

P–C Bond Splitting Reactions in Ruthenium(II) Complexes of Binap and MeO–Biphep Using CF₃SO₃H and HBF₄. A Novel Ru–F–H Interaction

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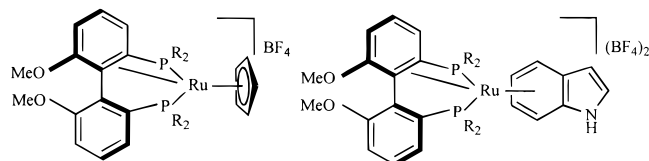
Reaction of Ru(OAc)₂(**1** or **2**), **1** = racemic Binap, or **2** = racemic MeO–Biphep, with wet CF₃SO₃H in 1,2-dichloroethane at 363 K results in P–C bond breaking to afford the cationic triflates [Ru(CF₃SO₃)(6′-diphenylphosphino-1-naphthyl)(PPh₂OH)](CF₃SO₃), **7a**, and [Ru(CF₃SO₃)(6′-diphenylphosphino-1′-(2-dimethoxy)biphenyl)(PPh₂OH)](CF₃SO₃), **7b**. Formally, the H⁺ protonates the acetate and water adds across the P–C bond with the resulting arene ring complexed η⁶ to the Ru(II). The solid-state structures of **7a** and **7b** are reported. A related reaction of Ru(OAc)₂(**1** or **2**) with HBF₄ gives P–C bond cleavage with the formation of compounds that contain the new phosphinite anion, **6** (C₁₂H₁₁BF₂O₂P), derived from hydrolysis of the BF₄[−] anion. NMR studies at 213 K on the reaction mixture derived from Ru(OAc)₂(**1**) and HBF₄ show an HF addition product containing a Ru–F–H moiety with ¹J(¹⁹F, ¹H) = 66 Hz. Warming of this mixture to 273 K gives P–C bond breaking and isolable complexes, **9**, containing the fluorophosphine, Ph₂PF. Complex **10**, a Ru–Cl analogue of **9** with complexed Ph₂PF, has also been isolated.

Introduction

There are a growing number of reactions involving chiral Ru(II) complexes. Specifically, Takaya,¹ Genêt,² and Schmid³ in olefin hydrogenation, Noyori⁴ in ketone reduction, and Kündig⁵ in Diels–Alder condensations, among others, have recently shown that Ru chemistry is suitable for a number of enantioselective transformations under relatively mild conditions.

We have been interested^{6–9} in the Ru chemistry of the atropisomeric chelating ligands Binap, **1**, and MeO–Biphep, **2**. When Ru(OAc)₂(**2**) reacts with 2 equiv of

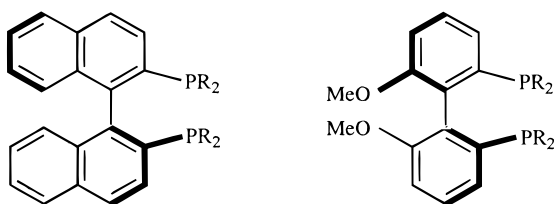
strate, an unexpected bonding mode is observed^{6,7} in which **2** acts as a six-electron donor, e.g., as in the MeO–Biphep complexes **3** and **4**. The complexation of



3, R = 3,5-di-*t*-Bu-phenyl

4, R = 3,5-di-*t*-Bu-phenyl

a double bond from the adjacent arene requires that the biaryl twist substantially so as to open the arene face to complexation with a concomitant low-frequency ³¹P chemical shift.^{6,7} The “precoordination” of the arene together with the strain in the biaryl results in facile protonation of a P–C bond and η⁶ arene complexation



1, R = Ph, 4-Tol, 3,5-di-*t*-Bu-phenyl

2, R = Ph

HBF₄ in the absence of a strongly coordinating sub-

(1) Takaya, H.; Ohta, T.; Mashina, K.; Noyori, R. *Pure Appl. Chem.* **1990**, *62*, 1135–1138. Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345. Takaya, H.; Noyori, R. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 8, p 443. Kumabayashi, H. *Recl. Trav. Chim. Pays-Bas* **1996**, *115*, 201–210.

(2) Genêt, J. P. *Agros Org. Acta* **1995**, *1*, 4–9. Genêt, J. P. *Pure Appl. Chem.* **1996**, *68*, 593–596.

(3) Schmid, R.; Broger, E. A.; Cereghetti, M.; Cramer, Y.; Foricher, J.; M., L.; Mueller, R. K.; Scalone, M.; Schoettel, G.; Zutter, U. *Pure Appl. Chem.* **1996**, *68*, 131. Schmid, R.; Cereghetti, M.; Heiser, B.; Schönholzer, P.; Hansen, H. J. *Helv. Chim. Acta* **1988**, *71*, 897–929. Cramer, Y.; Foricher, J.; Hengartner, U.; Jenny, C.; Kienzle, F.; Ramuz, H.; Scalone, M.; Schlageter, M.; Schmid, R.; Wang, S. *Chimia* **1997**, *51*, 303.

(4) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97–102. Kitamura, M.; Ohkuma, T.; Inoue, S.; Sayo, N.; Kumabayashi, H.; Akutagawa, S.; Ohta, T.; Noyori, R. *J. Am. Chem. Soc.* **1988**, *110*, 629–631.

(5) Kündig, E. P.; Saudan, C. M.; Bernadinelli, G. *Angew. Chem.* **1999**, *111*, 1298–1301.

(6) Feiken, N.; Pregosin, P. S.; Trabesinger, G. *Organometallics* **1997**, *16*, 5756–5762.

(7) Feiken, N.; Pregosin, P. S.; Trabesinger, G.; Scalone, M. *Organometallics* **1997**, *16*, 537.

(8) Feiken, N.; Pregosin, P. S.; Trabesinger, G. *Organometallics* **1997**, *16*, 3735.

(9) den Reijer, C. J.; Rüegger, H.; Pregosin, P. S. *Organometallics* **1998**, *17*, 5213–5215.

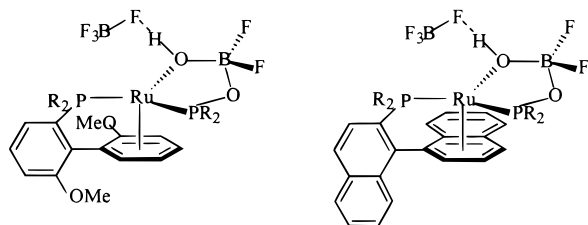
(10) Chan, A. S. C.; Laneman, S. A.; Miller, R. E. In *Selectivity in Catalysis*; ACS Symposium Series 517; American Chemical Society: Washington, DC, 1993; p 27.

(11) Goodson, F. E.; Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 12441–12453.

(12) Morita, D. K.; Stille, J. K.; Norton, J. R. *J. Am. Chem. Soc.* **1995**, *117*, 8576–8581. Kong, K. C.; Cheng, C. H. *J. Am. Chem. Soc.* **1991**, *113*, 6313.

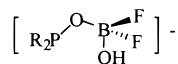
(13) Herrmann, W. A.; Thiel, W. R.; Brossmer, C.; Oefele, K.; Priemermeier, T.; Scherer, W. *J. Organomet. Chem.* **1994**, *461*, 51–60.

in the presence of strong acid.⁹ Adventitious water, together with very slow hydrolysis of the BF_4^- anion (over several weeks at 303 K), affords the somewhat exotic complex **5a**.



5a, R = Ph, 4-Tol, 3,5-di-t-Bu-phenyl **5b**, R = Ph

For **5a**, solution and solid-state structures have been solved.⁹ Although P–C bond cleavage in metal complexes is known, it is a relatively rare reaction and normally not induced by protonation.^{10–13} Formally, **5a** contains the new phosphinite anion, **6** ($\text{C}_{12}\text{H}_{11}\text{BF}_2\text{O}_2\text{P}$).

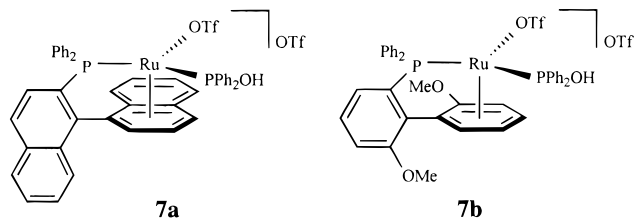


6, R = Ph

Our previous observations led us to believe that the P–C bond splitting was facile and the BF_4^- hydrolysis relatively slow (ca. 2 weeks), so that several intermediates might be detectable. We report here on an extension to Binap, a new and faster variation of this P–C cleavage reaction, and structural studies pertinent to the reaction mechanisms.

Results and Discussion

1. Ru–Triflate Chemistry. The synthesis of the arene complex **5a** was complicated due to the slow, but concurrent BF_4^- anion hydrolysis. To avoid this BF_4^- complication, $\text{Ru}(\text{OAc})_2$ (**1** or **2**) (**1** = racemic Binap, **2** = racemic MeO–Biphep) was allowed to react with slightly more than 2 equiv of wet $\text{CF}_3\text{SO}_3\text{H}$ in 1,2-dichloroethane at 363 K. These conditions gave the products **7a,b** in a few hours in good yield (see Scheme 1 and Experimental Section). Formally, the H^+ protonates the acetate and



the water adds across the P–C bond.

2. Solid-State Structures. The structures of **7a,b** were determined by X-ray diffraction, and views of the cations are shown in Figures 1 and 2. The immediate coordination spheres both contain an η^6 -arene, one oxygen of the triflate anion, and two phosphorus donors: one from the new monodentate $\text{P}(\text{OH})\text{Ph}_2$ ligand and the second from the $\text{P}(\text{biaryl})\text{Ph}_2$ ligand. The oxygen atoms attached to the P1 donors are clearly visible. Table 1 shows a list of selected bond lengths and bond angles for these complexes. The Ru–O bond lengths

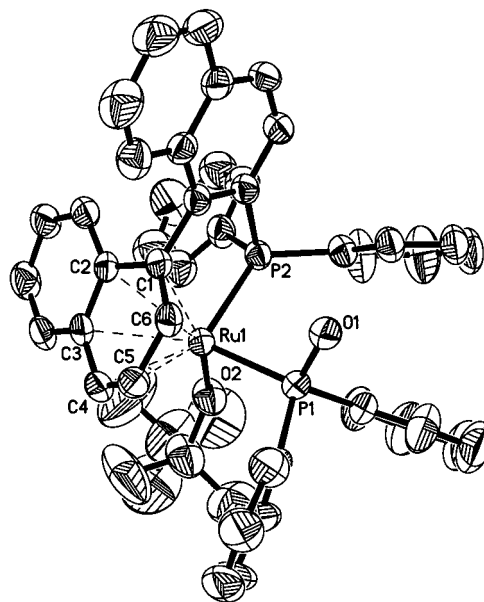


Figure 1. View of the structure of the cation of **7a**, 50% ellipsoids. The oxygen attached to P(1) is clearly visible, and the η^6 -complexation is indicated by dotted lines.

from the triflates are ca. 2.16 and 2.18 Å for **7a** and **7b**, respectively, and fall at the lower end of the known range (ca. 2.12–2.30 Å) for this bond.^{14–19}

The Ru–P separations are also routine; however, the six Ru–C arene bond lengths in both **7a** and **7b** are very different and seem to exist in three groups of two. Two distances are relatively short, Ru–C1 and Ru–C6, ca. 2.13–2.16 Å, but fairly normal;^{20–23} two are slightly long, Ru–C4 and Ru–C5, 2.29–2.32 Å; and two are quite long, Ru–C2 and Ru–C3, ca. 2.35–2.48 Å. Inspection of the X-ray literature for arene complexes of Ru(II) suggests that routine Ru–C separations in a variety of substituted and simple Ru–arene complexes should be on the order of 2.15–2.28 Å with the average at ca. 2.23 Å.²⁴ Specifically, the observed values at 2.480(5) and 2.477(5) Å for C2 and C3 in **7a** suggest a weak interaction. These differences might be related to steric effects, in that the longer distances involve the two sterically hindered fully substituted arene carbons. Further, in **7a** we find modest intramolecular ^{13}C coordination chemical shifts, $\Delta\delta$, 14.9 and 24.6 ppm, for the complexed arene carbons C2 and C3, relative to the 41.4 and 62.7 ppm values of $\Delta\delta$ found for C1 and C6

(14) Svetlanova-Larsen, A.; Zoch, C. R.; Hubbard, J. L. *Organometallics* **1996**, *15*, 3076–3087.

(15) Mauthner, K.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *16*, 1956–1961.

(16) Fong, T. P.; Lough, A. J.; Morris, R. H.; Mezzetti, A.; Rocchini, E.; Rigo, P. *J. Chem. Soc., Dalton Trans.* **1998**, 2111–2113.

(17) Burns, R. M.; Hubbard, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 9514–9520.

(18) Blosser, P. W.; Gallucci, J. C.; Wojcicki, A. *Inorg. Chem.* **1992**, *31*, 2376–2384.

(19) Abbenhuis, R. A. T. M.; del Rio, I.; Bergshoeff, M.; Boersma, J.; Veldman, N.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1998**, *37*, 1749–1758.

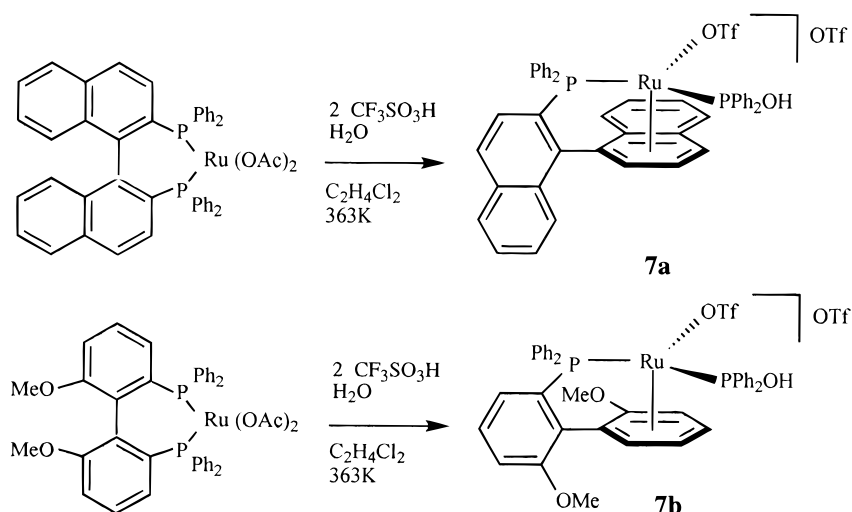
(20) Yamamoto, Y.; Sato, R.; Matsuo, F.; Sudoh, C.; Igoshi, T. *Inorg. Chem.* **1996**, *35*, 2329–2336.

(21) Brunner, H.; Oeschey, R.; Nuber, B. *Organometallics* **1996**, *15*, 3616–3624.

(22) Bhambri, S.; Tocher, D. A. *Polyhedron* **1996**, *15*, 2763–2770.

(23) Roethlisberger, M. S.; Salzer, A.; Buergi, H. B.; Ludi, A. *Organometallics* **1986**, *5*, 298–302.

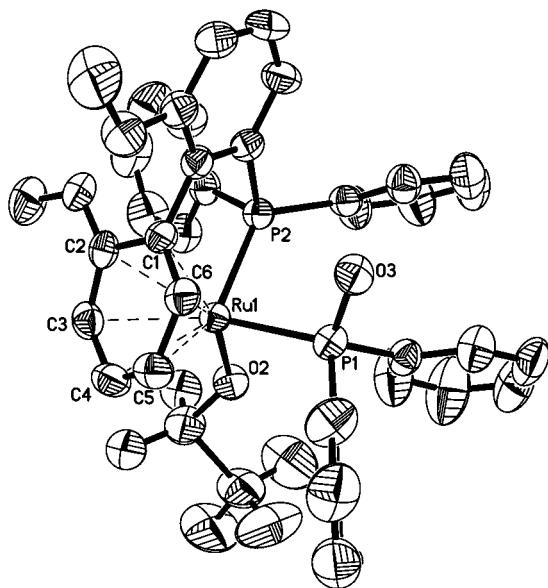
(24) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1–S83.

Scheme 1. Preparation of the Hydroxyphosphine–Arene Triflates, **7a** and **7b**Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for the Cations in **7a** and **7b**

	7a	7b
Ru–P(1)	2.2865(14)	2.3105(16)
Ru–P(2)	2.3389(14)	2.3529(16)
Ru–O (OTf)	2.155(4)	2.178(4)
Ru–C(1)	2.135(5)	2.136(5)
Ru–C(6)	2.161(5)	2.153(6)
Ru–C(4)	2.321(5)	2.306(6)
Ru–C(5)	2.300(5)	2.290(6)
Ru–C(2)	2.480(5)	2.408(6)
Ru–C(3)	2.477(5)	2.347(6)
P(1)–OH	1.591(4)	1.583(4)
P(1)–Ru–P(2)	91.76(5)	89.59(6)
P(1)–Ru–O(2)	94.64(11)	93.31(12)
P(2)–Ru–O(2)	94.73(11)	96.87(13)

Table 2. ^{13}C Coordination Chemical Shifts, $\Delta\delta$, for **7a** and **7b**

^{13}C position	$\Delta\delta$ ^{13}C 7a	$\Delta\delta$ ^{13}C 7b	^{13}C position	$\Delta\delta$ ^{13}C 7a	$\Delta\delta$ ^{13}C 7b
1'-1	41.4	33.3	5'-5	20.3	22.9
6'-6	62.7	64.4	2'-2	14.9	12.2
4'-4	32.0	34.2	3'-3	24.6	33.6

Figure 2. View of the structure of the cation of **7b**, 50% ellipsoids. The oxygen attached to P(1) is clearly visible, and the η^6 -complexation is indicated by dotted lines.

(see Table 2). These data support a weak interaction between Ru and C2 and C3.

We find it interesting that Ru–C1 and Ru–C6 are relatively short, as these were the two arene carbons involved in the η^2 olefin bonding shown in, for example, **3** and **4**. This suggests that the metal does not release C1 or C6 during the change from the η^2 -mode to the η^6

-mode, but has simply slipped across the face of the arene. However, it is also likely that P2, the phosphorus donor that was not involved in the P–C cleavage, serves as a tether which does not permit the Ru atom to move freely across the face of the hydrocarbon. For **7a** it is probably correct to consider the arene bonding as closer to η^4 than to η^6 . We do not find evidence for an intramolecular H-bond between the P(OH) and an oxygen of the complexed triflate; however, in **7b**, one finds a short 1.8 Å separation between the assigned position of the hydroxyl-H and an oxygen of the uncomplexed triflate.

3. NMR Studies on the Triflates. The solution structures for **7a,b** were confirmed by multinuclear, multidimensional NMR spectroscopy.^{25,26} Their ^{31}P spectra show the expected AX pattern, with the complexed Ph_2POH ligand appearing at higher frequency ($\delta = 114.5$ in **7a** and 104.1 in **7b**). Their ^{13}C spectra show six, and their ^1H spectra, three (**7a**) or four (**7b**) resonances, respectively, from the coordinated ring, all strongly shifted to lower frequencies, due to the complexation.^{23,27–29} The complexed arene protons were connected to their corresponding ^{13}C signals via a 2-D

(25) Pregosin, P. S.; Salzmann, R. *Coord. Chem. Rev.* **1996**, 155, 35–68.

(26) Pregosin, P. S.; Trabesinger, G. *J. Chem. Soc., Dalton Trans.* **1998**, 727–734.

(27) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, 1981; p 254.

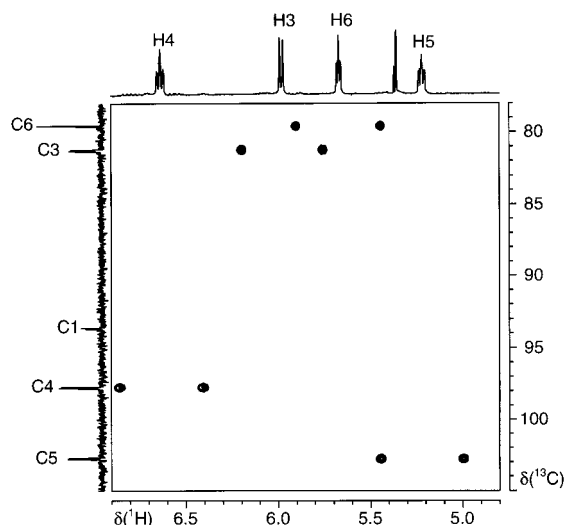


Figure 3. ^{13}C – ^1H correlation for **7b** showing cross-peaks for the four ^{13}C and ^1H resonances of the complexed ring. The chemical shifts appear at relatively low frequency, indicative of complexation (400 MHz, CD_2Cl_2 , ambient temperature). The one-bond coupling is retained in the proton direction.

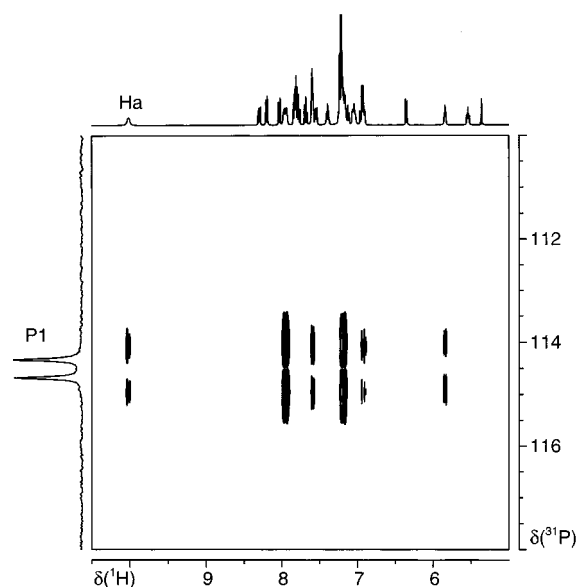


Figure 4. Section of the ^{31}P – ^1H correlation belonging to compound **7a**. The correlation to the OH proton (H^a) is clear, as is the two strong sets of cross-peaks due to the two sets of ortho P-phenyl protons. There are weak correlations to the meta protons and one of the protons of the complexed ring (400 MHz, CD_2Cl_2 , ambient temperature).

^{13}C , ^1H correlation, and a section of this is shown in Figure 3 for **7b**.

The OH proton is observed at $\delta = 10.02$ and 9.66 , respectively and for **7a** can be correlated to its ^{31}P signal; see Figure 4. The high-frequency position of the P(OH)-proton combined with its observed relatively slow exchange with water in the solvent (based on 2-D exchange spectroscopy) suggests that the OH may be hydrogen bonded (perhaps to an uncomplexed, anionic triflate oxygen atom, *vide supra*). A HOESY experiment

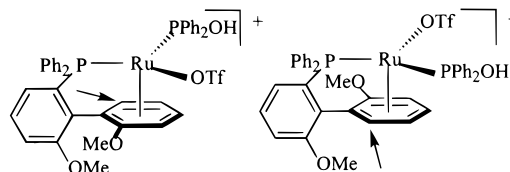
Table 3. NMR Data for the Complexes **7a** and **7b**^a

position	7a		7b	
	$\delta^{31}\text{P}$	$\delta^{19}\text{F}$	$\delta^{31}\text{P}$	$\delta^{19}\text{F}^e$
1	114.5	–78.2	104.1	–77.8
2	53.4	–79.5	50.2	–79.3
	$\delta^1\text{H}^{b,c,f}$	$\delta^{13}\text{C}$	$\delta^1\text{H}^{d,f}$	$\delta^{13}\text{C}$
1		99.6		93.7
2		116.9		146.4
3		110.6	5.98	81.4
4	7.54	100.0	6.63	97.6
5	5.54	107.6	5.22	102.7
6	5.84	77.9	5.67	79.5
7	6.34	127.4	2.99	56.9
8	6.94	135.4		
9	7.78	134.8		
10	8.03	131.8		
1'		141.0		127.8
2'		131.7		158.7
3'		135.2	7.25	115.0
4'	8.30	132.0	7.68	131.8
5'	7.81	127.9	7.15	125.6
6'		140.7		143.9
7'	7.81	129.1	3.94	56.4
8'	7.68	129.2		
9'	7.82	127.7		
10'	8.20	129.1		
OH	10.02		9.66	

^a 400 MHz, CD_2Cl_2 . ^b Exchange between OH and water. ^c Correlation between P1 and OH. ^d Exchange between OH and water. ^e No or slow exchange between OTf groups. ^f **7a**: **H4**, 7.54, $^3J(\text{H,H}) = 7.3$, $^3J(\text{P,H}) = 2.1$; **H5**, 5.54, $^3J(\text{H,H}) = 7.3$ and 5.3 , $^3J(\text{P,H}) = 2.3$; **H6**, 5.84, $J(\text{H,H}) = 5.3$, $^3J(\text{P,H}) = 4.3$. **7b**: **H3**, 5.98, $J(\text{H,H}) = 7.0$, 0.7 , $^3J(\text{P,H}) = 1.5$; **H4**, 6.63, $J(\text{H,H}) = 7.0$, 6.6 , and 1.4 , $^3J(\text{P,H}) = 2.1$; **H5**, 5.22, $J(\text{H,H}) = 6.6$, 5.2 , and 0.7 , $^3J(\text{P,H}) = 2.1$; **H6**, 5.67, $J(\text{H,H}) = 5.2$ and 1.4 , $^3J(\text{P,H}) = 3.7$.

(^{19}F , ^1H) shows a close contact between the uncomplexed OTf and the OH-proton. The ^{19}F spectrum reveals two separate triflate absorptions for each complex. Table 3 shows a selection of ^1H , ^{13}C , ^{19}F , and ^{31}P NMR data for **7a,b**.

The observation of a single diastereomer in the NMR spectra of **7a** and **7b** is thought to be due to kinetic control of the P–C bond splitting. Starting from, for example, racemic MeO–Biphep, the new phosphorus ligand moves from the position indicated by the arrows to the stereogenic Ru atom such that either the R,R or S,S diastereomer is formed. Solution NMR measure-



ments show that these complexes do not epimerize rapidly on the NMR time scale at ambient temperature.

4. Ru–BF₄ Chemistry. Since the use 1,2-dichloroethane at 363 K in the synthesis of **7a,b** reduced the

(28) Bennett, M. A.; McMahon, I. J.; Pelling, S.; Brookhart, M.; Lincoln, D. M. *Organometallics* **1992**, *11*, 127.

(29) Faller, J. W.; Chase, K. J. *Organometallics* **1995**, *14*, 1592–1600.

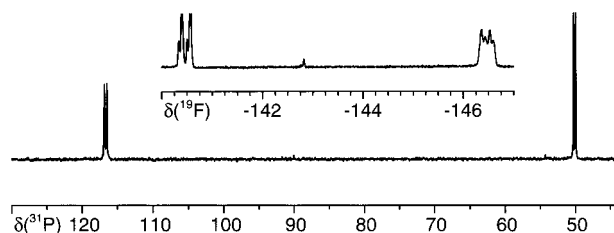
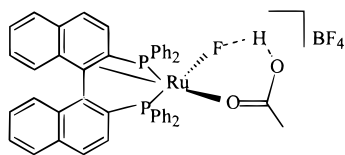


Figure 5. ^{19}F and ^{31}P spectra for **5b**. Top: BF_2 region showing two sets of ^{19}F resonances for each of the non-equivalent F atoms of the BF_2 . Bottom: The nonequivalent ^{31}P resonances. When expanded, one can see the second set of ^{31}P signals here as well (400 MHz, CD_2Cl_2 , ambient temperature).

reaction time without destroying the arene bonding, we allowed both $\text{Ru}(\text{OAc})_2$ (**1**) and $\text{Ru}(\text{OAc})_2$ (**2**) to each react with 2.1 equiv of HBF_4 (Et_2O) in this solvent at 363 K. Indeed, both **5a,b** could be obtained in a few days rather than weeks⁹ (see Experimental Section). Compound **5b** was not part of our earlier report,⁹ and it has been characterized via ^1H , ^{11}B , ^{13}C , ^{19}F , and ^{31}P NMR in conjunction with 2-D spectroscopy. Figure 5 shows ^{19}F and ^{31}P resonances for (in this case) the two diastereomers of **5b**. The slow kinetics combined with relatively large and awkward ligand **6** are thought to be responsible for the epimerization; that is, there is sufficient time for ligand dissociation which leads to epimerization.

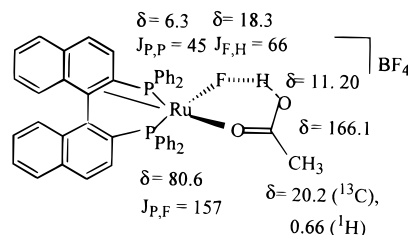
As the BF_4^- hydrolyzes slowly, we measured a set of NMR spectra after mixing cooled solutions of $\text{Ru}(\text{OAc})_2$ -(Binap) with 2.2 equiv of HBF_4 in CD_2Cl_2 at 213 K, with the goal of identifying intermediates in the P–C bond splitting reaction. We observe several species present in solution; however, the major component (ca. 8 times greater than the others) can be assigned to **8**, a structure



8 (at 213K)

in which the Binap functions as a six-electron donor,^{6,7,30} on the basis of the observed very low frequency ^{31}P chemical shift, $\delta = 6.3$ of the ^{31}P spin adjacent to the complexed olefin.^{6,7,30} This represents yet another (albeit rare) example of the complexation of the adjacent biaryl double bond. The second phosphorus signal appears at its normal position, $\delta = 80.6$, $^2J(^{31}\text{P}, ^{31}\text{P}) = 45$ Hz. The BF_4^- anion has been cleaved to afford a $\text{Ru}-\text{F}-\text{H}$ interaction plus $\text{Et}_2\text{O}-\text{BF}_3$ (whose identity has been confirmed via comparison with an independent sample³¹). Complex **8** shows a ^{19}F signal at $\delta = 18.3$, with a coupling to the proton of 66 Hz and a second spin–spin coupling to only one of the two ^{31}P signals, 157 Hz.³² There is a ^1H signal³³ at $\delta = 11.20$, with $^1J(^{19}\text{F}, ^1\text{H}) = 66$ Hz. The complexed acetate methyl signal is found

at relatively low frequency, $\delta = 0.66$, due to the anisotropy of a proximate P–phenyl ring; however, its ^{13}C chemical shift is routine, $\delta = 20.2$ ($\delta^{13}\text{CO} = 166.1$). Models suggest that if the acetate was bound in a bidentate mode, the methyl position would be incorrect for the observed ^1H chemical shift. However, H-bonding of the acetate oxygen to the hydrogen of the HF places the methyl group correctly. These NMR data for **8** are summarized below:



We cannot exclude the possibility that water is involved in the H-bond network and/or that it functions as a sixth ligand.

There are very few HF complexes,³⁴ although some $\text{M}(\text{HF}_2)$ derivatives are known.³⁵ In these literature complexes one often finds relatively large values of $^1J(^{19}\text{F}, ^1\text{H})$, ca. 400 Hz.³⁴ Consequently, given our value of 66 Hz, the H–F bond in **8** is weak, and we consider **8** as a stabilized $\text{Ru}-\text{F}$ complex. In the compound $\text{RuH}(\text{HF}_2)(\text{dmpe})$, reported by Perutz and co-workers,³⁶ one observes two different $^1J(^{19}\text{F}, ^1\text{H})$ values, one large, 274 Hz for the strong H–F interaction, and a much smaller one, <30 Hz, for the M–F moiety.³⁷

Warming the solution containing **8** to 273 K affords the fluorophosphine complex **9**. Formally, the proton of the HF (or one from proximate water) cleaves the P–C bond while forming the new P–F bond. The fluorophosphine complexes **9** exist as a mixture of two components, **9a** and **9b** in the ratio ca. 7:3, and show the characteristic very large $^1J(^{31}\text{P}, ^{19}\text{F})$ values,³⁸ ca. 948 Hz (and 956 Hz), as well as $^2J(^{31}\text{P}, ^{31}\text{P})$ values, 54 Hz (and 52 Hz). The η^6 -arene bonding is supported by the ^1H and ^{13}C data which reveal the expected low-frequency shifts (see Table 4). We know of only one other example in which a P–C bond is broken and a P–F bond made, and this

(32) We are not certain of the source of this selectivity. It might arise from the well-known geometric dependence of $^2J(^{31}\text{P}, \text{X})$, X = ^1H , ^{13}C , ^{31}P , ..., etc., with trans \gg cis. If the structure were indeed five-coordinate, the high-frequency ^{31}P spin would occupy a pseudo-trans position relative to the ^{19}F spin. Since both the ^{19}F and ^{31}P lines are broad, couplings of <5 Hz would not be observed.

(33) We also find a very weak proton signal at $\delta = 9.92$, as a doublet with $^1J(^{19}\text{F}, ^1\text{H}) = 267$ Hz, as well as a broad singlet at $\delta = 13.09$. These are assigned to solvated HF (a slight excess of HBF_4 , 2.2 equiv, is present) and HOAc , respectively. The 267 Hz value is similar to that found by Whittlesey et al.³⁶

(34) Lee, D. H.; Kwon, H. J.; Patel, B. P.; Liable-Sands, L. M.; Rheingold, A. L.; Crabtree, R. H. *Organometallics* **1999**, *18*, 1615–1621. Majez, Z.; Borrmann, H.; Lutar, K.; Zemva, B. *Inorg. Chem.* **1998**, *37*, 5912.

(35) Murphy, V. J.; Hascall, T.; Chen, J. Y.; Parkin, G. *J. Am. Chem. Soc.* **1996**, *118*, 7428–7429.

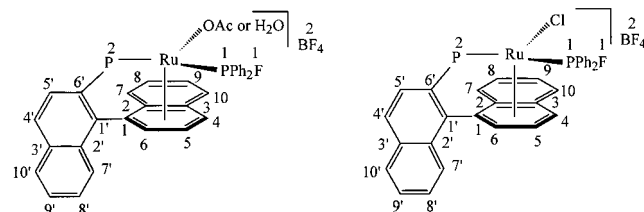
(36) Whittlesey, M. K.; Perutz, R. N.; Greener, B.; Moore, M. H. *Chem. Commun.* **1997**, 187–188.

(37) In the $\text{RuH}(\text{HF}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ analogue, the values are 392 and 36 Hz, respectively. Perutz, R. Personal communication, Nottingham, July, 1999.

(38) Verkade, J. G.; Mosbo, J. A. In *Stereospecificity in ^1J Coupling to Metals*; Verkade, J. G., Mosbo, J. A., Eds.; VCH: Deerfield Beach, FL, 1987; Vol. 8, pp 425–463.

(30) Pathak, D. D.; Adams, H.; Bailey, N. A.; King, P. J.; White, C. *J. Organomet. Chem.* **1994**, *479*, 237.

(31) Observed for an independent sample of $\text{Et}_2\text{O}-\text{BF}_3 = 4.23$ (q, 2H) and 1.38 (t, 3H). In-situ measurements on **8** show 4.23 (q, 2H) and 1.40 (t, 3H), both under the same conditions (CD_2Cl_2 , 400 MHz, 213 K).

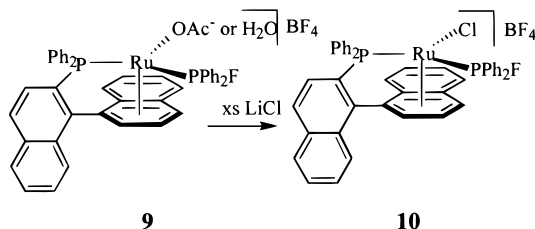
Table 4. ^1H , ^{13}C , ^{19}F , and ^{31}P NMR Data for **9** and **10**^a


9 ^{a,b,e}			10 ^d		
position	$\delta^{31}\text{P}$	$\delta^{19}\text{F}$	position	$\delta^{31}\text{P}$	$\delta^{19}\text{F}$
1	181.8	-121.7	1	176.7	-122.5
2	51.5		2	53.5	
	$\delta^1\text{H}$	$\delta^{13}\text{C}$		$\delta^1\text{H}$	$\delta^{13}\text{C}$
4	5.69	106.3	1		109.0
5	6.07	77.7	2		113.2
6	6.56	101.8	3		113.0
			4	5.95	108.7
			5	5.97	81.8
			6	6.93	101.4
			7	7.92	129.3
			8	7.98	136.4
			9	7.16	132.1
			10	6.57	128.7
			2'		131.5
			3'		135.0
			4'	8.24	132.1
			5'	7.61	128.0
			6'		144.2
			7'	7.94	129.0
			8'	7.84	130.0
			9'	7.73	129.6
			10'	8.20	125.5

9 ^{b,c,e}		
position	$\delta^{31}\text{P}$	$\delta^{19}\text{F}$
1	183.6	-115.5
2	41.4	
	$\delta^1\text{H}$	$\delta^{13}\text{C}$
4	5.60	108.8
5	5.82	78.4
6	6.55	103.8

^a 400 MHz, CD_2Cl_2 . ^b Major isomer, 213 K, assignment based on the observations for **10**. ^c Minor isomer, 213 K, assignment based on the observations for **10**. ^d Ambient temperature. ^e **9a**: **H4**, 5.69, $^3J(\text{H,H}) = 5.3$, $^3J(\text{P,H}) = 4.2$; **H5**, 6.07, $^3J(\text{H,H}) = 7.2$ and 5.3, $^3J(\text{P,H}) = 2.7$; **H6**, 6.56, $^3J(\text{H,H}) = 7.2$. **9b**: **H4**, 5.60, $^3J(\text{H,H}) = 5.2$, $^3J(\text{P,H}) = 4.2$; **H5**, 5.82, $^3J(\text{H,H}) = 7.3$ and 5.2, $^3J(\text{P,H}) = 2.3$; **H6**, 6.55 br d, 7.3.

concerns cleavage in a $\text{Ir}(\text{Me})(\text{PEt}_3)_3$ complex using C_6F_6 to form a FPet_2 donor.³⁹



Reaction of **9** with an excess of LiCl afforded the chlorofluorophosphine complex **10** as a single product, in which only the oxygen donor ligand has been substituted. This observation supports the idea that only one diastereomer is formed if the reaction proceeds quickly. Chloro compound **10** could be isolated in 74% yield and its structure proof followed in analogy to **9**. Figure 6 shows the ^{19}F and ^{31}P resonances for **10** with their characteristic large one-bond spin-spin interactions. A summary of this HF/BF_4 chemistry is given in Scheme 2, and further details are given in the Experimental Section.

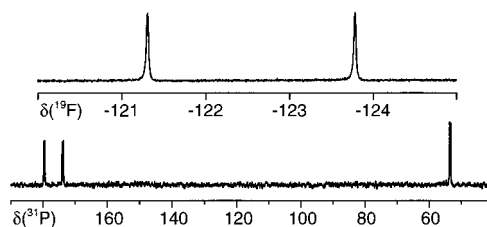


Figure 6. ^{19}F and ^{31}P for **10**. Top: ^{19}F showing the large $^1J(^{31}\text{P}, ^{19}\text{F})$ for the complexed $\text{Ph}_2\text{P}-\text{F}$ ligand. Bottom: ^{31}P showing both $^1J(^{31}\text{P}, ^{19}\text{F})$ and $^2J(^{31}\text{P}, ^{31}\text{P})$ (400 MHz, CD_2Cl_2 , ambient temperature).

Conclusions

The results described above clearly show that, in the absence of suitable ligands, acid-promoted $\text{P}-\text{C}$ bond cleavage and arene complexation can be facile in Ru complexes of both **1** and **2**. In the presence of triflic acid plus water, complexed diphenyl hydroxyphosphine is produced. With HBF_4 as acid, complexed diphenyl fluorophosphine is the product. Examples of both of these structural types have been isolated and characterized. In the HBF_4 chemistry with Binap, a novel $\text{Ru}-\text{F}-\text{H}$ intermediate was detected at 213 K in which the Binap acts as a six-electron donor, using both phosphorus atoms and one double bond of the adjacent biaryl ring. The appearance of **5a,b**, containing the exotic monodentate **6**, after long reaction times can now be rationalized in terms of slow hydrolysis of the $\text{P}-\text{F}$ and $\text{B}-\text{F}$ bonds. The new isolable arene complexes, **7a,b** (with PPh_2OH) and **10** (with Ph_2PF), are readily available and offer access to a wide variety of new organoruthenium derivatives with phosphinoarene chelates.

Experimental Section

All manipulations were carried out under an argon atmosphere. Diethyl ether was distilled from sodium benzophenone ketyl, 1,2-dichloroethane from P_4O_{10} , dichloromethane from CaH_2 , and hexane from sodium. All the other chemicals were commercial products and were used as received. *rac*-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (Binap) was purchased from Strem Chemicals. (*R,S*)-(6,6'-Dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine oxide) was a gift from F. Hoffmann-La Roche AG, Basel. The reduction of this diphosphine oxide by reported methods⁴⁰ (**1**) gave the ligand (*R,S*)-(6,6'-dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine) (MeO-Biphep).

X-ray. Crystals of **7a** and **7b** were mounted on glass capillaries, and data sets covering a hemisphere were collected on a Siemens SMART platform diffractometer equipped with a CCD detector (ω -scans with 0.3° step width). Data reduction plus corrections for Lorentz polarization and absorption was performed using the programs SAINT⁴¹ and SADABS.⁴² The structures were solved by direct methods and refined by full-matrix least-squares (versus F^2) with the SHELXTL program package.⁴³ All non-hydrogen atoms except the atoms belonging to disordered groups or solvent molecules were refined with anisotropic thermal parameters, but hydrogen atoms at calculated positions were refined with common isotropic thermal parameters for each group.

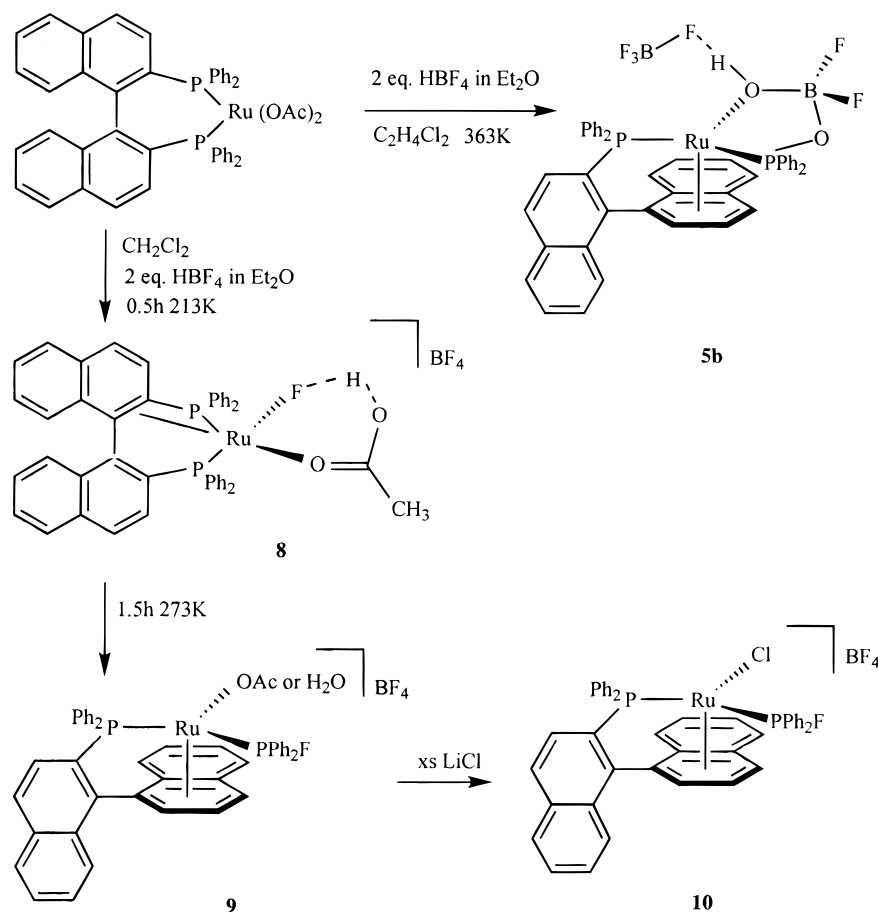
(40) Schmid, R.; Foricher, J.; Cereghetti, M.; Schoenholzer, P. *Helv. Chim. Acta* **1991**, *74*, 370.

(41) SAINT, Version 4; Siemens Analytical X-ray Systems, Inc.: Madison, WI.

(42) Sheldrick, G. *SADABS*; Göttingen, 1997.

(43) SHELXTL program package, Version 5.1; Bruker AXS, Inc.: Madison, WI.

(39) Blum, O.; Frolow, F.; Milstein, D. *Chem. Commun.* **1991**, 258.

Scheme 2. Chemistry of Ru(OAc)₂(Binap) with HBF₄

In **7a**, all the triflate anions, one phenyl group, and a not further specified solvent molecule showed a considerably strong positional disorder. Wherever possible, a split model was applied. The solvent molecule was described with partially occupied C atom positions with a common isotropic displacement parameter. In **7a** there are electron density peaks (C1L to C3L) located in a large void of the structure which could not be interpreted in terms of a clearly identified solvent. Nevertheless these peaks were included in the refinement; the effect of neglecting them on the *R*-value is relatively small (improvement of *R*₁ of about 0.4%).

In **7b** one triflate anion is strongly disordered and consequently was described by two partially occupied anion positions. The occupation factors refined to values of 0.533(4) and 0.467(4), respectively. The same geometric constraints were applied for both possible anion positions, and a common isotropic displacement parameter was used for the affected atoms. The somewhat larger *R*-values are certainly acceptable considering that there is now a model for the observed disorder available. Crystallographic data and details of the structure determinations are given in Table 5.

Synthesis of [Ru(C₁₂H₁₀BF₂O₂P)(6'-diphenylphosphino-1-naphthyl)(BF₄)](CF₃SO₃), **5b.** Ru(OAc)₂(**1**) (40.0 mg, 0.05 mmol) was dissolved in 2 mL of 1,2-dichloroethane. This was followed by addition of 2.3 equiv of tetrafluoroboric acid (15 μL, 7.3 M in Et₂O). After ca. 48 h at 363 K the resulting mixture was filtered using a glass filter and the 1,2-dichloroethane distilled under high vacuum. The crude reaction mixture was washed three times with 1 mL of hexane. The product was recrystallized from a dichloromethane–ether mixture to afford 36.8 mg (87%) of yellow **5b**. Anal. Calcd for C₄₄H₃₄O₂B₂F₆P₂Ru (893.38): C, 59.16; H, 3.84. Found: C, 59.07; H, 3.90. FAB-MS: calcd M⁺ 805.6; found 805.8. NMR (400 MHz, *J* in Hz, CD₂Cl₂, rt): ³¹P, 116.6 (d, P1, 52), 50.1 (d,

P2, 52); ¹⁹F, −140.4 (d, F1A, 62), −146.5 (d, F1A', 62), −140.5 (d, F1B, 62), −146.6 (d, F1B', 62), −150.8 (25%, F2), −150.8 (75%, F2); ¹³C, 142.3 (d, C6', 53), 141.5 (d, C3', 22), 136.3 (s, C9), 134.8 (s, C1'), 134.8 (s, C8), 131.7 (d, C4', 7), 131.4 (d, C2', 3), 130.3 (s, C10), 129.9 (s, C8'), 129.1 (s, C10'), 128.4 (s, C9'), 128.4 (s, C5'), 127.7 (s, C7), 125.4 (s, C7'), 113.6 (d, C2, 9), 110.0 (d, C3, 6), 105.7 (d, C5, 6), 102.7 (d, C1, 4), 95.1 (d, C4, 9), 73.3 (s, C6); ¹H, 8.43 (d, H10, 8.3), 8.24 (dd, H4', 8.8, 2.0), 8.20 (d, H10', 8.7), 7.95 (d, H7', 8.2), 7.92 (t, H9, 8.2, 7.8), 7.84 (ddd, H8', 8.3, 6.9, 1.2), 7.77 (dd, H5', 8.9, 6.9), 7.71 (ddd, H8', 8.3, 6.9, 1.2), 7.30 (br d, H4, 7.0, 2.1), 6.95 (H8, 8.6, 7.8), 6.26 (br d, H7, 8.6), 5.93 (br, Ha), 5.85 (dd, H6, 4.7, 2.7), 5.15 (ddd, H5, 7.0, 4.7, 2.3).

Synthesis of [Ru(CF₃SO₃)(6'-diphenylphosphino-1-naphthyl)(PPh₂OH)](CF₃SO₃), **7a.** Ru(OAc)₂(**1**) (65.0 mg, 0.08 mmol) was dissolved in 2 mL of 1,2-dichloroethane and then treated with 2.4 equiv of trifluoromethanesulfonic acid (16 μL, 0.18 mmol). The solution color turned immediately from yellow to orange. After heating for 1 h at 363 K, the solution was filtered using a glass filter. The 1,2-dichloroethane was evaporated under high vacuum. The crude reaction mixture was stirred and washed three times with 1 mL of ether, and the complex was then recrystallized from dichloromethane–ether. A suitable crystal for X-ray diffraction was obtained from the same mixture of solvents. Color: orange. Yield: 59.6 mg (74%). Anal. Calcd for C₄₆H₃₄O₇F₆P₂S₂Ru (1039.94): C, 53.13; H, 3.30. Found: C, 53.01; H, 3.44. FAB-MS: calcd 890.9; found 891.1.

Synthesis of [Ru(CF₃SO₃)(6'-diphenylphosphino-1-(2-dimethoxy)biphenyl)(PPh₂OH)](CF₃SO₃), **7b.** Ru(OAc)₂(**2**) (60.8 mg, 0.08 mmol) was dissolved in 2 mL of 1,2-dichloroethane and 2.1 equiv of trifluoromethanesulfonic acid (14 μL, 0.16 mmol) added. The solution color turned immediately from yellow to orange. After heating for 1 h at 363 K, the reaction

Table 5. Crystal Data and Structure Refinement for 7a and 7b

	7a	7b
formula	C ₄₆ H ₇₃ F ₆ O ₇ P ₂ RuS ₂	C ₄₀ H ₃₄ F ₆ O ₉ P ₂ RuS ₂
formula weight	1049.83	999.80
temperature, K	293(2)	293(2)
radiation	Mo K α (graphite-monochromated, $\lambda = 0.71073$ Å)	
cryst syst	triclinic	monoclinic
space group	P-1	<i>P</i> 2 ₁ / <i>c</i>
unit cell dimens		
a, Å	15.099(2)	21.020(3)
b, Å	16.131(2)	10.294(2)
c, Å	19.817(3)	21.626(3)
α , deg	108.20(3)	90
β , deg	103.14(3)	117.16(3)
γ , deg	94.34(3)	90
volume, Å ³	4408.7(12)	4163.4(11)
<i>Z</i>	4	4
density (calcd), Mg/m ³	1.580	1.595
abs coeff	0.601 mm ⁻¹	0.635 mm ⁻¹
<i>F</i> (000)	2122	2024
cryst size, mm ³	0.50 \times 0.18 \times 0.08	0.36 \times 0.32 \times 0.22
θ -range for data collection, deg	1.12–24.74	1.89–26.40
index ranges	–17 $\leq h \leq$ 17, –18 $\leq k \leq$ 18, –23 $\leq l \leq$ 23	–25 $\leq h \leq$ 26, –8 $\leq k \leq$ 12, –27 $\leq l \leq$ 27
no. of reflns colld	24 430	25 182
no. of ind reflns	14 887 [<i>R</i> _{int} = 0.0486]	8492 [<i>R</i> _{int} = 0.0545]
completeness to θ , deg, %	24.74, 98.9	26.40, 99.6
max. and min. transmission	0.9535 and 0.7533	0.8730 and 0.8037
no. of data/restraints/params	14 887/0/1156	8492/38/522
GOOF on <i>F</i> ²	0.976	1.040
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0500, <i>wR</i> ₂ = 0.1221	<i>R</i> ₁ = 0.0695, <i>wR</i> ₂ = 0.1793
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0885, <i>wR</i> ₂ = 0.1457	<i>R</i> ₁ = 0.1071, <i>wR</i> ₂ = 0.2061
largest diff peak and hole, e Å ⁻³	1.065 and –0.813	2.037 and –1.315

mixture was filtered using a glass filter. The 1,2-dichloroethane was evaporated under high vacuum. The crude reaction mixture was stirred and washed three times with 1 mL of ether. The complex was recrystallized from dichloromethane–ether. A suitable crystal for X-ray diffraction was obtained from the same mixture of solvents. Color: orange. Yield: 59.2 mg (78%). Anal. Calcd for C₄₀H₃₄O₉F₆P₂S₂Ru (999.84): C, 48.05; H, 3.43. Found: C, 48.00; H, 3.56. FAB-MS: calcd M⁺–OTf 701.7; found 701.3.

Preparation and/or Isolation of Compounds 8, 9, and 10. Ru(OAc)₂(**1**) (41.1 mg, 0.05 mmol) was dissolved in 2 mL of CD₂Cl₂. The solution was cooled to ca. 195 K before 2.2 equiv of tetrafluoroboric acid (15 μ L, 7.3 M in Et₂O) was added. The reaction was then immediately monitored by NMR at 213 K. After 30 min, intermediate **8** was observed as the main product. The mixture was then warmed to 273 K for 1.5 h to afford intermediate **9**. The reaction mixture was then cooled to 213 K (to stabilize this intermediate), and **9** was characterized via NMR methods. At 213 K, 23.6 mg (0.56 mmol) of LiCl was added to the yellow reaction mixture. The mixture became immediately red in color. After stirring overnight the reaction mixture was filtered through Celite. The solvent was evapo-

rated in vacuo and the product recrystallized from dichloromethane–ether to afford 32.3 mg (74%) of a red solid. Anal. Calcd for C₄₄H₃₄O₂B₂F₆P₂Ru·H₂O (893.38): C, 59.78; H, 3.99. Found: C, 59.76; H, 4.02. FAB-MS: calcd M⁺, 780.26; found, 780.89.

Acknowledgment. P.S.P. thanks the Swiss National Science Foundation and the ETH, for financial support. We also thank Johnson Matthey for the loan of metal salts and F. Hoffmann La-Roche, Basel, for the gift of MeO–Biphep ligands.

Supporting Information Available: Complete numbering scheme for the ORTEP diagrams. Table with experimental parameters (Table S1). Atomic coordinates and equivalent isotropic temperature factors (Table S2). Extended list of bond lengths and bond angles (Table S3). Anisotropic displacement parameters (Table S4). Calculated hydrogen coordinates and isotropic displacement parameters (Table S5). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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