Aqueous Organometallic Chemistry. 2. ^{1}H NMR Spectroscopic, Synthetic, and Structural Study of the Chemo- and Diastereoselective Reactions of [Cp*Rh-$(H_2O)_3]^{2+}$ with Nitrogen Ligands as a Function of pH

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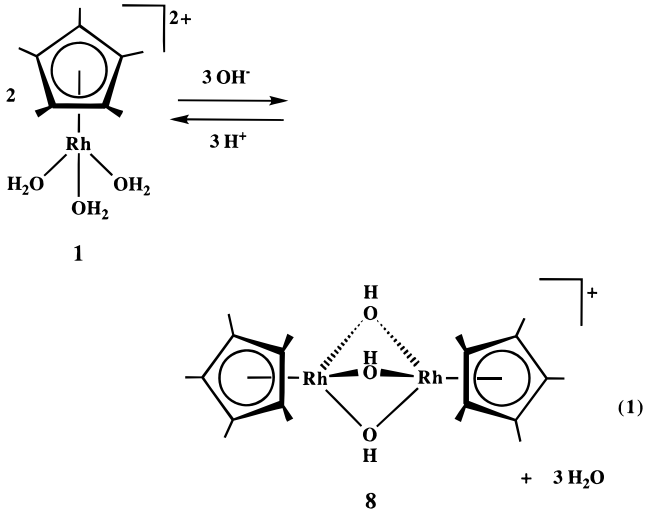
Received August 30, 1995[⊗]

The reactions of a new Cp*Rh aqua synthon, $[Cp^*Rh(H_2O)_3]^{2+}$ (**1**), at acidic pH values (2−6) with aniline (**2**), pyridine (**3**), and L-phenylalanine (**4**) have provided interesting chemo- and diastereoselectivities as studied by ^{1}H NMR, FAB/MS, and single-crystal X-ray crystallography. The reaction of **2** and aqua complex **1**, at pH values from 4 to 6, quantitatively provided $[Cp^*Rh(\eta^6\text{-aniline})]^{2+}$ (**5**); the structure of **5** was unequivocally determined by a single-crystal X-ray analysis, which also showed an approximate 25% η^5 component. Compound **3** reacted with **1**, at pH 2−6, to selectively provide $[Cp^*Rh(\eta^1\text{-pyridine})_n(H_2O)_{3-n}]^{2+}$ ($n = 1-3$) complexes **6a**−**c** as a function of pH. Surprisingly, complex **1** reacted with **4**, from pH 4 to 6, to provide only one diastereomer of the known cyclic trimer $[(Cp^*Rh)(\mu\text{-}\eta^1\text{-}(OCO)\text{:}\eta^2\text{-}(N,OCO)\text{-L- phenylalanine})]_3^{3+}$ (**7**; $S_C,S_C,S_C,S_{Rh},S_{Rh},S_{Rh}$), an example of a *one-step*, highly diastereoselective reaction in H_2O.

Recently, we elucidated the equilibrium between the Cp*Rh ($(\eta^5$-pentamethylcyclopentadienyl)rhodium) aqua complex $[Cp^*Rh(H_2O)_3]^{2+}$ (**1**) and $[(Cp^*Rh)_2(\mu\text{-}OH)_3]^+$ (**8**) by ^{1}H, ^{13}C, and ^{17}O NMR spectroscopy at pH values from 2 to 14 (eq 1).[2] In that study, we also determined the



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unequivocal structure of aqua complex **1** by X-ray crystallography. Thus, complex **1** appears to be a potential new synthon, at pH values <6, for the preparation of many types of Cp*Rh complexes with μ, η^1, η^2, η^6, etc. bonding modes, all in H_2O, a solvent of both biological and environmental compatibility. In this paper, we will describe an ^{1}H NMR, synthetic, and structural study of the H_2O-soluble nitrogen ligands **2**−**4** with aqua complex **1** as a function of pH and demonstrate that these various nitrogen ligands provide interesting chemo- and diastereoselectivities in aqueous solution.

Results and Discussion

Reactions of Complex 1 with Aniline (2) at pH Values of 2−6. Relatively few systematic studies have been reported on the reactions of Cp*Rh aqua complexes in H_2O with various ligands.[3] Maitlis and co-workers[3i] were the first to describe the reaction of aqua complex **8** with **2** in H_2O (pH ∼12). This reaction provided a poor yield of a μ-anilido complex, $[(Cp^*Rh)_2(\mu\text{-NHPh})(\mu\text{-OH})_2]^+$ (**9**). Furthermore, we have been studying the reactions of **1** and **8** with DNA/RNA bases and discovered that pH had a profound effect on the structures of the products formed.[3a−f] Therefore, we initially studied, by ^{1}H NMR spectroscopy, the reaction of **1** with **2** (eq 2) at pH 2−6 and found that this set of conditions exclusively provided $[Cp^*Rh(\eta^6\text{-aniline})]^{2+}$ (**5**)[4] (Figure 1).

Figure 1 clearly shows that as the pH is raised from 1.4 to 5.8 the formation of complex **5** increases, while

[⊗] Abstract published in *Advance ACS Abstracts*, March 15, 1996.

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(2) Eisen, M. S.; Haskel, A.; Chen, H.; Olmstead, M. M.; Smith, D. P.; Maestre, M. F.; Fish, R. H. *Organometallics* **1995**, *14*, 2806.

(3) (a) Smith, D. P.; Baralt, E.; Morales, B.; Olmstead, M. M.; Maestre, M. F.; Fish, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 10647. (b) Smith, D. P.; Olmstead, M. M.; Noll, B. C.; Maestre, M. F.; Fish, R. H. *Organometallics* **1993**, *12*, 593. (c) Smith, D. P.; Kohen, E.; Maestre, M. F.; Fish, R. H. *Inorg. Chem.* **1993**, *32*, 4119. (d) Smith, D. P.; Griffin, M. T.; Olmstead, M. M.; Maestre, M. F.; Fish, R. H. *Inorg. Chem.* **1993**, *32*, 4677. (e) Chen, H.; Maestre, M. F.; Fish, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 3631. (f) Chen, H.; Olmstead, M. M.; Smith, D. P.; Maestre, M. F.; Fish, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1514. (g) Kang, J. W.; Maitlis, P. M. *J. Organomet. Chem.* **1971**, *30*, 127. (h) Nutton, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1997. (i) Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2339.

(4) Espinet, P.; Baily, P. M.; Downey, R. F.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1980**, 1048.

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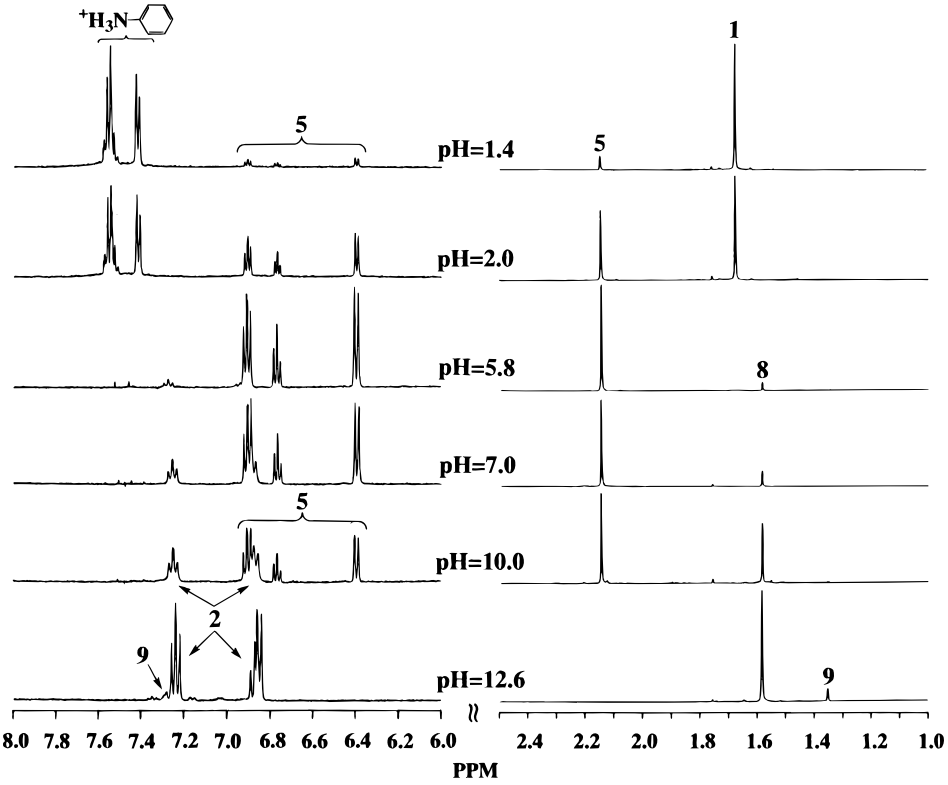
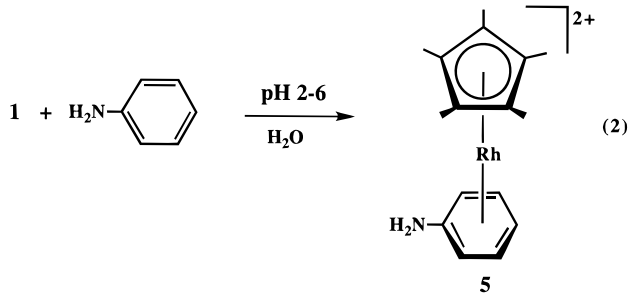


Figure 1. ^{1}H NMR spectral titration experiments for complex **5**, pH 1.4−12.6.



(2)

at higher pH values it decreases. The chemical shifts for the aromatic protons of free aniline are shifted to higher field upon complexation to the Cp*Rh group, indicating the formation of η^6 bonding.[5a] We attribute this efficient formation of η^6 bonding as a consequence of the increase in electron density to the aromatic ring from the powerful electron-donating H_2N group. In contrast, when the H_2N group is protonated at lower pH values (<2.0), the powerful electron-withdrawing H_3N^+ group causes a reversal of the reaction to the anilinium ion and **1**.

If we react complex **8**, formed exclusively at higher pH values (>7), with aniline, then only **8** and traces of the known complex $[(Cp^*Rh)_2(\mu\text{-NHPh})(\mu\text{-OH})_2]^+$ (**9**) are found; apparently complex **9** is not stable at these high pH values (Figure 1). However, when the pH is lowered back to 5.0, we again see the formation of **5** and the aqua complex **1**.

We were able to isolate complex **5** and determine its unequivocal structure by a single-crystal X-ray analysis (Tables 1 and 2 provide data for **5**), and Figure 2 shows the structure of **5**. In complex **5**, the Cp* and aniline groups are nearly parallel to one another; the angle between the normals to the planes of the five- and six-membered rings is 1.6°. Distances between the Rh atom and the ring carbons vary from 2.148(14) to 2.182(13) Å for the Cp* group and from 2.210(12) to 2.400(12) Å for the aniline group. However, the last distance of 2.400 Å is that of the amino-bonded carbon and is 0.166 Å longer than the average of the five other carbons of the six-membered ring. Reflecting this longer distance, the C(12)−C(11)−C(16) plane is tipped away from the

Table 1. Crystallographic Data for 5

compd	$[Cp^*Rh(aniline)](OTf)_2$
formula	$C_{18}H_{22}F_6NO_6RhS_2$
fw	629.40
a, Å	9.5272(7)
b, Å	13.9970(10)
c, Å	17.3226(6)
V, Å^3	2310.0(2)
Z	4
cryst syst	orthorhombic
space group	$P2_12_12_1$
T, K	130 (2)
λ, Å	1.54178
d(calcd), g/cm^3	1.810
2*θ* range, deg	8−114
μ(Mo Kα), mm^{-1}	8.460
range of transmissn factors	0.09−0.20
R1	0.0615
wR2	0.1558

Table 2. Selected Bond Distances (Å) and Angles (deg) for 5

Rh−C1	2.17(2)	Rh−C2	2.148(14)
Rh−C3	2.182(13)	Rh−C4	2.182(13)
Rh−C5	2.165(14)	Rh−C11	2.400(12)
Rh−C12	2.273(13)	Rh−C13	2.233(13)
Rh−C14	2.210(12)	Rh−C15	2.214(13)
Rh−C16	2.241(12)	N−C11	1.31(2)
N−C11−C12	121.8(13)	N−C11−C16	121.3(13)
C16−C11−C12	116.4(10)	C13−C12−C11	121.7(12)
C15−C16−C11	121.5(12)	C13−C14−C15	120.9(11)

(5) (a) Fish, R. H.; Baralt, E.; Kim, H.-S. *Organometallics* **1991**, *10*, 1965. (b) White, C. W.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1654.

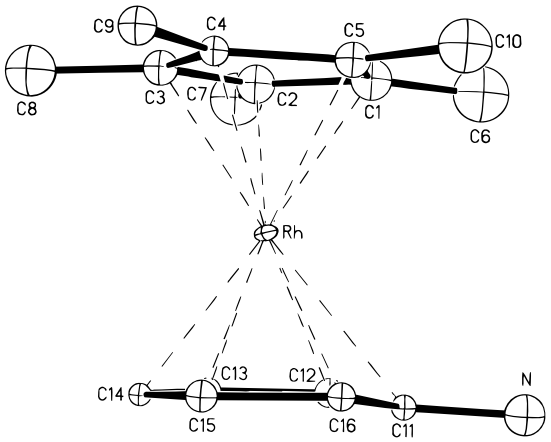


Figure 2. X-ray crystal structure of **5**.

Rh atom by 10.1° with respect to the plane of the five carbons C(12), C(13), C(14), C(15), and C(16). These structural parameters of **5** are consistent with an approximate 25% contribution from the η^5 component.[4] Furthermore, evidence for an η^5 component comes from the imino character of the C(11)-N bond (1.31 Å)[6] in the X-ray structure and the apparent lack of a coupling constant for the Rh−C(11) bond at 143 ppm in the ^{13}C NMR spectrum of **5** in D_2O (pH 5.0); it is interesting that this Rh−C(11) signal at 143 ppm is shifted ∼8 ppm upfield from the signal for free aniline, denoting η^6 bonding character.[5a]

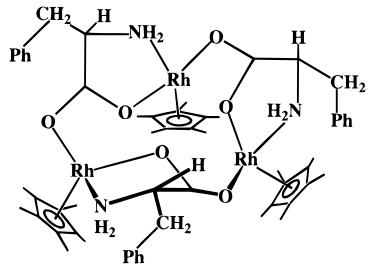
We compared the X-ray structural observations for **5** with results published by Maitlis et al.[4] for [Cp*Rh-(η^5-*N*-methylaniline)]$^{2+}$ (**10**). Although the structure of **10** was highly disordered, a slightly larger dihedral angle of ca. 13° was observed for the similar C(12)−C(11)−C(16) plane of **5**. Furthermore, the Rh atom of **5** is disposed almost symmetrically with respect to the planes of the five- and six-membered rings, with almost a straight line of 176.4° between the two ring centroids and Rh, while the Rh atom of **10** was displaced sideways with respect to the two-ring system, when it was viewed as a projection down the plane of the Cp* ring. This is probably due to the stronger electron-donating ability of the N−CH_3 group to the phenyl ring, thus causing increased C−N (1.28(4) Å) double-bond character in complex **10**. Therefore, we conclude that complex **10** possesses a larger η^5 bonding component than **5**.

Moreover, Maitlis et al.[4] also synthesized (from [Cp*Rh$(CH_3CN)_3$]$^{2+}$ in acetone) and then characterized **5**, by ^1H and ^{13}C NMR ($(CH_3)_2CO$-d_6) and IR spectroscopy, *as an* η^5 complex.[4] However, our IR data for **5** showed some discrepancies with those reported by Maitlis et al.[4] in terms of the C(ring)−N stretching frequencies. We observed a strong and characteristic C(ring)−N stretching band at 1282 cm^{-1}, whereas Maitlis reported a value of 1572 cm^{-1}.[4] Thus, on the basis of our total results, we prefer to assign **5** as an η^6 complex with the caveat that the structure has an ∼25% η^5 bonding component.

Reactions of Complex 1 with Pyridine (3) at pH Values of 2−6. Interestingly, reaction of **1** and **3** (in a 1:3 ratio) at pH 2−6 selectively provided η^1-pyridine complexes[5] [Cp*Rh(η^1-pyridine)$_n$$(H_2O)_{3-n}$]$^{2+}$ (n = 1−3; **6a**−**c**), as shown by ^1H NMR spectroscopy (Figure 3), depending on the pH of the solution. For example, at pH 2.2, the only complex observed was [Cp*Rh(η^1-pyridine)$(H_2O)_2$]$^{2+}$ (**6a**), while as the pH was raised to 5 [Cp*Rh(η^1-pyridine)$_2$$(H_2O)$]$^{2+}$ (**6b**) was predominant (**6b**/**6a**/**6c** = ∼65/29/6%), and at pH 6.6 both **6b** and **6c**, [Cp*Rh(η^1-pyridine)$_3$]$^{2+}$, were evident (**6b**/**6c** = ∼80/20%). Clearly, pH dictates selective substitution of the η^1-H_2O ligand by pyridine, and this represents a potentially powerful new synthetic approach to η^1 mono-, di-, or tri-ligand Cp*Rh complexes.

Reactions of Complex 1 with L-Phenylalanine (4) at pH Values of 4−6. More recently, Beck and co-workers studied the reactions of [(Cp*RhCl$_2$)]$_2$ with the amino acid L-phenylalanine (**4**) among others, *in methanol*, in the presence of a Ag^+ salt to provide both a mononuclear and a subsequently synthesized trinuclear (cyclic trimer) Cp*Rh complex from the above-mentioned mononuclear complex.[7] This latter cyclic trimer, [(Cp*Rh)(μ-η^1-(*OCO*):η^2-(*N*,*OCO*)-L- phenylalanine)]$_3^{3+}$ (**7**), one of several possible diastereomers (S_C,S_C,S_C,S_{Rh},S_{Rh},S_{Rh}), was assigned and characterized by X-ray crystallography. In solution, complex **7** was found to be an equilibrium mixture of two of all possible diastereomers, by ^1H NMR spectroscopy (MeOH-d_4), depending on the probe temperature; i.e., at −60 °C the ratio S_C,S_C,S_C,R_{Rh},R_{Rh},R_{Rh}/S_C,S_C,S_C,S_{Rh},S_{Rh},S_{Rh} was 36/64, while at 45 °C the ratio was 4/96 (1.81/1.66 ppm, Cp*).[7]

Since this process for the formation of **7** was stated to be an example of a chiral self-recognition process on the part of the Cp*Rh moiety,[7] we decided to study this interesting reaction of **4** with **1** in D_2O from pH 4 to 6 by ^1H NMR spectroscopy (Figure 4, pH 5.0 spectrum). *Importantly, we found that our one-step synthesis, in aqueous acidic solution, provided only one diastereomer,* ***7*** *(S_C,S_C,S_C,S_{Rh},S_{Rh},S_{Rh}, 1.57 ppm, Cp*); the other possible diastereomers were absent.*



7 $(S_cS_cS_cS_{Rh}S_{Rh}S_{Rh})$

In fact, a variable-temperature ^1H NMR experiment with **7** (S_C,S_C,S_C,S_{Rh},S_{Rh},S_{Rh}) in D_2O (pH 6), from 5 to 65 °C, showed no change in the diastereomer selectivity, the antithesis of the MeOH-d_4 NMR results. The diastereomer S_C,S_C,S_C,S_{Rh},S_{Rh},S_{Rh} appears to be more stable/favored in H_2O than the other possible diastereomers; e.g., S_C,S_C,S_C,R_{Rh},R_{Rh},R_{Rh}, possibly by virtue of the decreased interaction of the three benzyl groups on the asymmetric carbon atoms of **7** and favorable hydrogen bonding modes in D_2O.

Conclusions

We conclude that the utilization of the synthon, aqua complex **1**, represents a facile, one-step approach

(6) Courseille, C.; Geoffre, S.; Leroy, F.; Hospital, M. *Cryst. Struct. Commun.* **1974**, 583.

(7) Kramer, R.; Polborn, K.; Robl, C.; Beck, W. *Inorg. Chim. Acta* **1992**, *198*−200, 415 and references therein.

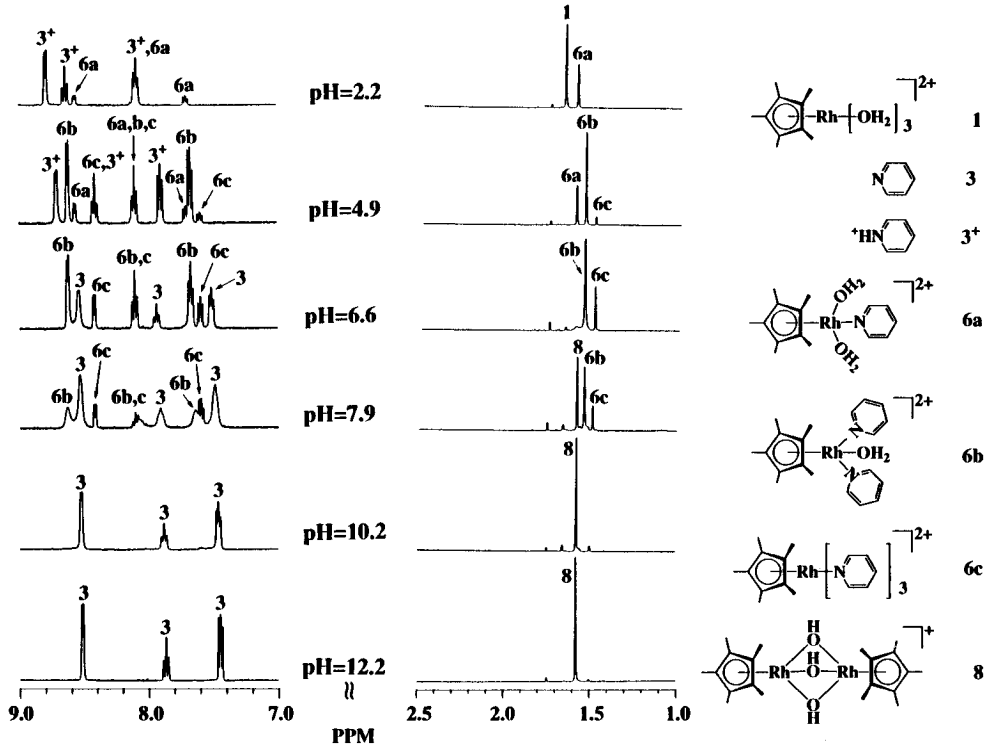


Figure 3. ^{1}H NMR spectral titration experiments for **6a**−**c**, pH 2.2−12.2.

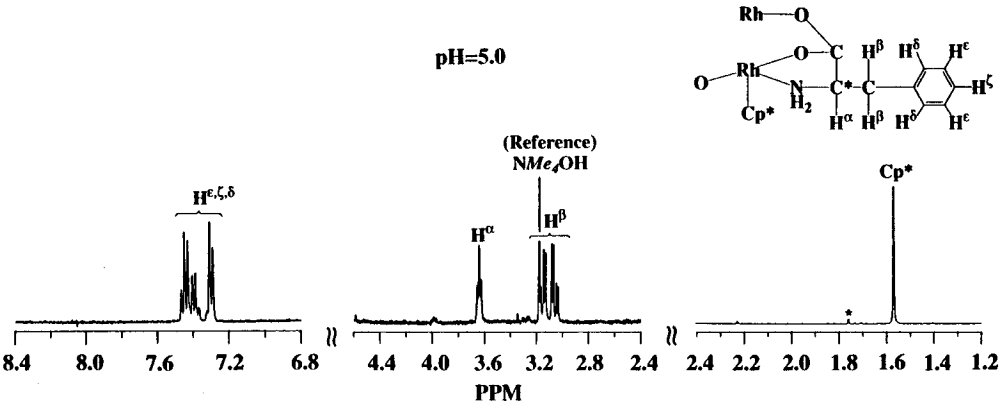


Figure 4. ^{1}H NMR spectra of **7**, pH 5.0. The starred peak denotes an impurity from the starting material.

to the synthesis of Cp*Rh complexes with a wide variety of bonding modes, as a function of pH. The use of H_2O as the environmentally safe solvent of choice is an important improvement over toxic organic solvents, while it allows an ease in isolation and crystallization of the products. Finally, we have demonstrated that complex **1**, with various water-soluble nitrogen ligands, provides high chemo- and diastereoselectivity at acidic pH values in excellent yields. We are in the process of studying the synthetic scope of synthon **1** with other water-soluble ligands, and we will report these results in future papers.

Experimental Section

General Procedures. Unless otherwise noted, all reactions and manipulations were conducted under an Ar/N_2 atmosphere in a Vacuum Atmospheres glovebox or using standard Schlenk techniques. The FT-IR spectra were determined as a solid (KBr matrix) in the mid-IR region (400−4000 cm^{-1}) with the use of a computer-controlled Nicolet Impact 400 FT-IR spectrometer. The 400 MHz ^{1}H NMR spectra, elemental analyses, and FAB/MS data were obtained at the Department of Chemistry, University of California, Berkeley, CA. All chemicals (highest purity available) were purchased from Aldrich Chemical Co. and used as received.

[Cp*Rh(η^6-aniline)](O_3SCF_3)$_2$ (5). To a solution of $[Cp^*RhCl_2]_2$ (200 mg, 0.32 mmol) in H_2O (40 mL) was added AgOTf (333 mg, 1.30 mmol) under an argon atmosphere. The reaction mixture was stirred at ambient temperature for 3 h, and then it was filtered. Then aniline (59 μL, 0.65 mmol) was added to the filtrate, and after it was stirred for 2 h at ambient temperature, the solution (measured pH 5.8) was evaporated *in vacuo* to leave a yellow solid of **5** in quantitative yield. A yellow crystal for X-ray structure analysis was obtained from ethanol/diethyl ether. ^{1}H NMR (400 MHz, D_2O, pH 5.8, 5 μL of 6×10^{-2} M Me_4NOH solution in D_2O as the internal reference with the methyl proton resonance set at 3.18 ppm, 25 °C, ppm, H_o = ortho H, H_m = meta H, H_p = para H): δ 6.91 (dd, $^3J_{H_o,H_m}$ = 6.6 Hz, $^3J_{H_m,H_p}$ = 6.6 Hz, 2H, Hm), 6.77 (t, $^3J_{H_m,H_p}$ = 6.6 Hz, 1H, H_p), 6.40 (d, $^3J_{H_o,H_m}$ = 6.6 Hz, 2H, H_o), and 2.15 (s, 15H, Cp*). ^{13}C NMR (Bruker AM400, D_2O, pH 6.0, 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid, sodium salt, as the internal standard, 25 °C, ppm): δ 89.0 (d, J_{C-Rh} = 4.7 Hz, C12/C16), 96.8 (d, J_{C-Rh} = 5.5 Hz, C14), 106.7 (d, J_{C-Rh} = 5.2 Hz, C13/C15), 111.8 (d, J_{C-Rh} = 8.0 Hz, C_5Me_5), 143.0 (s, C11); the C atom numbering is similar to that in Figure 2. IR (KBr,

cm^{-1}): NH_2, 3424; C(ring)—H, 3087; CH_3, 2926; C═C, 1572; C(ring)—N, 1282. FAB/MS (*m*-nitrobenzyl alcohol, *m*/*z* (relative intensity)): 480 (16%) [Cp*Rh(η^6-aniline) + OTf]$^+$; 331 (100%) [Cp*Rh(η^6-aniline) + e^-]$^+$; 166 (10%) [Cp*Rh(η^6-aniline)]$^{2+}$. Anal. Calcd for $C_{18}H_{22}F_6NO_6RhS_2$: C, 34.35; H, 3.53; N, 2.23. Found: C, 34.43; H, 3.73; N, 2.16.

The procedure for the NMR titration experiments (Figure 1) is as follows. Complex **5** was dissolved in argon-degassed D_2O (1 mL), and 5 μL of a 6×10^{-2} M $Me_4N(OH)$ solution in D_2O was used as the internal reference with the methyl proton resonance set at 3.18 ppm. The pH adjustments were carried out by adding the necessary amount of 0.65 M NaOD or 0.65 M CF_3SO_3D.

Cp*Rh(η^1-pyridine)$_n$(η^1-H_2O)$_{3-n}$](O$_3$SCF$_3$)$_2$ Complexes 6a—c. Samples of **6** for ^1H NMR analysis were prepared as follows: a solution of complex **1** (0.08 mmol) in D_2O (10 mL) was reacted with pyridine (0.243 mmol) and the mixture stirred for 2 h, after which a solution of Me_4NOH (50 μL) was added as an internal reference (pH 6.60). Then NMR samples (1 mL aliquots) were removed and the pH adjustments were carried out by adding the necessary amount of 0.65 M NaOD or 0.65 M CF_3SO_3D. See Figure 3 for ^1H NMR data concerning the substitution reactions of pyridine on complex **1** as a function of pH.

[(Cp*Rh)(μ-η^1-*OCO*:η^2-*N*,*OCO*)-L-phenylalanine)]$_3$(O$_3$SCF$_3$)$_3$ (7). To a solution of $[Cp^*RhCl_2]_2$ (25.0 mg, 0.04 mmol) in D_2O (5 mL) was added AgOTf (41.6 mg, 0.16 mmol) under an argon atmosphere. The reaction mixture was stirred at ambient temperature for 3 h, and then it was filtered. Then, L-phenylalanine (13.4 mg, 0.08 mmol) was added to the filtrate, and after all the L-phenylalanine was dissolved, the pH was adjusted to 5 by the addition of 0.1 N NaOD. After it was stirred for 1 h at ambient temperature, the solution was evaporated *in vacuo* to leave **7** in quantitative yield. ^1H NMR (400 MHz, D_2O, pH 5.0, 6×10^{-2} M Me_4NOH solution in D_2O as the internal reference with the methyl proton resonance set at 3.18 ppm, 25 °C, ppm): 7.5—7.2 (m, 15H, $H^{\epsilon,\xi,\delta}$), 3.64 (t, 3H, H^{α}), 3.2—3.0 (m, 6H, H^{β}), 1.57 (s, 45H, Cp*). FAB/MS (*m*-nitrobenzyl alcohol, *m*/*z*): 1203, [**7** − 3H]$^+$ (*R*(*I*) factor 0.008). Anal. Calcd for $C_{60}H_{75}F_9N_3O_{15}Rh_3S_3$: C, 43.57; H, 4.57; N, 2.54. Found: C, 43.30; H, 4.32; N, 2.50.

Samples of **7** for ^1H NMR analysis were prepared as follows: a solution of complex **1** (0.08 mmol) in D_2O (10 mL) was reacted with L-phenylalanine (0.08 mmol) and stirred for 2 h, after which a solution of Me_4NOH (50 μL) was added as an internal reference (pH 2.24). Then NMR samples (1 mL aliquots) were removed and the pH adjustments (4—6) were carried out by adding the necessary amount of 0.65 M NaOD or 0.65 M CF_3SO_3D. See Figure 4 for ^1H NMR data at pH 5.0 concerning the reaction of L-phenylalanine with complex **1**. In addition, verification of the NMR results in ref 7 of the diastereomer ratios in methanol, as a function of temperature, was also accomplished.

X-ray Data Collection, Solution, and Refinement of 5. The X-ray data for **5** were collected by using a Syntex $P2_1$ diffractometer equipped with an Enraf-Nonius low-temperature apparatus. All calculations were carried out on a MicroVAX 3200 computer using the SHELXS-86 program system. Crystals of **5** were transferred to a Petri dish and immediately covered with a layer of hydrocarbon oil. A single crystal was selected, mounted on a glass fiber, and immediately placed in a low-temperature N_2 stream.

Some details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information. The structure was solved in the space group $P2_12_12_1$ using direct methods. Hydrogen atoms were added geometrically and refined with a riding model. An absorption correction (XABS2)[8] was applied. The largest feature in the final difference map had a peak value of 3.094 e Å^{-3}. Selected bond distances and angles are listed in Table 2.

Acknowledgment. The studies at LBNL were generously supported by Laboratory Directed Research and Development Funds (R.H.F.), and the Department of Energy under Contract No. DE-ACO3-76SF00098. S.O. wishes to thank The Japan Scholarship Foundation for funds supporting this research between IMS and LBNL.

Supporting Information Available: Tables giving crystal data and data collection and solution and refinement details for **5**, tables of atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters for **5**, and Figures 5 and 6, giving a top view and the unit cell structure of **5** (11 pages). Ordering information is given on any current masthead page.

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(8) XABS2, an empirical absorption correction program: Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53.