) and aldehyde **12**[10] (1.33 g, 6.62 mmol) in dioxane (50 mL) was added $Pd(PPh_3)_4$ (0.371 g, 0.331 mmol, 5%) and anhydrous CuBr (0.095 g, 0.662 mmol, 10%). The mixture was heated to reflux for 7 h. The catalyst was filtered through a pad of Celite, and the solvent was removed in vacuo. The residue was dissolved in EtOAc and washed with a saturated solution of KF. After filtration through a pad of Celite, the organic layer was dried over $MgSO_4$ and the solvent removed in vacuo. The crude product was purified by column chromatography (10−30% EtOAc/hexanes) to yield the aldehyde (0.963 g, 58%) as a yellow solid: R_f 0.22 (30% EtOAc/hexanes); mp 136−137 °C; ^{1}H NMR ($CDCl_3$) δ 11.48 (s, 1H), 10.86 (s, 1H), 8.91 (d, 1H, J = 3.8 Hz), 8.22 (d, 1H, J = 8.2 Hz), 7.88 (d, 1H, J = 7.9 Hz), 7.77 (d, 1H, J = 6.6 Hz), 7.66 (m, 3H), 7.41 (m, 1H), 7.15 (t, 1H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ 200.3, 196.0, 159.3, 150.1, 146.1, 139.4, 136.6, 132.8, 131.4, 128.9 128.5, 128.3, 126.2, 121.1, 119.5; IR (film) 3550−3250, 1646, 1437, 1387, 1218 cm^{-1}; HRMS (CI) calcd *m*/*z* 250.0868 [MH$^+$], found *m*/*z* 250.0867. Anal. Calcd for $(C_{16}H_{11}NO_2)_4 \cdot H_2O$: C, 75.73; H, 4.57; N, 5.52. Found: C, 75.96; H, 4.65; N, 4.98.

Ethylene Quinoline−salenH$_2$ (17a). A mixture of aldehyde **16** (0.249 g, 1.00 mmol) and ethylenediamine (0.031 g, 0.50 mmol) in dry EtOH (4 mL) was heated at reflux for 2 h. The solution was cooled to 0 °C and filtered, and the resultant yellow solid was washed with cold EtOH. After it was dried in vacuo, the product (0.250 g, 96%) was obtained as a yellow solid: R_f unstable to SiO_2; mp 280 °C dec; ^{1}H NMR ($CDCl_3$) δ 13.66 (s, 1H), 8.91 (d, 1H, J = 3.2 Hz), 8.40 (s, 1H), 8.20 (d, 1H, J = 8.0 Hz), 7.85 (d, 1H, J = 8.0 Hz), 7.77 (d, 1H, J = 6.4 Hz), 7.61 (m, 1H), 7,36 (m, 3H), 6.99 (t, 1H, J = 7.8 Hz), 3.87 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 166.7, 150.3, 136.2, 134.9, 131.3, 131.2, 127.8, 126.0, 120.9, 118.1, 59.5; IR (film) 3550−3300, 1612, 1446 cm^{-1}; HRMS (CI) *m*/*z* (MH$^+$) calcd 523.2134, found 523.2152. Anal. Calcd for $C_{34}H_{26}N_4O_2$: C, 78.14; H, 5.01; N, 10.72. Found: C, 77.50; H, 5.14; N, 10.51.

Cyclohexane Quinoline−salenH$_2$ (17b). A mixture of aldehyde **16** (0.249 g, 1.00 mmol) and (−)-(1*R*,*2R*)-1,2-cyclohexanediamine (0.057 g, 0.50 mmol) in dry EtOH (4 mL) was heated to reflux for 2 h. The solution was cooled, and the

(28) (a) Galsbol, F.; Steenbol, P.; Sondergaard Sorensen, B. *Acta Chem. Scand.* **1972**, *26*, 3605−3611. (b) Larrow, J. F.; Jacobsen, E. N.; Gao, Y.; Hong, Y.; Nie, X.; Zepp, C. M. *J. Org. Chem.* **1994**, *59*, 1939−1942. (c) Larrow, J. F.; Jacobsen, E. N. *Org. Synth.* **1998**, *75*, 1−11.

solvent was removed to afford a yellow solid. This material was washed with hexanes and dried in vacuo, to yield the salenH_2 species (0.288 g, 100%) as a yellow solid: R_f unstable to SiO_2; mp 125−126 °C; $[\alpha] = -434°$ (*c* 0.72, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 13.87 (s, 1H), 8.99 (d, 1H, J = 3.4 Hz), 8.40 (s, 1H), 8.28 (d, 1H, J = 8.0 Hz), 7.94 (d, 1H, J = 8.0 Hz), 7.88 (d, 1H, J = 6.8 Hz), 7.72 (m, 1H), 7.48 (m, 2H), 7.32 (d, 1H, J = 7.4 Hz), 7.05 (t, 1H, J = 7.8), 3.32 (m, 1H), 2.37−0.83 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 164.9, 158.8, 150.2, 136.1, 134.7, 131.3, 131.2, 128.6, 127.7, 126.0, 120.8, 118.7, 118.0, 72.5, 33.1, 24.1; IR (film) 3580−3360, 1626, 1495 cm^{-1}; HRMS (CI) calcd *m*/*z* 577.2603 [MH$^+$], found *m*/*z* 577.2598.

(−)-(*R*,*R*)-Ru^{III}(quinoline-salen)(NO)Cl (20). NaH (10.1 mg, 0.42 mmol) was dissolved in DMF (0.5 mL). The salenH_2 compound **17b** (110 mg, 0.19 mmol) was added as a solution in DMF (0.5 mL) via cannula transfer, with the evolution of H_2. The dark yellow solution was stirred at room temperature for 20 min. A solution of Ru(NO)Cl_3 (59 mg, 0.25 mmol) in DMF (0.5 mL) was then added via cannula. The dark red solution was stirred at 110 °C for 20 h. After this solution was slowly cooled to 25 °C, the DMF was removed on a high-vacuum line. CH_2Cl_2 was added, and the solution was washed three times with distilled water, extracted with CH_2Cl_2, dried over Na_2SO_4 for 30 min, and concentrated to a brown solid. The solid was dissolved in CH_2Cl_2 and purified by preparative TLC (20% acetone/CH_2Cl_2) to provide the product in 50% yield (70 mg, 0.094 mmol) as a dark red solid: soluble in acetone, CH_3CN, and DMF (good), CH_3NO_2, CH_2Cl_2, and THF (moderate), and $CHCl_3$, EtOAc, Et_2O, and hexanes (poor); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.7 (d, J = 3.8 Hz, 1H), 8.4 (t, J = 2.3 Hz, 1H), 8.3 (s, 1H), 8.2 (s, 2H), 7.65 (t, J = 8.1 Hz, 2H), 7.6 (t, J = 7.4 Hz, 2H), 7.5 (m, 4H), 7.35 (d, J = 6.3 Hz, 1H), 7.32 (m, 1H), 7.3 (d, J = 6.3 Hz, 1H), 7.0 (bs, 1H), 6.8 (t, J = 7.6 Hz, 1H), 6.75 (t, J = 7.5 Hz, 1H), 6,78 (m, 1H), 4.1 (t, J = 11.0 Hz, 1H), 3.25 (t, J = 11.0 Hz, 1H), 2.85 (d, J = 9.2 Hz, 1H), 2.75 (d, J = 9.2 Hz, 1H), 2.0 (m, 2H), 1.8 (m, 1H), 1.6 (m, 1H), 1.4 (m, 2H); IR (film) 2932, 1832 (NO), 1629 (C═N), 1593, 1542, 1426, 1317 cm^{-1}; MS (ES) *m*/*z* 740 [M$^+$], 741 [MH$^+$], 751 [M − NO + CH_3CN^+].

Byproduct **21** (49 mg, 0.089 mmol) was isolated as a dark green solid: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.85 (m, J = 2.0 Hz, 1H), 8.2 (m, J = 2.0 Hz, 2H), 7.85 (dd, J = 5.7, 18.7 Hz, 2H), 7.60 (dd, J = 7.2, 13.4 Hz, 2H), 7.35 (m, 2H), 6.8 (t, J = 7.2 Hz, 1H), 4.4 (bs, 1H), 4.2 (bs, 1H), 3.8 (t, J = 7.4 Hz, 1H), 3.0 (m, 1H), 2.6 (d, J = 12.6 Hz, 1H), 2.2 (d, J = 13.0 Hz, 1H), 2.0 (d, J = 10.0 Hz, 1H), 1.8 (d, J = 10.0 Hz, 1H), 1.6 (m, 2H), 1.3 (m, 2H); MS (ES) *m*/*z* 546 [M$^+$], 558 [M − NO + CH_3CN^+].

Ru^{III}(salen)(NO)OTf (25). Complex **24**[13a] (5.63 mg, 0.013 mmol) and AgOTf (3.34 mg, 0.013 mmol) were dissolved in 600 μL of solvent (CD_2Cl_2 or 1:1 acetone-d_6/CD_2Cl_2) in a N_2-purged vial which was covered with aluminum foil. The solution was stirred for 1 h and then transferred to an N_2-purged NMR tube which was also covered with aluminum foil. The tube was shaken vigorously and then allowed to stand at 25 °C. AgCl was observed to precipitate out of solution and settle on the bottom of the tube. The reaction was monitored by ^{1}H NMR. Conversion was determined by a comparison of the integration values for the imine peaks of the starting material (δ 8.20) and product (δ 8.55): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.55 (s, 2H), 7.35 (m, 4H), 6.95 (d, J = 8.5 Hz, 2H), 6.7 (t, J = 7.4 Hz, 2H), 4.45 (m, 2H), 4.1 (m, 2H); IR (film) 1875 (NO), 1633 (C═N), 1603, 1441, 1283, 1270 cm^{-1}.

(−)-(*R*,*R*)-Cr^{III}(quinoline-salen)Cl (26). The salenH_2 species **17b** (50 mg, 0.087 mmol) and $CrCl_2$ (16 mg, 0.130 mmol) were combined in an inert-atmosphere glovebox and stirred in THF (1.8 mL) for 5.5 h. The dark yellow-brown slurry was then removed from the glovebox, and THF (1 mL) was added. After it was stirred under air for 24 h, the slurry was diluted with *tert*-butyl methyl ether (10 mL), washed with saturated NH_4Cl and brine, dried over Na_2SO_4, and concentrated to yield 20% of recovered **17b** (10 mg, 0.017 mmol) as a pale yellow solid. The remaining aqueous layer was then made basic with 3 N NaOH, extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated to provide the product in 80% yield (100% brsm) (46 mg, 0.0695 mmol) as a brown solid: IR (film) 3425 (br), 3049, 2932, 2849, 1623 (C═N), 1591, 1549, 1497, 1428, 1393, 1319, 1226 cm^{-1}; MS (ES) *m*/*z* 662 [M$^+$], 703 [M + CH_3CN^+]; HRMS (ES) calcd *m*/*z* 662.1540 [$C_{38}H_{31}N_4O_2ClCr^+$], found *m*/*z* 662.1533. Anal. Calcd for $C_{38}H_{30}ClCrN_4O_2 \cdot 3H_2O \cdot 2CH_2Cl_2$: C, 54.22; H, 4.55; N, 6.32. Found: C, 54.91; H, 4.17; N, 5.78.

(−)-(*R*,*R*)-Cr^{III}(quinoline-salen)(OTf) (27). A solution of AgOTf (20.4 mg, 0.079 mmol) in CH_3CN (1.0 mL) was added to a stirred solution of **26** (58 mg, 0.075 mmol) in CH_3CN (0.5 mL). The orange-brown slurry was stirred for 24 h at room temperature. The slurry was then filtered through a pad of Celite and washed excessively with CH_3CN. The washings were concentrated to provide the cationic complex in 95% yield (55 mg, 0.0709 mmol) as a red solid: MS (ES) *m*/*z* 776 [MH$^+$], 626 [M − OTf$^+$]; HRMS (ES) calcd *m*/*z* 776.1372 [$C_{39}H_{31}N_4O_5SF_3Cr^+$], found *m*/*z* 776.1370.

(−)-(*R*,*R*)-Ti^{IV}(quinoline-salen)(*p*-*t*BuC$_6$H$_4$OH)$_2$ (28). This reaction was performed in an inert-atmosphere glovebox. A solution of Ti(O*i*-Pr)$_4$ (30.1 mg, 0.1058 mmol) in CH_2Cl_2 (0.5 mL) was added to a solution of 4-*tert*-butylphenol (31.8 mg, 0.2115 mmol) in CH_2Cl_2 (0.5 mL). Ligand **17b** was then added to this bright yellow solution as a solution in CH_2Cl_2 (0.5 mL). The reaction turned bright orange-red immediately and was stirred for 10 min at room temperature. The solution was then removed from the glovebox and concentrated in vacuo to a sticky orange solid, which was further dried in vacuo with gentle heating for 3 h to provide the product as a bright orange solid in 100% yield (98 mg, 0.1058 mmol): mp 118−124 °C; soluble in benzene, toluene, $CHCl_3$, CH_2Cl_2, and DMF (good), DME and THF (moderate), and EtOAc, acetone, CH_3CN, Et_2O, hexane, and pentane (poor); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (m, 2H), 8.31 (s, 2H), 8.18 (d, J = 8.2 Hz, 2H), 7.83 (d, J = 8.1 Hz, 2H), 7.61 (m, 2H), 7.53 (dd, J = 7.9, 6.9 Hz, 4H), 7.30 (m, 2H), 7.18 (t, J = 7.5 Hz, 3H), 7.0 (t, J = 7.5 Hz, 3H), 6.88 (d, J = 8.6 Hz, 4H), 6.12 (d, J = 8.6 Hz, 3H), 3.39 (brd, J = 8.7 Hz, 2H), 2.46 (brd, J = 12.5 Hz, 2H), 2.20 (br d, J = 8.7 Hz, 2H), 1.15 (s, 18H); IR (film) 3036, 2958, 2864, 1800−1650, 1617 (C═N), 1587, 1559, 1503, 1433 cm^{-1}. The titanium complex **28** was found to undergo slow conversion to the μ-oxo dimer by ^{1}H NMR. X-ray-quality crystals of μ-oxo dimer **29** were grown from a solution of **28** in CH_2Cl_2 in an inert-atmosphere glovebox by slow diffusion with Et_2O.

Diethylzinc Addition to Benzaldehyde To Yield 1-Phenyl-1-propanol. 17b (0.025 mmol) was introduced into a dry Schlenk flask, and the system was purged with N_2. **17b** was dissolved in dry toluene (1 mL), and Et_2Zn (25 μL, 1.0 M in toluene, 0.025 mmol) was added. The mixture was stirred at room temperature for 1 h. Et_2Zn (500 μL, 1.0 M in toluene, 0.500 mmol) was added slowly. After 5 min, PhCHO was added dropwise. At various intervals, 100 μL aliquots were removed from the reaction mixture, quenched with 1 N HCl, and then extracted with pentane. The reaction progress was monitored by GC (carrier gas N_2, detector FID, 270 °C, injector 250 °C, oven 115 °C): t_R(PhCHO) = 3.0 min, t_R(*R*) = 16.0 min, t_R(*S*) = 16.7 min.

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Supporting Information Available: X-ray crystallographic methods and tables for **29** and figures giving the NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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