(Arene)ruthenium Complexes with Bis(oxazolines): Synthesis and Applications as Asymmetric Catalysts for Diels−Alder Reactions

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Reaction of the dimers $[RuCl_2(arene)]_2$ (arene = benzene, *p*-cymene, mesitylene) with bis(oxazolines) (N-N = bis(2-oxazoline) (box), 2,2-bis(2-oxazolinyl)propane (bop), 1,2-bis(2-oxazolinyl)benzene (benbox)) in the presence of $NaSbF_6$ gives the complexes $[RuCl(N\text{-}N)(arene)][SbF_6]$ (**1**−**8**), which have been fully characterized. Treatment of these cations with $AgSbF_6$ generates dications which in some cases are enantioselective catalysts for Diels−Alder reaction of methacrolein and cyclopentadiene. Two complexes, $[RuCl(^iPr\text{-}benbox)(p\text{-}cymene)][SbF_6]$ (**5**) and $[Ru(OH_2)(^iPr\text{-}bop)(mes)][SbF_6]_2$ (**10**; mes = mesitylene), have been characterized by X-ray crystallography.

Introduction

(Arene)ruthenium complexes with chiral bidentate ligands have been known since 1977;[1] however, their great potential as chiral catalysts has only recently been demonstrated. The best example so far is the asymmetric transfer hydrogenation of ketones, with enantiomeric excesses (ee) of >99%, using (arene)ruthenium complexes with a chiral ligand derived from a chiral diamine as catalyst.[2] (Arene)ruthenium complexes with chiral bidentate ligands containing at least one hard donor atom have attracted much study recently,[3−9] particularly their potential applications as chiral catalysts. With C_1-symmetry ligands the complexes can in principle exist as two diastereomers. The presence of two diastereomeric catalysts could lead to a reduction in enantioselectivty in a catalytic process. Very high diastereoselectivity has been found for some (arene)-ruthenium complexes; indeed, in favorable cases only one isomer is observed.[9] To avoid the possibility of diastereomers, C_2-symmetry chiral ligands can be used, in which case only one isomer is possible when coordinated to the metal. This approach has been very successful with chiral C_2-symmetric bis-phosphines, for example the use of $[RuCl(binap)(arene)]^+$ in asymmetric hydrogenation;[10] it should be noted, though, that during catalysis the arene dissociates from the metal, and hence, the active catalyst no longer has a half-sandwich structure. More recently, Kündig has reported a cyclopentadienylruthenium complex of a C_2-symmetry bis-phosphonite which retains the half-sandwich structure during catalysis of Diels−Alder reactions.[11]

In the past decade there has been a surge of interest in chiral nitrogen-donor ligands for use in asymmetric catalysis and bidentate, C_2-symmetry ligands such as semicorrins and particularly bis(oxazolines) have been very successful.[12,13] The use of C_2-symmetry nitrogen donor ligands in (arene)ruthenium complexes has been studied much less well. Kurosawa et al. have studied

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Table 1. Complex Numbering Scheme

complex	arene	N−N	complex	arene	N−N
1	mes	^{i}Pr -box	**5**	*p*-cymene	^{i}Pr-benbox
2	mes	^{i}Pr-bop	**6**	mes	Et-benbox
3	benzene	^{i}Pr-benbox	**7**	mes	^{i}Pr-benbox
4	*p*-cymene	Et-benbox	**8**	mes	Ph-benbox

bis(phenyloxazolinyl)propane complexes,[14] and a diaminobiphenyl complex in which the ligand has axial chirality has also been reported.[15] In this paper we report the synthesis of several (arene)ruthenium complexes with three different types of bis(oxazolines) (N-N), namely bis(2-oxazoline) (box), 2,2-bis(2-oxazolinyl)propane (bop), and 1,2-bis(2-oxazolinyl)benzene (benbox).

Results and Discussion

Synthesis and Characterization of [RuCl(N−N)(arene)][EF$_6$] (1−8; E = P, Sb). The complexes [RuCl(N-N)(arene)][EF$_6$] (**1**−**8**; E = P, Sb) (Table 1) were synthesized in high yield by treatment of the dimers [RuCl$_2$(arene)]$_2$ with 2 equiv of the bis(oxazoline) ligand (N-N) and NaSbF$_6$ (or KPF$_6$) in methanol at reflux. The complexes were characterized by ^{1}H NMR and mass spectroscopy, elemental analysis, and X-ray diffraction for **4**.

As explained above, only one isomer is possible, since the complexes are only chiral at the ligand, not at the metal. The free ligands have C_2 symmetry; however, the symmetry is lost on complexation and the ^{1}H NMR spectra of **1**−**8** are more complex as a result. In all of the complexes the oxazoline protons shift downfield on coordination; in complexes with ^{i}Pr substituents the CH proton shifts downfield compared to free ligand and the Me groups give rise to four doublets, one of which is often shifted upfield. The major ion in the mass spectrum of each complex corresponds to [RuCl(N-N)(arene)].

In the ^{1}H NMR spectra of **1** and **2** the signals for the η^6-mesitylene were observed at δ 2.32 and 5.67 for **1** and δ 2.25 and 5.71 for **2**, while for **6** and **7** the corresponding signals were considerably upfield (at δ 1.96 and 4.55 and at δ 1.95 and 4.77 for **6** and **7**, respectively). Such a substantial shift, almost 1 ppm in the case of the aromatic protons, is unlikely to be due to a difference in the donor properties of the ligands since they are all bis(oxazolines). The upfield shift in **7** is most likely due to a ring current effect from the benzene backbone of the benbox ligand. To test this hypothesis, a NOESY spectrum of **7** was run. This showed cross-peaks between both mesitylene signals (δ 1.95 and 4.77) and all three multiplets (total integration 4H) assigned to the benzene backbone of the ligand. In complex **8** the mesitylene signals were even more shielded (δ 1.74 and 4.07); in this case there may also be a ring current from one of the phenyl substituents on the oxazolines. Similar β-phenyl effects have been found in (arene)ruthenium salicylaldimine complexes.[4a]

Crystals of [RuCl(Et-benbox)(*p*-cymene)]PF$_6$ (**4**) were obtained that were suitable for X-ray crystallography, and the structure of the cation is shown in Figure 1.

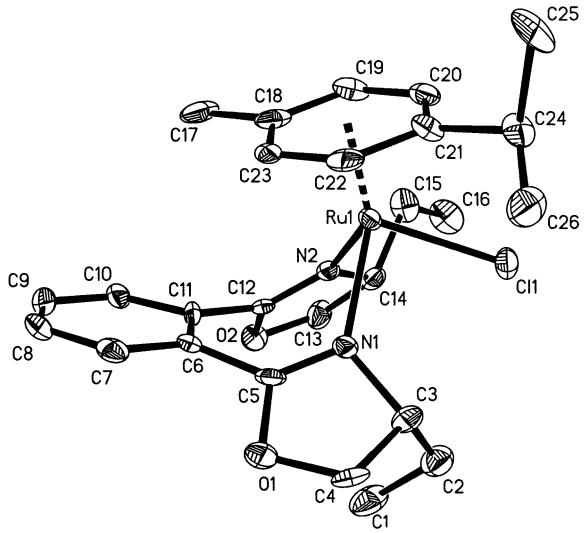

Figure 1. Structure drawing of the cation of **4**, showing the atom-labeling scheme. Displacement ellipsoids are shown at the 30% level. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ru(1)−N(1) = 2.127(8), Ru(1)−N(2) = 2.119(9), Ru(1)−Cl(1) = 2.403(2); N(2)−Ru(1)−N(1) = 80.2(4), N(2)−Ru(1)−Cl(1) = 88.6(3), N(1)−Ru(1)−Cl(1) = 88.1(2).

The ruthenium atom has a pseudooctahedral geometry with the arene occupying three adjacent sites of the octahedron. The most striking feature of the structure is that the oxazoline rings are rotated out of the plane of the benzene ring 48.3° (N1−O1) and 45.2° (N2−O2), allowing coordination to the ruthenium with a chelate bite angle of 80.2(4)°. A similar situation was found in the complex [Zn(^{i}Pr-benbox)Cl$_2$], which had torsion angles of 46.4 and 46.5°.[16] These rotations will tend to relieve steric interactions between the ethyl on C(14) and the η^6-arene while putting the ethyl on C(3) closer to the chloride. The benzene ring lies rather close to the *p*-cymene, with the C(6)−C(23) and C(11)−C(17) distances being 3.33 Å, consistent with the NOESY NMR data for **7** described above. The Ru−N(1) and Ru−N(2) distances, 2.127(8) and 2.119(9) Å, respectively, are statistically the same and are very similar to the Ru−N(oxazoline) distances found in (arene)ruthenium pyridyloxazoline complexes, 2.103(5)−2.128(5) Å.[9a]

Synthesis and Characterization of [Ru(L)(N−N)(arene)][SbF$_6$]$_2$ (9−12; L = OH$_2$, Acetone). To activate **1**−**8** for use in asymmetric catalysis, it is necessary to remove the strongly bound chloride ligand. This was done by treatment with AgSbF$_6$ in CH$_2$Cl$_2$/acetone to give a precipitate of AgCl and the solvent complexes [Ru(L)(N-N)(arene)][SbF$_6$]$_2$ (L = acetone, OH$_2$). The water ligand is obtained from the acetone solvent and/or during the workup, which is carried out in air. A few of these dicationic complexes (**9**−**12**), derived from **1**−**3** and **7** respectively, were isolated and characterized by ^{1}H NMR spectroscopy and mass spectrometry and in some cases elemental analysis; characterization of **10** was also carried out by X-ray diffraction. The ^{1}H NMR spectra of **9**−**12** provide evidence for a number of different processes: (i) exchange between acetone coordination and water coordination, (ii) exchange be-

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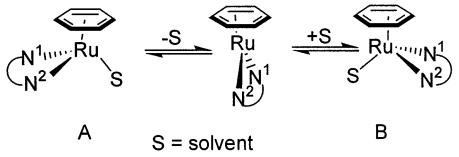
Scheme 1. Proposed Fluxionality of Solvent Complexes $[Ru(L)(N-N)(arene)][SbF_6]_2$ (L = Acetone, OH_2)



tween free and coordinated water, (iii) proton/deuterium exchange on the coordinated water, and (iv) a fluxional process which can reestablish C_2 symmetry for the bis-(oxazoline) (Scheme 1).

The ^{1}H NMR spectra of **9**, **11**, and **12** in d_6-acetone show evidence for acetone- and water-coordinated species. Addition of water shifts the position of the equilibrium and hence allows assignment of these species.[17] In the case of **9** the signals for the acetone-coordinated species are rather broad, suggesting that the fluxional process (iv) above (Scheme 1) is occurring at a rate similar to the NMR time scale and is faster for the acetone-coordinated complex than for the water-coordinated species. We have observed similar equilibria between acetone- and water-coordinated species, with faster exchange of acetone in related pyridyloxazoline complexes.[9a] The complexes **9**, **11**, and **12** each show a broad signal at ca. δ 3, due to free water, and two separate signals at ca. δ 7, due to coordinated H_2O and HOD. Addition of small aliquots of either H_2O or D_2O allowed assignment of these signals. Surprisingly, the signal for coordinated HOD is at higher frequency than that of H_2O. High-frequency deuterium isotope shifts, though uncommon, have been observed previously in systems where hydrogen bonding occurs.[18] Kurosawa et al. suggested, on the basis of kinetic measurements, that acetone may hydrogen bond to the coordinated water in $[Ru(OH_2)(Ph\text{-}bop)(C_6H_6)][BF_4]_2$ (**13**).[14] The observation of separate signals for coordinated H_2O and HOD shows that proton exchange is slow on the NMR time scale.

The ^{1}H NMR spectrum in d_6-acetone of $[Ru(L)(^i Pr\text{-}bop)(mes)]^{2+}$ (**10**), derived from **2**, showed evidence of exchange process (iv) above (Scheme 1) occurring at a rate comparable with the NMR time scale (400 MHz, 300 K). Thus, the CMe_2 group, which is expected to give rise to two inequivalent singlets, was observed as a broad signal at δ 1.7, while only two (of four) methyls of the isopropyl substituents and two of the six oxazoline protons were easily visible as a sharp doublet at δ 1.2 and a sharp doublet of doublets at δ 4.9, respectively. In addition, there was a broad hump at δ 2.9 due to water, with no signal visible due to coordinated water. At 233 K, all of the ^{1}H NMR signals were well-resolved, those due to the ^{i}Pr-bop ligand being much like those of the precursor **2**, though with the majority of the signals more deshielded, due to formation of a dication. Free water was observed as a broad singlet at δ 3.61 with singlets at δ 7.06 and 7.10 (ratio 7:3) in the region expected for coordinated water. Even at 233 K only one complex was observed, which suggests that coordination of acetone does not occur to any extent in this case. Similar fluxional behavior has been observed for the analogous complex $[Ru(OH_2)(Ph\text{-}bop)(C_6H_6)][BF_4]_2$ (**13**) reported by Kurosawa et al.;[14] in that case the exchange process was frozen out at 223 K, with free and coordinated water signals observed by ^{1}H NMR at δ 6.60 and 3.57, respectively (i.e. consistent with the chemical shifts reported here).

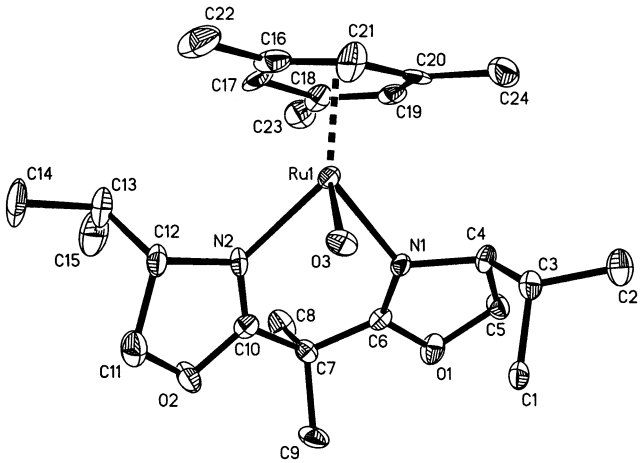


Figure 2. Structure drawing of the cation of **10**, showing the atom-labeling scheme. Displacement ellipsoids are shown at the 30% level. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ru(1)−N(1) = 2.135(11), Ru(1)−N(2) = 2.153(12), Ru(1)−O(3) = 2.160(10); N(2)−Ru(1)−N(1) = 83.5(5), N(2)−Ru(1)−O(3) = 81.1(4), N(1)−Ru(1)−O(3) = 85.1(4).

Recrystallization of **10** from acetone/ether gave crystals that were suitable for an X-ray structure determination. The structure of the dication is shown in Figure 2 with selected bond distances and angles. The bond distances and angles are similar to those for the known ruthenium analogue **13**.[14] Indeed, the Ru−N(1), Ru−N(2), and Ru−O(3) bond distances of **10** and **13** are statistically the same, and similar N(1)−Ru−N(2) chelate angles are found in each complex (83.5(5)° for **10** and 82.6(4)° for **13**). There is a significant difference (4°) between the angles N(2)−Ru(1)−O(3) (81.1(4)°) and N(1)−Ru(1)−O(3) (85.1(4)°), suggesting that the ligand is rotated slightly to reduce interaction between the isopropyl next to N(1) and the coordinated water. We noted a similar rotation to relieve steric interactions in pyridyloxazoline complexes.[9a] Examination of the structure of the related complex **13**[14] reveals an almost identical rotation with the larger N−Ru−O angle to the oxazoline bearing the substituent oriented toward the water, as seen in **10**.

Catalysis. The Diels−Alder reaction is one of the most important in organic chemistry, and great progress has been made in developing enantioselective versions. Recently there has been particular interest in using chiral transition-metal-based Lewis acid catalysts.[19] Chiral (arene)ruthenium complexes of bis-phosphine monoxides,[7a] phosphinooxazolines,[8a] pyridylimines,[5a] and pyridyloxazolines[9a] have been used to catalyze Diels−Alder reactions.

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Table 2. Enantioselective Diels−Alder Reaction of Methacrolein with Cyclopentadiene Catalyzed by [Ru(L)(N-N)(arene)][SbF_6]$_2$ (L = Acetone, OH_2), in Dichloromethane

entry	cat. precursor	cat. (%)	temp (°C)[d]	*t* (h)	yield[a] (%)	exo:endo	ee (%) (abs confign)
1	**1**	5	rt	24	47	94:6	10 (*S*)
2	**2**	5	rt	48	15[b]	88:12	0
3	**7**	5	rt	0.5	>95*	94:6	66 (*S*)
4	**3**	2	rt	2	90	88:12	31 (*S*)
5	**5**	2	rt	3	87	88:12	6 (*S*)
6	**7**	2	rt	0.5	>95*	94:6	65 (*S*)
7	**6**	2	0	24	94	94:6	45 (*R*)[c]
8	**7**	2	0	7	88	94:6	67 (*S*)
9	**8**	2	0	48	13	88:12	5 (*S*)
10			rt	48	15	85:15	0

[a] The isolated yield is quoted, except for those marked with an asterisk, which were experiments done in an NMR tube, where the yield is based on relative integrations. [b] Yields were somewhat variable with this catalyst, but the ee was always very low, suggesting an achiral catalytic impurity may have been present. Increasing the amount of hindered base[24] to 3 mol equiv led to the low yield reported. [c] The opposite configuration amino alcohol (i.e., R_C) was used in the ligand synthesis. [d] rt = room temperature.

As mentioned above, treatment of [RuCl(pymox)(arene)][SbF_6] (**1**−**8**) with $AgSbF_6$ gives the solvent complexes [Ru(L)(N-N)(arene)][SbF_6]$_2$ (L = acetone, OH_2); these dications are good Lewis acids and can catalyze the Diels−Alder reaction of methacrolein with cyclopentadiene. The catalysis can be carried out on freshly prepared solutions of these dications, either after filtration to remove the AgCl or after isolation, similar catalytic results being observed in either case. The results (Table 2) will be described in terms of the chloride precursor complexes **1**−**8**. Entries 1−3 show the effect of changing the type of oxazoline ligand with the same substituents and same arene. In this case the benbox complex **7** is the most successful catalyst in terms of activity and enantioselectivity. The bop complex **2** is inactive (the yield is comparable to the thermal reaction, entry 10), which is somewhat surprising, since this is the most frequently used bis-oxazoline in general. However, it is consistent with the fact that dication **10** showed no evidence of acetone coordination in d_6-acetone, whereas both **9** and **12** did.

The effect of changing the arene has been examined for the benbox catalysts (entries 4−6). All three complexes are quite active, giving high yields in a few hours. There is a large variation in enantioselectivity, with the mesitylene complex **7** being best, as found with related (arene)ruthenium pyridyloxazoline complexes,[9a] but with benzene complex **3** being rather better than the *p*-cymene complex **5**; notably, though, in both these cases the exo:endo selectivity is also poorer. The effect of changing the oxazoline substituents has been studied (entries 7−9): the alkyl substituents (Et, ^{i}Pr) are much better than phenyl, which has very low activity. Changing the catalyst loading from 5 to 2% (entries 3 and 6) has almost no effect, while lowering the temperature (entries 6 and 8) has surprisingly little effect on the enantioselectivity, though the rate of reaction is reduced as expected.

Using S_C ligands the major product was identified as (1*R*,2S,4*R*)-2-methylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde, by comparison of the sign of the optical rotation and the GC behavior of the acetal formed from (2*R*,4*R*)-pentanediol with literature values.[20] This is consistent with the isopropyl shielding the *Si* face of an *S-trans*-coordinated methacrolein leading to attack of cyclopentadiene at the *Re* face, as we have described previously for (arene)ruthenium pyridyloxazoline complexes.[9a]

In conclusion, we have synthesized a number of (arene)ruthenium complexes [Ru(Cl)(N-N)(arene)][SbF_6] with C_2-symmetry bis(oxazoline) ligands. Treatment of these with AgCl gave the dications [Ru(L)(N-N)(arene)]$^{2+}$ (L = acetone, OH_2), which in some cases were capable of catalyzing the Diels−Alder reaction of methacrolein and cyclopentadiene with moderate enantioselectivity. The best ligand in terms of the catalysis (benbox) has a flexible connection between the two oxazolines, allowing the ligand to adopt a nonplanar conformation. However, the enantioselectivity with the benbox catalyst derived from **7** is still less than that with the C_1-symmetry pyridyloxazoline complexes, which are the most enantioselective (arene)ruthenium catalysts for this reaction reported so far.[9a,26]

Experimental Section

Petroleum ether and diethyl ether were dried by refluxing over purple sodium/benzophenone under nitrogen, while dichloromethane was purified by refluxing over calcium hydride and acetone from calcium sulfate. The reactions described were carried out under nitrogen; however, once isolated as pure solids, the compounds are air-stable and precautions for their storage are unnecessary. ^{1}H NMR spectra were obtained using a Bruker spectrometer at 300 MHz in $CDCl_3$ unless stated otherwise; chemical shifts were recorded in ppm (referenced to tetramethylsilane or residual protons in the NMR solvent). FAB mass spectra were obtained on a Kratos Concept mass spectrometer using an NOBA matrix. Microanalyses were performed by Butterworth Laboratories Ltd., Middlesex, U.K.

The bis(oxazolines) were prepared by literature procedures (box,[21] bop,[22] benbox[16]) from the relevant amino alcohol, which in turn was prepared by reduction of the amino acid[23] (99% optical purity), except for phenylglycinol, which was a gift from NSC Technologies.

Preparations of [RuCl(bis(oxazoline))(arene)][SbF_6] (1−8). A solution of bis(oxazoline) ligand (2 equiv) and $NaSbF_6$ (2 equiv) in MeOH (10 cm^3) was added to [MCl_2(ring)]$_2$ (1 equiv), and the resulting suspension was heated to reflux for 2 h. A yellow-brown solution was obtained, which was then evaporated and the crude residue dissolved in CH_2Cl_2. Filtration through Celite (to remove NaCl and any black decomposition product), gave a red-orange solution, which was evaporated, and the crude complex was recrystallized from CH_2Cl_2/ether. The scale and yields for individual complexes are shown below. The PF_6 salts could be prepared similarly using KPF_6; the spectroscopic propeties were identical.

[RuCl(^{i}Pr-box)(mes)][SbF_6] (1). Complex **1** was prepared from [$RuCl_2$(mes)]$_2$ (80 mg, 0.137 mmol), ^{i}Pr-box (68 mg, 0.31 mmol), and $NaSbF_6$ (75 mg, 0.29 mmol) in 184 mg yield (94%). Anal. Calcd for $C_{21}H_{34}ClF_6N_2O_2RuSb\cdot H_2O$: C, 34.33; H, 4.66; N, 3.81. Found: C, 33.82; H, 4.22; N, 3.56. ^{1}H NMR: δ 0.74, 1.03, 1.04, 1.10 (4 × d, 3H, *J* = 7 Hz, CH*Me*$_2$), 2.14 (m, 1H, C*H*Me$_2$), 2.32 (s, 9H, C$_6$*Me*$_3$), 2.54 (m, 1H, C*H*Me$_2$) 4.26 (m, 1H, NC*H*), 4.66 (t, 1H, *J* = 10 Hz, OC*H*), 4.81 (m, 2H, OC*H*),

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4.95 (m, 1H, NC*H*), 5.15 (t, 1H, J = 9 Hz, OC*H*), 5.67 (s, 3H, $C_6H_3Me_3$) (water of solvation observed at δ 1.61). MS (FAB^+): m/z 481, $[M]^+$; 446, $[M - Cl]^+$.

[RuCl(ⁱPr-bop)(mes)][SbF$_6$] (2). Complex **2** was prepared from $[RuCl_2(mes)]_2$ (80 mg, 0.137 mmol), ⁱPr-bop (74 mg, 0.28 mmol), and $NaSbF_6$ (72 mg, 0.28 mmol) in 150 mg yield (72%). Anal. Calcd for $C_{24}H_{38}ClF_6N_2O_2PRu$: C, 43.15; H, 4.19; N, 5.73. Found: C, 43.15; H, 4.21; N, 5.73 (analysis on PF_6 salt). ^{1}H NMR: δ 0.55, 0.92, 0.95, 1.04 (4 × d, 3H, J = 7 Hz, CHMe_2), 1.38 (s, 3H, CMe_2), 1.61 (s, 3H, CMe_2), 2.25 (s, 9H, C_6Me_3), 2.47 (m, 2H, CHMe$_2$), 4.18 (t, 1H, J = 9 Hz, OC*H*), 4.37 (m, 1H, NCH), 4.45 (dd, 1H, J = 9, 1 Hz, OCH), 4.48 (m, 1H, NCH), 4.67 (m, 2H, NCH + OCH), 5.71 (s, 3H, $C_6H_3Me_3$). MS (FAB^+): m/z 523, $[M]^+$; 488, $[M - Cl]^+$.

[RuCl(ⁱPr-benbox)(C_6H_6)][SbF$_6$] (3). Complex **3** was prepared from $[RuCl_2(C_6H_6)]_2$ (60 mg, 0.12 mmol), ⁱPr-benbox (75 mg, 0.25 mmol), and $NaSbF_6$ (63 mg, 0.24 mmol) in 138 mg yield (77%). Anal. Calcd for $C_{24}H_{30}ClF_6N_2O_2RuSb$: C, 38.40; H, 4.03; N, 3.73. Found: C, 38.17; H, 3.92; N, 3.62. ^{1}H NMR: δ 0.53, 0.84, 0.96, 1.16 (4 × d, 3H, J = 7 Hz, CHMe_2), 2.59 (m, 1H, CHMe$_2$), 2.76 (m, 1H, CHMe$_2$), 4.42 (m, 1H, OC*H*), 4.58 (t, 1H, J = 9 Hz, OC*H*), 4.71 (m, 1H, NC*H*), 4.90 (m, 3H, 2 OC*H* + NC*H*), 5.68 (s, 6H, C_6H_6), 8.03 (m, 3H, C_6H_4), 8.25 (m, 1H, C_6H_4). MS (FAB^+): m/z 516, $[M + H]^+$.

[RuCl(Et-benbox)(*p*-MeC$_6$H$_4$Pr^i)][SbF$_6$] (4). Complex **4** was prepared from $[RuCl_2(p\text{-}MeC_6H_4Pr^i)]_2$ (80 mg, 0.13 mmol), Et-benbox (76 mg, 0.28 mmol), and $NaSbF_6$ (72 mg, 0.28 mmol) in 161 mg yield (79%). Anal. Calcd for $C_{26}H_{34}ClF_6N_2O_2PRu$: C, 45.39; H, 4.98; N, 4.07. Found: C, 45.22; H, 4.87; N, 3.85 (analysis on PF_6 salt). ^{1}H NMR (250 MHz): δ 0.71 and 0.98 (2 × t, 3H, J = 7 Hz, CH_2Me), 1.27 and 1.28 (2 × d, 3H, J = 7 Hz CHMe_2), 1.49 (m, 2H, CH_2Me), 1.64 (s, 3H, ArMe), 1.74 (m, 1H, CH_2Me), 2.42 (m, 1H, CH_2Me), 2.76 (sept, 1H, J = 7 Hz, CHMe$_2$), 4.10 (m, 1H, NCH), 4.35 (d, 1H, J = 7 Hz, *p*-Cy), 4.44 (m, 1H, NCH), 4.51 (m, 2H, OCH), 4.67 (dd, 1H, J = 9, 8 Hz, OCH), 4.84 (dd, 1H, J = 9.5, 8 Hz, OCH), 5.18 (d, 1H, J = 7 Hz, *p*-Cy), 5.54 (m, 2H, *p*-Cy), 7.87 (m, 3H, Ar H), 8.20 (m, 1H, Ar H). MS (FAB^+): m/z 543, $[M]^+$; 507, $[M - HCl]^+$.

[RuCl(ⁱPr-benbox)(*p*-MeC$_6$H$_4$Pr^i)][SbF$_6$] (5). Complex **5** was prepared from $[RuCl_2(p\text{-}MeC_6H_4Pr^i)]_2$ (80 mg, 0.13 mmol), ⁱPr-benbox (84 mg, 0.28 mmol), and $NaSbF_6$ (72 mg, 0.28 mmol) in 164 mg yield (78%). Anal. Calcd for $C_{28}H_{38}ClF_6N_2O_2PRu$: C, 41.68; H, 4.75; N, 3.47. Found: C, 41.45; H, 4.47; N, 3.58 (analysis on PF_6 salt). ^{1}H NMR: δ 0.44, 0.82, 1.00, and 1.12 (4 × d, 3H, J = 7 Hz, CHMe_2), 1.27 (s, 3H, ArMe), 1.30 and 1.35 (2 × d, 3H, J = 7 Hz, CHMe_2), 2.47 and 2.67 (2 × m, 1H, CHMe$_2$), 3.02 (sept, 1H, J = 7 Hz, CHMe$_2$), 4.20 (d, 1H, J = 7 Hz, *p*-Cy), 4.34 (t, 1H, J = 9 Hz, OCH), 4.57 (m, 2H, NCH + OCH), 4.78 (m, 1H, NCH), 4.91 (m, 2H, 2 × OCH), 5.19, 5.40, and 5.83 (3 × d, 1H, J = 7 Hz, *p*-Cy), 7.80 (m, 3H, C_6H_4), 8.29 (m, 1H, C_6H_4). MS (FAB^+): m/z 571, $[M]^+$; 535, $[M - HCl]^+$.

[RuCl(Et-benbox)(mes)][SbF$_6$] (6). Complex **6** was prepared from $[RuCl_2(mes)]_2$ (80 mg, 0.137 mmol), Et-benbox (76 mg, 0.28 mmol), and $NaSbF_6$ (72 mg, 0.28 mmol) in 168 mg yield (80%). Anal. Calcd for $C_{25}H_{32}ClF_6N_2O_2PRu$: C, 44.55; H, 4.79; N, 4.16. Found: C, 44.06; H, 4.76; N, 4.10 (analysis on PF_6 salt). ^{1}H NMR (250 MHz): δ 0.75 and 0.99 (2 × t, 3H, J = 7 Hz, CH_2Me), 1.56 (m, 2H, CH_2Me), 1.84 (m, 1H, CH_2Me), 1.96 (s, 9H, C_6Me_3), 2.40 (m, 1H, CH_2Me), 4.25 (t, 1H, J = 9 Hz, OCH), 4.43 (m, 1H, NCH), 4.55 (s, 3H, $C_6H_3Me_3$), 4.58 (m, 2H, OCH), 4.60 (m, 1H, OCH), 4.73 (m, 1H, NCH), 7.82 (m, 3H, C_6H_4), 7.94 (m, 1H, C_6H_4). MS (FAB^+): m/z 529, $[M]^+$.

[RuCl(ⁱPr-benbox)(mes)][SbF$_6$] (7). Complex **7** was prepared from $[RuCl_2(mes)]_2$ (80 mg, 0.137 mmol), ⁱPr-benbox (90 mg, 0.30 mmol), and $NaSbF_6$ (72 mg, 0.28 mmol) in 196 mg yield (90%). Anal. Calcd for $C_{27}H_{36}ClF_6N_2O_2RuSb$: C, 40.90; H, 4.58; N, 3.53. Found: C, 40.76; H, 4.51; N, 3.46. ^{1}H NMR (400 MHz): δ 0.47, 0.86, 0.97, and 1.13 (4 × d, 3H, J = 7 Hz, CHMe_2), 1.95 (s, 9H, C_6Me_3), 2.42 (m, 1H, CHMe$_2$), 2.75 (m, 1H, CHMe$_2$), 4.25 (m, 1H, NCH), 4.34 (dd, 1H, J = 9, 4 Hz, OCH), 4.68 (m, 3H, 2 OCH, NCH), 4.77 (s, 3H, $C_6H_3Me_3$), 4.84 (t, 1H, J = 9 Hz, OCH), 7.82 (m, 2H, C_6H_4), 7.93 (m, 1H, C_6H_4), 8.22 (d, 1H, J = 8 Hz, C_6H_4). MS (FAB^+): m/z 558, $[M + H]^+$.

[RuCl(Ph-benbox)(mes)][SbF$_6$] (8). Complex **8** was prepared from $[RuCl_2(mes)]_2$ (70 mg, 0.12 mmol), Ph-benbox (92 mg, 0.25 mmol), and $NaSbF_6$ (65 mg, 0.25 mmol) in 178 mg yield (86%). Anal. Calcd for $C_{33}H_{32}ClF_6N_2O_2RuSb$: C, 46.04; H, 3.75; N, 3.25. Found: C, 45.79; H, 3.63; N, 3.18%. ^{1}H NMR: δ 1.74 (s, 9H, C_6Me_3), 4.07 (s, 3H, $C_6H_3Me_3$), 4.55 (dd, 1H, OCH), 4.71 (t, 1H, J = 9 Hz, OCH), 5.06 (m, 2H, OCH + NCH), 5.43 (m, 2H, OCH + NCH), 6.84 (m, 2H, Ph), 7.27 (m, 4H, Ph), 7.52 (m, 4H, Ph), 7.97 (m, 2H, C_6H_4), 8.17 (d, 1H, J = 8 Hz, C_6H_4), 8.29 (d, 1H, J = 8 Hz, C_6H_4). MS (FAB^+): m/z 626, $[M + H]^+$.

Preparations of [Ru(L)(bis(oxazoline))(arene)][SbF$_6$]$_2$ (L = OH$_2$, acetone) (9−12). A solution of $AgSbF_6$ (1 equiv) in acetone (0.5 cm^3) was added to a solution of [RuCl(bis-(oxazoline))(arene)][SbF_6] (1 equiv) in CH_2Cl_2 (4 cm^3), giving a yellow-orange solution and an immediate precipitate of AgCl. The solution was stirred for 30 min at room temperature (protected from light) and then was filtered through Celite to remove AgCl. Evaporation, followed by washing with CH_2Cl_2, afforded solvent complexes as orange oils. In some cases the products could be recrystallized from acetone/ether, affording a crop of fine needles. The scale and yields for individual complexes are shown below.

[Ru(OH$_2$)(ⁱPr-box)(mes)][SbF$_6$]$_2$ (9). Complex **9** was prepared from **1** (50 mg, 0.070 mmol) and $AgSbF_6$ (25 mg, 0.073 mmol) in 63 mg yield (97%). The compound was only characterized in solution. ^{1}H NMR (d_6-acetone): δ 0.71, 1.05, 1.12, and 1.13 (4 × d, 3H, J = 7 Hz, CHMe_2), 2.42 (s, 9H, C_6Me_3), 2.46 (m, 1H, CHMe$_2$), 2.91 (m, 1H, CHMe$_2$), 4.72 (m, 1H, NCH), 4.87 (t, 1H, J = 10 Hz, OCH), 5.12 (m, 2H, OCH), 5.26 (m, 2H, OCH + NCH), 6.34 (s, 3H, $C_6H_3Me_3$), 7.15 (s, 2H, H_2O). MS (FAB^+): m/z 682, $[M - H_2O + SbF_6]^+$.

[Ru(OH$_2$)(ⁱPr-bop)(mes)][SbF$_6$]$_2$ (10). Complex **10** was prepared from **2** (27 mg, 0.038 mmol) and $AgSbF_6$ (13 mg, 0.038 mmol) in 34 mg yield (91%). Anal. Calcd for $C_{24}H_{40}F_{12}N_2O_3RuSb_2 \cdot Et_2O$: C, 31.99; H, 4.79; N, 2.66. Found: C, 31.90; H, 4.74; N, 2.61. ^{1}H NMR (400 MHz, 233 K, d_6-acetone): δ 0.54, 1.06, 1.08, 1.12 (4 × d, 3H, J = 7 Hz, CHMe_2), 1.53 and 1.77 (2 × s, 3H, CMe_2), 2.42 (m, 1H, CHMe$_2$), 2.42 (s, 9H, C_6Me_3), 2.96 (m, 1H, CHMe$_2$), 4.36 (t, 1H, J = 10 Hz, OCH), 4.52 (m, 1H, NCH), 4.88 (t, 1H, J = 10 Hz, OCH), 4.94 (m, 2H, 2 × OCH), 5.25 (m, 1H, NCH), 6.41 (s, 3H, $C_6H_3Me_3$), 7.06 (s, 2H, H_2O). MS (FAB^+): m/z 682, $[M - H_2O + SbF_6]^+$.

[Ru(OH$_2$)(ⁱPr-benbox)(C_6H_6)][SbF$_6$]$_2$ (11). Complex **11** was prepared from **3** (100 mg, 0.133 mol) and $AgSbF_6$ (48 mg, 0.14 mmol) in 107 mg yield (83%). Anal. Calcd for $C_{24}H_{32}F_{12}N_2O_3RuSb_2$: C, 29.74; H, 3.33; N, 2.89. Found: C, 29.89; H, 3.59; N, 2.80. ^{1}H NMR (d_6-acetone): δ 0.53, 0.84, 0.96, 1.16 (4 × d, 3H, J = 7 Hz, CHMe_2), 2.00 (m, 1H, CHMe$_2$), 2.78 (m, 1H, CHMe$_2$), 4.45 (ddd, 1H, J = 10, 2, 3 Hz, NCH), 4.81 (t, 1H, J = 10 Hz, OCH), 4.95 (m, 1H, NCH), 5.13 (m, 1H, OCH), 5.24 (m, 2H, OCH), 6.02 (s, 6H, C_6H_6), 7.65 (s, 2H, H_2O), 8.06 (m, 3H, C_6H_4), 8.31 (m, 1H, C_6H_4). MS (FAB^+): m/z 716, $[M - H_2O + SbF_6]^+$.

[Ru(OH$_2$)(ⁱPr-benbox)(mes)][SbF$_6$]$_2$ (12). Complex **12** was prepared from **7** (100 mg, 0.126 mmol) and $AgSbF_6$ (44 mg, 0.128 mmol) in 117 mg yield (92%). Anal. Calcd for $C_{27}H_{38}F_{12}N_2O_3RuSb_2 \cdot Me_2CO$: C, 33.70; H, 4.15; N, 2.62. Found: C, 33.75; H, 4.40; N, 2.61. ^{1}H NMR (d_6-acetone): δ 0.60, 0.93, 1.05, and 1.35 (4 × d, 3H, J = 7 Hz, CHMe_2), 2.1 (m, 1H, CHMe$_2$), 2.14 (s, 9H, C_6Me_3), 2.75 (m, 1H, CHMe$_2$), 4.23 (ddd, 1H, J = 10, 5, 3 Hz, NCH), 4.65 (t, 1H, J = 10 Hz, OCH), 4.83 (m, 1H, NCH), 5.08 (m, 3H, 3 × OCH), 5.30 (s, 3H, $C_6H_3Me_3$), 7.23 (s, 2H, H_2O), 8.12 (m, 2H, C_6H_4), 8.18 (m, 1H, C_6H_4), 8.43 (m, 1H, C_6H_4). MS (FAB^+): m/z 758 $[M - H_2O + SbF_6]^+$.

Catalysis Reactions. Schlenk Reactions (under N$_2$). The catalyst was prepared in situ from the chloride complex and 1 equiv of $AgSbF_6$ in CH_2Cl_2; the solution was filtered

through Celite into a Schlenk tube to remove AgCl. Alternatively, the isolated water-coordinated complexes could be used. Methacrolein (1 mmol) and 2,6-di-*tert*-butylpyridine (1 equiv/mol of catalyst)[24] were added to the catalyst solution (0.2 or 0.5 mmol) in CH_2Cl_2 (2 cm^3). The resulting yellow solution was equilibrated at the appropriate temperature before addition of cyclopentadiene (2 mmol). At the end of the reactions, the mixture was passed through a plug of silica, the solvent was removed, and the product was obtained as a colorless oil. The exo:endo ratio was determined by ^{1}H NMR spectroscopy, and the enantiomeric excess was determined by ^{1}H NMR or GC after conversion to the acetal with (2*R*,4*R*)-pentanediol.[20]

NMR Tube Experiments (in Air). Methacrolein (0.25 mmol) was added to a suspension of catalyst (5 μmol) in CD_2Cl_2 (0.5 cm^3), which led to rapid dissolution of catalyst to give a yellow solution. The solution was transferred to an NMR tube, and 2,6-di-*tert*-butylpyridine (1 equiv/mol of catalyst) and cyclopentadiene (0.5 mmol) were added. The ^{1}H NMR spectrum was run immediately and then repeated after suitable time intervals. The exo:endo ratio and enantiomeric excess were determined as described above.

X-ray Structure Determinations. Crystal data for **4**: orange block, crystal size 0.36 × 0.32 × 0.26 mm, $C_{26}H_{34}ClF_6N_2OPRu$, $M_r = 688.04$, orthorhombic, space group $P2_12_12_1$, $a = 11.569(1)$ Å, $b = 13.546(2)$ Å, $c = 18.480(2)$ Å, $V = 2896.1(6)$ Å^3, $Z = 4$, $D_c = 1.578$ g cm^{-3}, $T = 293(2)$ K, $\mu = 0.754$ mm^{-1}, $F(000) = 1400$, 3640 reflections collected with $5 < \theta < 25°$, 3448 unique ($R_{int} = 0.0285$), R1 = 0.0527 (for data $I > 2\sigma(I)$) and wR2 = 0.2416 (for all data), for 352 parameters, GOF = 1.135, Flack parameter −0.12(10).

Crystal data for **10**: orange block, crystal size 0.54 × 0.23 × 0.21 mm, $C_{24}H_{40}F_{12}N_2O_3RuSb_2 \cdot C_4H_{10}O$, $M_r = 1051.27$, orthorhombic, space group $P2_12_12_1$, $a = 13.0350(13)$ Å, $b = 16.5521(13)$ Å, $c = 17.945(2)$ Å, $V = 3871.7(6)$ Å^3, $Z = 4$, $D_c = 1.804$ g cm^{-3}, $T = 190(2)$ K, $\mu = 1.862$ mm^{-1}, $F(000) = 2072$, 4500 reflections collected with $2.6 < \theta < 25.0°$, 4344 unique ($R_{int} = 0.0110$), R1 = 0.0535 (for data $I > 2\sigma(I)$) and wR2 = 0.1502 (for all data), for 442 parameters, GOF = 1.115, Flack parameter 0.02(7).

Data for both **4** and **10** were collected on a Siemens P4 diffractometer using graphite-monochromated Mo Kα radiation; $\lambda = 0.7107$ Å, The data were corrected for Lorentz and polarization effects, and semiempirical absorption corrections based on ψ scans were applied. The structures were solved by Patterson methods and refined by full-matrix least squares on F^2 using the program SHELXTL-PC.[25] All hydrogen atoms bonded to carbon were included in calculated positions (C−H = 0.96 Å) using a riding model. The hydrogen atoms of the water molecule in **10** were not located and therefore are not included in refinement cycles. All non-hydrogen atoms were refined with anisotropic displacement parameters. High residual peaks (2.35 and −2.14 e Å^{-3}) in the final difference Fourier maps of **10** were located on the line *x*, 0.25, 0.75, which also passes through the Ru atom. We have no explanation for these high residual peaks; however, the data set is satisfactory in all other respects.

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Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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