Chloride Substitution Reactions of Cycloruthenated $(R)_C$-(+)-*N,N*-Dimethyl(1-phenylethyl)amine with Pseudohalides: Ruthenium Atom Stereochemistry

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The diastereoselectivity of chloride substitution by the pseudohalides azide, nitrite, thiocyanate, and cyanate in (S_{Ru},R_C)-$[\{\eta^6\text{-}C_6H_6\}RuCl[C_6H_4CH(Me)NMe_2]\}$ has been determined by a combination of ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, UV−visible spectroscopy, circular dichroism, infrared spectroscopy, and single-crystal X-ray crystallography. These chloride substitution reactions proceed with predominant retention of configuration at ruthenium. For the ambidentate ligands thiocyanate and nitrite, the major bonding mode is through their nitrogen donor atoms.

Introduction

Ligand substitution reactions of organometallic complexes wherein the metal is a stereocenter are of increasing interest.[1] In part, this interest stems from the fact that the stereochemical outcome of these simple reactions is related to the role that metal stereocenters could play in metal-mediated stereoselective organic transformations.[1o,2] Because of their potential application in catalysis, ruthenium complexes are of particular interest. For example, in situ catalysts formed from (arene)ruthenium complexes and chiral chelating Schiff base ligands gave moderate enantiomeric excesses (ee's) in the hydrogen transfer reduction of alkyl aryl ketones with 2-propanol.[3] Also, Noyori[4a] and Takaya[4b] obtained extremely high optical inductions in the hydrogenation of both prochiral alkenes and ketones using (arene)ruthenium procatalysts together with (*S*)- or (*R*)-BINAP cocatalysts.

We recently reported[5] that chloride substitution reactions of (S_{Ru},R_C)- and (R_{Ru},R_C)-$\{(\eta^6\text{-}C_6H_6)RuCl[C_6H_4CH(Me)NMe_2]\}$, $[(\eta^6\text{-}C_6H_6)Ru(TMBA)Cl]$ (**1a,a′**), with a variety of neutral and anionic ligands proceed with predominant retention of configuration at ruthenium. The chloride substitutions with anionic ligands were highly stereospecific. Chloride substitution reactions of the homologous α-(2-naphthyl)ethylamine complex, $[(\eta^6\text{-}C_6H_6)Ru(TMNA)Cl]$, especially those with halides and pseudohalides, occur with very high diastereoselectivities.[6] Because metal-mediated organic transformations often involve a sequence of steps, including ligand substitutions, there is a need for additional information concerning the stereochemistry of ligand substitution reactions of complexes wherein the metal is a stereocenter. This is especially so because there are only a limited number of such complexes that are configurationally stable at the metal center.[1d]

To ascertain whether chloride substitution by anionic ligands for these types of complexes generally occurs with high diastereoselectivity and to increase the limited database for ligand substitutions at stereogenic metal centers, we have investigated the stereochemical course of the substitution of chloride in the complexes **1a,a′** by the pseudohalides azide, nitrite, thiocyanate, and cyanate and report the results herein. We were also interested to learn whether linkage isomers would form for the ambidentate nitrite and thiocyanate ligands.

Results and Discussion

The mixture of the chloro complexes[7] (**1a, a′**; 20:1 ratio, 90.4% de) readily undergoes clean metathesis reactions with

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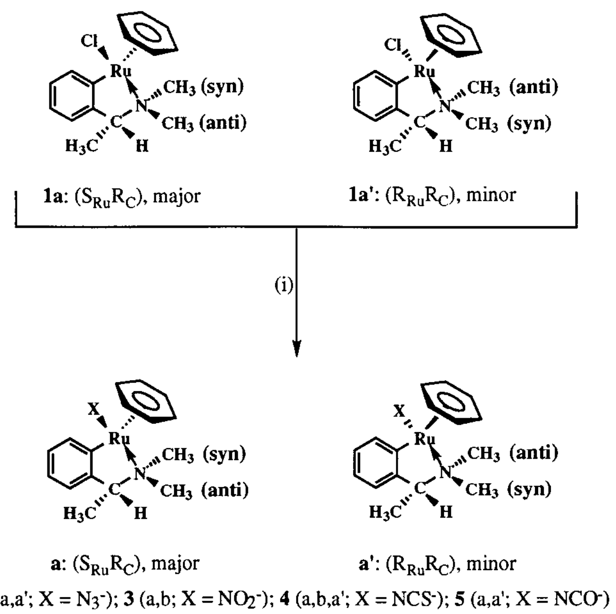
Scheme 1[a]



[a] (i) Stirred in EtOH (95%)/CH_2Cl_2 (20:1) mixture with appropriate anion salt at room temperature.

excess NaN_3, $NaNO_2$, NaNCS, or a stoichiometric amount of AgNCO[8] in a CH_2Cl_2/(95%) EtOH mixture to form the corresponding azido (**2a,a′**), nitro (**3a**), nitrito (**3b**), isothiocyanato (**4a,a′**), thiocyanato (**4b**), and cyanato (**5a,a′**) analogues, respectively (Scheme 1), with high chemical and optical yields. The ratios of the isomers and diastereomers were determined by ^1H NMR spectroscopy[7] by integration of the H_2 resonances for each species (see Experimental Section and Figure 1 for proton labeling scheme). The ^1H and $^{13}C\{^1H\}$ NMR spectra (see Experimental Section) of the azide and cyanate complexes in $CDCl_3$ solution are essentially the same, except for minor chemical shift differences, as those previously reported for the chloride starting complexes (**1a,a′**). Over a period of days, both the azide and cyanate complexes react with adventitious HCl present in old $CDCl_3$ to form minor amounts of the major (S_{Ru},R_C) diastereomer of the chloride complex, **1a**, as can be seen by the presence of its H_2 resonance in the spectrum of an aged sample of the cyanate complex (Figure 1). Both complexes are stable in acetone-d_6 solutions for several days. The azide (96.4% de) and cyanate (87.2% de) reactions are slightly more and less stereoselective, respectively, than the previously reported[5] bromide (93.2% de) and iodide (94.3% de) reactions. Only one species is detectable by infrared spectroscopy in CH_2Cl_2 solutions for both the azide [$\nu_a(N_3)$ 2040 cm^{-1}] and cyanate [ν_a(NCO) 2223 cm^{-1}; ν_s(NCO) 1304 cm^{-1}] complexes.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of the nitrite complex show the presence of two species in solution in a 5.3 to 1 ratio. For the chloride, bromide, azide, and cyanate complexes, where no linkage isomers are present, the average chemical shift difference of the H_2 resonances for the (S_{Ru},R_C) and (R_{Ru},R_C) diastereomers is 0.44 ppm. The chemical shifts of the two H_2 resonances for the nitrite complex differ by only 0.17 ppm, and on this basis we attribute the more upfield resonance to the less abundant nitrito linkage isomer with the (S_{Ru},R_C) absolute configuration. The more downfield H_2 resonance is attributed to the more abundant (S_{Ru},R_C) nitro linkage isomer. Previous studies[9] of Ru(II) nitrite complexes have generally shown that the nitro linkage isomer is more stable than the nitrito linkage isomer, and observation of the latter is rare. The infrared spectrum in CH_2Cl_2 solution supports the presence of linkage isomers [$\nu_{as}(NO_2)$ 1430 cm^{-1}; $\nu_s(NO_2)$ 1320 cm^{-1} (nitro) and ν(N=O) 1470 cm^{-1}; ν(N−O) 979 cm^{-1} (nitrito)].[10]

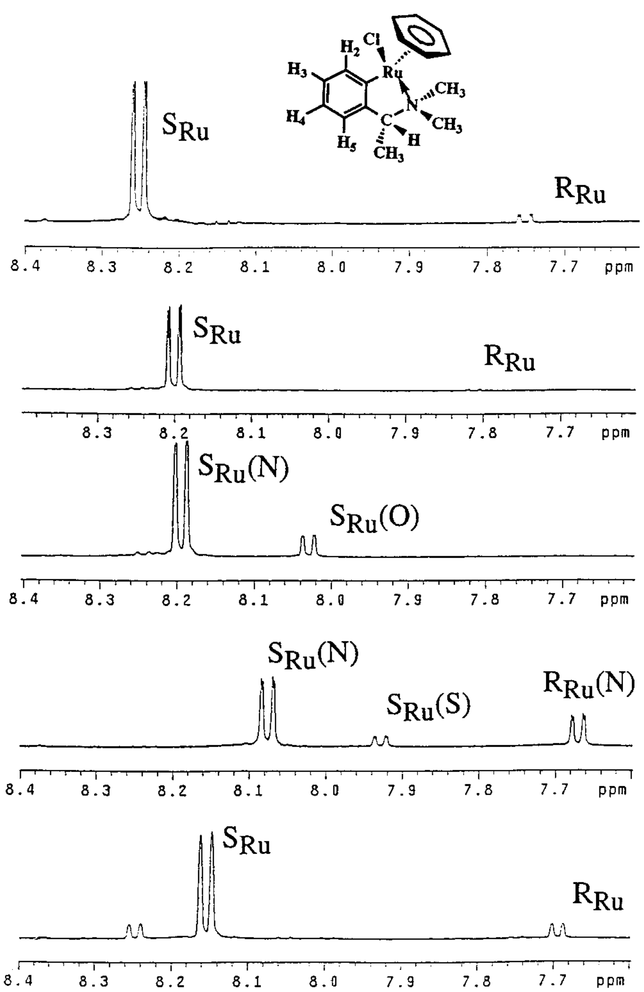


Figure 1. Expansions of the 500 MHz ^1H NMR spectra ($CDCl_3$) in the H_2 region of, from top to bottom, **1a,a′**, **2a,a′**, **3a,b**, **4a,b,a′**, and **5a,a′**. Note that in the aged spectrum of **5a,a′** the H_2 resonance for **1a** is present.

For the thiocyanate reaction, three species (Figure 1), viz. (S_{Ru},R_C, NCS, 63.2%), (S_{Ru},R_C, SCN, 10.5%), and (R_{Ru},R_C, NCS, 26.3%), were formed. To the best of our knowledge, this represents one of a small number of examples of thiocyanate linkage isomers for Ru(II) complexes.[11] The steric bulk of the other ligands in the ruthenium coordination sphere is expected to destabilize the S-bound thiocyanate linkage isomer (as it is bent rather than linear),[12] consistent with it being a minor product. The infrared spectrum of this mixture in CH_2Cl_2 solution shows two ν(CN) vibrations (2120 and 2090 cm^{-1}) in concert with the presence of thiocyanate linkage isomers.[10,13]

The above conclusions on the ruthenium absolute configurations for the major diastereomers **2a**, **3a**, **4a**, and **5a** (and hence

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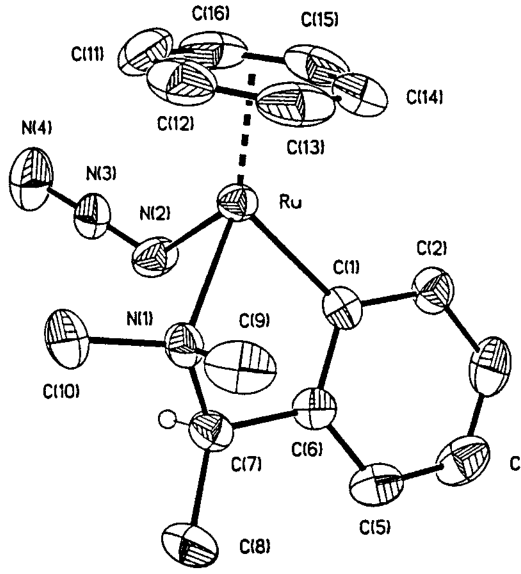

Figure 2. Structural drawing of **2a**, showing the atom numbering scheme (40% probability ellipsoids, the hydrogen atom has an arbitrary radius of 0.1 Å). Selected bond lengths (Å) and angles (deg) are Ru(1)−C(1), 2.069(6); Ru(1)−C(arene, ave.), 2.202(7); Ru(1)−N(1), 2.174(5); Ru(1)−N(2), 2.144(6); N(2)−N(3), 1.158(7); N(3)−N(4), 1.170(7); C(1)−Ru(1)−N(1), 77.5(2); C(1)−Ru(1)−N(2), 84.2(2); N(1)−Ru(1)−N(2), 84.3(2); Ru(1)−N(2)−N(3), 122.6(5); N(2)−N(3)−N(4), 176.2(8).

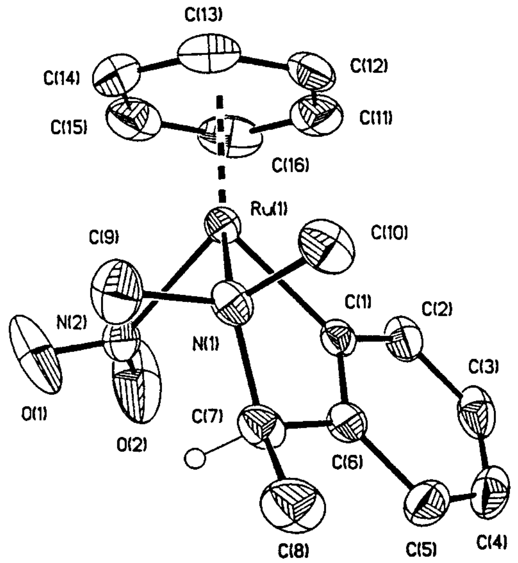

Figure 3. Structural drawing of **3a**, showing the atom numbering scheme (40% probability ellipsoids, the hydrogen atom has an arbitrary radius of 0.1 Å). Selected bond lengths (Å) and angles (deg) are Ru(1)−C(1), 2.068(3); Ru(1)−C(arene, ave.), 2.227(5); Ru(1)−N(1), 2.177(3); Ru(1)−N(2), 2.088(3); N(2)−O(1), 1.219(5); N(2)−O(2), 1.197(5); C(1)−Ru(1)−N(1), 77.9(1); C(1)−Ru(1)−N(2), 85.1(1); N(1)−Ru(1)−N(2), 90.2(1); O(1)−N(2)−O(2), 115.3(4).

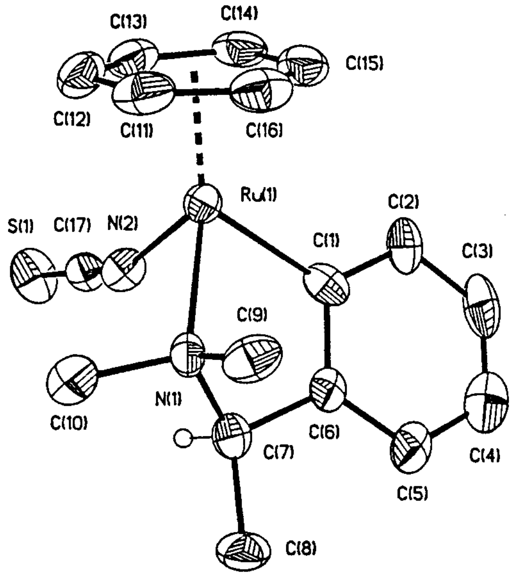

Figure 4. Structural drawing of one of the independent molecules of **4a**, showing the atom numbering scheme (40% probability ellipsoids, the hydrogen atom has an arbitrary radius of 0.1 Å). Selected bond lengths (Å) and angles (deg) are Ru(1)−C(1), 2.068(13); Ru(1)−C(arene, ave.), 2.214(14); Ru(1)−N(1), 2.182(10); Ru(1)−N(2), 2.076(9); N(2)−C(17), 1.152(12); C(17)−S(1), 1.623(10); C(1)−Ru(1)−N(1), 78.8(5); C(1)−Ru(1)−N(2), 86.8(4); N(1)−Ru(1)−N(2), 87.7(3); Ru(1)−N(2)−C(17), 157.2(9); N(2)−C(17)−S(1), 178.6(14).

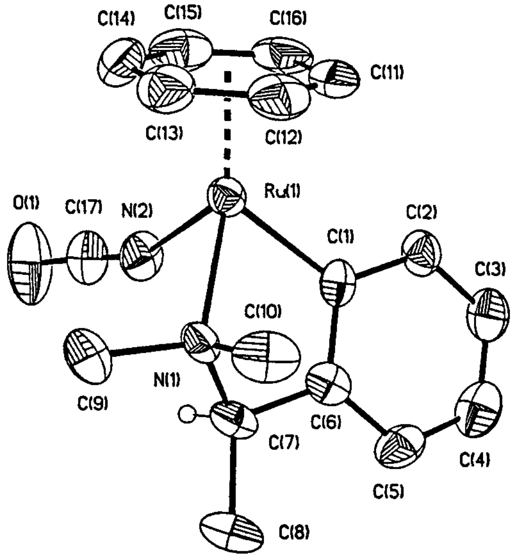

Figure 5. Structural drawing of **5a**, showing the atom numbering scheme (40% probability ellipsoids, the hydrogen atom has an arbitrary radius of 0.1 Å). Selected bond lengths (Å) and angles (deg) are Ru(1)−C(1), 2.053(7); Ru(1)−C(arene, ave.), 2.205(8); Ru(1)−N(1), 2.170(5); Ru(1)−N(2), 2.113(7); N(2)−C(17), 1.077(9); C(17)−O(1), 1.239(10); C(1)−Ru(1)−N(1), 77.7(2); C(1)−Ru(1)−N(2), 87.3(2); N(1)−Ru(1)−N(2), 84.6(2); Ru(1)−N(2)−C(17), 156.8(7); N(2)−C(17)−O(1), 176.9(11).

the stereochemistry of the reactions leading to their formation) were confirmed by their crystal structures (Figures 2−5). Crystallographic data are given in Table 1. Each structure consists of isolated molecules with no unusual intermolecular contacts. **3a** crystallizes as a CH$_3$OH solvate, and for **4a** there are two inequivalent molecules in the asymmetric unit. The major difference in the structures of these two molecules is in the Ru−N−C bond angles of the isothiocyanate [Ru(1)−N(2)−C(17), 157.2(9)° and Ru(2)−N(4)−C(34), 177.9(9)°]. The metal−NCS bond angles in metal isothiocyanate complexes have been reported to vary from 130° to 180° and are usually expected to be near 180° for Ru(II) complexes.[12] The difference here is probably a result of crystal packing effects. The metrical parameters of the four complexes worthy of note are the Ru−

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Table 1. Crystallographic Data for **2a**, **3a**, **4a** and **5a**

compound	**2a**	**3a**	**4a**	**5a**
emp formula	$C_{16}H_{20}N_4Ru$	$C_{16}H_{20}N_2O_2Ru{\cdot}CH_3OH$	$C_{17}H_{20}N_2RuS$	$C_{17}H_{20}N_2ORu$
fw	369.43	405.45	385.48	369.42
cryst syst	orthorhombic	monoclinic	monoclinic	orthorhombic
a (Å)	9.269(1)	7.3026(5)	10.111(1)	8.934(1)
b (Å)	12.773(2)	14.337(1)	10.187(1)	13.043(1)
c (Å)	13.142(1)	8.1670(1)	15.660(2)	13.386(2)
α (deg)	90	90	90	90
β (deg)	90	92.25(1)	91.524(8)	90
γ (deg)	90	90	90	90
V (Å^3)	1555.9(3)	854.5(1)	1612.3(3)	1559.8(3)
z	4	2	2[a]	4
space group	$P2_12_12_1$	$P2_1$	$P2_1$	$P2_12_12_1$
ρ_{calcd} (mg/m^3)	1.577	1.572	1.588	1.573
μ (mm^{-1})	1.006	0.933	1.096	1.005
trans. max/min	0.8979/0.8443	0.9375/0.8185	0.9100/0.8596	0.9322/0.8770
$R(F)^b$ ($I > 2\sigma(I)$)	0.0290	0.0184	0.0402	0.0408
$R\omega(F^2)^c$	0.0521	0.0462	0.0786	0.0604

[a] Two inequivalent molecules per asymmetric unit. [b] $R(F) = \sum(|F_o| - |F_c|)/\sum(|F_o|)$. [c] $R\omega(F) = [\sum[\omega(F_o^2 - F_c^2)^2]/\sum[\omega(F_o^2)^2]]^{0.5}$; $\omega = 1/\sigma^2(F)^2 = \sigma^2(\text{counts}) + (\rho I)^2$.

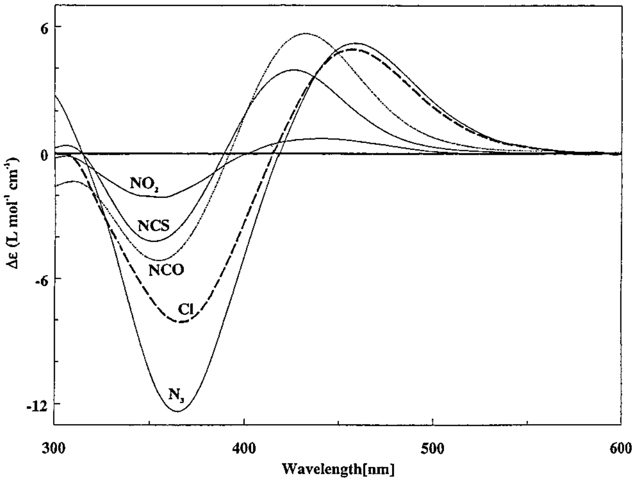

Figure 6. CD spectra of **1a,a′** (90.4% de), **2a,a′** (96.4% de), **3a,b**, **4a,a′,b** (47.4% de), **5a,a′** (87.2% de) in CH_2Cl_2, 1 cm path length.

C(1) (2.053 to 2.068 Å; 2.065 Å ave.), Ru−N(1) (2.170 to 2.191 Å; 2.179 Å ave.), and Ru−N(pseudohalide) N_3 (2.144(6) Å), NO_2 (2.088(3) Å), NCS (2.076(9) Å; 2.044(9) Å), NCO (2.113(7) Å) distances. These distances differ very little among the entire series, and the metrical parameters of the benzylamine complexes and the analogous naphthylamine complexes[6] are very similar. The ambidentate ligands NCO^-, NCS^-, and NO_2^- all bind to ruthenium through their nitrogen donor atoms in the major diastereomer. The major diastereomer has the (S_{Ru},R_C) absolute configuration in each case. The five-membered chelate ring has the puckered envelope conformation with the benzylic $C-CH_3$ group pseudoequatorial and nearly in the plane of the aryl ring[14] for all four complexes.

Table 2. Comparative Diastereoselectivities[a] of Cl^- Substitution Reactions of [(η^6-C_6H_6)Ru(R-TMBA)Cl] and [(η^6-C_6H_6)Ru(R-TMNA)Cl][b]

	diastereoselectivity (% de)	
X	[(η^6-C_6H_6)Ru(R-TMBA)Cl]	[(η^6-C_6H_6)Ru(R-TMNA)Cl][b]
Cl	90.4[c]	92.0
Br	93.2[c]	93.3
I	94.3[c]	94.9
N_3	96.4	100
NCO	87.2	100
NCS	47.4[d]	100
NO_2	100[e]	100

[a] % de = (% major diastereomer − % minor diastereomer). [b] Reference 6. [c] Reference 5. [d] 89.5% isothiocyanato; 10.5% thiocyanato linkage isomer. [e] 84.1% nitro; 15.9% nitrito linkage isomer.

The absolute configurations of the bulk samples were investigated by CD spectroscopy (Figure 6). The signs and morphologies of the CD spectra of this series of complexes are very similar, suggesting that the absolute configurations of the major species in solution are the same.[1h−j,o,15] The absolute configuration at the Ru center of the major diastereomer of the chloro complex has been established as S_{Ru}.[7] Since these diastereomers are configurationally stable and the stereochemistry at the benzylic carbon remains R_C during the course of these substitution reactions, we assign to all of these complexes the (S_{Ru},R_C) and (R_{Ru},R_C) absolute configurations for the major and minor diastereomers, respectively.

For both the benzylamine[5] and naphthylamine[6] complexes, all the halide and pseudohalide ligand substitution reactions proceed with predominant retention of configuration at Ru. The diastereoselectivities are compared in Table 2. A search through the literature related to this subject[1,5,15] reveals that retention of configuration at the metal center has been the most common stereochemical outcome in these studies. While epimerization and/or racemization is sometimes observed, net inversion of metal configuration appears to be rare.

As can be seen from the data in Table 2, the diastereoselectivity of the chloride substitutions is generally greater for the substitutions of the TMNA complex than for the TMBA analogue. To assess whether this has an electronic origin, the redox potentials for the Ru(II)/(III) couples (Table 3) were determined by cyclic voltammetry. For both of the chloride complexes the Ru(II)/(III) couples are both chemically and electrochemically reversible processes. Within experimental

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Table 3. Ru(II)/(III) Couples for [(η^6-C_6H_6)Ru(R-TMNA)Cl] and [(η^6-C_6H_6)Ru(R-TMBA)X] Complexes[a]

complex	$E_{1/2}$ (V) ($E_{p_a} - E_{p_c}$, mV)
[(η^6-C_6H_6)Ru(TMNA)Cl]	0.41 (111)
[(η^6-C_6H_6)Ru(TMBA)Cl]	0.41 (111)
[(η^6-C_6H_6)Ru(TMBA)Br]	0.40 (104)
[(η^6-C_6H_6)Ru(TMBA)I]	0.38[b,d]
[(η^6-C_6H_6)Ru(TMBA)N_3]	0.29[b](129)
[(η^6-C_6H_6)Ru(TMBA)NO_2]	0.52[c,d]
[(η^6-C_6H_6)Ru(TMBA)NCS]	0.51[b,d]
[(η^6-C_6H_6)Ru(TMBA)NCO]	0.42 (161)

[a] Measured in CH_2Cl_2 solution at a glassy carbon working electrode, Ag/AgCl (aqueous) reference electrode, 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. All potentials are vs F_c/F_c^{+}, scan rate 50 or 100 mV s^{-1}. [b] Quasireversible. [c] Irreversible. [d] E_{p_a} only.

error, the redox potentials of the two complexes are the same. This implies[16] that there is no perceptible difference in the electronic donor or acceptor properties of the TMNA and TMBA ligands. Thus, we believe that the differences in the diastereoselectivities, as well as the fact that NO_2^- and SCN^- linkage isomers are observed for the TMBA complexes and not for the TMNA complexes, has a steric origin. For the TMBA complexes, the five-membered chelate ring is flexible[5,6] and interconverts in solution between two limiting conformations, wherein the CCH_3 group is either pseudoaxial or pseudoequatorial. For the TMNA complexes, the five-membered chelate ring is rigid with the CCH_3 group remaining pseudoequatorial.[6] This probably emanates from the larger naphthyl than benzyl ring systems. For the former, more mass, including solvent molecules, must be moved in order for λ to δ or vice-versa ring conformational interchange to occur. This gives rise to a greater steric buttressing toward the approach of an incoming ligand for the chloride substitutions in the TMNA complex than in the TMBA complex and results in generally greater diastereoselectivity regardless of whether these reactions occur by an associative or dissociative mechanism.[5]

All of these complexes slowly decompose in solution (over a period of days) to produce greenish-black decomposition products. To better understand these decomposition processes, we have determined the redox potentials of these complexes by cyclic voltammetry (Table 3). As can be seen from the data in Table 3, there are only small changes in the Ru(II)/(III) oxidation potentials as a function of the identity of the coordinated halide or pseudohalide. Their oxidation potentials are similar to those reported for *trans*-[L_4RuX_2] (L = PMe_3, $AsMe_2Ph$, $SbMe_2Ph$; X = Cl, Br, I).[17] Thus, it is not surprising that separate potentials were not observed for the nitrite and thiocyanate linkage isomers. Oxidation of the iodide, azide, and thiocyanate complexes is quasireversible, and that of the nitrite complex is irreversible. On the basis of the above results, we believe that for the iodide, azide, thiocyanate, and nitrite complexes the oxidation is a Ru(II)/(III) couple.

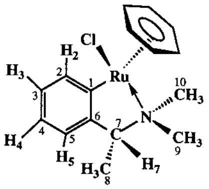
Thus, the mode of decomposition of the complexes in solution is likely oxidation followed sequentially by electron transfer from the halide or pseudohalide to ruthenium,[18] ligand dissociation, and ultimate formation of finely divided insoluble black particles.

Experimental Section

1. Physical Measurements. NMR spectra were recorded on a Varian Unity Plus-500 FT NMR spectrometer operating at 500 MHz for ^1H and 125 MHz for ^{13}C. Chemical shifts were referenced to residual solvent resonances with all shifts to low-field, high-frequency positive. FT-IR spectra were obtained as CH_2Cl_2 solutions on NaCl windows on a Perkin-Elmer BX Spectrometer for the mid-IR region (400−4000 cm^{-1}) (abbreviations: shp = sharp, sh = shoulder, st = strong, w = weak, br = broad). UV−visible spectra were recorded at 25 °C on a Perkin-Elmer Lambda-11 UV−visible spectrophotometer as CH_2Cl_2 solutions in 1.00 cm quartz cells. CD spectra were recorded at 25 °C on a JASCO J-600 spectropolarimeter with a CH_2Cl_2 solution of each compound in 1.00 cm quartz cells. Cyclic voltammograms were recorded at 25 °C in freshly distilled CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate using a BAS CV 50-W voltammetric analyzer. A three-electrode system was used. The working electrode was a glassy carbon disk, and the reference electrode was Ag/AgCl (aqueous) separated from the cell by a luggin capillary. The F_c/F_c^{+} couple occurred at 480 mV[19] under the same conditions. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

2. Synthesis and Characterization of the Products of Ligand Substitution Reactions: {(η^6-C_6H_6)Ru[$C_6H_4CH(Me)NMe_2$]X} (X = N_3 (2a,a′), NO_2 (3a,b), NCS (4a,a′,b), NCO (5a,a′)). The substitution products were all prepared by the same general method. This involved metathetic reactions of **1a,a′**[7] with an excess of the appropriate sodium salt or a stoichiometric amount of AgNCO[8] in a mixture of CH_2Cl_2 and EtOH (95%), with the salt added as an aqueous solution. Reaction mixtures were not air sensitive, and no precautions were taken to exclude air. Since AgNCO is light-sensitive, its reaction was performed in the dark. The following preparation of **2a,a′** is representative.

2a,a′ (X = N_3). To a solution of **1a,a′** (0.400 g, 1.10 mmol) in a mixture of 5 mL CH_2Cl_2 and 25 mL of 95% EtOH was added a solution of 0.987 g (15.2 mmol) NaN_3 in 4 mL of H_2O. Then 35 mL of 95% EtOH was added. The resulting transparent, red-orange solution was stirred at ambient temperature for 17 h, and the solvents were removed on a rotary evaporator. The red-orange, solid residue was dissolved in CH_2Cl_2 and gravity-filtered through Celite to remove NaCl and excess NaN_3. The solvent was removed from the filtrate on a rotary evaporator, and the remaining orange powder was dried under vacuum to afford 0.324 g (80%), mp 165 °C (dec). Anal. Calcd for $C_{16}H_{20}N_4Ru$: C, 52.04; H, 5.42; N, 15.17. Found: C, 51.91; H, 5.53; N, 15.01. ^1H NMR (500 MHz, $CDCl_3$):



2a (major) δ 1.20 (d, $^3J(H_7H_8)$ = 7.0 Hz, 3H, $CH_3(8)$), 2.45 (s, 3H, $NCH_3(9)$), 3.15 (s, 3H, $NCH_3(10)$), 3.91 (apparent qt, $^3J(H_7H_8)$ = 7.0 Hz, $^4J(H_5H_7)$ = $^6J(H_3H_7)$ =1.0 Hz, 1H, H_7), 5.32 (s, 6H, η^6-C_6H_6), 6.79 (ddd, $^3J(H_4H_5)$ = 7.5 Hz, $^4J(H_3H_5)$ = 1.5 Hz, $^4J(H_5H_7)$ = 1.0 Hz, 1H, H_5), 7.00 (apparent td, $^3J(H_3H_4)$ = $^3J(H_4H_5)$ = 7.5 Hz, $^4J(H_2H_4)$ = 1.3 Hz, 1H, H_4), 7.11 (apparent tdd, $^3J(H_2H_3)$ = $^3J(H_3H_4)$ = 7.5 Hz, $^4J(H_3H_5)$ =1.5 Hz, $^6J(H_3H_7)$ = 1.0 Hz, 1H, H_3), 8.20 (dd, $^3J(H_2H_3)$ = 7.5 Hz, $^4J(H_2H_4)$ = 1.3 Hz, 1H, H_2). **2a′** (minor) δ 1.22 (d, $^3J(H_7H_8)$ = 7.0 Hz, 3H, $CH_3(8)$), 1.83 (s, 3H, $NCH_3(9)$), 3.39 (s, 3H, $NCH_3(10)$), 3.82 (apparent qt, $^3J(H_7H_8)$ = 7.0 Hz, $^4J(H_5H_7)$ = $^6J(H_3H_7)$ =1.0 Hz, 1H, H_7), 5.29 (s, 6H, η^6-C_6H_6), 6.77 (ddd, $^3J(H_4H_5)$ = 7.5 Hz, $^4J(H_3H_5)$ = 1.5 Hz, $^4J(H_5H_7)$ = 1.0 Hz, 1H, H_5), 7.01 (apparent td,

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$^3J(H_3H_4) = {}^3J(H_4H_5) = 7.5$ Hz, $^4J(H_2H_4) = 1.3$ Hz, 1H, H_4), 7.18 (apparent tdd, $^3J(H_2H_3) = {}^3J(H_3H_4) = 7.5$ Hz, $^4J(H_3H_5) = 1.5$ Hz, $^6J(H_3H_7) = 1.0$ Hz, 1H, H_3), 7.81 (dd, $^3J(H_2H_3) = 7.5$ Hz, $^4J(H_2H_4) = 1.3$ Hz, 1H, H_2). The relative intensities of the two H_2 resonances (55 to 1) established the 96.4% de. $^{13}C\{^1H\}$ NMR(125 MHz, $CDCl_3$): **2a** (major) δ 9.7 (C_8), 49.4 (C_9), 52.2 (C_{10}), 67.6 (C_7), 85.2 (η^6-C_6H_6), 123.4 (C_4, C_5), 126.2 (C_3), 137.0 (C_2), 149.5 (C_6), 166.3 (C_1). IR: (CH_2Cl_2 solution) $\nu_a(N_3)$ 2040 cm^{-1} (st, shp); (Nujol) $\nu_s(N_3)$ 1262 cm^{-1} (w), $\delta(N_3)$ 658 cm^{-1} (vw). UV−Vis: ($c = 5.5 \times 10^{-5}$ M in CH_2Cl_2 at 25 °C). λ_{max}, nm (ϵ, L mol^{-1} cm^{-1}) 227 (1.9×10^4), 256 (1.7×10^4). ($c = 4.4 \times 10^{-4}$ M in CH_2Cl_2). 414 (1.1×10^3). CD: molecular ellipticity $[\theta]_\lambda$ (deg cm^2 dmol^{-1}) where $[\theta]_\lambda = 3300$ x $(\Delta\epsilon)_\lambda$ and $(\Delta\epsilon)_\lambda$ is the measured CD quantity (in units of L mol^{-1} cm^{-1}) at a given wavelength: $c = 5.5 \times 10^{-4}$ M in CH_2Cl_2 at 25 °C: $[\theta]_{600}$ (0), $[\theta]_{459}$ (+17093); $c = 1.1 \times 10^{-4}$ M, $[\theta]_{365}$ (−40795).

3a,b (X = NO$_2$): yield 0.179 g (87%) yellow powder (mp 130−6 °C). Anal. Calcd for $C_{16}H_{20}N_2O_2Ru{\cdot}CH_3OH$: C, 50.38; H, 5.92; N, 6.91. Found: C, 50.52; H, 6.03 N, 6.45. ^1H NMR (500 MHz, $CDCl_3$): **3a** (major) δ 1.18 (d, $^3J(H_7H_8) = 6.5$ Hz, 3H, $CH_3(8)$), 2.49 (s, 3H, $NCH_3(9)$), 3.46 (s, 3H, $NCH_3(10)$), 3.88 (q, $^3J(H_7H_8) = 6.5$ Hz, 1H, H_7), 5.42 (s, 6H, η^6-C_6H_6), 6.74 (d, $^3J(H_4H_5) = 7.5$ Hz, 1H, H_5), 7.00 (apparent td, $^3J(H_3H_4) = {}^3J(H_4H_5) = 7.5$ Hz, $^4J(H_2H_4) = 0.8$ Hz, 1H, H_4), 7.13 (apparent t, $^3J(H_2H_3) = {}^3J(H_3H_4) = 7.5$ Hz, 1H, H_3), 8.20 (dd, $^3J(H_2H_3) = 7.5$ Hz, $^4J(H_2H_4) = 0.8$ Hz, 1H, H_2). **3b** (minor) δ 1.29 (d, $^3J(H_7H_8) = 7.0$ Hz, 3H, $CH_3(8)$), 1.95 (s, 3H, $NCH_3(9)$), 3.43 (s, 3H, $NCH_3(10)$), 3.86 (q, $^3J(H_7H_8) = 7.0$ Hz, 1H, H_7), 5.36 (s, 6H, η^6-C_6H_6), 6.77 (d, $^3J(H_4H_5) = 7.5$ Hz, 1H, H_5), 7.01 (apparent td, $^3J(H_3H_4) = {}^3J(H_4H_5) = 7.5$ Hz, $^4J(H_2H_4) = 0.8$ Hz, 1H, H_4), 7.20 (apparent t, $^3J(H_2H_3) = {}^3J(H_3H_4) = 7.5$ Hz, 1H, H_3), 8.03 (dd, $^3J(H_2H_3) = 7.5$ Hz, $^4J(H_2H_4) = 0.8$ Hz, 1H, H_2). The relative intensities of the two H_2 resonances (5.3 to 1) established the linkage isomer ratio. $^{13}C\{^1H\}$ NMR(125 MHz, $CDCl_3$): **3a** (major) δ 10.1 (C_8), 50.9 (C_9), 51.9 (C_{10}), 68.4 (C_7), 88.4 (η^6-C_6H_6), 123.4 (C_5), 123.5 (C_4), 126.6 (C_3), 138.0 (C_2), 149.3 (C_6), 165.3 (C_1). IR: (CH_2Cl_2 solution) $\nu_{as}(NO_2)$ 1430 cm^{-1} (m), $\nu_s(NO_2)$ 1320 cm^{-1} (w) (nitro), $\nu(N{=}O)$ 1470 cm^{-1} (sh), $\nu(N{-}O)$ 979 cm^{-1} (sh) (nitrito). UV−Vis: ($c = 1.1 \times 10^{-4}$ M in CH_2Cl_2 at 25 °C). λ_{max}, nm (ϵ, L mol^{-1} cm^{-1}) 330 (2.5×10^3), 252 (9.9×10^3). CD: $c = 5.5 \times 10^{-4}$ M in CH_2Cl_2 at 25 °C: λ_{max}, nm ($[\theta]_\lambda$, deg cm^2 dmol^{-1}) 600 (0), 578 (−225), 441 (+2265); $c = 1.1 \times 10^{-4}$ M, 356 (−6922).

4a,a′,b (X = NCS): yield 0.147 g (79%) red powder (mp 190 °C, dec). Anal. Calcd for $C_{17}H_{20}N_2RuS$: C, 52.99; H, 5.19; N, 7.27. Found: C, 52.78; H, 5.06 N, 7.13. ^1H NMR (500 MHz, $CDCl_3$): **4a** (major − $S_{Ru}R_C$(NCS)) δ 1.21 (d, $^3J(H_7H_8) = 7.0$ Hz, 3H, $CH_3(8)$), 2.44 (s, 3H, $NCH_3(9)$), 3.21 (s, 3H, $NCH_3(10)$), 3.90 (qdd, $^3J(H_7H_8) = 7.0$ Hz, $^4J(H_5H_7) = 1.5$ Hz, $^6J(H_3H_7) = 1.0$ Hz, 1H, H_7), 5.37 (s, 6H, η^6-C_6H_6), 6.78 (apparent dt, $^3J(H_4H_5) = 7.0$ Hz, $^4J(H_3H_5) = {}^4J(H_5H_7) = 1.5$ Hz, 1H, H_5), 6.98 (ddd, $^3J(H_3H_4) = 7.5$ Hz, $^3J(H_4H_5) = 7.0$ Hz, $^4J(H_2H_4) = 1.0$ Hz, 1H, H_4), 7.06 (apparent tdd, $^3J(H_2H_3) = {}^3J(H_3H_4) = 7.5$ Hz, $^4J(H_3H_5) = 1.5$ Hz, $^6J(H_3H_7) = 1.0$ Hz, 1H, H_3), 8.08 (dd, $^3J(H_2H_3) = 7.5$ Hz, $^4J(H_2H_4) = 1.0$ Hz, 1H, H_2). **4b** ($S_{Ru}R_C$(SCN)) δ 1.23 (d, $^3J(H_7H_8) = 7.0$ Hz, 3H, $CH_3(8)$), 2.54 (s, 3H, $NCH_3(9)$), 3.27 (s, 3H, $NCH_3(10)$), 4.30 (qdd, $^3J(H_7H_8) = 7.0$ Hz, $^4J(H_5H_7) = 1.5$ Hz, $^6J(H_3H_7) = 1.0$ Hz, 1H, H_7), 5.43 (s, 6H, η^6-C_6H_6), 6.77 (apparent dt, $^3J(H_4H_5) = 7.0$ Hz, $^4J(H_3H_5) = {}^4J(H_5H_7) = 1.5$ Hz,1H, H_5), 6.97 (ddd, $^3J(H_3H_4) = 7.5$ Hz, $^3J(H_4H_5) = 7.0$ Hz, $^4J(H_2H_4) = 1.0$ Hz, 1H, H_4), 7.04 (apparent tdd, $^3J(H_2H_3) = {}^3J(H_3H_4) = 7.5$ Hz, $^4J(H_3H_5) = 1.5$ Hz, $^6J(H_3H_7) = 1.0$ Hz, 1H, H_3), 7.93 (dd, $^3J(H_2H_3) = 7.5$ Hz, $^4J(H_2H_4) = 1.0$ Hz, 1H, H_2). **4a′** ($R_{Ru}R_C$(NCS)) δ 1.27 (d, $^3J(H_7H_8) = 7.0$ Hz, 3H, $CH_3(8)$), 1.93 (s, 3H, $NCH_3(9)$), 3.29 (s, 3H, $NCH_3(10)$), 3.80 (qdd, $^3J(H_7H_8) = 7.0$ Hz, $^4J(H_5H_7) = 1.5$ Hz, $^6J(H_3H_7) = 1.0$ Hz, 1H, H_7), 5.32 (s, 6H, η^6-C_6H_6), 6.76 (apparent dt, $^3J(H_4H_5) = 7.0$ Hz, $^4J(H_3H_5) = {}^4J(H_5H_7) = 1.5$ Hz,1H, H_5), 6.98 (ddd, $^3J(H_3H_4) = 7.5$ Hz, $^3J(H_4H_5) = 7.0$ Hz, $^4J(H_2H_4) = 1.0$ Hz, 1H, H_4), 7.09 (apparent tdd, $^3J(H_2H_3) = {}^3J(H_3H_4) = 7.5$ Hz, $^4J(H_3H_5) = 1.5$ Hz, $^6J(H_3H_7) = 1.0$ Hz, 1H, H_3), 7.67 (dd, $^3J(H_2H_3) = 7.5$ Hz, $^4J(H_2H_4) = 1.0$ Hz, 1H, H_2). The relative intensities of the H_2 resonances (6.0:1:2.5) established the ratio of **4a:4b:4a′** as 63.2%:10.5%:26.3% or 73.7% ($S_{Ru}R_C$) species. $^{13}C\{^1H\}$ NMR(125 MHz, $CDCl_3$): **4a**: δ 10.4 (C_8), 49.7 (C_9), 53.4 (C_{10}), 69.7 (C_7), 87.9 (η^6-C_6H_6), 123.8 (C_5), 124.1 (C_4), 126.5 (C_3), 139.0 (C_2), 150.8 (C_6), 165.9 (C_1). **4a′**: δ 11.0 (C_8), 45.3 (C_9), 56.2 (C_{10}), 76.6 (C_7), 87.3 (η^6-C_6H_6), 123.2 (C_5), 123.4 (C_4), 127.2 (C_3), 139.9 (C_2), 150.0 (C_6), 172.5 (C_1). IR: (CH_2Cl_2 solution) ν(CN) 2120, 2090 cm^{-1} (shp, st); (Nujol) ν(CS) 805, 785, 750 cm^{-1} (w). UV−Vis: ($c = 5.5 \times 10^{-4}$ M in CH_2Cl_2 at 25 °C). λ_{max}, nm (ϵ, L mol^{-1} cm^{-1}) 403 (6.9×10^2). ($c = 1.1 \times 10^{-4}$ M in CH_2Cl_2). 228 (1.1×10^4), 250 (1.0×10^4). CD: $c = 5.5 \times 10^{-4}$ M in CH_2Cl_2 at 25 °C: λ_{max}, nm ($[\theta]_\lambda$, deg cm^2 dmol^{-1}) 600 (0), 426 (+12908), 352 (−13922), 306 (+1158).

5a,a′ (X = NCO). AgNCO was reacted with **1a,a′** in a 1:1 ratio, and the reaction was performed in the dark. After filtration of the reaction mixture through Celite and removal of the solvents on a rotary evaporator, the green and orange solid residue was dissolved in a minimum amount of CH_2Cl_2 and subjected to filtration chromatography over a short (∼7 × 2 cm^2) column of alumina which had been packed with a mixture of hexane and ether (1:1) and was eluted with CH_2Cl_2. This resulted in a dark green band (containing elemental ruthenium and organic impurities) at the top of the column and an orange band which moved with the solvent front. Solvents were removed from the eluant on a rotary evaporator, and the resulting yellow powder was dried under vacuum to yield 0.428 g (71%) (mp 180 °C, dec). Anal. Calcd for $C_{17}H_{20}N_2ORu$: C, 55.29; H, 5.42; N, 7.59. Found: C, 55.51; H, 5.27; N, 7.43. ^1H NMR (500 MHz, $CDCl_3$): **5a** (major) δ 1.16 (d, $^3J(H_7H_8) = 6.5$ Hz, 3H, $CH_3(8)$), 2.39 (s, 3H, $NCH_3(9)$), 3.20 (s, 3H, $NCH_3(10)$), 3.99 (q, $^3J(H_7H_8) = 6.5$ Hz, 1H, H_7), 5.27 (s, 6H, η^6-C_6H_6), 6.75 (d, $^3J(H_4H_5) = 7.0$ Hz, 1H, H_5), 6.94 (apparent td, $^3J(H_3H_4) = {}^3J(H_4H_5) = 7.0$ Hz, $^4J(H_2H_4) = 1.0$ Hz, 1H, H_4), 7.04 (apparent t, $^3J(H_2H_3) = {}^3J(H_3H_4) = 7.0$ Hz, 1H, H_3), 8.14 (dd, $^3J(H_2H_3) = 7.0$ Hz, $^4J(H_2H_4) = 1.0$ Hz, 1H, H_2). **5a′** (minor) δ 1.23 (d, $^3J(H_7H_8) = 6.5$ Hz, 3H, $CH_3(8)$), 2.44 (s, 3H, $NCH_3(9)$), 3.26 (s, 3H, $NCH_3(10)$), 3.77 (q, $^3J(H_7H_8) = 6.5$ Hz, 1H, H_7), 5.22 (s, 6H, η^6-C_6H_6), 6.74 (d, $^3J(H_4H_5) = 7.0$ Hz, 1H, H_5), 6.93 (apparent td, $^3J(H_3H_4) = {}^3J(H_4H_5) = 7.0$ Hz, $^4J(H_2H_4) = 1.0$ Hz, 1H, H_4), 7.07 (apparent t, $^3J(H_2H_3) = {}^3J(H_3H_4) = 7.0$ Hz, 1H, H_3), 7.67 (dd, $^3J(H_2H_3) = 7.0$ Hz, $^4J(H_2H_4) = 1.0$ Hz, 1H, H_2). The relative intensities of the two H_2 resonances (14.7 to 1) established the 87.2% de. $^{13}C\{^1H\}$ NMR(125 MHz, $CDCl_3$): **5a** (major) δ 9.9 (C_8), 49.2 (C_9), 52.7 (C_{10}), 68.7 (C_7), 86.9 (η^6-C_6H_6), 123.4 (C_5), 123.8 (C_4), 126.2 (C_3), 138.5 (C_2), 150.9 (C_6), 167.8 (C_1). IR: (CH_2Cl_2 solution) ν_a(NCO) 2223 cm^{-1} (st, br), ν_s(NCO) 1304 cm^{-1} (st, shp). UV−Vis: ($c = 9.1 \times 10^{-4}$ M in CH_2Cl_2 at 25 °C). λ_{max}, nm (ϵ, L mol^{-1} cm^{-1}) 410 (6.0×10^2). ($c = 8.0 \times 10^{-5}$ M in CH_2Cl_2 at 25 °C). 255 (1.1×10^4), 227 (1.4×10^4). CD: $c = 5.8 \times 10^{-4}$ M in CH_2Cl_2 at 25 °C: λ_{max}, nm ($[\theta]_\lambda$, deg cm^2 dmol^{-1}) 600 (0), 432 (+18581), 355 (−16951).

3. X-ray Data Collection and Processing. Suitable yellow plates of **2a**, **3a**, **4a**, and **5a** were obtained from $ClCH_2CH_2Cl$, CH_3OH/ether, CH_2Cl_2, and CH_2Cl_2/ether/hexane, respectively. They were mounted on glass fibers and placed on a Siemens P4 diffractometer. Intensity data were taken in the ω mode at 25 °C with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Three check reflections, monitored every 100 reflections, showed random (<2%) variation during the data collections. The data were corrected for Lorentz, polarization effects, and absorption (using an empirical model derived from azimuthal data collections). Scattering factors and corrections for anomalous dispersion were taken from a standard source.[20] Calculations were performed with the Siemens SHELXTL Plus (Version 5.03) software package on a PC. The structures were solved by direct methods. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were refined at calculated positions with a riding model in which the C−H vector was fixed at 0.96 Å. The CH_3OH hydrogen for **3a** was not included in the refinement. The data were refined by the method of full-matrix least squares on F^2. Final cycles of refinement converged to the $R(F)$ and $R\omega(F)$ values given in Table 1, where $\omega^{-1} = \sigma^2F + 0.001F^2$. Absolute configurations were determined by refinements of the Flack parameter.[21] The known absolute configuration of the benzylic carbon in **1a,a′**[7] also served as an internal reference in verifying the absolute configuration at the Ru(II) center in each of the complexes.

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Supporting Information Available: X-ray crystallographic files in CIF format for complexes **2a**, **3a**, **4a**, and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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