Synthesis, Kinetics, and Stereochemistry of P−C Bond Breaking and P−C Bond Making Reactions: Ruthenium−Arene Binap Chemistry

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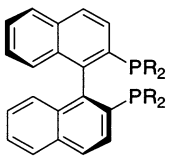
Received March 26, 2001

The syntheses of a set of new arene Ru complexes containing the ligand P(OH)(OR)Ph are reported. Kinetic results for the rapid stereospecific alcoholysis of a Ru−{$P(OH)Ph_2$} moiety with ROH to give a phenyl RuP(OH)(OR)Ph fragment are given. The protonation chemistry of this new Ru−phenyl {P(OH)(OR)Ph} species, using an excess of triflic acid in CD_2Cl_2, affords a reaction in which the Ru−phenyl group migrates from the metal back to the P atom without loss of stereogenicity at the Ru atom. The ease and stereospecificity of these reactions are rationalized.

Introduction

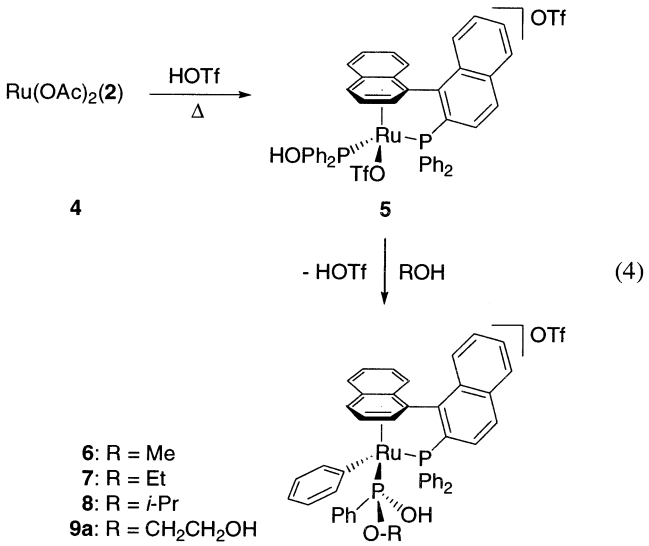
The splitting of P−C bonds in phosphine complexes can lead to interesting new phosphorus-and-carbon-donor metal complexes,[1−5] and eqs 1−3 in Scheme 1 show examples from Pt,[2] Mo,[4] and Ru[5] chemistry. The Ru complex **1** is rather exotic and arises via an intermediate in which HF has been added across a P−C bond; however, such examples are scarce. Regrettably, P−C bond cleavage can represent an undesirable side reaction in homogeneously catalyzed processes[6−10] in which complexed tertiary phosphines are attacked by nucleophiles. Nevertheless, this reaction type is mechanistically significant in terms of understanding how catalysts function.

We have reported[11] that the complexed racemic Binap ligand, **2**, (and subsequently, **3**) reacts with triflic acid



2: R = Ph
3: R = p-Tolyl

in the complex $Ru(OAc)_2$(**2**), **4**, to afford the P−C bond cleavage product **5** (see eq 4). This product appears to have arisen via the addition of water across the P−C bond of complexed Binap. Further reaction of **5** with



(4)

several simple alcohols ROH, R = Me, Et, *i*-Pr, CH_2-CH_2OH, results in the compounds **6**−**9**, which contain the relatively rare ligand type P(OH)(OR)Ph.[12] During this chemistry, a new Ru−C(aryl) bond forms due to migration of a P-phenyl group to the metal center. These new phenyl complexes are unique in that they are produced in only one diastereomeric form; that is, the phenyl migration and P−O bond formation are stereospecific. Moreover, these new derivatives contain *three different forms of stereogenicity*: atropisomerism, from the biaryl moiety, a chiral transition metal,[13] and the newly formed stereogenic P atom. Reaction with *tert*-butyl alcohol was shown to produce the unexpected

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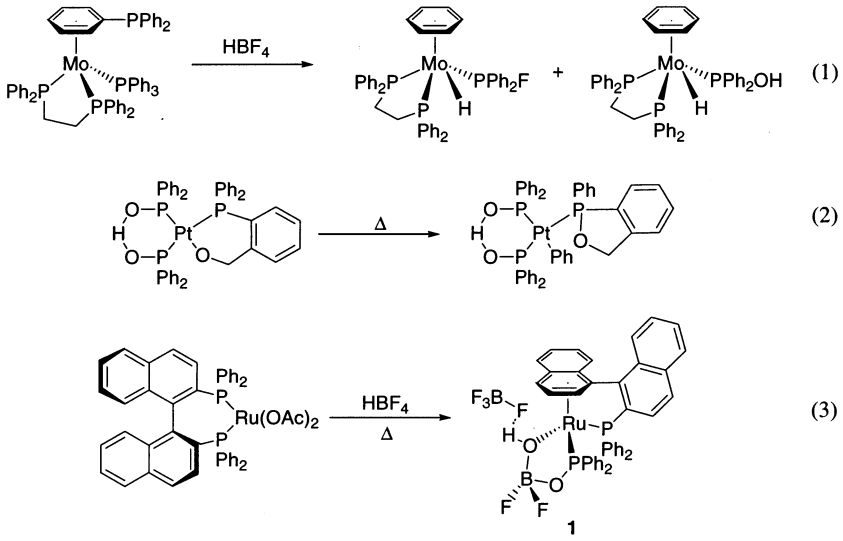
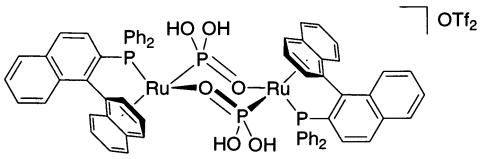
10.1021/om0102394 CCC: $20.00
Publication on Web 06/07/2001

Scheme 1



(1) (2) (3)

dinuclear species **10**, in which a phosphorus acid ligand has been produced.[14]



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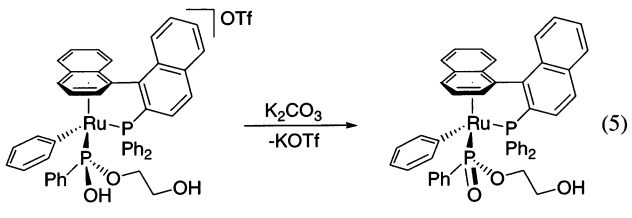
We report here (a) a kinetic study for the alcoholysis chemistry of eq 4 and (b) that reaction of **6** or **8** with an excess of triflic acid affords a reverse migration in which the Ru−phenyl group returns from the metal to the P atom without loss of stereogenicity at the Ru center.

Results and Discussion

Synthesis and Characterization. The new complexes **6**−**9** were prepared in good yield and characterized via ^{31}P, ^{13}C, and ^{1}H NMR and mass spectroscopic data together with microanalytical results (see Experimental Section). The solid-state structure of **8** has been reported in an earlier communication.[12] Typically, the ^{31}P NMR spectra show the signal for the phosphonite ligand at high frequency, e.g., for **8**, $\delta P^1 = 140.7$ and $\delta P^2 = 57.6$ (see Scheme 2 for the numbering).

In the chemistry of eq 4, the final product was isolated by evaporation of the low-boiling alcohol followed by removal of the product triflic acid by washing with ether.

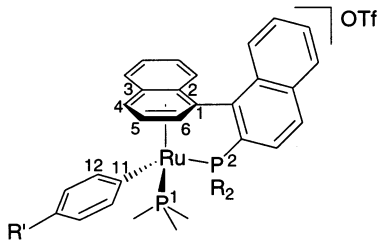


(5)

9a **9b**

The standard preparation for **9a** (extracting with dichloromethane and subsequent washing with water) unexpectedly gave **9b**. To facilitate the isolation of **9b**, a synthetic route involving base was employed (see eq 5). However, in the absence of base, **9a** was clearly the initial product in the alcohol solution (based on ^{31}P NMR). For the stereochemical discussion, which follows later, we prepared enantiopure *p*-tolyl Binap, **3**, analogues of **6** and **9**. For these compounds, the oxide structure and not the P(OH) variant was deliberately isolated via addition of base, as the high solubility of the cationic complex prevented an easy separation from the side-product triflic acid (see eq 6).

Scheme 2



The deprotonation of the hydroxy alkoxy phosphine is accompanied by a low-frequency change in ^{31}P chemical shift by ca. 30 ppm. The characterization of the P−C bond splitting products is helped by a ^{31}P,^{1}H correlation (see Figure 1 for **13b**). Relative to **11** the high-frequency ^{31}P spin in **13b** is now associated with one and not two sets of ortho aromatic protons (see arrows). The expansion of the cross-peaks in the aliphatic region shows which of the three closely spaced multiplets stem from the $POCH_2$ protons.[15]

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(15) We observe the OH-proton as a doublet, $\delta = 5.74$, $^{3}J_{HH} = 9.1$, arising from one of the two diastereotopic CH_2OH protons. The lack of exchange plus the specific coupling suggests a possible H-bond arising from an interaction with the P=O.

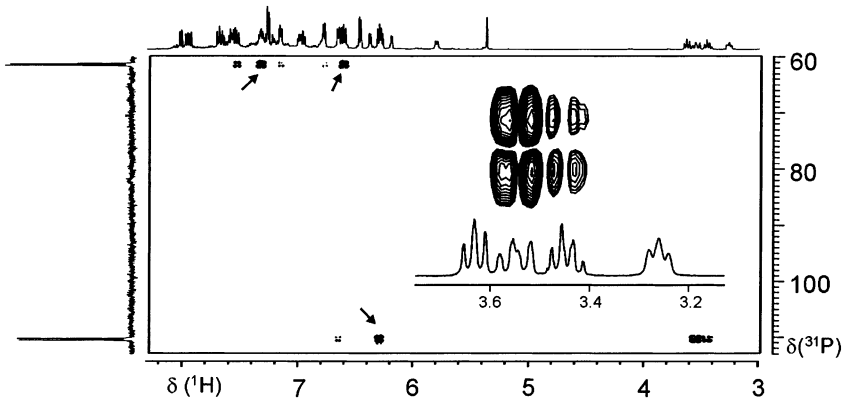
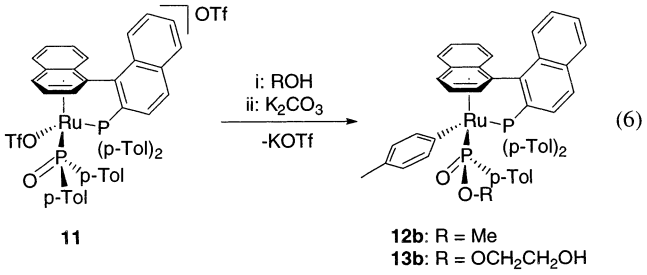


Figure 1. $^{31}P,^{1}H$ correlation for **13b** showing the cross-peaks from the ^{31}P signals. The two strong peaks from the phosphine (top arrows) arise from the two sets of ortho-tolyl protons. In addition to that, one observes cross-peaks stemming from the meta protons (weak) and from the ortho Binap proton (moderate). For the high-frequency signal, only one cross-peak for the ortho (bottom arrow) and meta protons is observed. The inset shows the two cross-peaks for the $POCH_2$ protons of the glycol.



(6)

Kinetics of the Formation of 6−8. The reactions of **5** with ROH were followed by ^{31}P NMR methods. For convenience, only the high-frequency signals will be discussed, as these are more responsive to change in structure. Reaction of **5** using either methanol or ethanol as solvent proceeds essentially within the time necessary to obtain a ^{31}P NMR spectrum to afford **6** and **7**, respectively. The difference in reaction rates as a function of the alcohol concentration becomes obvious when **5** is allowed to react using 4:1 alcohol/benzene-d_6 mixtures at 21 °C.

For methanol with this solvent pair, complex **5** is no longer observed just after mixing, whereas one finds signals at $\delta = 91.6$, $^2J(^{31}P,^{31}P) = 52$ Hz, and $\delta = 86.0$, $^2J(^{31}P,^{31}P) = 48$ Hz.[16] After 15 min, complex **6** is observed as the only species at $\delta = 138.4$, $^2J(^{31}P, ^{31}P) = 62$ Hz. For simplicity, we shall hereafter refer to $^2J(^{31}P, ^{31}P)$ as ^2J.

A ^{31}P NMR spectrum of **5** in ethanol/benzene-d_6 after ca. 2 min from the time of mixing shows a signal at $\delta = 87.1$, $^2J = 48$ Hz. This signal decreases in intensity during the course of the reaction. The low-frequency change from ca. 110 ppm for the starting material[16] to 87.1 ppm indicates that the ligand environment of the $P(OH)Ph_2$ phosphorus has been perturbed by the presence of ethanol. The conversion to product **7**, $\delta = 138.0$, $^2J = 62$ Hz, is quantitative and requires ca. 20 min. The

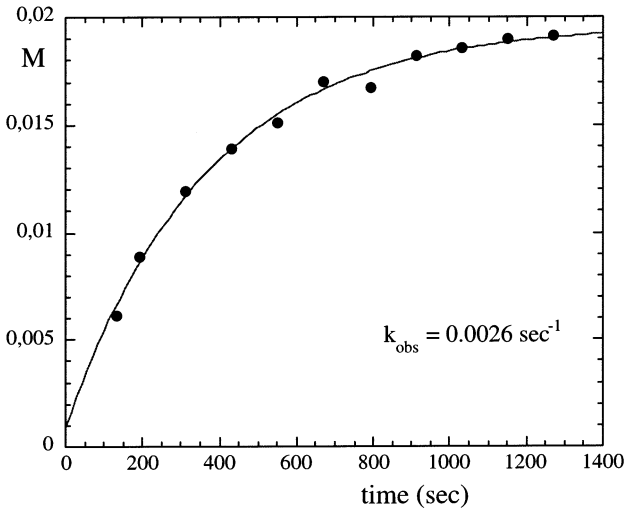


Figure 2. Plot of the concentration of complex **7**, obtained from the intensity values of the ^{31}P NMR peak at $\delta = 138.3$, against time, for the reaction of complex **5** with ethanol, in 4:1 ethanol/benzene-d_6, at 20.5 °C. The best exponential decay fitted to the set of data points is shown.

best fit of concentration vs time (via the intensity values of the product signal at 138.3 ppm) using the first-order rate expression (eq 7) gives a value for the observed rate constant $k_{obs} = 2.6 \times 10^{-3}$ s^{-1} (see Figure 2).

$$c_t = c_\infty - (c_\infty + c_0) \exp -(k_{obs} t) \qquad (7)$$

In the reaction of **5** with 2-propanol/benzene-d_6, the first ^{31}P spectrum after mixing shows **5** and **8**, plus two new species characterized by $\delta = 91.8$, $^2J = 51$ Hz, and $\delta = 83.5$, $^2J = 48$ Hz. Relative to methanol and ethanol, the reaction proceeds sluggishly.

To further reduce the reactivity of complex **5** and to obtain rate data at similar alcohol concentrations, ROH/benzene-d_6 mixtures using an alcohol concentration of ca. 4.9M were studied (see Table 1). For methanol, the ^{31}P signal observed at $\delta = 99.8$, $^2J = 51$ Hz (note, again, the solvent effect on this signal) disappears as the product **6** forms: $\delta = 140.0$, $^2J = 62$ Hz. The observed rate constant, k_{obs}, for the formation of **6** is 6.4×10^{-4} s^{-1} at 21 °C. In a separate experiment, ^{19}F measurements show that (for a solution of 8 mg of **5** dissolved in 1:4 MeOH/benzene-d_6) only compound **5** has com-

(16) The reactions of complex **5** (ca. 0.01 mmol, 0.019 M) with alcohols were followed by ^{31}P NMR spectroscopy, in solvent mixtures alcohol/benzene-d_6. For **5** in $CDCl_3$ the ^{31}P values are $\delta = 112.5$, $^2J = 54$ Hz, $\delta = 53.2$, $^2J = 54$ Hz. In (a) methanol/benzene-d_6, one finds $\delta = 112.5$, $^2J = 54$ Hz and $\delta = 53.8$, $^2J = 54$ Hz, whereas in 1:2.5 ethanol/benzene-d_6, these change to $\delta = 109.7$, $^2J = 57$ Hz and $\delta = 53.3$, $^2J = 57$ Hz. Consequently the complexes with $\delta = 91.6$, $^2J = 52$ Hz or $\delta = 86.0$, $^2J = 48$ Hz (methanol) and $\delta = 87.1$, $^2J = 48$ Hz (ethanol) do not represent **5**.

Table 1. Observed Rate Constants for the Reaction of 5 with Alcohols[a]

alcohol (M)	temp (°C)	k_{obs} (s^{-1})[b]
methanol (4.93)[c]	20.5	6.4×10^{-4} [d]
ethanol (13.7)[e]	20.5	2.6×10^{-3} [d]
ethanol (4.92)[f]	20.5	5.6×10^{-4} [d]
2-propanol (4.96)[h]	27.1	8.8×10^{-5} [i]

[a] [**5**] = 0.013−0.023 M. [b] All values ±12%. [c] 100/400 (μL) MeOH/benzene-d_6. [d] d[product]/dt. [e] 400:100 (μL) EtOH/benzene-d_6. [f] 145:360 (μL) EtOH/benzene-d_6. [h] 190:310 (μL) *i*-PrOH/benzene-d_6. [i] −d[**5**]/dt.

plexed triflate. The remaining species show the ^{19}F signal for free OTf^-.

For the reaction of **5** with ethanol the rate constant, $k_{obs} = 5.6 \times 10^{-4}$ s^{-1}, is calculated from the intensities of the high-frequency peak of the product. This value indicates that, for these somewhat more dilute alcohol solutions, the reactions with MeOH and EtOH at 21 °C proceed at similar rates.

Due to its relatively slow rate, the reaction with 2-propanol was carried out at 27 °C, and not 21 °C. The major peaks observed are those of the starting material, $\delta = 106.5$, $^2J = 55$ Hz, together with a weak, unresolved resonance at ca. 94 ppm. The signal for complex **5**, initially not well resolved, shifts gradually to $\delta = 109.2$ ($^2J = 56$ Hz) toward the end of the reaction. The product **8**, $\delta = 138.9$, $^2J = 59$ Hz, slowly reacts to form a new species, $\delta = 114.9$, $^2J = 72$ Hz and $\delta = 60.7$, $^2J = 72$ Hz. On the basis of subsequent observations we believe this species to arise from hydrolyses/protonation reactions, i.e., to form a P(=O)(OR)(OH) ligand. This is based partially on the relatively large ^2J value of 72 Hz and partially on the known tendency of **6**−**8** to slowly hydrolyze.[14] After 16 h, the two product compounds appear present in similar amounts. The reaction rate was calculated using the disappearance of the substrate, according to eq 8, giving a value of $k_{obs} = 8.8 \times 10^{-5}$ s^{-1} (27 °C).

$$c_t = c_\infty + (c_0 - c_\infty) \exp -(k_{obs}t) \qquad (8)$$

The concentration dependence of **5** (via the intensity of the tertiary phosphine substrate peak at $\delta = 53.9$) vs time is shown in Figure 3. The reaction with 2-propanol can be considered to be 1 order of magnitude slower than with either methanol or ethanol.

The good fit obtained for the reaction with 2-propanol, as well with those for methanol and ethanol, indicates that the reactions are first order with respect to complex **5**. A comparison of the values of k_{obs} obtained using different amounts of EtOH (13.7 and 4.96 M) indicates a rate dependence on the concentration of the alcohol (see Table 1).

The reaction of **5** with 2-propanol (1:1.6 *i*-PrOH/benzene-d_6, 4.96 M) was also studied in the presence of an excess of sodium triflate (NaOTf, 0.133 mmol in 605 μL, 0.22 M). The substrate **5** was consumed after 4 h, whereas in the same time, without added sodium triflate, ca. 70% of substrate had reacted; that is, addition of triflate increases the reaction rate. Mechanistically speaking, if triflate dissociation was important, the rate should be slower. As described above, the product **8** reacts to form the species previously observed. Regrettably, due to the presence of species whose ^{31}P resonances overlap and/or are too broad to determine precisely, it was not possible to obtain a reliable valuable of k_{obs}.

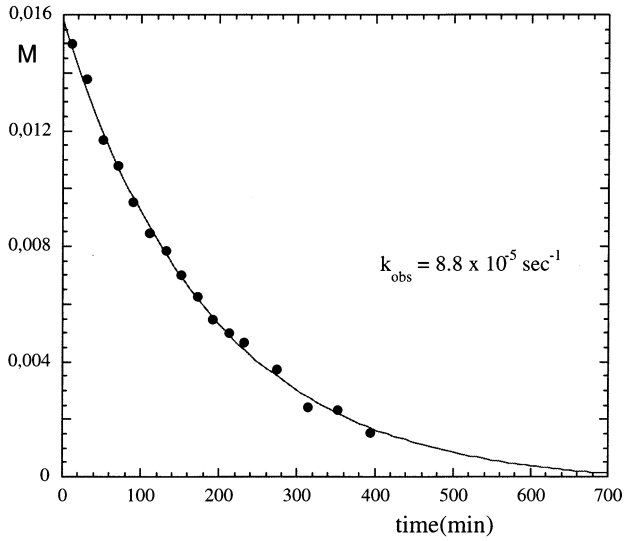
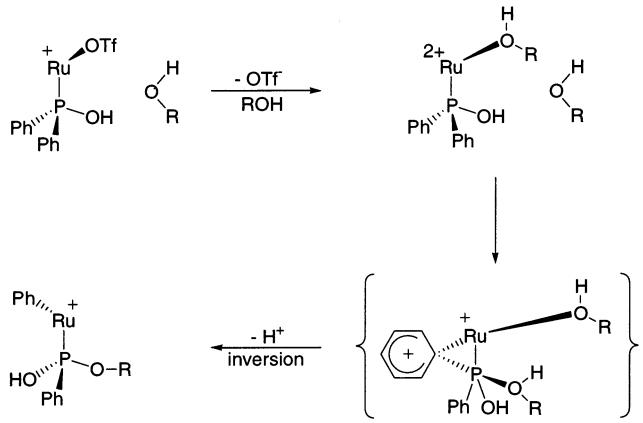


Figure 3. Plot of the concentration of complex **5**, obtained from the intensity values of the ^{31}P NMR peak at $\delta = 53.9$, against time, for the reaction with 2-propanol, in 1:1.6 2-propanol/benzene-d_6, at 27 °C, showing the best exponential decay fitted to the set of data points.

Scheme 3



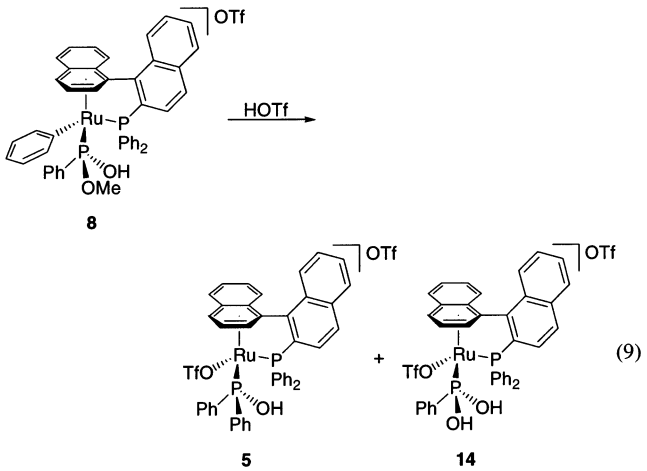
The reaction of complex **5** (0.023 M) with 2-propanol ([*i*-PrOH] = 4.96 M) using the solvent mixture 1:1.6 *i*-PrOH/$CDCl_3$ at 27 °C is slower than in the corresponding *i*-PrOH/benzene-d_6 mixture. After 5 h, the solution contained comparable amounts of **5** and the two products. In contrast to the experiments involving benzene-d_6, the first spectrum after mixing did not show peaks due to **8**. Only the resonances of **5** and two intermediate species, $\delta = 93.2$ and $\delta = 82.4$, are observed.

A possible reaction pathway, which rationalizes the transformation of complex **5** into products **6**, **7**, and **8**, respectively, is shown in Scheme 3 (only the reactive sites of these molecules are shown). Using the alcohol as solvent favors the formation of the dicationic solvent complex (as might the presence of excess charged triflate). This solvated dication could be one of the two observed intermediates. There is always solvent alcohol close by, partially due to hydrogen bonding[17] to both the triflate anion and POH moieties (another possible source of an intermediate structure). In the transition state the complexed solvent begins to dissociate. Simultaneously,

the phenyl bridges the Ru and P atoms and the proximate H-bonded solvent begins to form the new P−O bond via a pseudo-backside attack. Possibly, these steps occur sequentially, although the alcohol must be in the rate-determining step. This mechanism is reminiscent of the formation of a classical arenium ion[18] (a typical intermediate in 1,2 shifts of aryl rings) and would be consistent with the observed stereospecificity. Since the alcohol is involved in the transition state, it is reasonable that both its concentration and size affect the kinetics.

Concluding this section, the transformation of complex **5** into products **6**−**8** can be envisaged as proceeding through rapid conversion of **5** into intermediate species, characterized by a significant alteration of the ligand environment of the complexed $P(OH)Ph_2$ ligand. At high alcohol content (for methanol and ethanol), where a mass action effect shifts the equilibrium toward the intermediates, complex **5** disappears on mixing. It is likely that these intermediate species result from ligand exchange of the ruthenium-coordinated triflate anion with the alcohol and/or hydrogen bonding. The presence of excess sodium triflate does not retard the process. There is an obvious concentration effect of the alcohol, which, in combination with the slowing effect of the larger R group, e.g., 2-propanol, provides a hint as to why hydrolysis (and eventual formation of **10**) becomes competitive for wet higher alcohol homologues.

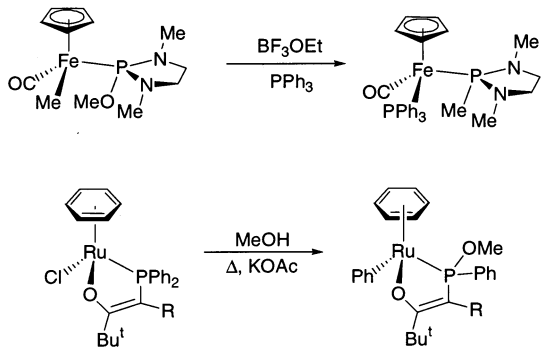
Stereochemistry and Protonation Studies. With a view to preparing chiral complexes with an open coordination site, two of the Ru−{P(OH)OR)Ph} compounds, **6**, R = Me, and **8**, R = *i*-Pr, were allowed to react with excess triflic acid in methylene chloride solution. Surprisingly, instead of removing the Ru−phenyl ligand, the observed protonation product was either exclusively **5** (R = Me) or primarily **5** (R = *i*-Pr), and some of these results are shown in eq 9.



(9)

From the reaction leading from **8** to **5** we find a minor amount of a new $P(OH)_2Ph$ compound, **14** (whose NMR details are provided in the Experimental Section). Complex **14** presumably arises from some competitive Ru−C protonation together with P(OMe) hydrolysis. For these acid reactions with both **6** and **8**, only a single diastereomer is observed; that is, epimerization at the Ru atom is not found.

This type of migration reaction is known[19,20] (see eqs 10 and 11), but rare.



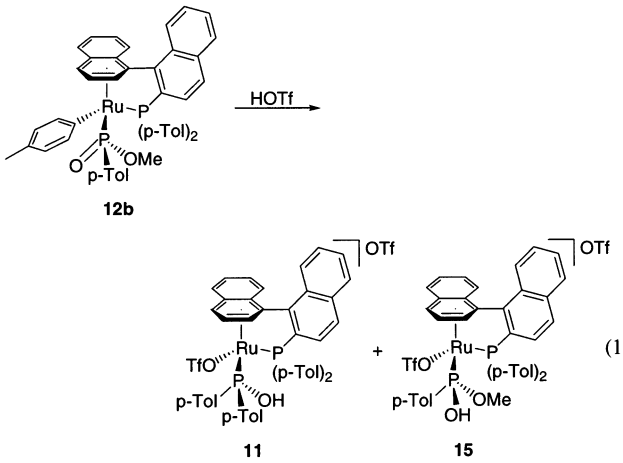
(10)

(11)

The product of eq 10 arises due to alcohol loss to the Lewis acid, followed by methyl migration.[20] The new Ru−Ph in eq 11 may arise via solvolysis of the Ru−Cl bond.[19]

As an additional check on the stereospecificity of the formation of **5** from **6**, we carried out several protonation reactions using optically pure, commercially available (*S*)-*p*-tolyl Binap, **3**. While only marginally different from **2**, this ligand affords yet another subset of complexes, namely, **11** and the alcohol adducts **12b** and **13b** (see eq 6). The neutral P(=O)(OMe)(*p*-tolyl) complex, **12b**, differs somewhat from **6**; however, addition of HOTf clearly generates the P(OH)(OMe)(*p*-tolyl) analogue of **6** as initial product before the reaction proceeds.

In direct analogy with the chemistry of **6**, reaction of **12b** with excess triflic acid affords the (observed and isolated) single diastereomer of **11** under the chosen conditions, plus a modest amount of **15** due to protonation of the tolyl ligand (see eq 12).



(12)

Consequently, both the formation of **6** (**12**) and the reformation of **5** (**11**) proceed stereospecifically. The presence of side products is sensitive to the reaction conditions (see Experimental Section).

It is recognized that epimerization at Ru can (but need not always[21−26]) be facile. Consequently, we repeated

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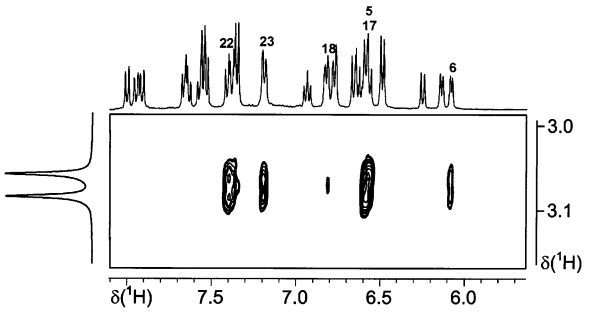


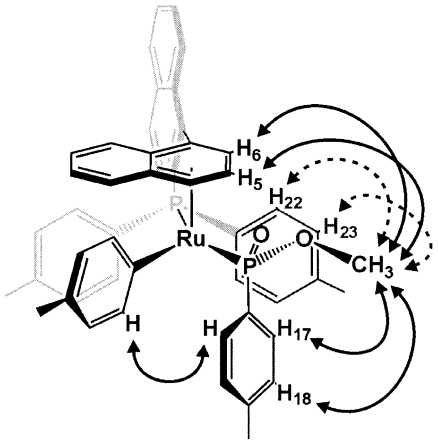
Figure 4. Cross-section from the ^{1}H NOESY NMR spectrum for **12b**. There are contacts from the methoxy group (vertical) to H5 and H6 (weak, from the complexed arene), H22 and H23, the ortho and meta protons of a proximate P-phenyl group of the tertiary phosphine, and H17 and H18 from the *p*-tolyl of the P(=O)(OMe)(*p*-tolyl) ligand (methylene chloride-d_2, 400 MHz, 293 K).

the protonation of **12b** with excess triflic acid in methylene chloride at dry ice acetone temperature. After transferring to a precooled NMR probe at 220 K, we observed only a single product with a broad resonance at $\delta = 123.2$ and a sharp doublet at $\delta = 52.4$. Slowly warming using 10 deg increments to 270 K eventually affords a sharp ^{31}P NMR spectrum of the pure P(OH)-(*p*-tolyl)$_2$ analogue, **11** (with no trace of **15** under these mild conditions). Since there is no evidence for a second diastereomer, we conclude that the reaction is very facile and, indeed, proceeds stereospecifically.

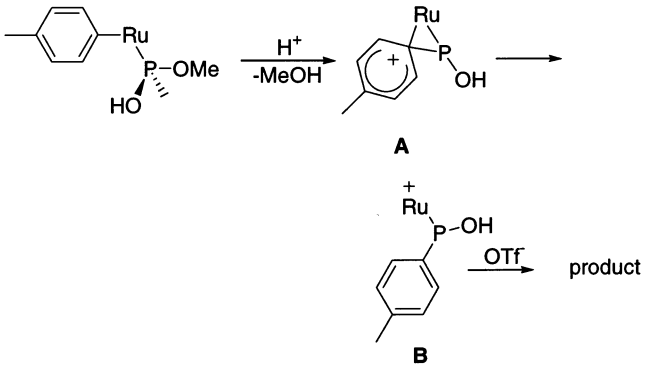
To help in understanding the specificity of this transformation, we have determined the 3-D solution structure of the {P(=O)(OMe)(*p*-tolyl)} derivative **12b**, in methylene chloride, using NOE methods.[27,28] A cross section from this NOESY spectrum is given in Figure 4, and the most relevant results are summarized in Scheme 4. The important contacts stem from the P(=O)(OMe)(*p*-tolyl) group. The methoxy group is proximate to two *p*-tolyl groups, one from each of the two P-donors. However, it is *remote* from the Ru−*p*-tolyl ligand. This methyl group shows NOEs to both ortho and meta protons of one P−aryl ring of the tertiary phosphine as well as weakish contacts to two of the η^6-arene protons. The ortho protons of the P(=O)(OMe)(*p*-tolyl) group show contacts to the Ru−*p*-tolyl group.

From these and additional NOE results it can be seen that the Ru−aryl ring is positioned in a ca. anti periplanar position relative to the methoxy group. This structural feature allows us to rationalize both the ease and specificity of the reaction (see Scheme 5).[29] The positive charge, which would develop from facile protonation of the P(OMe) group by the strong acid, can be stabilized by the Ru−*p*-tolyl group, again, in analogy with carbon cation chemistry (see structure **A**). Complete transfer of the aryl to the P atom is then accompanied by rapid triflate capture by the ruthenium cation, **B**, to afford product. Since **A** and **B** are positively charged, in methylene chloride the triflate anion will be close by. The excess of triflic acid helps to facilitate rapid capture before epimerization.

Scheme 4



Scheme 5



Comments. The chemistry described above allows us to access a series of novel Ru compounds containing P(OH)(OR)(Aryl) ligands. Their formation can be facile and is most likely driven by the electrophilic Ru^{2+} metal center, which arises after solvolysis. Apparently, the chiral atropisomeric character of the original Binap is not lost, with the result that new stereogenic centers are produced. Experiments designed to exploit these new complexes are currently in progress.

Experimental Section

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Pentane and diethyl ether were distilled from sodium−potassium alloy. Dichloromethane was distilled from CaH_2, 1,2-dichloroethane from P_4O_{10}, and toluene from potassium. Water was deoxygenated prior to use; all other chemicals were commercial products und were used as received. (*S*)-*p*-Tolyl-Binap was purchased from Strem. NMR spectra were recorded with Bruker DPX-300 and Avance 400 and 500 spectrometers. Chemical shifts are given in ppm, and coupling constants (*J*) are given in Hz. Elemental analyses and mass spectroscopic studies were performed at ETHZ.

Preparation of 6. Compound **5** (54 mg, 0.052 mmol) was dissolved in 12 mL of methanol and stirred at room temper-

(24) Onitsuka, K.; Dodo, N.; Matsushima, Y.; Takahashi, S. *Chem. Commun.* **2001**, 521.

(25) Faller, J. W.; Patel, B. P.; Albrlizzio, M. A.; Curtis, M. *Organometallics* **1999**, *18*, 3096. Faller, J. W.; Parr, J. *Organometallics* **2000**, *19*, 3556. Faller, J. W.; Parr, J. *Organometallics* **2000**, *19*, 1829.

(26) Zanetti, N. C.; Spindler, F.; Spencer, J.; Togni, A.; Rihs, G. *Organometallics* **1996**, *15*, 860.

(27) The correct ^{1}H NMR assignments arise from a combination of homonuclear and heteronuclear X,H-correlation experiments. The ^{31}P,^{1}H experiment is crucial in that it allows the facile recognition of the ortho protons of the P-tolyl rings, i.e., one set for the P=O and two sets for the tertiary phosphine donors.

(28) Pregosin, P. S.; Trabesinger, G. *J. Chem. Soc., Dalton Trans.* **1998**, 727. Pregosin, P. S.; Valentini, M. *Enantiomer* **2000**, *4*, 529.

(29) One can consider the chemistry of, for example, eq 9 and Scheme 5 as involving equilibria. However, on the preparative scale we do not observe starting material and not all the experimental conditions are identical.

ature for 30 min. The solvent was removed in vacuo and the remaining residue washed three times with ether. Complex **6** is obtained as an orange-yellow solid. Yield: 46 mg (96%).

^{1}H NMR (d_8-thf, 400 MHz): 9.64 (d, $^2J_{PH}$ = 8.1, 1H, O*H*), 8.15 (d, $^3J_{HH}$ = 7.5, 1H), 8.13 (d, $^3J_{HH}$ = 8.2, 1H), 8.02 (d, $^3J_{HH}$ = 8.5, 1H). 7.86 (d, $^3J_{HH}$ = 8.5, 1H), 7.77 (m, 1H), 7.73 (t, $^3J_{HH}$ = 7.8, 1H), 7.69 (m, 1H), 7.67 (m, 1H), 7.64 (m, 1H), 7.63 (m, 2H), 7.55 (m, 2H), 7.37 (H5, m, 1H), 7.35 (m, 2H), 7.28 (H12, d, $^3J_{HH}$ = 7.7, 2H), 7.24 (t, $^3J_{HH}$ = 7.9, 1H), 7.15 (m, 2H), 7,11 (m, 2H), 6.90 (m, 2H), 6.89 (H4, d, $^3J_{HH}$ = 5.6, 1H,), 6.79 (t, $^3J_{HH}$ = 7.2, 1H), 6.75 (H6, m, 1H), 6.71 (m, 1H), 6.62 (m, 3H), 3.68 (d, $^3J_{PH}$ = 12.0, 3H, C*H*$_3$). ^{13}C NMR (d_8-thf, 100 MHz): 150.3 (C11), 148.5, 147.3(C12, d, $^2J_{CP}$ = 5), 140.9, 137.9, 135.6 (d, $^2J_{CP}$ = 11), 134.8, 134.7, 133.9, 131.4, 131.0, 130.9, 130.8 (d, $^2J_{CP}$ = 11), 130.6, 130.5, 129.4, 129.0, 128.6, 128.5, 127.9 (d, $^3J_{CP}$ = 10.1), 127.7, 126.6, 126.1, 123.1, 117.8 (C1), 116.2 (C3), 106.8 (C2), 101.1 (C5, d, $^2J_{CP}$ = 5), 93.5 (C6), 91.6 (C4, d, $^2J_{CP}$ = 9), 53.6 (d, $^2J_{CP}$ = 13). ^{19}F NMR (d_8-thf, 282 MHz): −78.17. ^{31}P NMR (d_8-thf, 162 MHz): 144.7 (P1, d, $^2J_{PP}$ = 61), 60.3 (P2, d, $^2J_{PP}$ = 61). MS (FAB): 773.0 (M^+), 695.0 (M^+ − Ph), 539.0 (Ru(**2**)$^+$ − PPh$_2$; 100%). Anal. Calcd for $C_{46}H_{37}F_3O_5P_2RuS{\cdot}H_2O$: C, 58.78; H, 4.19. Found: C, 58.66; H, 4.78.

Preparation of 7. Compound **5** (50 mg, 0.048 mmol) was dissolved in 12 mL of ethanol and stirred at room temperature for 45 min. The solvent was removed in vacuo and the remaining residue washed three times with ether/pentane, 2:1. Product **7** is obtained as an orange-yellow solid. Yield: 38 mg (83%). ^{1}H NMR (d_8-thf, 400 MHz): 9.71 (d, $^2J_{PH}$ = 6.6, 1H, O*H*), 8.14 (m, 2H), 8.02 (d, $^3J_{HH}$ = 8.1, 1H), 7.80 (d, $^3J_{HH}$ = 8.3, 1H), 7.76 (d, $^3J_{HH}$ = 7.9, 1H), 7.71 (m, 2H), 7.60 (m, 4H), 7.50 (m, 3H), 7.34 (m, 1H), 7.30 (m, 1H), 7.21 (m, 3H), 7.11 (m, 4H), 6.88 (m, 3H), 6.78 (t, $^3J_{HH}$ = 7.0, 1H), 6.71 (H6, d, $^3J_{HH}$ = 5.4, 1H), 6.62 (m, 5H), 3.69 (m, 1H, C*H*$_2$), 3.46 (m, 1H, C*H*$_2$) 1.30 (t, $^3J_{HH}$ = 7.0, 3H, C*H*$_3$). ^{13}C NMR (d_8-thf, 100 MHz): 150.3 (C11, d, $^1J_{CP}$ = 21),148.4, 147.0 (C12, d, $^2J_{CP}$ = 5), 140.8, 138.1, 135.4, 134.7, 134.1, 130.9, 130.8, 130.4, 129.5, 129.0, 128.5, 128.4, 127.9, 127.8, 127.6, 126.6, 126.1, 123.1, 118.3 (C1), 116.6 (C3), 108.1 (C2), 100.9 (C5), 91.0 (C4), 93.5 (C6), 63.2 (d, $^2J_{CP}$ = 12, *C*H$_2$), 15.7 (d, $^2J_{CP}$ = 7, *C*H$_3$). ^{19}F NMR (d_8-thf, 282 MHz): −79.40. ^{31}P NMR (d_8-thf, 162 MHz): 142.4 (P1, d, $^2J_{PP}$ = 60), 59.7 (P2, d, $^2J_{PP}$ = 60). MS (FAB): 787.0 (M^+, 100%), 709.0 (M^+ − Ph), 539.0 (Ru(**2**)$^+$ − PPh$_2$). Anal. Calcd for $C_{47}H_{39}F_3O_5P_2RuS{\cdot}H_2O$: C, 59.18; H, 4.33. Found: C, 58.58; H, 4.30.

Preparation of 8. Complex **5** (50 mg, 0.048 mmol) was dissolved in 12 mL of 2-propanol and stirred at room temperature for 70 min. The solvent was removed in vacuo and the remaining residue washed three times with ether/pentane, 2:1. Product **8** is obtained as an orange-yellow solid. Yield: 39 mg (85%). Crystals suitable for X-ray diffraction were obtained upon slow evaporation of a saturated benzene solution.^{1}H NMR (d_8-thf, 400 MHz): 10.07 (s, 1H, O*H*), 8.15 (d, $^3J_{HH}$ = 8.2, 1H), 8.10 (d, $^3J_{HH}$ = 7.9, 1H), 8.00 (d, $^3J_{HH}$ = 8.3, 1H). 7.77 (m, 1H), 7.76 (m, 1H), 7.60 (m, 1H), 7.53 (d, $^3J_{HH}$ = 3.8, 2H), 7.48 (m, 6H), 7.35 (t, $^3J_{HH}$ = 7.4, 1H), 7.25 (t, $^3J_{HH}$ = 7.6, 1H), 7.18 (m, 1H), 7.13 (m, 2H), 7.03 (d, $^3J_{HH}$ = 7.1, 2H), 6.97 (m, 3H), 6.87 (d, $^3J_{HH}$ = 5.3, 1H), 6.71 (m, 4H), 6.60 (m, 4H), 4.00 (m, 1H, C*H*), 1.38 (d, $^3J_{HH}$ = 6.0, 3H, C*H*$_3$) 1.01 (d, $^3J_{HH}$ = 6.1, 3H, C*H*$_3$). ^{13}C NMR (d_8-thf, 100 MHz): 148.5 (C11, dd, $^2J_{CP}$ = 21, 8.9), 148.1 (d, $^1J_{CP}$ = 50), 145.3 (C12, d, $^3J_{CP}$ = 5), 140.8 (d, $^2J_{CP}$ = 19), 137.9 (d, $^1J_{CP}$ = 76), 134.8 (d, $^2J_{CP}$ = 10), 134.7, 134.5, 134.5 (d, $^2J_{CP}$ = 10), 132.9 (d, $^1J_{CP}$ = 48), 131.5 (d, $^3J_{CP}$ = 13), 131.4 (d, $^2J_{CP}$ = 11), 131.0 (d, $^3J_{CP}$ = 7), 130.7, 130.4, 129.4 (d, $^1J_{CP}$ = 42), 129.3, 129.0, 128.7 (d, $^3J_{CP}$ = 11), 128.6, 128.6 (d, $^2J_{CP}$ = 4), 128.1 (d, $^3J_{CP}$ = 10), 127.4 (d, $^3J_{CP}$ = 11), 126.8, 126.7, 122.7, 119.8 (C1, d, $^2J_{CP}$ = 15), 117.7 (C3, d, $^2J_{CP}$ = 4), 106.8 (C2, d, $^2J_{CP}$ = 12), 100.2 (C5, d, $^2J_{CP}$ = 5), 93.9 (C6), 89.2 (C4, d, $^2J_{CP}$ = 10), 72.2 (d, $^2J_{CP}$ = 13), 23.6 (*C*H$_3$), 23.1 (*C*H$_3$). ^{19}F NMR (d_8-thf, 282 MHz): −79.40. ^{31}P NMR (d_8-thf, 162 MHz): 140.7 (P1, d, $^2J_{PP}$ = 59), 57.6 (P2, d, $^2J_{PP}$ = 59). MS (FAB): 801.0 (M^+), 723.0 (M^+ − Ph), 538.9 (Ru(**2**)$^+$ − PPh$_2$). Anal. Calcd for $C_{48}H_{41}F_3O_5P_2RuS$: C, 60.69; H, 4.35. Found: C, 60.62; H, 4.54.

Preparation of 9b. Complex **5** (30 mg, 0.028 mmol) was dissolved in 5 mL of ethylene glycol and stirred at room temperature for 10 min. Potassium carbonate (15 mg, 0.16 mmol) was added, and the color of the solution changed immediately from yellow to orange. Stirring was continued for another 5 min, after which toluene (10 mL) was added, and the mixture washed very thoroughly with water. The solvent was removed in vacuo, and the residue was dried, redissolved in toluene, filtered, and taken to dryness again. Washing the orange residue with a small amount of pentane afforded **9b** as an orange solid. Yield: 14 mg (64%). ^{1}H NMR (CD_2Cl_2, 300 MHz): (CD_2Cl_2, 500 MHz) 8.03 (d, $^3J_{HH}$ = 8.3, 1H), 7.98 (d, $^3J_{HH}$ = 8.9, 1H), 7.93 (d, $^3J_{HH}$ = 8.3, 1H), 7.69 (d, $^3J_{HH}$ = 8.3, 1H), 7.67 (m, 1H), 7.59 (m, 1H), 7.58 (m, 1H), 7.54−7.48 (m, 2H), 7.39 (m, 1H), 7.33 (H12, d, $^3J_{HH}$ = 7.7, 2H), 7.28 (t, $^3J_{HH}$ = 7.9, 1H), 7.19 (m, 2H), 7.05 (m, 1H), 6.95 (m, 2H), 6.89 (dt, $^3J_{HH}$ = 7.7, $^4J_{PH}$ = 2.8, 2H), 6.74 (m, 2H), 6.71 (m, 1H), 6.56 (t, $^3J_{HH}$ = 7.6, 2H), 6.54 (m, 2H), 6.32 (H4, d, $^3J_{HH}$ = 6.5, 1H), 6.30 (d, $^3J_{HH}$ = 8.5, 1H), 6.24 (H6, d, $^3J_{HH}$ = 5.0, 1H), 5.66 (d, $^2J_{HH}$ = 9.4, O*H*), 3.70−3.50 (m, 3H, C*H*$_2$), 3.26 (m, 1H, C*H*$_2$-OH). ^{13}C NMR (CD_2Cl_2, 75 MHz): 155.9 (C11), 149.5, 147.4 (C12, d, $^3J_{PC}$ = 5), 141.3, 135.3 (d, $^2J_{PC}$ = 11), 134.9 (d, $^2J_{PC}$ = 10), 134.3, 132.4, 131.7, 130.5 (d, $^2J_{PC}$ = 10), 130.2, 129.8, 128.6, 128.5, 128.4, 128.3, 127.5 (d, $^3J_{PC}$ = 10), 127.0 (d, $^3J_{PC}$ = 10), 126.2, 126.1, 122.6, 115.8 (C3), 113.0 (C1), 111.2 (C2, d, $^3J_{PC}$ = 10), 101.3 (C5, d, $^3J_{PC}$ = 5), 91.5 (C6), 89.4 (C4, d, $^3J_{PC}$ = 11), 69.4 (d, $^3J_{PC}$ = 12, P-O-*C*H$_2$), 62.8 (*C*H$_2$-OH). ^{31}P NMR (CD_2Cl_2, 202 MHz): 109.2 (P1, d, $^2J_{PP}$ = 56), 62.8 (P2, d, $^2J_{PP}$ = 56). MS (FAB): 802.2 (M^+), 724.2 (M^+ − Ph), 646.2 (M^+ − 2Ph), 538.5 (Ru(**2**)$^+$ − PPh$_2$). Anal. Calcd for $C_{46}H_{38}O_5P_2Ru{\cdot}2\ H_2O$: C, 65.94; H, 5.06. Found: C, 66.26; H, 5.23. Two equivalents of water are observed in the ^{1}H NMR spectrum.

Preparation of 11. To a solution of (*S*)-Ru(*p*-Tol)Binap(OAc)$_2$ (150 mg, 0.167 mmol) in 5 mL of dichloroethane was added triflic acid (35 μL, 0.399 mmol). The orange solution was stirred at 90 °C for 60 min. After this time the solvent was removed in vacuo and the remaining residue washed three times with ether/pentane, 1:1. Product **11** is obtained as a yellow solid. Yield: 147 mg (82%). ^{1}H NMR (CD_2Cl_2, 300 MHz): 8.27 (dd, $^4J_{PH}$ = 8.6, $^3J_{HH}$ = 8.6, 1H), 8.19 (d, $^3J_{HH}$ = 8.5, 1H), 8.02 (d, $^3J_{HH}$ = 8.5, 1H), 7.85−7.62 (m, 7H). 7.51 (H4, d, $^3J_{HH}$ = 7.3, 1H), 7.34 (m, 2H), 7.09 (m, 2H), 7.07−6.92 (m, 7H), 6.79 (m, 4H), 6.36 (d, $^3J_{HH}$ = 8.4, 1H), 5.77 (H6, m, 1H), 5.57 (H5, m, 1H), 2.45 (s, 3H, C*H*$_3$), 2.35 (s, 3H, C*H*$_3$), 2.22 (s, 3H, C*H*$_3$), 2.18 (s, 3H, C*H*$_3$). ^{13}C NMR (CD_2Cl_2, 75 MHz): 142.8 (d, $^4J_{CP}$ = 3), 142.7 (d, $^4J_{CP}$ = 3), 142.1 (d, $^4J_{CP}$ = 3), 141.7 (d, $^4J_{CP}$ = 3), 141.2 (d, $^1J_{CP}$ = 47), 140.8 (d, $^2J_{CP}$ = 11), 139.0 (d, $^1J_{CP}$ = 63), 135.3 (d, $^4J_{CP}$ = 2), 135.1, 134.8, 134.6 (d, $^2J_{CP}$ = 11), 132.8 (d, $^2J_{CP}$ = 11), 132.0 (d, $^3J_{CP}$ = 8), 131.8, 131.7, 131.4 (d, $^2J_{CP}$ = 10.6), 130.2 (d, $^3J_{CP}$ = 12.4), 129.6 (d, $^3J_{CP}$ = 12.0), 129.5 (d, $^3J_{CP}$ = 11), 129.3 (d, $^3J_{CP}$ = 11), 129.2, 129.0, 128.8 (d, $^3J_{CP}$ = 13), 127.5, 125.1, 123.7 (d, $^1J_{CP}$ = 54), 123.6 (d, $^1J_{CP}$ = 54), 117.0 (C2, d, $^3J_{CP}$ = 7), 110.8 (C3), 107.7 (C5, d, $^3J_{CP}$ = 6), 99.9 (C4, d, $^3J_{CP}$ = 9), 99.4 (C1, d, $^3J_{CP}$ = 4), 77.8 (C6), 21.6, 21.4. ^{19}F NMR (CD_2Cl_2, 282 MHz): −78.2 (Ru-Otf), −79.3 (OTf$^-$). ^{31}P NMR (CD_2Cl_2, 162 MHz): 115.2 (P1, d, J_{PP} = 56), 52.9 (P2, d, J_{PP} = 56). MS (FAB): 947.0 (M^+), 797.3 (M^+ − OTf, 100%), 567.2 (Ru(**3**)$^+$ − P(*p*-Tol)$_2$). Anal. Calcd for $C_{50}H_{42}F_6O_7P_2RuS_2{\cdot}H_2O$: C, 53.91; H, 3.98. Found: C, 53.84; H,4.29.

Preparation of 12b. In 15 mL of methanol **11** (70 mg, 0.064 mmol) was dissolved and the solution stirred at room temperature for 15 min. Potassium carbonate (35 mg, 0.25 mmol) was added, resulting in an immediate color change from yellow to orange. After 10 min, the solvent was removed in vacuo, the orange residue redissolved in toluene, and the solution washed thoroughly with water. Filtration and drying afforded product **12b** as an orange solid. Yield: 40 mg, 76%. ^{1}H NMR (d_8-thf, 300 MHz): 8.01 (d, $^3J_{HH}$ = 8.3, 1H), 7.96 (d, $^3J_{HH}$ = 8.8, 1H),

7.88 (d, $^3J_{HH}$ = 8.3, 1H), 7.73 (d, $^3J_{HH}$ = 8.1, 1H), 7.61−7.38 (m, 8H), 7.24 (m, 2H), 6.92 (t, $^3J_{HH}$ = 7.6, 1H), 6.81 (m, 2H), 6.72−6.64 (m, 6H), 6.53 (H5, m, 1H), 6.45 (d, $^3J_{HH}$ = 7.4, 2H), 6.26 (H4, d, $^3J_{HH}$ = 6.7, 1H), 6.22 (d, $^3J_{HH}$ = 8.3, 1H), 6.06 (H6, m, 1H), 3.08 (d, $^3J_{PH}$ = 10.3, 3H, OCH_3), 2.41 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 2.10 (s, 3H, CH_3). ^{13}C NMR (d_8-thf, 75 MHz): 152.0 (C11), 150.2 (d, $^1J_{CP}$ = 51), 147.6 (C12, d, $^3J_{CP}$ = 5), 143.0, 141.4, 140.2, 140.1, 137.2, 135.5 (d, $^2J_{CP}$ = 12), 135.0 (d, $^2J_{CP}$ = 10), 134.4, 131.9, 131.7, 130.8, 130.4 (d, $^2J_{CP}$ = 10), 129.8, 129.4, 129.3, 128.7 (d, $^3J_{CP}$ = 11), 128.5, 128.3, 128.2, 128.1, 128.0 (d, $^3J_{CP}$ = 10.8), 127.9, 127.4 (d, $^3J_{CP}$ = 10.4), 127.0, 126.7, 126.0, 116.3 (C3), 112.5 (C2), 111.2 (C1), 102.0 (C5), 90.7 (C6), 89.2 (C4), 50.6 (O-*C*H$_3$), 21.0 (*C*H$_3$), 20.7 (*C*H$_3$), 20.6 (*C*H$_3$), 20.5 (*C*H$_3$). ^{31}P NMR (d_8-thf, 121 MHz): 104.3 (P1, d, $^2J_{PP}$ = 57), 62.6 (P2, d, $^2J_{PP}$ = 57). MS (FAB): 828.3 (M^+), 737.3 (M^+ − *p*-Tol), 567.2 (Ru(**3**)$^+$ − P(*p*-Tol)$_2$, 100%). Anal. Calcd for $C_{49}H_{44}O_2P_2Ru$: C, 71.09; H, 5.36. Found: C, 70.81; H, 6.09.

Preparation of 13b. Complex **11** (30 mg, 0.027 mmol) was dissolved in ethylene glycol (3 mL) and stirred at room temperature for 10 min, then potassium carbonate (15 mg, 0.11 mmol) was added and the color of the solution changed immediately from yellow to orange. Toluene (7 mL) was added to the solution and the resulting suspension washed very thoroughly with deoxygenated water. The solvent was removed in vacuo and the residue washed with a small amount of pentane to afford **13b** as orange solid. Yield: 17 mg (71%). ^{1}H NMR (CD_2Cl_2, 400 MHz): 8.01 (d, $^3J_{HH}$ = 8.1, 1H), 7.95 (d, $^3J_{HH}$ = 8.6, 1H), 7.92 (d, $^3J_{HH}$ = 8.3, 1H), 7.69 (d, $^3J_{HH}$ = 8.6, 1H), 7.65 (m, 1H), 7.60−7.50 (m, 3H), 7.31 (dd, $^3J_{PH}$ = 11.0, $^3J_{HH}$ = 8.0, 2H), 7.25 (H12, d, $^3J_{HH}$ = 7.8, 2H), 7.14 (m, 1H), 7.01−6.94 (m, 2H), 6.77 (m, 2H), 6.66−6.57 (m, 4H), 6.46 (d, $^3J_{HH}$ = 7.6, 2H), 6.39 (H4, d, $^3J_{HH}$ = 6.9, 1H), 6.26 (m, 3H), 6.18 (H6, m, 1H), 5.74 (d, $^3J_{HH}$ = 9.1, 1H, O*H*), 3.57 (m, 1H), 3.45 (m, 1H), 3.24 (m, 1H), 2.44 (s, 3H, CH_3), 2.21 (s, 6H, CH_3), 2.17 (s, 3H, CH_3). ^{13}C NMR (CD_2Cl_2, 125 MHz): 151.7 (C11), 150.1 (d, $^1J_{PC}$ = 50), 147.4 (C12, d, $^3J_{PC}$ = 5), 141.5 (d, $^2J_{PC}$ = 22.5), 141.0, 140.5, 140.3, 137.7, 135.2 (d, $^2J_{PC}$ = 12), 134.9 (d, $^2J_{PC}$ = 10), 134.2, 131.8, 131.5, 130.9 (d, $^2J_{PC}$ = 10), 130.0 (d, $^2J_{PC}$ = 6), 129.5, 128.9 (d, $^3J_{PC}$ = 11), 128.4, 128.2 (d, $^3J_{PC}$ = 10), 128.0, 127.3 (d, $^3J_{PC}$ = 10), 127.1, 126.9, 126.1, 115.7 (C3, d, $^2J_{PC}$ = 4), 112.0 (C1, d, $^2J_{PC}$ = 8), 111.7 (C2), 101.6 (C5, d, $^2J_{PC}$ = 6), 91.6 (C6), 89.2 (C4, d, $^2J_{PC}$ = 11), 69.5 (d, $^2J_{PC}$ = 13), 62.9, 21.7, 21.3, 20.9. ^{31}P NMR (CD_2Cl_2, 202 MHz): 110.6 (P1, d, $^2J_{PP}$ = 57), 61.4 (P1, d, $^2J_{PP}$ = 57). MS (FAB): 858.2 (M^+), 797.2 (M^+ − ethylene glycol), 767.2 (M^+ − *p*-Tol), 567.3 (Ru(**3**)$^+$ − P(*p*-Tol)$_2$). Anal. Calcd for $C_{50}H_{46}O_3P_2Ru$: C, 70.00; H, 5.40. Found: C, 69.54; H, 6.16.

Kinetics. The reactions of complex **5** (0.01 mmol, 0.019 M) were monitored by ^{31}P NMR spectroscopy using a Bruker AC300 NMR instrument at 121.5 MHz, in solvent mixtures (0.50 mL) of alcohol with benzene-d_6, used to provide the lock signal. H_3PO_4 was used as an external standard for peak calibration, in EtOH/benzene-d_6, 400/100 (v/v, μL), as well as in EtOH/ benzene-d_6, 145/360 (v/v, μL). The temperature in the NMR probe was determined from the chemical shift difference between the OH and CH_2 signals of a solution of ethylene glycol containing 20% DMSO-d_6. MeOH was distilled from magnesium; EtOH and 2-propanol were analytical grade commercial solvents with water content estimated as <0.2%. The alcohol was added to the heterogeneous mixture of complex **5** and benzene-d_6 in the NMR tube, to obtain a clear solution upon mixing. Spectra were collected immediately, using a macro sequence. Identical acquisition parameters were used for each experiment, e.g., 100−200 scans with acquisition time 0.5 s, and the appropriate delay between each spectrum was employed. The first-order rate constants were obtained from a nonlinear least-squares regression analysis by fitting the exponential dependence of concentration, *c*, calculated via peak intensities, against time, which yields values of c_∞, k_{obs}, and correlation coefficient (*r* better than 0.998 for all values of k_{obs}).

Protonation of 6. Triflic acid (50 μL, 0.566 mmol) was added to a solution of **6** (3 mg, 0.0032 mmol) in 0.5 mL of CD_2Cl_2 at room temperature. Within minutes, ca. 90% of the starting material had been converted to compound **5** (as determined by ^{31}P NMR). After removal of excess triflic acid and washing the residue with pentane/Et_2O, 1:1, the resulting spectra for compound **5** were identical with those reported previously.

Protonation of 8. A solution of **8** (5 mg, 0.0052 mmol) in 0.5 mL of CD_2Cl_2 was added dropwise to a stirred solution of 10 μL (0.11 mmol) of HOTf in 0.5 mL of CD_2Cl_2 at 0 °C. After 10 min, the starting material had virtually disappeared. The observed product ratio **5/14** is ca. 6:1 (determined by ^{31}P NMR). A higher ratio of **14** is obtained using the following sequence: A stirred solution of **8** (5 mg, 0.0052 mmol) in 0.7 mL of CD_2Cl_2 was treated dropwise with 30 μL (0.34 mmol) of HOTf at room temperature over a period of 30 min. The observed product ratio **5/14** is ca. 1:2 (determined by ^{31}P NMR) with traces left of starting material. Compound **14** has been characterized by NMR and FAB-MS methods but was not isolated as pure compound.

^{1}H NMR (CD_2Cl_2, 400 MHz): 9.33 (s, br, 2H, O*H*), 8.35 (dd, $^3J_{HH}$ = 8.7, $^3J_{PH}$ = 8.7, 1H), 8.21 (d, $^3J_{HH}$ = 8.3, 1H), 8.12 (dd, $^3J_{HH}$ = 8.6, $^3J_{PH}$ = 7.3, 1H), 8.00 (d, $^3J_{HH}$ = 8.3, 1H), 7.88−7.75 (m, 6H), 7.73−7.34 (m, 9H), 7.27−6.94 (m, 6 H), 6.36 (m, 1H), 5.69 (H5, m, 1H), 5.49 (H6, m, 1H). ^{13}C NMR (CD_2Cl_2, 100 MHz): 141.4, 140.3, 135.3, 135.2, 134.6, 134.3, 132.3, 132.0, 131.4, 131.3, 129.8, 129.6, 129.1, 128.6, 127.7, 127.1, 124.9, 117.7 (C2), 110.2 (C3), 105.6 (C5), 99.3 (C4), 98.4 (C1), 76.7 (C6). ^{19}F NMR (CD_2Cl_2, 376 MHz): −78.30 (s, P-OTf), −79.50 (s, OTf). ^{31}P NMR (CD_2Cl_2, 161 MHz): 131.8 (P1, d, $^2J_{PP}$ = 61), 55.8 (P2, d, $^2J_{PP}$ = 61). MS (FAB): 831.1 (M^+), 681.1 (M^+ − OTf), 539.1 (Ru(**2**)$^+$ − PPh_2).

Protonation of 12b. To a stirred solution of 10 μL (0.11 mmol) of HOTf in 0.5 mL of CD_2Cl_2 was added a solution of **12b** (5 mg, 0.0060 mmol) in 0.5 mL of CD_2Cl_2 at 0 °C in a dropwise fashion. The starting material was no longer present after a few minutes. The observed product ratio, **11/15**, was ca. 4:1 (determined by ^{31}P NMR). After removal of excess triflic acid and washing the residue with pentane/Et_2O, 1:1, the spectra of compound **11** are identical with those recorded via an independent synthesis. FAB-MS of the isolated mixture shows peaks for both compounds. **11**: 947.2 (M^+), 797.3 (M^+ − OTf, 100%), 567.1 (M^+ − OTf, − P(*p*-Tol)$_2$OH). **15**: 887.2 (M^+), 737.3 (M^+ − OTf), 567.1 (M^+ − OTf, − P(*p*-Tol)(OMe)(OH)).

Acknowledgment. We thank the Swiss National Science Foundation, the ETH Zurich, and COST CHEMISTRY D12 (D12 0025.99, Ruthenium Catalysts for Fine Chemistry) for financial support. P.S.P. also thanks F. Hoffmann-La Roche AG Basel for the gift of chemicals as well as Johnson Matthey for the loan of precious metal salts.

OM0102394