Pyridine Adducts of Chiral Arene Ruthenium Compounds. Diastereoselective Synthesis and Characterization

J. W. Faller,* Brian J. Grimmond, and Michael Curtis

Yale University, Department of Chemistry, 225 Prospect Street, New Haven, Connecticut 06520

Received April 18, 2000

The compounds [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)L][SbF_6]$_2$, where Cy = *p*-$CH_3C_6H_4CH(CH_3)_2$; L = pyridine, **2**; 3,5-lutidine, **3**; isoquinoline, **4**, were synthesized by chloride abstraction from [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)Cl][SbF_6], **1**, followed by treatment of the intermediate Lewis acid [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)][SbF_6]$_2$ with the appropriate ligand. Characterization by elemental analysis, ^{1}H, ^{31}P{^{1}H}, VT NMR spectroscopy, and IR spectroscopy indicated that **2**−**4** were obtained as a mixture of *exo* and *endo* diastereomers (de = 14−60%). The endo diastereomer of compound **2** was also characterized by X-ray crystallography which revealed the (R_{Ru}*,R_C*) relative configuration of the two stereogenic centers within the molecule. In contrast to analogues with other neutral donors, ^{31}P{^{1}H} NMR spectroscopy experiments demonstrated that **2**−**4** were stable to diastereomer interconversion in solution. This suggests that epimerization of the ruthenium center in an intermediate *exo*-[CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)][SbF_6]$_2$ occurred by a path unavailable to **2**−**4** by inversion of the Ru-(η^2-$Ph_2PCH(Me)Ph_2PO$) ring.

Downloaded by NORTH CAROLINA CONSORTIUM on June 29, 2009
Published on November 1, 2000 on http://pubs.acs.org | doi: 10.1021/om000319s

Introduction

Organometallic ruthenium compounds are becoming increasingly important as catalysts of numerous organic reactions.[1] Furthermore, chiral arene ruthenium complexes are potentially capable of catalytic asymmetric synthesis, making them attractive synthetic targets.[2] One approach to the synthesis of such chiral compounds is to bind a heterobidentate auxiliary ligand to an arene−Ru−Cl fragment and thereby generate a stereogenic metal center.[3] Our research of heterobidentate complexes currently centers on the synthesis of bisphosphine monoxide [PP(O)] ligands[4] and an investigation of their unsymmetrical binding to arene−Ru precursors with applications of the resulting chiral complexes as Lewis acid catalysts in asymmetric synthesis.[5]

We have previously shown that *endo*-[CyRu(η^2-$Ph_2PCH(R)Ph_2PO$)Cl]SbF_6, where Cy = *p*-$CH_3C_6H_4CH(CH_3)_2$ and R = CH_3, **1**, is formed diastereoselectively upon treatment of $CyRuCl_2L$, L= the PP(O) ligand series (±)-$Ph_2PCH(R)Ph_2PO$, with 1 equiv of $AgSbF_6$. This diastereoselectivity was attributed to a preferential *endo* orientation of the PP(O) ligand substituent R, which places R remote to Cl so that steric interactions are minimized. Upon $AgSbF_6$ abstraction of the remaining chloride ligand from the metal center, the resulting electron-deficient species [CyRu(η^2-$Ph_2PCH(R)Ph_2PO$)-L′](SbF_6)$_2$ (L′ = free coordination site; solvent) could feasibly serve as a Lewis acid catalyst. However, since the PP(O) ligand was racemic, the observed diastereomer of the metal complex was also racemic and therefore usually considered unsuitable for catalytic asymmetric synthesis.

We are currently investigating a chiral poisoning strategy to avoid the need for resolution of the phosphine. Chiral poisoning typically involves deactivating one enantiomer of a racemic catalyst by its selective binding to an enantiopure chiral additive, prior to any given catalytic reaction.[1c,6] For this approach to be successful here, the additive must display sufficient selectivity for one antipode of the racemic catalyst, and the remaining nonracemic active catalyst should not be subject to rapid epimerization. This report describes initial attempts to study the extent of epimerization in the intermediate [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)L′][SbF_6]$_2$

(1) (a) Brunner, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1195−1208. (b) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97, (c) Faller, J. W.; Mazzieri, M. R.; Nguyen, J. T.; Parr, J.; Tokunaga, M. *Pure Appl. Chem.* **1994**, *66*, 1463. (d) Brunner, H. *Adv. Organomet. Chem.* **1980**, *18*, 151.

(2) (a) Kundig, E. P.; Saudan, C. M.; Bernardinelli, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1220. (b) Carmona, D.; Cativiela, C.; Elipe, S.; Lahoz, F. J.; Lamata, M. P.; Pilar, M.; de Viu, L. R.; Oro, L. A.; Vega, C.; Viguri, F. *Chem. Commun.* **1997**, 2351. (c) Davies, D. L.; Fawcett, J.; Garratt, S. A.; Russell, D. R. *Chem. Commun.* **1997**, 1351. (d) Davies, D. L.; Fawcett, J.; Krafczyk, R.; Russell, D. R. *J. Organomet. Chem.* **1997**, *546*, 581. (e) Mandal, S. K.; Chakravarty, A. R. *J. Chem. Soc., Dalton Trans.* **1992**, 1627. (f) Mandal, S. K.; Chakravarty, A. R. *J. Organomet. Chem.* **1991**, *417*, C59. (g) Faller, J. W.; Ma, Y.; Smart, C. J.; Diverdi, M. J. *J. Organomet. Chem.* **1991**, *420*, 237.

(3) Examples of heterodentate ligand complexes: (a) Hayashi, T. *J. Organomet. Chem.* **1999**, *576*, 195. (b) Singewald, E. T.; Shi, X. B.; Mirkin, C. A.; Schofer, S. J.; Stern, C. L. *Organometallics* **1996**, *15*, 3062. (c) Hayashi, T. *Acta Chim. Scand.* **1996**, *50*, 259. (d) Chooi, S. Y. M.; Leung, P.-h.; Mok, K. F. *Inorg. Chim. Acta* **1993**, *205*, 245. (e) Hayashi, T.; Uozumi, Y. *Pure Appl. Chem.* **1992**, *64*, 1911. (f) Vonmatt, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 566. (g) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27. (h) Uozumi, Y.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 9887.

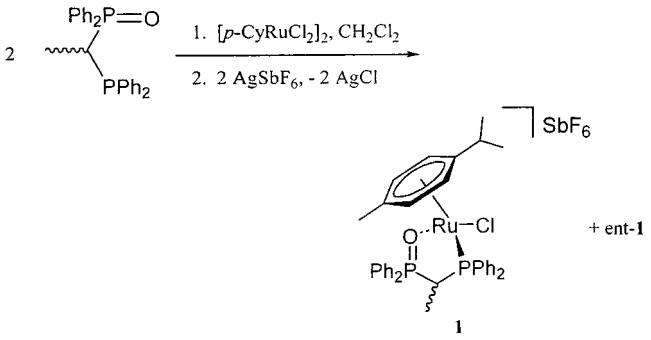
(4) Faller, J. W.; Patel, B. P.; Albrizzio, M. A.; Curtis, M. *Organometallics* **1999**, *18*, 3096.

(5) (a) Faller, J. W.; Liu, X.; Parr, J. *Chirality* **2000**, *12*, 325. (b) Faller, J. W.; Parr, J. *Organometallics* **2000**, *19*, 1829. (c) For a related example: Faller, J. W.; Smart, C. J. *Tetrahedron Lett.* **1989**, *30*, 1189.

(6) (a) Sablong, R.; Osborn, J. A.; Faller, J. W. *J. Organomet. Chem.* **1997**, *527*, 65. (b) Faller, J. W.; Liu, X. *Tetrahedron Lett.* **1996**, *37*, 3449. (c) Faller, J. W.; Sams, D. W. I.; Liu, X. *J. Am. Chem. Soc.* **1996**, *118*, 1217. (d) Faller, J. W.; Tokunaga, M. *Tetrahedron Lett.* **1993**, *34*, 7359. (e) Faller, J. W.; Parr, J. *J. Am. Chem. Soc.* **1993**, *115*, 804.

10.1021/om000319s CCC: $19.00 © 2000 American Chemical Society
Publication on Web 11/01/2000

Scheme 1. Preparation of Lewis Acid Precursors



(L′ = free coordination site or solvent) by trapping experiments with various pyridine bases. In the case of no bonding with the solvent, the intermediate would be coordinatively unsaturated. The isolated complexes [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)L][SbF_6]$_2$ (L = pyridine, **2**; 3,5-lutidine, **3**; isoquinoline, **4**) were characterized by standard techniques and found to exist as a mixture of two diastereomers, whose ratio varied with the base used.

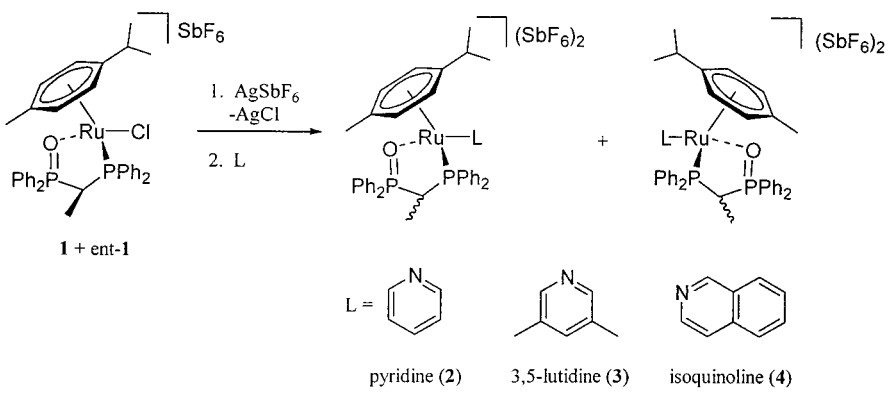
Results

Synthesis and Characterization of *endo*-[CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)Cl][SbF_6], 1. The previous synthesis of [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)Cl][SbF_6], **1**, from $(CyRuCl_2)_2$ and (±)-$Ph_2PCH(Me)Ph_2PO$ required the chromatographic isolation of the intermediate complex CyRu($Ph_2PCH(Me)Ph_2PO$)Cl_2 as a mixture of η^1 and η^2 isomers. Subsequent chloride extraction with 1 equiv of $AgSbF_6$ provided **1** as a single diastereomer. A more convenient one-pot synthesis involves the in situ formation of the intermediate η^1- and η^2-CyRu($Ph_2PCH(Me)Ph_2PO$)Cl_2 in CH_2Cl_2 followed by $AgSbF_6$ chloride extraction to afford **1** (Scheme 1). Filtration through Celite provided a clear red solution of crude **1**, which could then be isolated by chromatography (silica/EtOAc). Characterization of **1** by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy verified that the *endo* diastereomer was obtained in good yield (86%).

Synthesis of [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)L][SbF_6]$_2$ [L = py, 2; 3,5-lutidine, 3; isoquinoline, 4]. The $AgSbF_6$ extraction of the remaining chloride ligand from **1** in CH_2Cl_2 provided the Lewis acid [CyRu($Ph_2PCH(Me)Ph_2PO$)L′][SbF_6]$_2$, which was observed by $^{31}P\{^1H\}$ NMR spectroscopy but not isolated. The generation of the Lewis acid was further evidenced by the formation of an AgCl precipitate and an orange-colored solution. After stirring at ambient temperature, the AgCl byproduct was removed by filtration through Celite to afford a clear orange solution. As shown in Scheme 2, quenching of the in situ Lewis acid with an excess of the appropriate pyridine bases provided the corresponding pyridine adducts [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)L][SbF_6]$_2$ (L = pyridine, **2**; lutidine, **3**; isoquinoline, **4**). The formation of compounds **2**−**4** was demonstrated by the prompt formation of clear yellow-orange solutions, which were then stirred for 12 h. The addition of pentane to the crude reaction mixtures precipitated the pyridine adducts as yellow solids or oils, which were then isolated and washed with pentanes. Drying in vacuo typically gave analytically pure samples of **2** and **4** as yellow powders. Compound **3** required further washing with Et_2O to remove excess 3,5-lutidine and provide **3** as an Et_2O solvate, as established by ^1H NMR spectroscopy. Compounds **2**−**4** were characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, IR spectroscopy, and elemental analysis. The $^{31}P\{^1H\}$ NMR data for the compounds, which are summarized in Table 1, illustrated that whereas **1** was obtained as a single diastereomer, the base adducts **2**, **3**, and **4** were produced as an unequal mixture of diastereomers. While compounds **2**−**4** were soluble in common chlorinated solvents and aromatic hydrocarbons, they proved insoluble in aliphatic hydrocarbons and Et_2O. In the solid state, **2**−**4** were obtained as yellow powders which were stable upon prolonged exposure to air. However, exposure of solutions of **2**−**4** to air resulted in their gradual decomposition. This was marked by a color change from yellow to blue over a period of days.

Characterization of [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)py][SbF_6]$_2$, 2. The addition of pyridine to [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)L′][SbF_6]$_2$ gave [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)py][SbF_6]$_2$, **2**, as two diastereomers in a ratio of 1.00:1.32 (de = 14%). This was established most conveniently by $^{31}P\{^1H\}$ NMR spectroscopy (Table 1), where each diastereomer was represented by a set of AX doublets. A crystalline sample of **2** suitable for study by X-ray diffraction was obtained from a CH_2Cl_2/Et_2O solvent system. An ORTEP representation of **2** is presented in Figure 1, with relevant crystallographic data and selected bond lengths and angles summarized in Tables 2 and 3, respectively. As shown in Figure 1, the η^2 binding of the racemic (±)-$Ph_2PCH(Me)Ph_2PO$ ligand to the Ru center created two stereogenic sites located at the Ru center and the methyne carbon C(11)

Scheme 2 . Preparation of Pyridine Adducts



Downloaded by NORTH CAROLINA CONSORTIUM on June 29, 2009
Published on November 1, 2000 on http://pubs.acs.org | doi: 10.1021/om000319s

Table 1. $^{31}P\{^1H\}$ NMR Data for [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)Cl][SbF_6] (1) and [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)L][SbF_6]$_2$ [L = Pyridine (2), 3,5-Lutidine (3), Isoquinoline (4)]

	major diastereomer			minor diastereomer			
L	P(O)	P	$^2J_{PP}$ (Hz)	P(O)	P	$^2J_{PP}$ (Hz)	de (%)
Cl (**1**)[a]	66.50 (d)	49.00 (d)	27.5				100
py (**2**)[a]	73.70 (d)	57.33 (d)	30.4	73.04 (d)	54.82 (d)	29.4	14
lut (**3**)[b]	73.81 (d)	56.35 (d)	29.7	75.14 (d)	58.81 (d)	31.3	60
iso (**4**)[a]	73.42 (d)	56.93 (br)	29.2	72.45 (d)	54.20 (d)	27.6	50

[a] Data recorded at ambient temperature on a GE OMEGA 300 or 500 MHz and referenced to external H_3PO_4(aq). [b] Data recorded on a Bruker 400 MHz spectrometer.

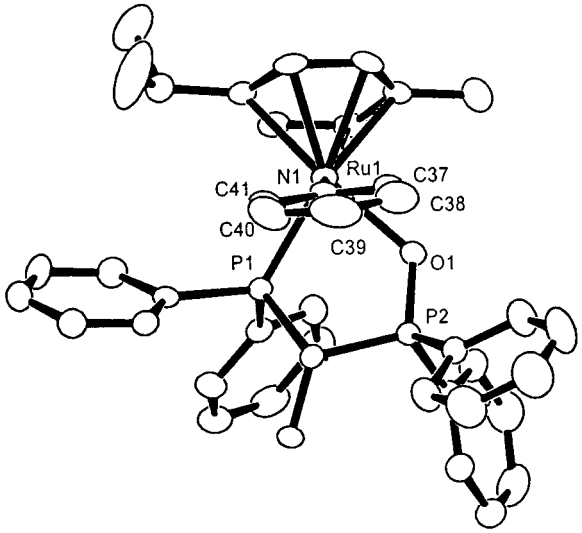


Figure 1. ORTEP representation of [CyRu(η^2-$Ph_2PCH(Me)Ph_2P(O)py$][SbF_6]$_2$ (**2**) with 50% probability ellipsoids.

Table 2. Crystallographic Data for X-ray Diffraction Study of [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)L][SbF_6]$_2$, 2

formula	$Sb_2Ru_2P_2F_{12}OC_{41}H_{43}$
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	12.6033(3)
b, Å	20.7488(5)
c, Å	17.2835(4)
β, deg	102.307(1)
V, Å^3	4415.8(2)
fw	1200.30
ρ_{calcd}, g/cm^3	1.805 (Z = 4)
abs coeff (cm^{-1})	17.07
cryst size, mm	0.05 × 0.15 × 0.17
diffractometer	Nonius KappaCCD
monochromator	graphite
radiatn	Mo Kα (0.71073 Å)
max 2 Å, deg	55
no. of refl measd	27 628 (unique 10 157)
data used, $F^2 > 3\sigma(F^2)$	5950
no. of params refined	541
p factor	0.02
final residuals R, R_w	0.035; 0.034
convergence, largest shift/error	0.00
GOF	1.24
largest + $\Delta(\rho)$, e Å^{-3}	0.56

of the ligand backbone. The Ru center was also η^6-bound to the ancillary Cy ligand and η^1-bound to the pyridine ligand to maintain a pseudo-octahedral geometry. Only one of the two possible diastereomers was observed in the isolated crystalline sample with a R_{Ru}*,R_C* relative configuration of the two stereocenters present. In agreement with the structurally related benzaldehyde complex [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)C_6H_5CHO][SbF_6]$_2$, the PP(O) ligand contained a *endo* methyl substituent, with the methyl oriented toward the Cy ring and away from the pyridine donor ligand.[4] Additionally, it was noted in the analogous benzaldehyde complex that when benzaldehyde was η^1-coordinated to the Ru center, it was tilted with P−Ru−O−C and O−Ru−O−C dihedral angles of 153.4(2)°, ϕ(1), and 70.7(2)°, ϕ(2), respectively. The difference from perfect alignment (0°) was [180 − ϕ(1)] } = 26.6° and indicated a clear bias in the orientation of the O=C π plane to facilitate alignment with the Ru−P bond. This has been proposed to accommodate favorable metal−benzaldehyde dπ−pπ* interactions in agreement with literature precedents.[7] In contrast, for **2**, the P(1)−Ru(1)−N(1)−C(37), ϕ(1), and O(1)−Ru(1)−N(1)−C(37), ϕ(2), dihedral angles of 128.2° and 48.2°, respectively, with [180 − ϕ(1)] = 51.8 illustrated that the pyridine ligand π-plane was not significantly canted toward either the Ru(1)−P(1) or Ru(1)−O(1) bonds.[8]

Table 3. Selected Bond Distances (Å) and Angles (deg) for [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)L][SbF_6]$_2$, 2

Ru(1)	P(1)	2.360(1)	Ru(1)	N(1)		2.128(3)
Ru(1)	O(1)	2.141(3)	P(2)	O(1)		1.528(3)
P(1)	Ru(1)	O(1)	80.16(8)	P(1)	Ru(1)	N(1)	90.93(9)
N(1)	Ru(1)	O(1)	84.0(1)	Ru(1)	O(1)	P(2)	165.9(3)

This lack of alignment with the Ru(1)−P(1) or Ru(1)−O(1) bonds can be seen in Figure 1. Metrically, this can perhaps be appreciated more fully by consideration of a difference in angles $\Delta\phi' = |\phi(2) - [180 - \phi(1)]|$. For the pyridine complex, the difference between P(1)−Ru(1)−N(1)−C(37), ϕ(1), and O(1)−Ru(1)−N(1)−C(37), ϕ(2), respectively, yields a $\Delta\phi'$ of only 3.6°. In contrast, the $\Delta\phi' = 44.1°$ for the aldehyde complex indicates the bias for O=C π*-orbital alignment with the Ru(1)−P(1) bond.

The unit cells of several randomly selected crystalline samples of **2** were examined by X-ray crystallography and found to be that of the *endo* diastereomer of **2**. It was then assumed that the crystalline sample in hand was that of diastereoenriched *endo*-**2**. The remaining crystals of *endo*-[CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)py][SbF_6]$_2$, **2**, were dissolved in methylene chloride-d_2 and characterized by NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum indicated the predominance of one diastereomer (δ 73.04, 54.82; PO, P) (dr = 5:1) with minor amounts of the resonances corresponding to the second diastereomer (δ 73.70, 57.33; PO, P). The signals for the major diastereomer in solution were assigned to *endo*-**2**, which

(7) (a) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592−598. (b) Huang, Y. H.; Gladysz, J. A. *J. Chem. Educ.* **1988**, *65*, 298−303. (c) Dalton, D. M.; Fernandez, J. M.; Emerson, K.; Larsen, R. D.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9198−9212. (d) Gladysz, J. A.; Boone, B. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 51−583.

(8) It is possible that the orientation of the pyridine ring parallel to the *p*-Cy aromatic plane may occur despite the favorable Ru−py dπ−pπ* interaction in the solid state owing to the need to minimize the overriding steric interactions between the pyridine and *p*-Cy ring.

Downloaded by NORTH CAROLINA CONSORTIUM on June 29, 2009
Published on November 1, 2000 on http://pubs.acs.org | doi: 10.1021/om000319s

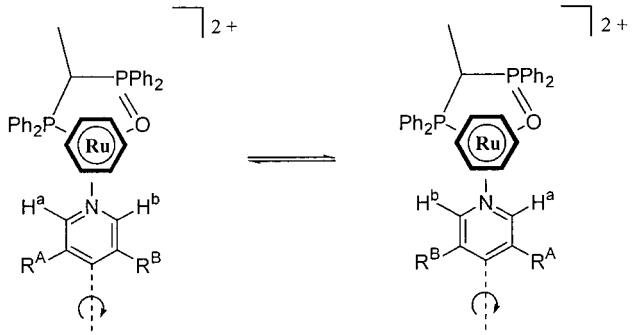


Figure 2. Plane view of [CyRu(η^2-$Ph_2PCH(Me)Ph_2P(O)L$]-$[SbF_6]_2$ (L = py (**2**), lut (**3**)) illustrating the rotation of the pyridine ligand ring about the Ru−N bond. The ligand rotation leads to exchange of the inequivalent *ortho*-protons H^a and H^b and exchange of the inequivalent *meta* substituents R^a and R^b [L = H (**2**), Me (**3**)]. Note that the substituents on the Cy ring have been removed for clarity.

Downloaded by NORTH CAROLINA CONSORTIUM on June 29, 2009
Published on November 1, 2000 on http://pubs.acs.org | doi: 10.1021/om000319s

was observed in the X-ray diffraction study. This was made under the confident assumption that, when redissolved, *endo*-**2** was not subject to instantaneous inversion of stereochemistry at the metal center to produce the alternative diastereomer *exo*-**2**. The minor signals observed were then assigned to *exo*-**2**. It should be noted that the comparison of the $^{31}P\{^1H\}$ NMR spectra of diastereoenriched *endo*-**2** (dr = 5:1) to the crude reaction mixture of *exo*/*endo*-**2** indicated that the major diastereomer of the crude product (dr = 3:4) was in fact *exo*-**2**. On standing for 1 week at ambient temperature under an inert atmosphere, the NMR sample of *endo*-**2** was reexamined by $^{31}P\{^1H\}$ NMR spectroscopy. The *endo*/*exo* diastereomer peak ratio was essentially identical to that obtained originally, indicating negligible metal center epimerization under these conditions. Furthermore, the ratio of diastereomers remained intact when the same NMR solution of **2** was treated with a large excess of pyridine. This again demonstrated that the stereochemistry of the metal center was stable, even in the presence of a potential ligating base.

The ^1H NMR spectrum of *endo*-**2** displayed the expected resonances; the Cy ligand signals were particularly diagnostic of diastereoenriched **2**. Four Cy aromatic proton signals were observed, in addition to a methyl singlet, two diastereotopic *i*-Pr doublets, and one *i*-Pr methine septet. The resonance for the potentially inequivalent *ortho* protons of the pyridine ring was not obscured by the aryl-phosphine protons. The fact that one resonance for the *ortho* protons δ 8.6 was obtained suggested that, at ambient temperature, the pyridine ligand was subject to rapid rotation about the Ru−N bond axis (Figure 2).[9] As can be seen in Figure 2, rapid rotation of the pyridine ring leads to exchange of the inequivalent *ortho* protons, labeled H^a and H^b, to provide the averaged *ortho* proton signal observed. Upon cooling the methylene chloride-d_2 solution of *endo*-**2** to the solvent low-temperature limit of −80 °C, only the time-averaged signal was observed. This indicated that the H^a and H^b sites were still in the fast exchange regime at −80 °C ($\Delta G^‡ < 10.7$ kcal mol^{-1}). (In all of the cases we will discuss we assume that rotation about the ruthenium−arene bond is rapid.)

Characterization of [CyRu(η^2-$Ph_2PCH(Me)Ph_2$-PO)lut][SbF_6]$_2$, 3. Treatment of the Lewis acid [CyRu-(η^2-$Ph_2PCH(Me)Ph_2PO)L'$][SbF_6]$_2$ with an excess of 3,5-lutidine provided the adduct [CyRu(η^2-$Ph_2PCH(Me)Ph_2$-PO)lut][SbF_6]$_2$, **3**, as a mixture of *endo* and *exo* diastereomers. In contrast with the pyridine analogue **2**, the $^{31}P\{^1H\}$ NMR spectrum of **3** revealed a distinct diastereoselectivity in the binding of the Lewis acid complex to the sterically demanding lutidine ligand (Table 1). The major diastereomer obtained with a dr = 4:1 was presumed to be the *endo* form because this provided minimal steric conflict between the bulky 3,5-lutidine and the methyl substituent of the PP(O) ligand.

In methylene chloride-d_2 the ^1H NMR spectrum of **3** displayed resonances for the Cy ligand which were similar to those described for **2**. Additionally, a singlet of relative intensity six was noted at δ 1.86 and assigned to the lutidine methyl protons. The observation of a single resonance indicated that the lutidine ring was also subject to rapid rotation (Figure 2) and time averaging at ambient temperature, in a manner similar to that observed for **2**. However, when cooled to −80 °C, the inequivalent lutidine methyl groups (Me^a and Me^b in Figure 2) could be distinguished as two separate resonances at δ 1.93 and 1.75, each of relative intensity three. On heating to ambient temperature in 10 °C increments, the methyl resonances broadened ($T_I = -70$ °C, $\Delta G^‡ = 11.3$ kcal mol^{-1}) and eventually coalesced ($T_c = -30$ °C, $\Delta G^‡ = 11.8$ kcal mol^{-1}) to provide a time-averaged methyl resonance of relative intensity six.[10] This fluxional behavior was consistent with exchange of the inequivalent methyl sites (L^a and L^b in Figure 2) upon rotation of the bulky 3,5-lutidine ligand about the Ru−N bond axis.

Characterization of [CyRu(η^2-$Ph_2PCH(Me)Ph_2$-PO)isoquinoline][SbF_6]$_2$, 4. A combination of ^1H and $^{31}P\{^1H\}$ NMR spectroscopy indicated that the Lewis acid [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO)L'$][SbF_6]$_2$ demonstrated the moderate diastereoselectivity when binding to isoquinoline (dr = 3:1, Table 1). The ^1H chemical shifts of the Cy ligands for the *exo* and *endo* isomers of **2**, **3**, and **4** were nearly identical. This suggests that the *exo* diastereomer was the major isomer of **4**. Similar to the AX spin patterns obtained for **2** and **3**, the $^{31}P\{^1H\}$ NMR spectrum for compound **4** revealed four resonances at ambient temperature, consistent with the presence of two diastereomers in a ratio of 3:1. The resonances for the minor diastereomer appeared as two typical AX doublets (δ 71.69, d; 53.49, d; $^2J = 29.2$ Hz). However, the AX spin system signals for the major diastereomer (δ 72.71, d, $^2J = 28.8$ Hz; 56.20, br) were observed as a doublet and a broad resonance, which indicated that an exchange phenomenon was taking place. To examine this process, a methylene chloride-d_2 solution of **4** was characterized by $^{31}P\{^1H\}$ VT and ^1H VT NMR spectros-

(9) Hapticity interconversion between ruthenium(II) complexes, such as CpRu(II)(η^6-py) and CpRu(II)(η^1-py)$(CH_3CN)_n$, has been observed to occur only in the coordinating solvent CD_3CN. (a) Fish, R. H.; Kim, H. S.; Fong, R. H. *Organometallics* **1991**, 10(3), 770. (b) Fish, R. H.; Kim, H. S.; Fong, R. H. *Organometallics* **1989**, *8*, 1375. Given the lack of readily available coordination sites at the Ru center in **2**, the VT ^{1}HNMR spectroscopy, and the low solvating characteristics of CD_2Cl_2, it is unlikely that a similar reversible haptatropic shift of the coordinated pyridine ring could take place here.

(10) Faller, J. W. In *Encyclopedia of Inorganic Chemistry*; King, R. B. Ed.; John Wiley and Sons: New York, 1994; p 3914. Mann, B. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergammon: New York, 1982; Vol. 3, Chapter 20.

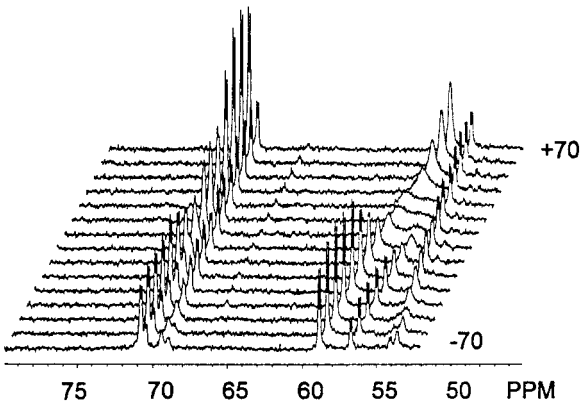


Figure 3. $^{31}P\{^1H\}$VT NMR spectrum of [CyRu(η^2-Ph_2-PCH(Me)Ph_2P(O)iso][SbF_6]$_2$ (**4**) from −70 to 70 °C. On cooling from 70 °C, the resonances for the P(V) and P(III) nuclei of the each diastereomer broadened and decoalesced into two AX doublets with a ratio of 2.1:1.0. This VT behavior was attributed to the exchange of two conformational isomers for each diastereomer of **4** in a ratio of 2.1:1.0.

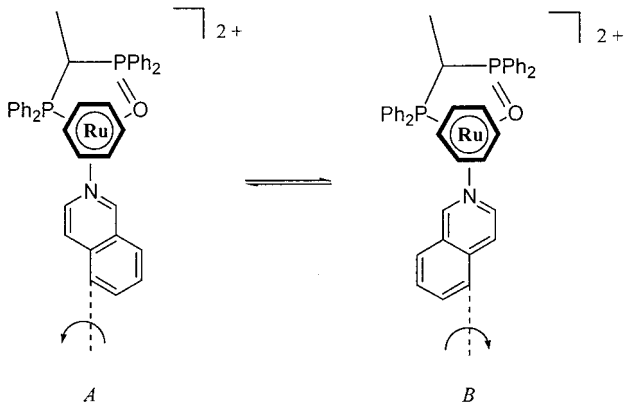


Figure 4. Plane view of [CyRu(η^2-PhPCH(Me)Ph_2P(O)-iso][SbF_6]$_2$ (**4**) illustrating the exchange of the conformation isomers of **4**. The unsymmetrical isoquinoline ligand can bind to the Ru center with ring 2 of isoquinoline oriented toward the Ph_2P(O) or Ph_2P substituents, generating two conformers, *A* and *B*, respectively. Rotation of the isoquinoline ligand leads to the interconversion of the two conformational isomers. The steric interaction of the isoquinoline ligand with aryl phosphine groups disfavors the formation of conformer *B*.

Downloaded by NORTH CAROLINA CONSORTIUM on June 29, 2009
Published on November 1, 2000 on http://pubs.acs.org | doi: 10.1021/om000319s

copy; the $^{31}P\{^1H\}$VT NMR spectra are presented in Figure 3. Upon cooling to −70 °C, the two ambient-temperature signals representing the P(V) and P(III) nuclei of the major diastereomer each resolved into two sets of AX doublets. In the region of the P(V) nuclei, the ratio between the two doublets (δ 72.91, 72.50) was 2.2:1.0. Similarly for the P(III) region, two doublets (δ 58.05, 55.38) of relative intensity 2.2:1.0 were observed. These data indicated that two inequivalent forms of the major diastereomer were present and in rapid exchange with one another. Furthermore, because the intensities of the signals for the exchange partners were inequivalent, i.e., 2.2:1.0, it is obvious that one of the two conformers of the major diastereomer of **4** was present in a greater amount. As illustrated in Figure 4, the two conformers presumably arise from two possible orientations of the unsymmetrical η^1-isoquinoline ligand to the chiral Ru metal center in relation to the phosphine−phosphine oxide ligand. Furthermore, it is likely that the dominant conformer *A* (δ 72.91, d; 58.05, d; ^2J = 29.5 Hz) was the sterically preferred isomer, where the arene isoquinoline ring was accommodated in the large Ru−O=PPh_2 pocket. The minor conformer *B* (δ 72.50, d; 55.38, d; ^2J = 31.5 Hz) involved greater steric interaction of the isoquinoline moiety with the phenyl groups of the adjacent PPh_2 functionality. On heating to ambient temperature in 10 °C increments, the conformer P(V) and P(III) resonances broadened (T_I = −30 °C, $\Delta G^{\ddagger}$ = 13.6 kcal mol^{-1} major → minor;) and eventually coalesced (P(V) T_c = 0 °C, P(III) T_c = 40 °C) to provide P(V) and P(III) averaged resonances.[11]

As shown in Figure 3, at −70 °C two conformers of the minor diastereomer were also observed. Both the P(V) and P(III) signals of the minor diastereomer were separated into two signals, which appeared to be poorly resolved doublets. Integration of these resonances indicated that the ratio of the two conformers observed was approximately 2.0:1.0. Upon warming in 10 °C increments from −80 °C, the onset of line broadening due to exchange between the two conformers of the minor diastereomer was initially observed at T_I = − 70 °C, indicating an activation energy for rotation of $\Delta G^{\ddagger}$ ∼11.3 kcal mol^{-1}. The resonances for the conformers of the minor diastereomer coalesced at P(V) T_C = − 50 °C, P(III) T_C = −40 °C.

Discussion

Source of Diastereoselectivity for *exo*/*endo*-[CyRu(η^2-Ph_2PCH(Me)Ph_2PO)L][SbF_6]$_2$. The adducts *exo*/*endo*-[CyRu(η^2-Ph_2PCH(Me)Ph_2PO)L][SbF_6]$_2$ (L = py, **2**; lut, **3**; iso, **4**) were synthesized, and trapped as their kinetic products, by quenching the intermediate [CyRu(η^2-Ph_2PCH(Me)Ph_2PO)L′][SbF_6]$_2$, L′ = solvent or a free coordination site) with the appropriate base. When the unsubstituted pyridine was bound to the metal center, there was low *exo*/*endo* differentiation owing to a negligible Me···py steric interaction. This, in fact, culminated in the formation of a slight excess of *exo*-**2** (de = 14%). However, when binding to more sterically encumbered bases such as 3,5-lutidine, a significant diastereoselectivity (dr = 4:1) was observed. The substituents on these substituted pyridines would appear to be remote for direct interactions with other

(11) The ^{1}H variable-temperature NMR data of **4** was consistent with rotation of the isoquinoline ligand about the Ru−N bond axis. At ambient temperature, the downfield resonances for the isoquinoline ligand (δ > 8.5 ppm) were not observed owing to rapid conformational exchange. However, upon cooling to −80 °C, two isoquinoline resonances (δ 9.03, s; 9.92, s) were observed in a ratio of 1.0:0.3, respectively. These signals were tentatively assigned to the isolated *ortho*-isoquinoline proton of the major and minor conformers of *endo*-**4**, respectively, on the basis of chemical shift, multiplicity, and intensity. Irradiation of the resonance (δ 9.03), which corresponded to the major conformer of *endo*-**4**, resulted in saturation transfer to the resonance (δ 9.92) assigned to the minor conformer of *endo*-**4**, verifying that the two protons were exchange partners. A further resonance (δ 9.20, d, J = 6.1 Hz, relative intensity 1.0) was also detected at −80 °C. This was assigned to the remaining *ortho*-isoquinoline proton of endo-**4** on the basis of its chemical shift, multiplicity, and intensity. Irradiation of this proton indicated that its exchange partner, i.e. the *ortho*-isoquinoline proton of the minor conformer of *endo*-**4**, was located within the main body of the aryl region. We attempted to confirm that the major conformer of *endo*-**3** had the second aryl ring of the isoquinoline ligand oriented toward the P=O functional group (conformer *B* in Figure 4). However, line selective irradiation of the *ortho*-isoquinoline protons failed to provide satisfactory NOE effects to neighboring phosphine aryl protons as evidence for this assignment.

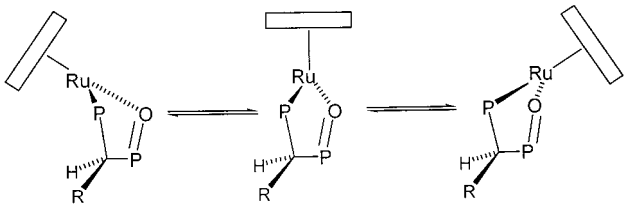


Figure 5. Illustration of the proposed mechanism for the interconversion of the *exo* and *endo* diastereomers of the Lewis acid [CyRu(η^2-$Ph_2PCH(Me)Ph_2P(O)$][SbF_6]$_2$. A cyclopentane-type ring inversion mechanism can account for the exchange between the two diastereomers.

ligands in the vicinity of the metal. Nevertheless, it would appear that some more remote steric interactions with the ancillary ligands are minimized, which yields a preference for the *endo* diastereomer for L = lutidine and the *exo* isomer for the L = isoquinoline. The Me···py steric interaction should be similar for all cases, if the pyridine ring is oriented in the same way. Other interactions may force a different preferred orientation of the ring than that observed in **2** and thus influence the diastereomer preference via modulation of the Me···py steric interaction. Attempts to unambiguously assign the diastereomers by Overhauser effects with ^{1}H NMR spectroscopy were inconclusive.

Mechanism of *exo*/*endo* Diastereomer Interconversion. When *endo*-**1** was converted to the Lewis acid *endo*-[CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)L′][SbF_6]$_2$ (L′ = solvent, vacant site), the generation of the coordination site at the Ru center led to the epimerization of the Lewis acid and yielded a mixture of *exo* and *endo* diastereomers (Figure 5). As discussed previously, there were at least two possible dissociation mechanisms that could cause complex epimerization. The first involved hemilability of the η^2-(PPO) ligand probably occurring via dissociation of the P(O) donor from the metal center to create a transient free coordination site at the metal center. This hemidissociation would be followed by rotation of the η^1-PP(O) ligand about the Ru−P bond axis and finally reassociation of the dangling P(O) functional group to the metal center. Inverting the PP(O) binding to the Ru center would invert the metal center stereochemistry and consequently interconvert *exo* and *endo* diastereomers. An alternative mechanism for diastereomer epimerization required dissociation of any labile solvent or substrate molecule (S) from the metal center to create a vacant site. This could facilitate a five-membered ring inversion of the CyRu[η^2-$Ph_2PCH(Me)Ph_2PO$] moiety (Figure 5), effecting diastereomer interconversion upon reassociation of a labile ligand S.

On trapping the Lewis acid species [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)][SbF_6]$_2$ with various pyridines, the corresponding adducts **2**−**4** were obtained as a mixture of *exo* and *endo* diastereomers, indicating that diastereomer interconversion can occur prior to binding of the pyridine ligand. For compound **2**, a diastereoenriched sample of endo-**2** in 67% de was obtained by fractional recrystallization and monitored by NMR spectroscopy over a period of weeks. It was observed that *endo*-**2** was stable to epimerization over this time, suggesting that a mechanism involving P(O) dissociation was unlikely. This can be surmised because if P(O) dissociation were to be the source of epimerization, diastereoenriched **2** would also undergo epimerization via P(O) hemidissociation/reassociation to provide an equilibrium mixture of *exo*/*endo* diastereomers.

Significantly, an *exo*/*endo* mixture of **2** (de = 14%) did not exhibit any change in the *exo*/*endo* ratio under the same conditions. This would tend to eliminate the possibility that an initial kinetic product of *exo*/*endo*-**2** (de = 14%) was interconverting during a fractional recrystallization to a thermodynamic product ratio of predominantly *endo*-**2**.

Thus it appears that the compound *endo*-**2** was stable to epimerization because the pyridine ligand was not subject to dissociation[12] and not because it was a thermodynamic product of diastereomer interconversion.[13] Dissociation of the pyridine ligand was necessary to provide the coordinately unsaturated Lewis acid, which only then could undergo epimerization through an η^2-PP(O) ring inversion mechanism.

Fluxionality and Nonrigid Behavior of [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)L][SbF_6]$_2$. The pyridine adducts **2**, **3**, and **4** displayed temperature-dependent NMR behavior associated with rotation of the appropriate η^1-pyridine ligand about the Ru−N bond. For compound **2**, the rate of ligand rotation was sufficiently rapid that the inequivalent pyridine *ortho* protons were subject to fast exchange averaging at −80 °C ($\Delta G^{\ddagger}$ < 10.7 kcal mol^{-1}). However, the bulkier amine ligands 3,5-lutidine and isoquinoline slowed the rate of Ru−N ligand rotation that it could be observed by VT NMR spectroscopy in the slow exchange regime. For compound **3**, the exchange of the inequivalent 3,5-lutidine methyl groups was observed at temperatures above −70 °C ($\Delta G^{\ddagger}$ = 11.8 kcal mol^{-1}), whereas exchange between two conformers of the isoquinoline adduct **3** was observed at temperatures greater than −33 °C, $\Delta G^{\ddagger}$ = 13.6 kcal mol^{-1}. Each exchange process was facilitated by rotation of the pyridine ligand about the Ru−N bond, which has particular relevance to the application of complexes [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)S][SbF_6]$_2$ (S = free coordination site, substrate) to Lewis acid-catalyzed asymmetric synthesis. The VT NMR spectroscopy study discussed here indicated that ligands bound to the Ru(II) metal center undergo rapid rotation about the Ru−ligand bond axis. For unsymmetrical ketone, aldehyde, or imine substrates η^1-bound to and activated by the same metal complex, ligand rotation similar to that observed for **2**−**4** exposes different diastereotopic π-faces of the ligand to attack by external reagents. Thus, it is likely that adjustments would be necessary to control the rotation of bound prochiral substrates in order to improve diatereofacial discrimination during any asym-

(12) Recent examples of Ru complexes involving bidentate ligand conformer interconversion upon prior dissociation of a labile monodentate ligand include: (a) Slugovc, C.; Simanko, W.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1999**, *18*, 3865. (b) Asano, H.; Katayama, K.; Kurosawa, H. *Inorg. Chem.* **1996**, *35*, 5760. (c) Therrien, B.; Ward, T. R. *Angew. Chem., Int. Ed.* **1999**, *38*, 405. (d) Ward, T. R.; Schafer, O.; Daul, C.; Hofmann, P. *Organometallics* **1997**, *16*, 3207. Pyridine and phosphine complexes of chiral Schiff base Ru(II)−arene cations have been synthesized previously and isolated as a mixture of diastereomers. The ^{1}H NMR and CD spectroscopy data suggested that the metal center was not subject to epimerization. Although not addressed directly, this was presumably also due to the inert nature of the complexes with pyridine or phosphine ligands. Mandal, S. K.; Chakravarty, A. R. *J. Chem. Soc., Dalton Trans.* **1992**, 1627.

(13) A recent case of thermodynamic versus kinetic control of stereochemistry in chiral arene−Ru(II) compounds can be found in: Davenport, A. J.; Davies, D. L.; Fawcett, J.; Garratt, S. A.; Russell, D. R. *Chem. Commun.* **1999**, 2331.

Downloaded by NORTH CAROLINA CONSORTIUM on June 29, 2009
Published on November 1, 2000 on http://pubs.acs.org | doi: 10.1021/om000319s

metric reaction. It should be noted that the conformational preference exhibited by [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)C_6H_5CHO][SbF_6]$_2$ in the solid state would expose one face of the carboxaldehyde to reagent attack if it were maintained in solution.[14] With minimal conversion to the other conformer via Ru−O bond rotation, a significant degree of enantioselectivity could be anticipated with an enantiopure catalyst. Further studies into solution and solid-state binding of ketones and aldehydes are under investigation.

Conclusion

The chiral compounds [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)L][SbF_6]$_2$ [L = py, **2**; 3,5-lutidine, **3**; isoquinoline, **4**] were synthesized as a mixture of *exo* and *endo* diastereomers from *endo*-[CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)Cl][SbF_6]. For pyridine, no significant selectivity was observed in the formation of the complex. With increasing steric bulk of the pyridine ligand (L) the diastereoselectivity increased up to 4:1 dr. The mixture of diastereomers obtained indicated that the intermediate Lewis acid *exo*-[CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)][SbF_6]$_2$ was subject to *exo*/*endo* conversion prior to quenching with the appropriate pyridine. Epimerization of the Lewis acid is believed to occur via a ring inversion mechanism.

Experimental Section

The reactions were carried out using standard inert atmosphere techniques where necessary. The solvents CH_2Cl_2 and pentane were distilled from CaH_2 prior to use and degassed by three freeze−pump−thaw cycles where necessary. Reagent grade Et_2O, isoquinoline, and $AgSbF_6$ (Aldrich) were used without further purification. Silica gel was purchased from EM Separation Technologies and was used as received. The compounds $(CyRuCl_2)_2$[15] and (±)-$Ph_2PCH(Me)Ph_2PO$[16] were prepared according to literature procedures. Pyridine and 3,5-lutidine (Aldrich) were distilled from KOH and stored over KOH prior to use. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on GE Omega 300 or 500 MHz instruments and on a Bruker 400 MHz spectrometer at 25 °C unless stated otherwise. The deuterated solvents $CDCl_3$ and CD_2Cl_2 (Aldrich) were stored over molecular seives and used without purification. The ^1H NMR chemical shifts for the major diastereomers of **2**, **3**, and **4** are fully reported along with the detected resonances for the minor diastereomers. The relative intensities of the protons for each diastereomer of compounds **2**, **3**, and **4** do not reflect the ratio between the diastereomers (Table 1). IR spectra were recorded on a MDAC M-1200 spectrometer.

Synthesis of [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)Cl][SbF_6], 1. In a glovebox, a Schlenk tube was charged with (±)-($Ph_2PCH(Me)POPh_2$ (0.83 g, 2.0 mmol) and transferred to a Schlenk line, where it was evacuated for 10 min and backfilled with N_2. A sample of $(CyRuCl_2)_2$ (0.30 g, 0.46 mmol) was dissolved in degassed CH_2Cl_2 (15 mL), and the solution was introduced by syringe into the Schlenk tube to give a red solution. The reaction mixture was stirred for 10 min, and then $AgSbF_6$ (0.31 g, 0.92 mmol) in CH_2Cl_2 (5 mL) was added, which immediately produced a cloudy red solution. After stirring for 12 h, the reaction mixture was filtered through Celite, the Celite cake was washed with CH_2Cl_2 (5 mL), and the filtrates were combined as a clear red solution. The solvent was removed in vacuo to afford a red solid, which was redissolved in a minimal amount of CH_2Cl_2 (0.5 mL) and chromatographed on silica, eluting with EtOAc. An orange band was isolated and the solvent removed in vacuo to provide **1** as an orange powder (0.61 g, 86% yield). $^{31}P\{^1H\}$ NMR is given in Table 1. The ^1H NMR was in agreement with literature values.[4]

Synthesis of [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)C_5H_5N][SbF_6]$_2$, 2. A Schlenk tube was charged with $AgSbF_6$ (0.04 g, 0.11 mmol) and **1** (0.10 g, 0.11 mmol), wrapped in foil to exclude light, and attached to a vacuum line in a darkened fume hood. The vessel was evacuated for 10 min and backfilled with N_2. Upon addition of CH_2Cl_2 (10 mL), a cloudy red solution was obtained and stirred for 1 h. The reaction mixture was filtered through Celite, and the Celite pad was washed with CH_2Cl_2 (5 mL). The filtrates were then combined to give a clear red solution. An aliquot of freshly distilled pyridine (0.22 mL, 2.6 mmol) was introduced by syringe, producing a yellow-orange solution, which was then stirred for 1 h. The solvent was reduced in vacuo to ∼4 mL and pentane (10 mL) added by syringe to afford a cloudy yellow solution, which was stored at −20 °C. Filtration of the reaction mixture by cannula gave a yellow residue, which was washed with pentane (3 × 2 mL) and dried in vacuo to give **2** as a yellow powder (0.09 g, 65% yield). Anal. Calcd for $C_{41}H_{43}NOF_{12}RuSb_2$: C, 41.03. H, 3.61. Found: C, 41.04. H, 3.71. IR (CH_2Cl_2, 20 °C): $\nu_{(P=O)}$ 1121 cm^{-1}. ^1H NMR (CD_2Cl_2, 300 MHz, δ): *endo* diastereomer: 8.14 (m, py−*H*), 8.04−7.40 (m, Ar−*H*), 7.10 (app-t, 2 H, J = 6.8 Hz, Ar−*H*), 6.15 (d, 1 H, J = 6.2 Hz, Cy C*H*), 6.05 (d, 1 H, J = 6.2 Hz, Cy C*H*), 6.00 (d, J = 6.2 Hz, Cy C*H*), 5.43 (d, 1 H, J = 6.2 Hz, Cy C*H*), 2.95 (m, 1 H, C*H*Me), 2.76 (spt, 1 H, J = 6.8 Hz, Cy C*H*Me$_2$), 2.08 (s, 3 H, Cy C*H*$_3$), 1.29 (d, J = 6.8 Hz, Cy CHC*H*$_3$), 1.26 (d, 3 H, J = 6.8 Hz, Cy CHC*H*$_3$) 1.11 (m, 3 H, CHC*H*$_3$). *exo* diastereomer: 8.04−7.40 (m, Ar-*H*), 6.85 (app-t, 2 H, J = 7.4 Hz, Ar-*H*), 6.39 (dd, 2 H, J = 11.4, 8.2 Hz, Ar-*H*), 5.86 (d, 1 H, J = 6.2 Hz, Cy C*H*), 5.41 (obs d, 1 H, J = 6.2 Hz, Cy C*H*) 4.97 (d, 1 H, J = 6.2 Hz, Cy C*H*), 4.58 (m, 1 H, C*H*Me), 1.73 (spt, 1 H, J = 6.9 Hz Cy C*H*Me$_2$), 1.44 (s, 3 H, Cy CHC*H*$_3$), 1.11 (m, 3 H, CHC*H*$_3$), 0.98 (d, 3 H, J = 6.9 Hz, Cy CHC*H*$_3$) 0.88 (d, 3 H, J = 6.9 Hz, Cy CHC*H*$_3$). Note one Cy C*H* proton (δ 5.31 ppm) was obscured by the residual CH_2Cl_2 peak.

Synthesis of [CyRu(η^2-$Ph_2PCH(Me)Ph_2PO$)η^1-C_7H_9N], 3. In a glovebox, a Schlenk tube was charged with $AgSbF_6$ (0.04 g, 0.11 mmol) and **1** (0.10 g, 0.11 mmol), wrapped in foil to exclude light, and transferred to a Schlenk line in a darkened fume hood. The vessel was evacuated for 10 min and backfilled with N_2. Upon addition of CH_2Cl_2 (5 mL), a cloudy red solution was obtained and stirred for 0.5 h. The reaction mixture was filtered through Celite, and the Celite pad was washed with CH_2Cl_2 (5 mL). The filtrates were then combined to give a clear red solution. An aliquot of freshly distilled 3,5-lutidine (0.15 mL, 1.3 mmol) was added by syringe to give an orange solution, which was then stirred for 12 h. The solution volume was reduced to ∼3 mL, precipitating a gray solid which was removed from the reaction mixture by syringe filtration of the solution. Pentane (5 mL) was added by syringe, resulting in the separation of an oil from which the remaining solution was removed by syringe. The oily residue was washed with pentane (5 mL) and dried in vacuo to give crude **3** as a yellow powder. ^1H NMR analysis of the powder revealed the presence of **3** and excess 3,5-lutidine, which could not be removed on further washing with pentanes or extended drying in vacuo. Compound **3** was then washed with Et_2O (3 H 5 mL) to remove the 3,5-lutidine and provide **3** as an Et_2O solvate as established by ^1H NMR spectroscopy (0.09 g, 65% yield). Anal. Calcd for $C_{43}H_{47}NOF_{12}RuSb_2(Et_2O)_{0.5}$: C, 42.71 H, 4.14. Found: C, 42.70 H, 4.13. IR (CH_2Cl_2, 20 °C): $\nu_{(P=O)}$ 1120 cm^{-1}. ^1H NMR (CD_2Cl_2, 400 MHz, δ): *endo* diastereomer: 8.29−7.27 (m, Ar−*H*),

(14) Gladysz, J. A.; Boone, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 550.

(15) Bennett, M. A.; Huang T. N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth.* **1982**, *21*, 74.

(16) (a) Visseaux, M.; Dormond, A.; Baudry, D. *Bull. Soc. Chim. Fr.* **1993**, *130*, 173. (b) Higgins, S. J.; Taylor, R.; Shaw, B. L. *J. Organomet. Chem.* **1987**, *325*, 285. (c) Grim, S. O.; Satek, L. C.; Tolman, C. A.; Jesson, J. P. *Inorg. Chem.* **1975**, *14*, 656.

Downloaded by NORTH CAROLINA CONSORTIUM on June 29, 2009
Published on November 1, 2000 on http://pubs.acs.org | doi: 10.1021/om000319s

6.12 (d, 1 H, J = 6.2 Hz, Cy C*H*), 6.09 (d, 1 H, J = 6.2 Hz, Cy C*H*), 5.95 (d, 1 H, J = 6.2 Hz, Cy C*H*), 5.37 (d, 1 H, J = 6.2 Hz, Cy C*H*), 3.40 (q, J = 7.0 Hz, Et_2O CH_2), 2.97 (m, 1 H, C*H*CH_3), 2.80 (spt, 1 H, J = 7.0 Hz, Cy C*H*Me_2), 2.06 (s, 3 H, Cy CH_3), 1.88 (s, 6 H, lut CH_3), 1.33 (d, 3 H, J = 7.0 Hz, Cy CHCH_3), 1.30 (d, 3 H, J = 7.0 Hz, Cy CHCH_3), 1.15 (t, J = 7.0 Hz, Et_2O CH_3), 1.09 (m, 3 H, CHCH_3). *exo* diastereomer: 8.29−7.27 (m, Ar−*H*), 6.85 (td, 2 H, J = 7.8, 2.6 Hz, Ar−*H*), 6.37 (dd, 2 H, J = 11.4, 8.6 Hz), 6.01 (d, 1 H, J = 6.3 Hz, Cy C*H*), 5.90 (d, 1 H, J = 6.3 Hz, Cy C*H*), 5.42 (d, 1 H, J = 6.3 Hz, Cy C*H*), 4.99 (d, 1 H, J = 6.3 Hz, Cy C*H*), 4.52 (m, 1 H, C*H*CH_3), 1.76 (spt, 1 H, J = 6.8 Hz, Cy C*H*Me_2), 1.47 (s, 3 H, Cy CH_3), 1.09 (m, 3 H, CHCH_3) 0.99 (d, 3 H, J = 6.8 Hz, Cy CHCH_3), 0.86 (d, 3 H, J = 6.8 Hz, Cy CHCH_3).

Synthesis of [CyRu(η^2-Ph_2PCH(Me)Ph_2PO)C_9H_7N], 4. In a glovebox, a Schlenk tube was charged with $AgSbF_6$ (0.04 g, 0.11 mmol) and **1** (0.10 g, 0.11 mmol), wrapped in foil to exclude light, and transferred to a Schlenk line in a darkened fume hood. The vessel was evacuated for 10 min and backfilled with N_2. Upon addition of CH_2Cl_2 (10 mL), a cloudy red solution was obtained and stirred for 1 h. The reaction mixture was filtered through Celite, and the Celite pad was washed with CH_2Cl_2 (5 mL). The filtrates were then combined to give a clear red solution. An aliquot of isoquinoline (0.03 g, 0.52 mmol) dissolved in CH_2Cl_2 (1 mL) was added by syringe to the reaction mixture and stirred for 1 h. The resulting clear yellow solution was reduced in volume to ∼3 mL and pentane (10 mL) added by syringe to precipitate a yellow residue. The solution was removed by syringe and the remaining yellow residue washed with pentane (2 H 5 mL) before drying in vacuo to give **4** as a yellow solid (0.05 g, 37% yield). Anal. Calcd for $C_{45}H_{45}NOF_{12}RuSb_2$: C, 43.23 H, 3.63. Found: C, 42.82 H, 3.89. IR (CH_2Cl_2, 20 °C): $\nu_{(P=O)}$ 1121 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 500 MHz, 40 °C, δ): *endo* diastereomer: 8.25−7.32 (m, Ar-*H*), 6.27 (d, 1 H, J = 6.2 Hz, Cy C*H*), 6.13 (d, 1 H, J = 6.2 Hz, Cy C*H*), 6.02 (d, 1 H, J = 6.2 Hz, Cy C*H*), 5.49 (d, 1 H, J = 6.2 Hz, Cy C*H*), 3.00 (m, 1 H, C*H*Me), 2.68 (spt, J = 6.9 Hz, Cy C*H*Me_2), 2.17 (s, 3 H, Cy CH_3), 1.27 (d, 3 H, J = 6.9 Hz, Cy CHCH_3), 1.24 (d, 3 H, J = 6.9 Hz, Cy CHCH_3), 1.02 (m, 3 H, CHCH_3). *exo* diastereomer: 9.36 (br, iso-*H*) 8.58 (br, iso-*H*), 8.25−7.32 (m, Ar−*H*), 6.83 (br, Ar−*H*), 6.55 (td, 2 H, J = 7.9 Hz, 2.6 Hz, Ar−*H*), 6.35 (dd, 2 H, J = 10.9, 8.3 Hz, Ar−*H*), 5.99 (d, J = 6.3 Hz, Cy C*H*), 5.52 (d, J = 6.5 Hz, Cy C*H*), 5.47 (d, 1 H, J = 6.5 Hz, Cy C*H*), 5.05 (d, 1 H, J = 6.3 Hz, Cy C*H*), 4.59 (m, 1 H, C*H*Me), 1.80 (spt, 1 H, J = 6.6 Hz, Cy C*H*Me_2), 1.47 (s, 3 H, Cy CH_3), 1.17 (m, 3 H, CHCH_3), 0.97 (d, 3 H, J = 6.6 Hz, Cy CHCH_3), 0.83 (d, 3 H, J = 6.6 Hz, Cy CHCH_3).

X-ray Crystallography. Orange crystals of [CyRu(η^2-Ph_2-PCH(Me)Ph_2PO)C_5H_5N], **2**, suitable for X-ray diffraction were obtained from a very slow crystallization from 1:1 CH_2Cl_2/Et_2O solution of **2** at −5 °C. Crystallographic data are summarized in Table 2. The structures were determined from data collected with a Nonius KappaCCD at −90 °C. Lorentz and polarization corrections were applied to all data. An empirical absorption correction was applied using SORTAV.[17] Intensities of equivalent reflections were averaged. The structure was solved by heavy-atom Patterson and difference Fourier methods using the teXan crystal structure analysis package, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. Hydrogen atoms were placed at calculated positions before each refinement and were included in the refinement, but were not refined.

Acknowledgment. This research was supported by grants from the National Science Foundation (CHE-9726423) and the Petroleum Research Fund administered by the American Chemical Society.

Supporting Information Available: Tables of crystal data, positional and thermal parameters, and bond lengths and angles for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000319S

(17) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.

Downloaded by NORTH CAROLINA CONSORTIUM on June 29, 2009
Published on November 1, 2000 on http://pubs.acs.org | doi: 10.1021/om000319s