Contribution to the Chemistry of Metal Complexes with Stereogenic Metal Centers: Diastereoselective Formation of Ruthenium Half-Sandwich Complexes

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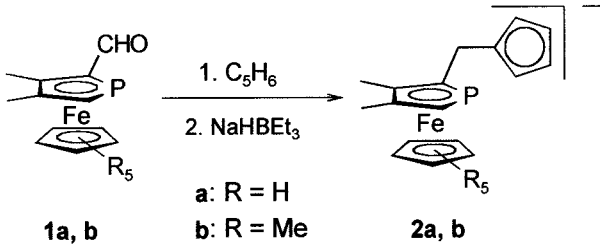
Received December 4, 2000

The chiral half-sandwich complexes **3** and **4** are formed with high diastereoselectivities in the reaction of cyclopentadienides **2a**,**b**, bearing tethered phosphaferrocene donor moieties with planar chirality, and $[(PPh_3)_3RuCl_2]$ in toluene at 90 °C. The diastereoisomers of the Cp complex **3** are obtained in a 95:5 ratio, whereas for the Cp* derivative **4** only one isomer is detectable, the structure of which has been determined by X-ray diffraction. Substitution of the chloride ligand in **4** by other anionic (H^-, I^-) or neutral (H_2, py) ligands proceeds stereospecifically in all cases. In contrast, conversion of the chlorides **3a**,**b** (95:5) to the respective hydrides **9a**,**b** proceeds with complete epimerization at Ru. In $CHCl_3$ the 1:1 mixture of hydrides **9a**,**b** is reconverted to the chlorides to give a kinetically controlled 4:1 mixture of isomers **3a**,**b**. Equilibration of this mixture in toluene at 90 °C restores the original ratio of isomers of 95:5, which we therefore believe to reflect the thermodynamically controlled value. The cationic H_2 complex **7**, generated via Cl abstraction from **4** in the presence of H_2, was characterized to be a η^2-dihydrogen complex by measuring the T_1 value of the coordinated H_2 ligand.

Introduction

The selective formation of chiral nonracemic metal complexes is a challenging goal in coordination chemistry with potential implications for enantioselective catalysis. The proper choice of chiral ligands plays a crucial role in the "predetermination of metal chirality", a term recently coined by von Zelewsky.[1] One topic that has received increasing attention over the last few years is the formation of chiral half-sandwich complexes, in which a cyclopentadienyl ligand is tethered to an additional donor function.[2] Several attempts have been made to introduce an element of chirality into this type of Cp−L chelate ligand in order to enable a diastereoselective complexation reaction, and ruthenium complexes $Cp-LRu(PR_3)X$ have been studied in particular detail.[3] In this contribution we wish to report our results in the stereoselective formation of ruthenium complexes using the chiral Cp−P chelate ligands **2** (Scheme 1).

Scheme 1



Results and Discussion

Synthesis of Half-Sandwich Complexes 3 and 4. On the basis of our previous work on chiral phosphaferrocene chelate ligands,[4] we have launched a research project to explore the coordination chemistry of the cyclopentadienyl anion **2a**, which is easily prepared as its Na salt in a two-step procedure starting from aldehyde **1a**, and the formation of the homoleptic ferrocene from **2a** and $FeCl_2$ was recently reported.[5] For the preparation of half-sandwich complexes we chose $[(PPh_3)_3RuCl_2]$ as a starting material in order to obtain the half-sandwich complex $[Ru(\eta^5:\eta^1\text{-}\mathbf{2a})(PPh_3)Cl]$ (**3**). An equimolar mixture of **2a** and $[(PPh_3)_3RuCl_2]$ was

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10.1021/om0010262 CCC: $20.00
Publication on Web 03/17/2001

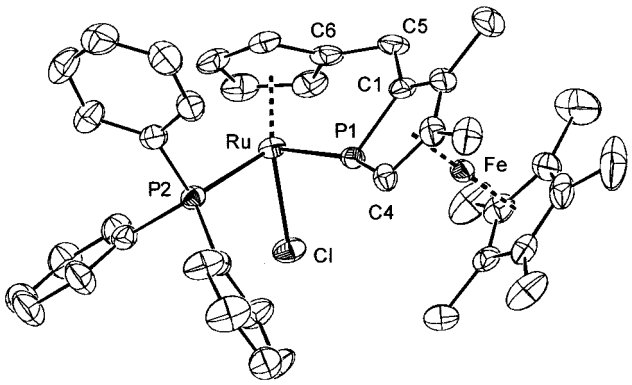
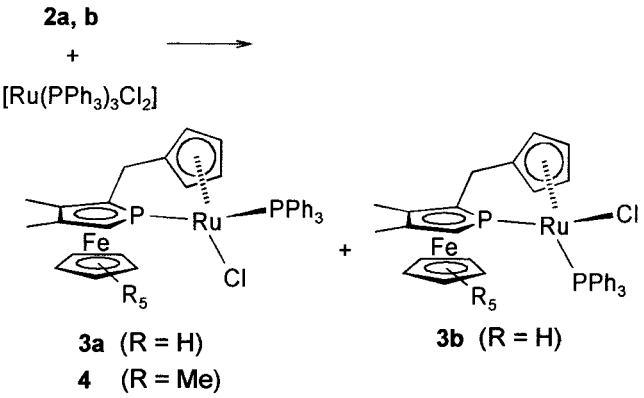


Figure 1. Molecular structure of complex **4**. Selected bond lengths (Å) and angles (deg): Ru(1)−P(1) = 2.2549(14), Ru(1)−P(2) = 2.2912(14), Ru(1)−Cl(1) = 2.4285(12); P(1)−Ru(1)−P(2) = 94.45(5), P(1)−Ru(1)−Cl(1) = 99.37(5), P(2)−Ru(1)−Cl(1) = 90.41(5), C(1)−P(1)−C(4) = 90.4(3), C(1)−P(1)−Ru(1) = 108.3(2), C(4)−P(1)−Ru(1) = 155.21(17), C(6)−C(5)−C(1) = 110.4(5).

Scheme 2



heated in toluene at 90 °C overnight (Scheme 2). The ^{31}P NMR spectrum of the crude reaction mixture indicated complete conversion and showed a signal for uncoordinated PPh_3 and two pairs of doublets in a 95:5 ratio, attributable to the two diastereomeric complexes **3a**,**b**, which were isolated as red crystals in 63% yield from the reaction mixture. The isomer ratio of 95:5 was unaffected by the workup procedure; moreover, attempts to separate the isomers by chromatography or fractional crystallization were unsuccessful. The anticipated connectivity of complex **3** was proven by an X-ray diffraction study carried out on a crystal selected from the 95:5 mixture of isomers.[6] The observed relative configuration of the central and planar elements of chirality in the examined crystal is that depicted in formula **3a**, which results in a minimal interference of the PPh_3 ligand and the CpFe moiety of the phosphaferrocene. (The relative configuration is identical with that found for the Cp* analogue in complex **4**, as depicted in Figure 1; see below.) We believe that this arrangement corresponds to the thermodynamically more stable diastereomer, because models indicate a severely unfavorable interaction between the CpFe fragment and the PPh_3 ligand in the diastereomeric complex **3b**.

Next, we turned our attention to possible modifications of our ligand system to further improve the stereoselectivity of the complexation reaction. On the basis of the steric argument given above, substitution of the Cp for a sterically more demanding Cp* ligand in the phosphaferrocene seemed promising for this purpose. The Cp*-modified cyclopentadienide **2b** was prepared in a similar manner from the corresponding aldehyde **1b**, which was obtained according to a procedure closely related to those reported by Mathey[7] and Fu.[8] The complexation reaction was carried out under the same conditions as reported above, and the ^{31}P NMR spectrum of the crude mixture indicated the formation of only one diastereomeric complex, which was obtained in crystalline form in 68% isolated yield after chromatography. The diastereomeric purity of complex **4** can be regarded as de > 98%. Thus, a virtually complete control of the metal configuration is exerted by the ligand-based chirality. To the best of our knowledge, this is the highest selectivity observed so far for this kind of complexation reaction, leading to complexes of the type [Cp−LRu(PR_3)X]. Similar complexation experiments with the ligand systems reported in ref 3 gave de values in the range of 18−83%. Although Hidai and co-workers reported the synthesis of a diastereomerically pure complex,[3b] this result was obtained after recrystallization of the crude product and does therefore not allow conclusions to be drawn regarding the selectivity of the complexation reaction itself.

An X-ray diffraction study allowed the unambiguous assignment of the relative configuration of the two elements of chirality. An ORTEP plot of the structure is given in Figure 1, together with selected distances and angles. Complex **4** crystallizes in the monoclinic space group *Pn* with $Z = 2$. The orientation of the PPh_3 ligand and the Cp*Fe moiety are qualitatively the same as in complex **3a**, in accord with the above assumption that increasing the steric demand of the CpFe fragment leads to a higher selectivity in the complexation reaction. The basic conformational feature of the structure is that the phospholyl and Cp* rings of the phosphaferrocene moiety are almost perpendicular to the substituted Cp ring coordinated to the Ru atom. The Ru−P bonds differ slightly in length, the distance Ru−P1 (225.5(1) pm) being shorter than the distance Ru−P2 (229.1(1) pm). This is in accord with our earlier observations that metal−phosphaferrocene bonds generally tend to be shorter than metal−PR_3 bonds in trialkyl- or triarylphosphine complexes, although the difference of ca. 4 pm in the present case is rather small.[4b] In the related complex [$CpCH_2CH_2PPh_2Ru(PPh_3)Cl$] the bonds between Ru and the electronically quite similar phosphorus atoms are 230.7(2) and 231.1(1) pm; i.e., they are identical within the experimental error.[9] For comparison, the Ru−P distances in the complex [CpRu(PPh_3)$_2$Cl] are 233.7(1) and 233.5(1) pm, respectively.[10]

(6) The X-ray structure determination suffered from poor crystal quality, leading to a low precision data set. However, the structure solution is significant as far as the constitution and relative configuration of the complex are concerned. Since the related complex **4** could be characterized by X-ray diffraction with high accuracy, no details of the structure determination for complex **3** will be discussed. The assumption that the crystal of **3** investigated by X-ray diffraction belongs to the major diastereomer served to us as a plausible working hypothesis based on probability. The examined crystal was not characterized by NMR spectroscopy.

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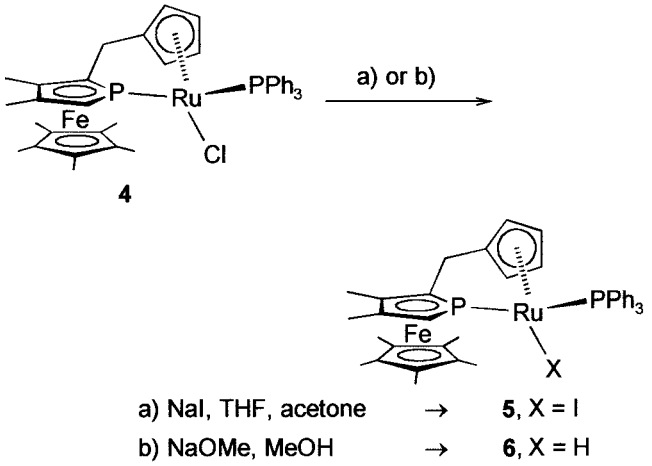
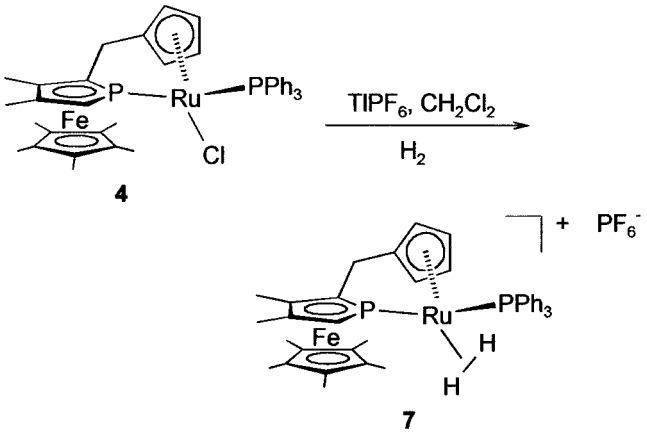
Scheme 3



Scheme 4



Reactivity of Complexes 3 and 4. We have started to explore the reactivity of complexes **3** and **4** with respect to the configurational stability of the Ru center. Results for the Cp* complex **4** are described first. The exchange of the chloride ligand for iodide occurred smoothly within a period of 36 h on stirring complex **4** with an excess of solid NaI in a THF/acetone mixture (Scheme 3). The NMR spectra indicated a clean quantitative conversion with the formation of the single diastereomeric iodide complex **5**. Similarly, reaction of the chloride **4** with an excess of NaOMe in refluxing MeOH leads within 1 h to the quantitative formation of the Ru−H complex **6**, obtained again as a single diastereomer. This reaction protocol is a known procedure in Ru chemistry, and the reaction is believed to occur by successive substitution of the Cl ligand by methoxide, followed by β-hydrogen elimination and release of formaldehyde.[11] The reaction is accompanied by a color change from orange-red to yellow. The most significant feature of the hydride complex **6** is the ^{1}H NMR resonance for the hydride proton, which appears as a doublet of doublets due to the coupling to the two inequivalent P nuclei at δ −9.54 ppm. The hydride complex **6** turned out to be rather reactive, as workup manipulations with chlorinated solvents or chromatography led partially to the re-formation of the starting chloride complex **4**.[12] The hydride to chloride transformation occurred quantitatively within 1 h when a C_6D_6 solution of the hydride complex was treated with a few drops of $CDCl_3$. The chloride complex **4** was formed as a single diastereomer, which showed the same NMR resonances as the starting material. Thus, the cycle chloride−hydride−chloride proceeds with overall retention of configuration at the Ru center. This is in accord with literature reports that most substitution reactions of CpRuLL′Cl proceed with retention.[3h]

Further substitution reactions could be carried out by treating the chloride complex **4** with $TlPF_6$ in CH_2Cl_2, followed by addition of a ligand suitable to occupy the vacant coordination site on the Ru atom. For example, treatment of a solution of the cation with hydrogen gas at normal pressure led to the formation of the cationic dihydride complex **7** in quantitative yield, as monitored by NMR spectroscopy (Scheme 4). The ^{1}H NMR spectrum features one broad resonance for the metal-bound hydrogen atoms at δ −6.8 ppm, whereas two doublets are observed in the ^{31}P NMR spectrum. Thus, again, complex **7** is formed as a single diastereomer. When solutions are evaporated in vacuo, complex **7** reversibly loses dihydrogen and the NMR spectra of the residue in CD_2Cl_2 show broad and unspecific resonances. When dihydrogen is bubbled through this CD_2Cl_2 solution, the dihydride complex **7** is quantitatively regenerated. However, once the dihydride **7** is obtained as a powdery solid by cooling a CH_2Cl_2 solution layered with hexane, the H_2 ligand is not liberated under vacuum. Because of the sensitivity of complex **7** a satisfactory elemental analysis could not be obtained; hence, the compound was characterized only by NMR methods in solution. Different results were observed for the reaction of the cationic dihydride with triethylamine and pyridine, respectively: the alkylamine acts as a Brønsted base, abstracting a proton from the complex, leading to the neutral monohydride complex **6** (formed as a single diastereomer with the same NMR resonances as described above). On the other hand, addition of pyridine leads to the loss of H_2 and formation of the cationic pyridine complex **8** (single diastereomer) (Scheme 5). The different behaviors of amines and pyridine toward cationic dihydride complexes have been described in the literature.[13] With the synthesis of complex **7** the question arose as to whether this compound has to be considered as a classical dihydride or a η^2-dihydrogen complex, and the T_1 relaxation time of the hydride resonance was determined by the inversion recovery technique in order to address this question. The value of $T_1 = 15$ ms measured at room temperature in CD_2Cl_2 is characteristic of dihydrogen complexes, which generally feature short T_1 values.[13] The observation of a broad ^{1}H NMR resonance with an unresolved ^{1}H−^{31}P coupling is in accord with this classification, as is the easy and reversible loss of the coordinated H_2 molecule from the complex in solution, although the latter

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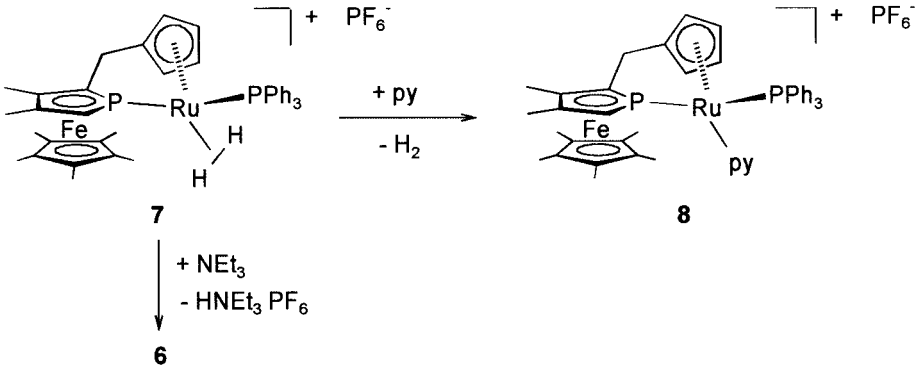
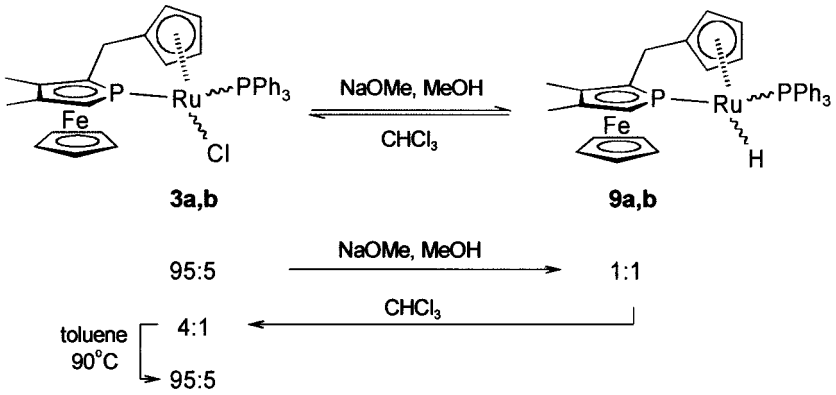
Scheme 5



Scheme 6



criterion is of less diagnostic value.[13] Quite a number of complexes of the type $CpRuL_2H_2^+$ have been prepared and characterized. The nature of the RuH_2 fragment, i.e., the dihydride vs the η^2-dihydrogen character, is strongly dependent on the nature of the ligand L, and many cases are known where both forms coexist in an equilibrium. Strongly basic ligands such as alkylphosphines render the Ru center electron rich, and the equilibrium usually lies on the dihydride side. As the phosphines become less basic, the equilibrium is shifted in favor of the η^2-H_2 complex. If one phosphine is replaced by the strong π-acceptor ligand CO, the η^2-H_2 form is usually the only observed species.[11a,14] Thus, the fact that only this form is observed in the case of our complex **7** is another nice confirmation of the π-acidic character of the phosphaferrocene ligand, which has been described earlier to behave more like a phosphite $P(OR)_3$ than a phosphine PR_3 in terms of donor/acceptor properties.[15]

All reactions of the Cp* derivative **4** described in the preceding section have been carried out as well with the sterically less demanding Cp complex **3**. While constitutionally similar products were obtained, the stereochemical course of the reactions was different and deserves a brief discussion. Specifically, when a 95:5 mixture of chlorides **3a**,**b** was treated with NaOMe in MeOH as described above, the formation of the diastereomeric hydrides **9a**,**b** was observed in a ratio of 1:1, indicating complete epimerization at the Ru center. This result is in striking contrast to the selectivity of the analogous reaction of the Cp* derivative **4** (see above) and to the literature report of Consiglio et al., who observed a stereospecific formation of hydride complexes from diastereomeric CpRuP*PCl complexes with retention of configuration at the Ru atom.[16] The hydrides **9a**,**b** were converted back to the chlorides **3** with interesting results (Scheme 6): a solution of the 1:1 mixture of hydrides in $CDCl_3$ is transformed to the chloride smoothly at room temperature within 2 h. However, the ratio of diastereomers **3a**:**3b** is 4:1 under these conditions, as determined from the integrated ^{31}P NMR spectra. When the $CDCl_3$ solution is evaporated to dryness and the residue is dissolved in toluene and heated to 90 °C for 2 h, the isomer ratio is shifted to 95:5, the value which was observed after the synthesis of complex **3** according to Scheme 2. We therefore conclude that the 95:5 ratio reflects the thermodynamic equilibrium of the diastereomers, while the 4:1 result of the hydride−chloride transformation is under kinetic control. Consiglio et al. have reported the preparation and configurational stability of CpRu(P*P)Cl complexes, where P*P represents enantiopure, C_1-symmetric diphosphines.[16,17] The diastereomers were formed in almost equal amounts under kinetic control, and isomerization of the Ru centers to approach the thermodynamic ratio of isomers was brought about by heating the mixture in chlorobenzene to 80 °C for a period of several hours. However, the highest thermodynamic ratio observed was 2.4:1, which is in pronounced contrast to the high degree of thermodynamic preference of the major dia-

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stereomers of the chloro complexes **3** and **4** described in this work.

On the basis of the result of the X-ray diffraction analysis of complex **4**, we anticipate the same relative configuration at the Ru atom for all complexes of the Cp* series, i.e., **5**−**8**, as indicated in Schemes 3−5, respectively. This assumption is corroborated by two observations (vide supra): (1) the sequence **4**−**6**−**4** leads back to the same diastereomer of **4** as the starting material; (2) the same diastereomer of hydride **6** is obtained either by deprotonation of the dihydrogen complex **7** or by chloride−hydride exchange from complex **4**. We are trying to grow crystals of the respective complexes suitable for X-ray diffraction in order to substantiate this assumption. Furthermore, we are currently exploring further reactions of the chloride complexes **3a**,**b** and **4** which will hopefully allow us to exploit the complex based chirality to induce some stereoselective transformations of suitable substrates in the coordination sphere of the Ru atom.

Experimental Section

General Procedures. Reactions were carried out under an atmosphere of nitrogen by means of conventional Schlenk techniques. Solvents were purified and deoxygenated by conventional methods. Silica was heated at 220 °C for 12 h, cooled to room temperature under high vacuum, and stored under dinitrogen.

NMR spectra were recorded on a Varian Unity 500 spectrometer (^{1}H, 500 MHz; ^{31}P{^{1}H}, 202 MHz; ^{13}C{^{1}H}, 126 MHz) and a Varian Mercury 200 (^{1}H, 200 MHz; ^{31}P, 81 MHz). ^{1}H spectra are referenced to the residual solvent signal and ^{31}P spectra to external H_3PO_4 (85%). Mass spectra were recorded on a Finnigan MAT-95 spectrometer (EI, 70 eV nominal electron energy). The anions **2a**,**b**[5] and $[Ru(PPh_3)_3Cl_2]$[18] were prepared as described in the literature.

Synthesis of Chloride Complexes 3 and 4. A mixture of Na−**2a** or Na−**2b** (0.92 mmol) and $[Ru(PPh_3)_3Cl_2]$ (0.92 mmol) in dry toluene (25 mL) was heated to 90 °C overnight. Most of the solvent was removed under vacuum, and the residue was purified by chromatography on silica. PPh_3 was removed first with toluene, and the complexes were eluted with 2:1 toluene/ether. Recrystallization gave red crystals of **3** (from toluene, 0.58 mmol, 63%) or **4** (from CH_2Cl_2/Et_2O, 0.63 mmol, 68%). ^{1}H NMR (500 MHz, $CDCl_3$): **3a** (major isomer), 2.03 (s, Me), 2.14 (s, Me), 2.47 (m, 1 H, C_5H_4), 2.49−2.67 (m, 2 H, CH_2), 2.76 (d, ^2J(H,P) = 31.7 Hz, 1 H, α-H), 4.43 (s, Cp), 4.43 (m, 1 H, C_5H_4), 5.10 (m, 1 H, C_5H_4), 5.19 (m, 1 H, C_5H_4), 7.28−7.60 (m, 15 H, PPh_3); **3b** (minor isomer), 2.04 (s, Me), 2.07 (s, Me), 3.75 (s, Cp), 2.91 (d, ^2J(H,P) = 31.5 Hz, 1 H, α-H); **4**, 1.59 (d, ^2J(H,P) = 30.8 Hz, 1 H, α-H), 1.88 (s, Me), 1.90 (s, Cp*), 1.92 (s, Me), 2.11 (m, 1 H, C_5H_4), 2.31 (dd, ^2J(H,H) = 15.2 Hz, ^3J(H,P) = 23.5 Hz, 1 H, CH_2), 2.43 (dd, ^2J(H,H) = 15.2 Hz, ^3J(H,P) = 6.2 Hz, 1 H, CH_2), 4.35, 5.04, 5.27 (3 m, 3 H, C_5H_4), 7.24−7.52 (m, 15 H, PPh_3). ^{13}C NMR (126 MHz, $CDCl_3$): **3a** (major isomer), 14.6 (s, CH_3), 16.5 (s, CH_3), 24.6 (d, ^2J(C,P) = 15.9 Hz, CH_2), 61.2 (d, ^1J(C,P) = 29.1 Hz, phospholyl α-CH), 65.2 (s, Cp CH), 73.8 (s, C_5H_5), 80.3 (s, Cp CH), 82.4 (d, J(C,P) = 12.1 Hz, Cp CH), 82.8 (d, J(C,P) = 11.0 Hz, Cp CH), 86.2 (s, phospholyl α-C(q)), 88.9 (s, Cp C(q)), 110.3 (d, ^1J(C,P) = 9.8 Hz, phospholyl β-C), 116.5 (s, phospholyl β-C), 128−137 (PPh_3); **4**, 10.4 (s, Cp* CH_3), 11.8 (d, ^3J(C,P) = 4.4 Hz, phospholyl CH_3), 13.9 (d, ^3J(C,P) = 3.8 Hz, phospholyl CH_3), 22.1 (d, ^2J(C,P) = 17.0 Hz, CH_2), 61.3 (d, ^1J(C,P) = 22.0 Hz, phospholyl α-CH), 62.9 (s, Cp CH), 80.3 (d, J(C,P) = 7.1 Hz, Cp CH), 81.6 (s, Cp CH), 83.7 (d, J(C,P) = 8.2 Hz, Cp CH), 84.1 (s, Cp* C(q)), 86.5 (s, Cp C(q)), 87.3 (s, phospholyl α-C(q)), 104.9 (d, J(C,P) = 7.7 Hz, phospholyl β-C), 116.3 (d, J(C,P) = 9.0 Hz, phospholyl β-C), 127−137 (PPh_3). ^{31}P NMR (202 MHz, $CDCl_3$): **3a**, 23.4 (d, ^2J(P,P) = 64 Hz, phospholyl P), 48.0 (d, ^2J(P,P) = 64 Hz, PPh_3); **3b**, 21.2 (d, ^2J(P,P) = 62 Hz, phospholyl P), 50.3 (d, ^2J(P,P) = 62 Hz, PPh_3); **4**, 31.3 (d, ^2J(P,P) = 64 Hz, phospholyl P), 47.7 (d, ^2J(P,P) = 64 Hz, PPh_3). SIMS for **3**: *m*/*e* 708 (M^+), 673 (M^+ − Cl), 411 (M^+ − Cl − PPh_3). Anal. Calcd for $C_{35}H_{33}ClP_2FeRu$ (708.0): C, 59.38, H, 4.70. Found: C, 59.28, H, 4.79. MS for 4: *m*/*e* 778 (M^+), 516 (M^+ − PPh_3). Anal. Calcd for $C_{40}H_{43}ClP_2FeRu$ (778.1): C, 61.75, H, 5.57. Found: C, 61.55, H, 5.62.

Crystal Data and Structure Refinement Details for 4: $C_{40}H_{43}ClFeP_2Ru$, M_r = 778.05, red block, 0.2 × 0.2 × 0.15 mm^3, T = 293 K, Bruker SMART CCD, Mo Kα radiation, λ = 0.710 73 Å, monoclinic, space group *Pn*, a = 13.7601(13) Å, b = 9.2059(9) Å, c = 15.3591(14) Å, β = 115.160(2)°, V = 1761.0(3) Å^3, Z = 2, D_c = 1.467 Mg/m^3, μ(Mo Kα) = 1.035 mm^{-1}, F(000) = 800, total of 10 335 reflections, 5650 unique reflections, R(int) = 0.0386, 4916 reflections with $I > 2\sigma(I)$, full-matrix least-squares refinement on F^2, 406 parameters, final results R1 = 0.0374, wR2 = 0.0787 ($I > 2\sigma(I)$), R1 = 0.0433, wR2 = 0.0814 (all data), GOF = 0.832, maximum/minimum residual electron density +0.73/−0.35 eÅ^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-154123. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, int. +1223/336-033; E-mail, teched@chemcrys.cam.ac.uk).

Synthesis of Iodide 5. A solution of **4** (50 mg, 0.06 mmol) in THF/acetone was stirred in the presence of excess solid NaI for 36 h at room temperature. Reaction progress is easily monitored by measuring ^{31}P NMR spectra of the reaction mixture. The solvent was removed in a vacuum and the residue was chromatographed on silica with toluene/ether 4:1 to give 53 mg (95%) of **5** as a red solid after removal of the solvent. ^{1}H NMR (500 MHz, $CDCl_3$): 1.53 (d, ^2J(H,P) = 30.5 Hz, 1 H, α-H), 1.86 (s, Me), 1.89 (s, Cp*), 1.96 (s, Me), 2.29−2.38 (m, 2 H, CH_2), 2.42 (m, 1 H, C_5H_4), 4.40 (m, 1 H, C_5H_4), 5.07 (m, 1 H, C_5H_4), 5.31 (m, 1 H, C_5H_4), 7.2−7.5 (m, 15 H, PPh_3). ^{13}C NMR (126 MHz, $CDCl_3$): 10.6 (s, Cp* CH_3), 11.7 (s, phospholyl CH_3), 13.9 (s, phospholyl CH_3), 21.7 (d, ^2J(C,P) = 16.5 Hz, CH_2), 60.2 (d, ^1J(C,P) = 19.0 Hz, phospholyl α-CH), 69.5 (s, Cp CH), 80.8 (s, Cp CH), 81.1 (d, J(C,P) = 11.0 Hz, Cp CH), 84.3 (s, Cp* C(q)), 86.9 (s, Cp C(q)), 88.0 (s, phospholyl α-C(q)), 104.9 (d, J(C,P) = 9.3 Hz, phospholyl β-C), 116.4 (s (br), phospholyl β-C), 127−138 (PPh_3). ^{31}P NMR (202 MHz, $CDCl_3$): 23.7 (d, ^2J(P,P) = 65 Hz, phospholyl P), 45.1 (d, ^2J(P,P) = 65 Hz, PPh_3). MS: *m*/*e* 870 (M^+), 608 (M^+ − PPh_3), 481 (M^+ − PPh_3 − I). Anal. Calcd for $C_{40}H_{43}IP_2FeRu$ (869.5): C, 55.25; H, 4.99. Found: C, 54.57; H, 5.04.

Synthesis of Hydrides 6 and 9a,b. Sodium methoxide was prepared by dissolving 30 mg of Na (1.3 mmol) in 3 mL of MeOH. To this solution was added a solution of **4** (106 mg, 0.14 mmol) in 2 mL of toluene, and the mixture was heated to reflux for 2 h, during which time a color change from red to light orange was observed. The mixture was evaporated to dryness and the residue chromatographed on silica with 10:1 hexane/ether. A total of 86 mg (84%) of **6** was obtained as a yellow powder after removal of the solvent. ^{1}H NMR (500 MHz, C_6D_6): −9.54 (dd, ^2J(H,P) = 40.2, 30.6 Hz, 1 H, Ru−H), 1.69 (d, ^2J(H,P) = 30.7 Hz, 1 H, α-H), 1.60 (s, Me), 1.68 (s, Me), 1.74 (s, Cp*), 2.14 (dd, ^2J(H,H) = 15.3 Hz, ^3J(H,P) = 9.5 Hz, 1 H, CH_2), 2.41 (dd, ^2J(H,H) = 15.3 Hz, ^3J(H,P) = 18.4 Hz, 1 H, CH_2), 4.47 (m, 1 H, C_5H_4), 4.56 (m, 1 H, C_5H_4), 4.88 (m, 1 H, C_5H_4), 5.52 (m, 1 H, C_5H_4), 6.8−7.07 (m, PPh_3), 7.73−7.84 (m, PPh_3). ^{13}C NMR (126 MHz, C_6D_6): 10.2 (s, Cp* CH_3), 11.8 (d, ^3J(C,P) = 4.9 Hz, phospholyl CH_3), 14.4 (d, ^3J(C,P) = 4.4 Hz, phospholyl CH_3), 22.5 (d, ^2J(C,P) = 17.0 Hz, CH_2), 61.8 (d,

(18) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *12*, 237−241.

^1J(C,P) = 13.1 Hz, phospholyl α-CH), 72.5 (d, J(C,P) = 9.9 Hz, Cp CH), 77.7 (s, Cp CH), 79.2 (d, J(C,P) = 6.6 Hz, Cp CH), 81.9 (s, Cp* C(q)), 84.1 (d, J(C,P) = 4.4 Hz, Cp CH), 84.2 (s, Cp C(q)), 85.4 (d, ^2J(C,P) = 4.9 Hz, phospholyl α-C(q)), 109.1 (s, phospholyl β-C), 117.0 (s, phospholyl β-C), 127−143 (PPh_3). ^{31}P NMR (202 MHz, C_6D_6): 58.1 (d, ^2J(P,P) = 43 Hz, phospholyl P), 70.2 (d, ^2J(P,P) = 43 Hz, PPh_3). HRMS: *m/e* calcd for $C_{40}H_{44}P_2FeRu$ (743.7), 744.1305; found, 744.1295.

9a,**b** was obtained in a completely analogous manner by treatment of 192 mg (0.27 mmol) of **3a**,**b** with NaOMe (31 mg, 1.36 mmol) in 10 mL of MeOH at reflux for 3 h. The solvent was removed and the residue purified by chromatography on silica with 5:1 hexane/ether to give a yellowish solid of **9a**,**b** (152 mg, 84%, isomer ratio 1:1) after removal of the solvent. Signal assignments to either **9a** or **9b** were deduced from ^{1}H−^{1}H-COSY and ^{1}H−^{13}C-HMQC spectra. ^{1}H NMR (500 MHz, C_6D_6): **9a**, −9.52 (dd, ^2J(H,P) = 40.6, 29.7 Hz, 1 H, Ru−H), 1.75 (s, Me), 1.76 (s, Me), 2.22 (dd, ^2J(H,H) = 15.2 Hz, ^3J(H,P) = 7.3 Hz, 1 H, CH_2), 2.46 (dd, ^2J(H,H) = 15.2 Hz, ^3J(H,P) = 11.9 Hz, 1 H, CH_2), 2.57 (d, ^2J(H,P) = 31 Hz, 1 H, α-H), 3.98 (s, 5 H, Cp), 4.59 (m, 1 H, C_5H_4), 4.64 (m, 1 H, C_5H_4), 4.99 (m, 1 H, C_5H_4), 5.33 (m, 1 H, C_5H_4), 7.07−7.79 (m, PPh_3); **9b**, −10.16 (dd, ^2J(H,P) = 41.5, 36.2 Hz, 1 H, Ru−H), 1.79 (s, Me), 1.83 (s, Me), 2.25 (dd, ^2J(H,H) = 15.3 Hz, ^3J(H,P) = 5.9 Hz, 1 H, CH_2), 2.33 (dd, ^2J(H,H) = 15.3 Hz, ^3J(H,P) = 12.9 Hz, 1 H, CH_2), 2.60 (d, ^2J(H,P) = 31 Hz, 1 H, α-H), 3.76 (s, 5 H, Cp), 4.70 (m, 2 H, C_5H_4), 4.81 (m, 1 H, C_5H_4), 5.02 (m, 1 H, C_5H_4), 5.16 (m, 1 H, C_5H_4), 7.06−7.83 (m, PPh_3). ^{31}P NMR (202 MHz, C_6D_6): **9a**, 47.3 (d, ^2J(P,P) = 44 Hz, phospholyl P), 68.7 (d, ^2J(P,P) = 44 Hz, PPh_3); **9b**, 46.7 (d, ^2J(P,P) = 40 Hz, phospholyl P), 68.5 (d, ^2J(P,P) = 40 Hz, PPh_3). ^{13}C NMR (126 MHz, C_6D_6): **9a**, 74.0 (d, J(C,P) = 8.9 Hz, C_5H_4), 77.7 (d, J(C,P) = 8.8 Hz, C_5H_4), 79.1 (s, C_5H_4), 82.5 (d, J(C,P) = 4.9 Hz, C_5H_4), 74.8 (s, Cp CH); **9b**, 72.9 (d, J(C,P) = 7.6 Hz, C_5H_4), 75.6 (d, J(C,P) = 7.7 Hz, C_5H_4), 82.7 (s, C_5H_4), 84.0 (d, J(C,P) = 5.5 Hz, C_5H_4), 73.8 (s, Cp CH); signals attributable to **9a** or **9b**, 14.2 (d, ^3J(C,P) = 6.0 Hz, Me), 14.3 (d, ^3J(C,P) = 4.4 Hz, Me), 16.3 (d, ^3J(C,P) = 4.4 Hz, Me), 16.4 (d, ^3J(C,P) = 4.9 Hz, Me), 25.1 (d, ^2J(C,P) = 17.0 Hz, CH_2), 25.2 (d, ^2J(C,P) = 17.5 Hz, CH_2), 60.0 (d, ^1J(C,P) = 12.6 Hz, phospholyl α-CH), 61.1 (d, ^1J(C,P) = 14.2 Hz, phospholyl α-CH), 84.7 (s, C(q)), 85.0 (s, C(q)), 87.4 (d, J(C,P) = 5.0 Hz, C(q)), 87.5 (d, J(C,P) = 4.9 Hz, C(q)), 111.9 (d, J(C,P) = 5.5 Hz, C(q)), 112.8 (d, J(C,P) = 10.4 Hz, C(q)), 117.6 (d, J(C,P) = 7.7 Hz, C(q)), 117.9 (d, J(C,P) = 7.1 Hz, C(q)). HRMS: *m/e* calcd for $C_{35}H_{34}P_2FeRu$, 674.0522; found, 674.0518.

Synthesis of Cationic Dihydrogen Complex 7. Solid $TlPF_6$ (68 mg, 0.19 mmol) was added to a solution of **4** (151 mg, 0.19 mmol) in 3 mL of CH_2Cl_2, and the mixture was stirred for 3 h under an atmosphere of hydrogen at room temperature. TlCl was removed by filtration, and **7**·PF_6 was precipitated from the filtrate by addition of ether to give 111 mg (79%) of a yellow powder. ^{1}H NMR (500 MHz, CD_2Cl_2): −6.80 (b s, 2 H, Ru−H_2), 1.52 (d, ^2J(H,P) = 32.0 Hz, 1 H, α-H), 1.73 (s, Cp*), 1.90 (s, Me), 1.94 (s, Me), 2.34 (dd, ^2J(H,H) = 15.7 Hz, ^3J(H,P) = 6.4 Hz, 1 H, CH_2), 2.62 (dd, ^2J(H,H) = 15.7 Hz, ^3J(H,P) = 25.0 Hz, 1 H, CH_2), 3.37 (m, 1 H, C_5H_4), 4.95 (m, 1 H, C_5H_4), 5.39 (m, 1 H, C_5H_4), 5.45 (m, 1 H, C_5H_4), 7.17−7.54 (m, PPh_3). ^{13}C NMR (126 MHz, CD_2Cl_2): 10.1 (s, Cp* CH_3), 11.7 (d, ^3J(C,P) = 5.0 Hz, phospholyl CH_3), 13.9 (d, ^3J(C,P) = 4.5 Hz, phospholyl CH_3), 21.5 (d, ^2J(C,P) = 15.4 Hz, CH_2), 60.2 (s, phospholyl α-CH), 79.6 (d, J(C,P) = 6.0 Hz, Cp CH), 77.9 (s, Cp CH), 83.6 (d, J(C,P) = 6.0 Hz, Cp CH), 84.8 (s, Cp* C(q)), 88.6 (s, Cp CH), 88.8 (s, Cp C(q)), 90.7 (d, ^2J(C,P) = 6.5 Hz, α-C(q)), 107.5 (d, ^2J(C,P) = 12.6 Hz, phospholyl β-C), 123.2 (d, ^2J(C,P) = 9.4, Hz, phospholyl β-C), 129−136 (PPh_3). ^{31}P NMR (202 MHz, CD_2Cl_2): −144.3 (sept, ^1J(P,F) = 710 Hz, PF_6^-), 35.7 (d, ^2J(P,P) = 49 Hz, phospholyl P), 51.5 (d, ^2J(P,P) = 49 Hz, PPh_3).

Synthesis of Cationic Pyridine Complex 8. To a solution of **7** in CH_2Cl_2—prepared in the manner described above from 88 mg (0.11 mmol) of **4** and 43 mg (0.11 mmol) of $TlPF_6$—was added 8.9 mg (0.11 mmol, 1 equiv) of pyridine via syringe. The solvent was removed from the red solution, and the residue was purified by chromatography on silica with 1:1 CH_2Cl_2/THF to give 79.2 mg (72%) of **8** as a red oil after removal of the solvent. Crystalline material was obtained by layering a CH_2Cl_2 solution with ether. ^{1}H NMR (500 MHz, CD_2Cl_2): 1.76 (s, Cp*), 1.95 (s, Me), 2.00 (s, Me), 2.06 (d, ^2J(H,P) = 32.2 Hz, 1 H, α-H), 2.35 (dd, ^2J(H,H) = 15.4 Hz, ^3J(H,P) = 9.2 Hz, 1 H, CH_2), 2.41 (dd, ^2J(H,H) = 15.4 Hz, ^3J(H,P) = 20.2 Hz, 1 H, CH_2), 3.13 (m, 1 H, C_5H_4), 4.69 (m, 1 H, C_5H_4), 5.17 (m, 1 H, C_5H_4), 5.33 (m, 1 H, C_5H_4), 7.00−7.69 (m, py + PPh_3), 8.81 (d, J = 5.6 Hz, 2 H, NCH). ^{13}C NMR (126 MHz, CD_2Cl_2): 10.6 (s, Cp* CH_3), 11.7 (d, ^3J(C,P) = 4.4 Hz, phospholyl CH_3), 14.2 (d, ^3J(C,P) = 4.4 Hz, phospholyl CH_3), 21.3 (d, ^2J(C,P) = 16.4 Hz, CH_2), 61.4 (d, ^1J(C,P) = 14.8 Hz, phospholyl α-CH), 67.9 (s, Cp CH), 79.5 (d, J(C,P) = 9.8 Hz, Cp CH), 82.8 (d, J(C,P) = 6.6 Hz, Cp CH), 84.6 (s, Cp* C(q)), 88.7 (d, J(C,P) = 6.6 Hz, Cp CH), 90.1 (s, Cp C(q)), 90.2 (s, phospholyl α-C(q)), 105.5 (d, ^1J(C,P) = 13.2 Hz, β-C), 115.1 (d, ^2J(C,P) = 7.1 Hz, phospholyl β-C), 125.3 (s, py *m*-C), 129−135 (PPh_3), 137.9 (s, py *p*-C), 158.5 (d, J(C,P) = 9.3 Hz, py *o*-C). ^{31}P NMR (202 MHz, CD_2Cl_2): −144.3 (sept, ^1J(P,F) = 710 Hz, PF_6^-), 23.5 (d, ^2J(P,P) = 55 Hz, phospholyl P), 50.4 (d, ^2J(P,P) = 55 Hz, PPh_3). Anal. Calcd for $C_{45}H_{48}P_3NF_6FeRu$ (966.7): C, 55.91; H, 5.00. Found: C, 55.45; H, 5.41.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft (DFG; SFB 380 and Graduiertenkolleg 440) and the Fonds der Chemischen Industrie for financial support.

Supporting Information Available: X-ray structural information for compound **4**. This material is available free of charge via the Internet at http://www.acs.org.

OM0010262