Phosphino−Arene Ruthenium Complexes Containing the Phosphorus Acid Anion {P(=O)(OR)$_2$} as P-Donor

Tilmann J. Geldbach and Paul S. Pregosin*

Laboratory of Inorganic Chemistry, ETH Zentrum, 8092 Zürich, Switzerland

Alberto Albinati and Frank Rominger

Chemical Pharmacy, University of Milan, I-20131 Milan, Italy

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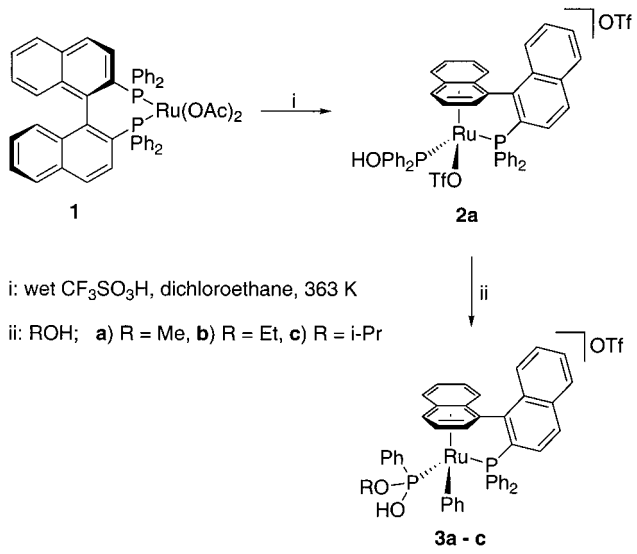
The cationic complex [Ru(OTf)(P(OH)Ph$_2$){Ph$_2$P-(η^6-arene)}]OTf, **2** (**2a** = 6′-diphenylphosphino-1′-naphthyl-$\eta^6{}_{(1-6)}$-naphthalene, **2b** = 6,6′-dimethoxy-2′-diphenylphosphino-$\eta^6{}_{(1-6)}$-biphenyl), is shown to react with water/*tert*-butyl alcohol/THF mixtures to afford [Ru(P(=O)(OH)$_2${Ph$_2$P-(η^6-arene)}]$_2$(OTf)$_2$, **4**. The solid-state structure of a derivative, [Ru{P(=O)(OH)(OMe)}{Ph$_2$P-(naphthyl-η^6-naphthalene}]$_2$(OTf)$_2$, **6**, is reported and found to possess extremely asymmetric η^6-arene bonding. Complexes **4** and **6**, plus a mononuclear dimethoxy analogue, Ru(P(=O)-(OMe)$_2$(Ph$_2$P-(naphthyl-η^6-naphthalene)](OTf), **8**, represent the first examples of Ru-compounds that contain the phosphorus acid anion P(=O)(OR)$_2$ (R = H and/or Me) as an anionic P-donor ligand. PGSE diffusion measurements are shown to be helpful in distinguishing between dinuclear oxygen bridging species and their mononuclear analogues.

Introduction

The chemistry of the biaryl-based atropisomeric chiral bidentate ligands Binap[1−3] and MeO−Biphep[4−7] continues to attract interest. There are an increasing number of applications in homogeneous catalysis, and some of these reactions center on ruthenium chemistry.[8,9]

We have recently reported[10] that the simple hydrogenation catalyst precursor Ru(OAc)$_2$(Binap), **1**, reacts with 2 equiv of CF_3SO_3H and water in a P−C bond-cleaving transformation to form the arene complex **2a** (see Scheme 1). This new hydroxydiphenylphosphino−arene derivative reacts further under mild conditions with alcohols, e.g., MeOH, EtOH, and i-PrOH, to produce the ruthenium−phenyl arene compounds **3**, in which a phenyl group has migrated to the metal from the hydroxydiphenylphosphino ligand.[11] All of the reactions proceed stereospecifically. We report here that the reaction of **2a** with *tert*-butyl alcohol takes a different and unexpected course.

Scheme 1



Results and Discussion

Preparation of 4. In contrast to the reactions leading to **3a**−**c**, addition of *tert*-butyl alcohol to **2a** did not result in a homogeneous solution; consequently THF was added to facilitate contact between these two reagents. Stirring for several hours afforded a mixture

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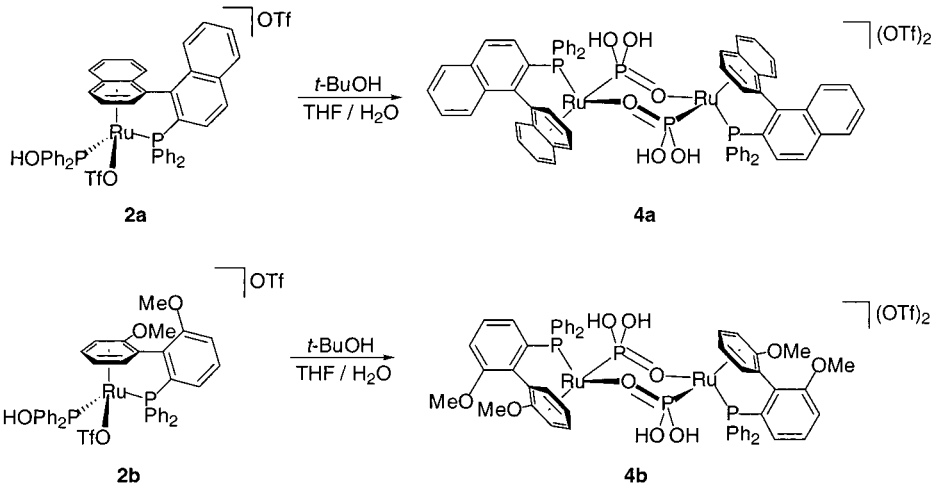
Scheme 2



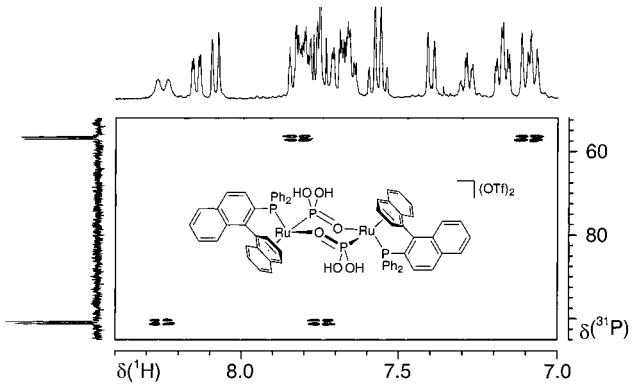
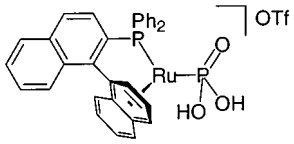


Figure 1. $^{31}P,^{1}H$-correlation showing the four proton cross-peaks from the two ^{31}P signals. The two from the phosphine (top) arise from ortho protons. The two from the high-frequency signal (bottom) arise from the exchangeable OH protons (one of which is under the biaryl aromatic signals (400 MHz, CD_2Cl_2)).

of products whose preliminary NMR analysis suggested the presence of several complexes. The crude reaction mixture was then treated with water in order to increase the polarity and thereby facilitate a P−C-bond cleavage (see Experimental Section). After stirring for several hours, workup afforded complex **4a** (see Scheme 2).

The formulation of the structure is based on mass spectroscopic, NMR, and microanalytical data. The ^{31}P NMR spectrum of **4a** reveals an AX spin system with one resonance at relatively high frequency, δ 100.9. Figure 1 shows the P,H-correlation for **4a**. The two cross-peaks stemming from the high-frequency ^{31}P signal, δ 8.25 and δ 7.74, can both be shown to stem from *exchangeable protons* (via D_2O addition) so that the oxygen-containing P-donor no longer possesses a phenyl substituent (which would show a strong correlation due to the P-phenyl ortho protons). ^{13}C measurements, see Table 1, confirm the presence of an asymmetric η^6-arene moiety.[12,13] The C1 and C6 signals are fairly typical for Ru−arene complexes and appear at relatively low frequency, 96.5 and 78.3 ppm, respectively, whereas the remaining four complexed arene resonances are found at higher frequency, 100.5−120.9 ppm. Addition of *tert*-butyl alcohol to **2b** led to the analogous dimer **4b**.



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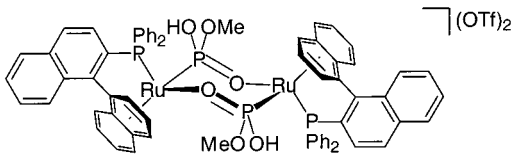
Originally, we considered the mononuclear 16e structure **5**; however, FAB mass spectoscopic data reveal prominent peaks for the molecular ion at *m/e* 1241.5 (twice the weight of **5**) as well as a signal at *m/e* 1223.4 due to water loss. We believe that **4a** represents the first Ru-complex containing the phosphorus acid anion $P(=O)(OH)_2$ as a ligand. Phosphonate compounds of the type $R^1P(=O)(OR^2)_2$ are well known,[14a] and $HP(=O)(OEt)_2$ has recently been shown to add to Pd(0) to afford $Pd-P(=O)(OEt)_2$ complexes.[14b]

During the attempted recrystallization of **3a**, a crystal of complex **6**, whose structure is closely related to that of **4a**, was obtained. We presume that compound **6** forms slowly from **3a** due to solvolysis via traces of water.



6

Structure of 6. Complex **6** was (accidentally) crystallized from wet THF. The molecule can be seen to arise from the dimerization of a fragment related to **5**, in which the P=O moiety bridges the two Ru-centers.

The immediate coordination sphere for each Ru(II) atom comprises an asymmetric η^6-arene, one PPh_2 type donor, one phosphorus acid monomethyl ester anion P-donor, and the phosphine oxide oxygen of a symmetry-

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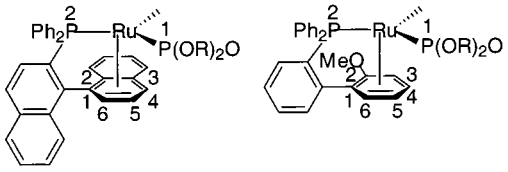
Table 1. Selected ^{1}H and ^{13}CNMR Data for 4a, 4b, 8, and 10



position	4a		4b		8		10	
	δ ^{31}P 1	δ ^{31}P 2	δ ^{31}P 1	δ ^{31}P 2	δ ^{31}P 1	δ ^{31}P 2	δ ^{31}P 1	δ ^{31}P 2
	100.9	56.7	100.3	53.2	87.5	55.7	78.3	60.2
	δ ^{1}H	δ ^{13}C	δ ^{1}H	δ ^{13}C	δ ^{1}H	δ ^{13}C	δ ^{1}H	δ ^{13}C
1		96.5		90.0		98.5		109.4
2		120.9		149.9		116.8		114.7
3		113.1		82.2		110.7		112.0
4	5.29	100.5	5.46	98.9	7.51	94.1	7.40	93.1
5	6.55	104.9	4.89	96.5	6.80	102.6	7.13	103.7
6	5.27	78.3	6.01	80.6	5.35	76.5	5.90	85.9

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 6[a]

Ru1−P1	2.2552(18)	P1−Ru1−P2	91.2(2)
Ru1−P2	2.3152(17)	O3*−Ru1−P1	89.4(1)
Ru1−O3*	2.085(4)	O3*−Ru1−P2	100.5(1)
Ru1−C1	2.138(7)	Ru1−P1−O3	117.7(2)
Ru1−C6	2.146(6)	Ru1−P1−O1	112.0(2)
Ru1−C4	2.300(7)	Ru1−P1−O2	111.0(2)
Ru1−C5	2.278(7)	Ru1−O3*−P1*	138.5(3)
Ru1−C2	2.514(7)	O3−P1−O1	104.4(3)
Ru1−C3	2.511(7)	O3−P1−O2	106.8(3)
P1−O1	1.581(5)	O1−P1−O2	103.9(3)
P1−O2	1.590(5)		
P1−O3	1.517(4)		

[a] The starred atoms are obtained from those unstarred by the symmetry operation 1/2 − *x*; 1/2 − *y*; −*z*.

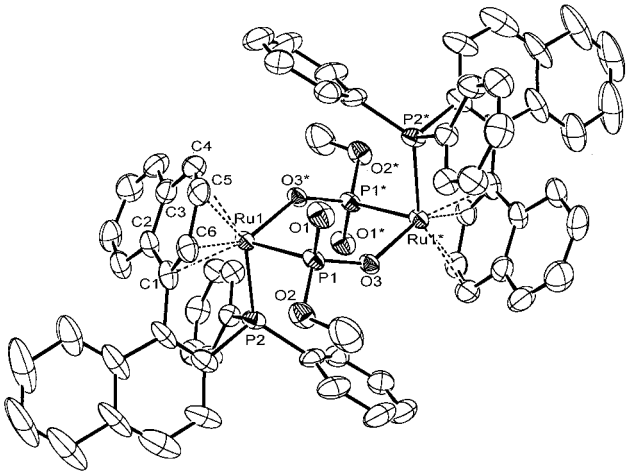


Figure 2. ORTEP plot showing the cation of **6**. The starred atoms are obtained from those unstarred by the symmetry operation 1/2 − *x*; 1/2 − *y*; −*z*. Ellipsoid probability at 50%.

related monomer (see Experimental Section). A list of selected bond lengths and bond angles is given in Table 2, and an ORTEP view of the molecule is shown in Figure 2.

The six-membered ring formed from the two Ru atoms, and the two P═O moieties can be seen from Figure 3 to have a chair conformation. The two P(OH) groups assume axial and the two P(OMe) groups equatorial positions. As is frequently found,[15,16] one of the

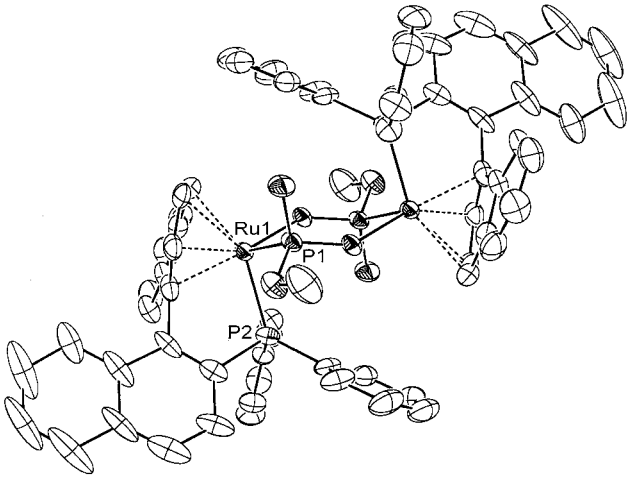


Figure 3. ORTEP view of **6** from the side showing the chair conformation of the six-membered ring.

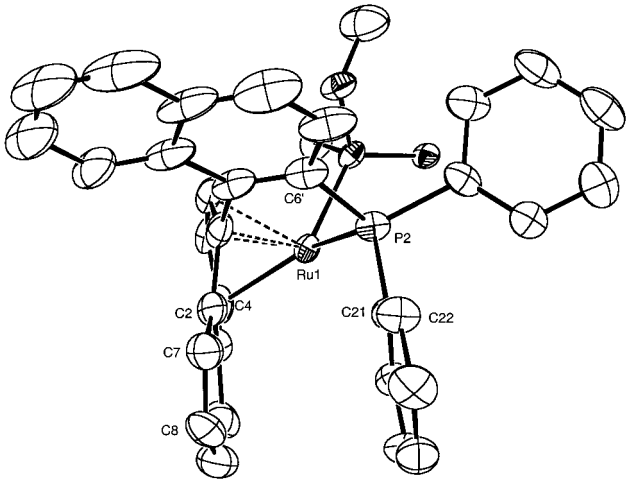


Figure 4. ORTEP view of **6** showing the parallel arrangement of the two aryl rings.

two PPh_2 rings stacks with an arene ring of the biaryl containing the asymmetric η^6-arene (see Figure 4). In **6** this stacking involves the C7−C10 biaryl ring and the C21−C26 P-phenyl ring. The ring−ring separations fall in the range 3.5−3.8 Å and are consistent with previous observations.

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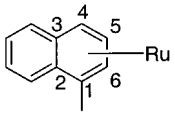
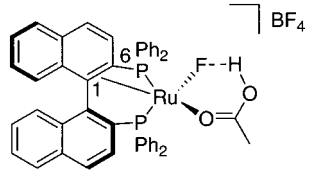
The decision to consider the P1−O3 bond as a phosphine oxide type double bond stems from a comparison of the three P−O separations: P1−O1, 1.581(5) Å, P1−O2, 1.590(5) Å, and P1−O3, 1.517(4) Å. The latter is clearly shorter than the two former and is in good agreement with literature P−O bond lengths for phosphine oxides.[17]

The O−P1−O angles (104−107°) and the Ru1−P1−O angles 111.0(2)−117.7(2)° reveal that the local geometry around P1 is distorted from that expected for an ideal tetrahedral arrangement; on the other hand the P1−Ru1−P2 angle of 91.18(6)° is normal and the bond lengths Ru1−P1, 2.255(2) Å, and Ru1−P2, 2.315(2) Å, are as expected.

Somewhat unexpected are the six Ru−C bond lengths associated with the arene complexation. As can be seen from Table 2 these fall into three groups of two: Ru1−



C1, 2.138(7) Å, and Ru1−C6, 2.146(6) Å, are the shortest. Ru1−C4, 2.300(7) Å, and Ru1−C5, 2.278(7) Å, are intermediate in length, and Ru1−C2, 2.514(7) Å, and Ru1−C3, 2.511(7) Å, are quite long. Since routine Ru−C(arene) separations are on the order of 2.20−2.30 Å,[18−25] the bonding is clearly strongly asymmetric. Two points are worth emphasizing in connection with the arene bonding: (a) The observed short bond distances to C1 and C6 are to those carbons that were complexed in an η^2-mode in related complexes such as **7**[10,26−28] before any P−C bond cleavage occurred. We interpret



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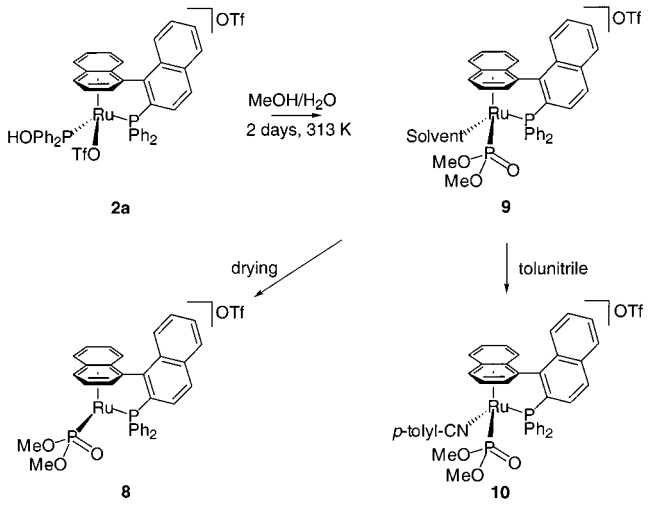
these bond length data to indicate that the Ru atom need only slide across the face of the arene (e.g., during the P−C cleavage chemistry) to reach the strongly asymmetric η^6-mode. Asymmetry in the η^6-bonding for

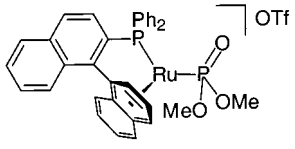
Scheme 3



related complexes is not uncommon and has been observed previously,[29a] e.g., in the triflate complexes **2**[10] and the naphthalene complex Ru(η^6-$C_{10}H_8$)(η^4-1,5-C_8H_{12}).[29b] (b) The ^{13}C coordination chemical shifts, $\Delta\delta$, for C2 and C3 in **4a** (relative to C2′ and C3′) are 10.9 and 21.4 ppm, respectively, suggesting some interaction with the Ru. Consequently, we believe that an η^4-description would be too extreme. Indeed, the C−C separations within the complexed arene ring do not suggest localized bonding. However, it is clear that **6** could easily attain a 16e (instead of an 18e) configuration without very much movement of the Ru atom.

We also note an interesting distortion of the coordinated naphthyl moiety. The least-squares plane through atoms C1−C6 reveals a deviation from planarity. C1 and C4 are out of the best plane by ca. 0.1 Å, leading to a boatlike shape for this six-membered ring, in which C1 and C4 are displaced toward the Ru atom. Very marked boatlike distortions[30] are typical for η^4 derivatives of naphthalene complexes; however, the bending in **6** is not quite so pronounced as that referred to above.

Synthesis of a P(OMe)$_2$ Analogue 8. Given the serendipity involved with **6**, we have prepared the dimethoxy analogue **8** of **4a** via addition of MeOH/H_2O and show this chemistry in Scheme 3. In contrast to



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what we observed for **4a**, the mass spectral and diffusion data are now consistent with a mononuclear complex. With structural problems of this type, pulsed gradient spin diffusion (PGSE) measurements can provide a useful complement to mass spectroscopy.[31−35] PGSE

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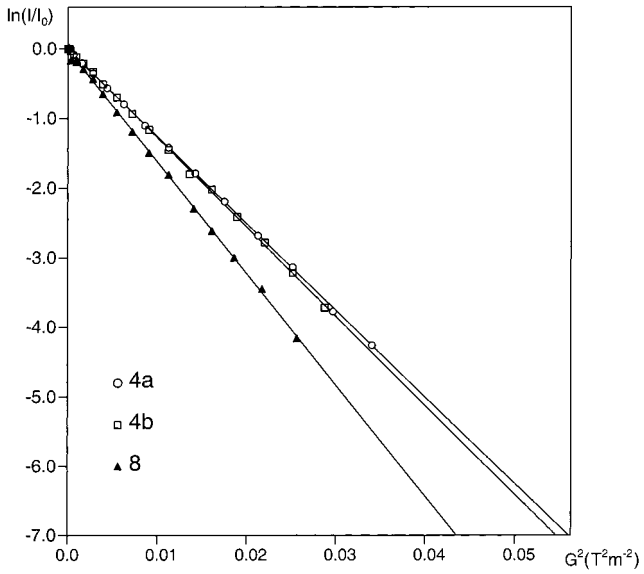

Figure 5. Plot of the $\ln(I/I_0)$ vs the square of gradient amplitude (expressed in $T^2\ m^{-2}$), for **4a**, **4b**, and **8**. The larger slope for **8** is indicative of a smaller molecular volume (see text).

results reflect translation and thus molecular volumes. Our experience[33,34] suggests that decreases in the diffusion constant, *D*, on the order of 20% correspond to changes in molecular size of about a factor of 2. Figure 5 shows PGSE results for **4a**,**b** and **8**. Obviously, **4a** and **4b** have much larger volumes in keeping with the mass spectroscopic data. Moreover, the ratio of the diffusion constants **8**/**4a**, 0.77, is consistent with about twice the volume for **4a**. The routine NMR characterization of **8** follows that for **4** and is described in the Experimental Section. The 16e species **8** is most likely solvated in solution; that is, it exists as **9** in Scheme 3. Prolonged drying leads to **8**. The presence of an open coordination position in **8** is demonstrated by the reaction with *p*-tolunitrile which affords the 18e complex **10**. The presence of the donor nitrile ligand leads to a change in the coordination of the arene as seen from the ^{13}C NMR data (see Table 1).

Comment. There are still relatively few examples of P−C bond-breaking reactions involving Ru(II).[10,29,36] Mechanistically, it is reasonable to believe that the chemistry leading to **4** begins with a solvolysis reaction to produce a dication (see Scheme 4). Under the given reaction conditions this solvolysis of the triflate induces phenyl migration; however, relative to step ii in Scheme 1, protonation of the new Ru−C bond is now facile. The resulting new dication (presumably with a $P(OH)_2Ph$ ligand) is now the source of a second phenyl migration. This second Ru−C bond is also protonated (perhaps via the $P(OH)_3$ ligand), thus giving the $P(=O)(OH)_2$ anion and a second equivalent of benzene. Dimerization of the product affords **4**.[37]

In terms of understanding the observed difference between the chemistry of Scheme 1 and the development of **4**, it is likely that the relative acidities of water and *tert*-butyl alcohol are important. Water possesses a ca. 10^2 larger pK_a than the alcohol,[38] and although, under the chosen conditions, the *tert*-butyl alcohol/water ratio is >2, the water reacts much faster than the larger, less acidic alcohol in this cationic chemistry.

Experimental Section

All manipulations were carried out under an argon atmosphere. Diethyl ether was distilled from sodium−potassium alloy, THF was distilled from potassium, and pentane and dichloromethane were distilled from CaH_2. All the other chemicals were commercial products and were used as received. (*RS*)-(6,6′-Dimethoxybiphenyl-2,2′-diyl)bis(diphenylphosphine oxide) was a gift from F. Hoffmann-La Roche AG, Basel.

The ^1H PGSE experiments were performed on a Bruker AVANCE 400 spectrometer equipped with a microprocessor-controlled gradient unit and a multinuclear probe with an actively shielded Z-gradient coil. About 0.8 mg of the complexes was dissolved in 0.6 mL of CD_2Cl_2 and measured at 298 K without spinning. The sequence used was the "three pulses stimulated-echo", the shape of the gradient was rectangular, their length was 5 ms, the time between the midpoints of the gradient was 100 ms, and the strength varied automatically in the course of the experiment.

Crystallography. Air stable, yellow crystals of **6** were obtained from THF upon slow evaporation of the solvent. For the data collection, a prismatic single crystal was mounted on a Bruker SMART CCD diffractometer. The space group was determined from the systematic absences, while the cell constants were refined at the end of the data collection, using 6503 reflections, using the data reduction software SAINT.[39] A total of 2142 frames were collected, by using an ω scan in steps of 0.3° with a counting time of 20 s. The intensities were corrected for Lorentz and polarization factors[39] and empirically for absorption using the SADABS program.[40] Selected crystallographic and other relevant data are listed in Table 3 and in Supplementary Table S1.

The standard deviations on intensities were calculated in terms of statistics alone, while those on F_o^2 were calculated as shown in Table 3. The structure was solved by direct and Fourier methods. In the crystal structure, each dinuclear species lies across a crystallographic symmetry element, so that only half of the dimeric moiety is independent. The data were refined by full matrix least squares[41] minimizing the function $[\sum w(F_o^2 - (1/k)F_c^2)^2]$. During the refinement anisotropic displacement parameters were used for all atoms except for the H atoms, which were treated isotropically.

Toward the end of the refinement, two disordered solvent molecules (THF) were located from difference Fourier maps. The first molecule was refined without constraints, using anisotropic temperature factors, while for the second solvent molecule intra-ring distances[42] were constrained at the beginning of the refinement. No extinction correction was deemed

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Scheme 4

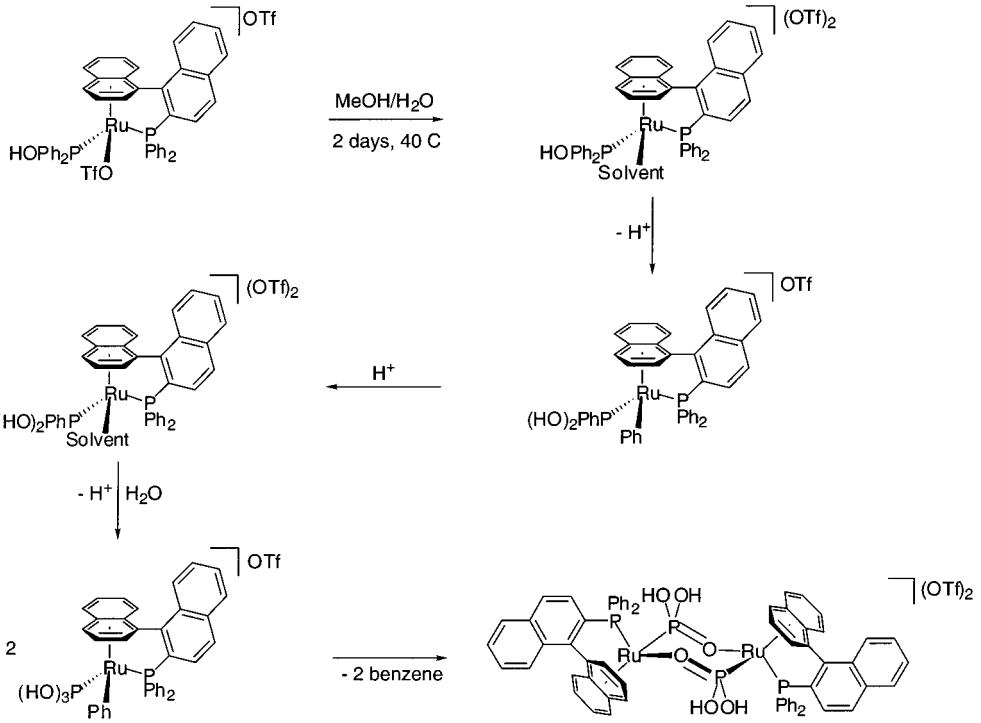

Table 3. Experimental Data for the X-ray Diffraction Study of 6·2 THF

Formula	$C_{42}H_{35}F_3O_8P_2RuS$
mol wt	919.77
data coll. *T*, K	200(2)
diffractometer	SMART CCD
cryst syst	monoclinic
space group (no.)	*C*2/*c* (15)
a, Å	24.3765(5)
b, Å	17.6565(4)
c, Å	21.8961(5)
β, deg	112.916(1)
V, Å^3	8680.4(3)
Z	8
$\rho_{(calcd)}$, g cm^{-3}	1.408
μ, cm^{-1}	5.45
radiation	Mo Kα (graphite monochrom., $\lambda = 0.71073$ Å)
θ range, deg	$1.81 < \theta < 27.47$
no. indep data	9919
no. obsd reflns (n_o) $[\lvert F_o\rvert^2 > 2.0\sigma(\lvert F\rvert^2)]$	5495
transmission coeff	0.83−0.96
no. of params refined (n_v)	489
R^a (obsd reflns)	0.072
$R^2{}_w{}^b$ (obsd reflns)	0.1346
GOF^c	0.959

[a] $R = \sum(|F_o - (1/k)\ F_c|)/\sum|F_o|$. [b] $R^2{}_w = [\sum w(F_o{}^2 - (1/k)F_c{}^2)^2/\sum w|F_o{}^2|^2]$. [c] GOF $= [\sum_w(F_o{}^2 - (1/k)F_c{}^2)^2/(n_o - n_v)]^{1/2}$.

Table 4. ^{1}H PGSE Results for 4a, 4b, and 8

	$-m^a$/T^{-2} m^2	10^{10} D/m^2 s^{-1} [b]
4a	117(1)[c]	6.71(6)[c]
4b	122(1)	7.00(6)
8	153(1)	8.77(6)

[a] Measured using $\delta = 5$ ms and $\Delta = 100$ ms. [b] Estimated using the diffusion coefficient of HDO in D_2O as reference.[34] [c] Standard deviation.

necessary. Upon convergence (see Supplementary Table S1), the final difference Fourier map showed no significant peaks.

The contribution of the hydrogen atoms in their calculated position (C−H = 0.95 Å, B(H) = 1.3B(C_{bonded}) Å^2) was included in the refinement using a riding model. All calculations were carried out by using the PC version of the SHELX-97 programs.[41] The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[42]

Preparation of 4a. Complex **2a** (41 mg, 0.040 mmol) was suspended in 6 mL of *tert*-butyl alcohol, and 5 mL of THF was added. The solution was stirred at 40 °C for 3 h, and then 0.5 mL of H_2O was added. The mixture was stirred for another 12 h at 40 °C, during which time an orange solid precipitated. Filtration and washing with pentane afforded **4a**. Yield: 27 mg (87%). ^{1}H NMR (CD_2Cl_2, 400 MHz): 8.25 (d, $^2J_{PH}$ = 13.0, 2H, O*H*), 8.14 (m, 2H), 8.08 (d, $^3J_{HH}$ = 8.3, 2H), 7.86−7.63 (m, 18H). 7.57 (m, 4H), 7.40 (d, $^3J_{HH}$ = 8.1, 2H), 7.29 (m, 2H), 7.17 (m, 4H), 7.09 (m, 4H), 6.70 (d, $^3J_{HH}$ = 7.7, 2H), 6.55 (m, 2H), 5.96 (d, $^3J_{HH}$ = 8.3, 2H), 5.29 (m, 2H), 5.27 (m, 2H). ^{13}C NMR (CD_2Cl_2, 100 MHz): 144.6, 140.9, 136.9, 134.5, 133.9, 133.2, 131.8, 131.3, 131.0, 130.3, 129.3, 128.8, 128.7, 128.5, 127.8, 127.4, 125.6, 125.2, 120.9, 113.1, 104.8, 100.5, 96.5, 78.3. ^{19}F NMR (CD_2Cl_2, 376 MHz): −79.36. ^{31}P NMR (CD_2Cl_2, 162 MHz): 100.9 (d, $^2J_{PP}$ =70.0), 56.7 (d, $^2J_{PP}$ = 71.1). MS (FAB): 1241.5 (M^+), 1223.4 ($M^+ - H_2O$, 100%), 621.1 (monomer). Anal. Calcd for $C_{33}H_{26}F_3O_6P_2RuS$: calcd C: 51.43, H: 3.40; found C, 51.36; H, 3.65. Mp > 250 °C.

Preparation of 4b. Complex **2b** (40 mg, 0.040 mmol) was suspended in 6 mL of *tert*-butyl alcohol, and 4 mL of THF was added. The solution was stirred at 40 °C for 3 h and then treated with 0.7 mL of H_2O. The mixture was stirred for 2 days at 40 °C, during which time a yellow precipitate formed. Most of the THF was removed in vacuo, and subsequent filtration and washing with pentane afforded **4b** as a yellow solid. Yield: 19 mg (65%). ^{1}H NMR (CD_2Cl_2, 500 MHz): 8.10 (dd, $^3J_{PH}$ = 11.9, $^3J_{HH}$ = 7.3, 4H), 7.67−7.45 (m, 22H), 7.23 (t, $^3J_{HH}$ = 7.9, 2H), 7.08 (d, $^3J_{HH}$ = 8.3, 2H), 6.01 (t, $^3J_{HH}$ = 5.7, 2H), 5.46 (d, $^3J_{HH}$ = 6.6, 2H), 5.08 (t, $^3J_{HH}$ = 3.7, 2H), 4.89 (t, $^3J_{HH}$ = 6.4, 2H), 3.82 (s, OCH_3, 6H), 2.87 (s, OCH_3, 6H). The OH chemical shifts were determined by PH-COSY (CD_2Cl_2, 500 MHz): 7.62 (d, $^2J_{PH}$ = 17.2, 2H), 7.53 (d, $^2J_{PH}$ = 17.2, 2H). ^{13}C NMR (CD_2Cl_2, 162 MHz): 158.2, 149.9, 148.5, 136.0, 134.8, 134.4, 131.9, 131.6, 130.8, 128.9, 127.7, 124.5, 113.6, 98.8, 96.5, 82.2, 80.6, 56.4, 56.2. ^{19}F NMR (CD_2Cl_2, 376 MHz): −79.36.

^{31}P NMR (CD_2Cl_2, 202 MHz): 100.3 (d, $^2J_{PP}$ = 77.8), 53.2 (d, $^2J_{PP}$ = 78.6). MS (FAB): 1311.1 (M − OTf), 1160.7 (M^+), 1142.7 ($M^+ - H_2O$), 581.3 (monomer). Anal. Calcd for $C_{54}H_{50}F_6O_{16}P_4Ru_2S_2$: C, 44.45; H, 3.45. Found: C, 44.29; H, 3.64.

Preparation of 8. Complex **2a** (50 mg, 0.048 mmol) was dissolved in 7 mL of MeOH and stirred at room temperature for 30 min. A 2.0 mL portion of H_2O was added and the mixture stirred at 40 °C for 2 days. The resulting yellow solution was concentrated, extracted with CH_2Cl_2, and dried over $MgSO_4$. Most of the CH_2Cl_2 was removed in vacuo and then Et_2O added. The precipitate was collected by filtration, washed with pentane, and dried to afford **8** as a yellow solid. Yield: 23 mg (59%). ^{1}H NMR (CD_2Cl_2, 400 MHz): 8.23 (m, 1H), 8.19 (d, $^3J_{HH}$ = 8.4, 1H), 8.14 (d, $^3J_{HH}$ = 8.2, 1H), 7.90−7.05 (m, 16H). 6.97 (t, $^3J_{HH}$ = 7.7, 1H), 6.80 (t, $^3J_{HH}$ = 6.1, 1H), 6.31 (d, $^3J_{HH}$ = 8.8, 1H), 5.35 (under solvent signal, 1H), 3.52 (d, $^3J_{PH}$ = 11.0, 3H, O-CH_3), 3.21 (d, $^3J_{PH}$ = 11.4, 3H, O-CH_3)**.** ^{13}C NMR (CD_2Cl_2, 100 MHz): 142.5, 141.8, 134.9, 134.5, 134.0, 133.6, 133.1, 133.0, 132.7, 132.1, 131.4, 131.2, 129.8, 129.5, 129.0, 128.8, 128.6, 128.2, 127.7, 126.9, 125.4, 116.8, 110.7, 102.6, 98.5, 94.1, 76.5, 52.0, 51.6. ^{19}F NMR (CD_2Cl_2, 282 MHz): −79.31. ^{31}P NMR (CD_2Cl_2, 162 MHz): 87.5 (d, $^2J_{PP}$ = 66.0), 55.7 (d, $^2J_{PP}$ = 67.0). MS (FAB): 648.5 (monomer), 538.6 (RuBinap − PPh_2). Anal. Calcd for $C_{35}H_{29}F_3O_6P_2RuS$: C, 52.70; H, 3.66. Found: C, 52.65; H, 3.78.

Preparation of 10. Complex **2a** (20 mg, 0.019 mmol) was dissolved in 2.5 mL of MeOH and stirred at room temperature for 30 min. Addition of 0.5 mL of H_2O was followed by stirring at 40 °C for 2 days. The resulting yellow solution was concentrated, extracted with CH_2Cl_2, and dried over $MgSO_4$. After filtration, 50 μL of *p*-tolunitrile was added and the mixture stirred at room temperature for 20 min. Concentration of the solvent followed by addition of pentane led to the precipitation of a yellow solid. The crude product was collected and then washed with 1:1 pentane/Et_2O and dried in vacuo to yield 10 mg (56%) of **10**. ^{1}H NMR (CD_2Cl_2, 400 MHz): 8.20 (m, 1H), 8.16 (d, $^3J_{HH}$ = 7.6, 1H), 8.14 (d, $^3J_{HH}$ = 7.5, 1H), 7.97 (t, $^3J_{HH}$ = 7.6, 1H), 7.89 (d, $^3J_{HH}$ = 8.6, 1H), 7.82−7.50 (m, 4H). 7.46 (d, $^3J_{HH}$ = 8.3, 2H), 7.43−7.37 (m, 6H), 7.35 (d, $^3J_{HH}$ = 8.1, 2H), 7.33−7.21 (m, 3H), 7.13 (m, 1H), 6.89 (m, 2H), 6.55 (d, $^3J_{HH}$ = 8.6, 1H), 5.90 (m, 1H), 3.45 (d, $^3J_{PH}$ = 11.8, 3H), 2.99 (d, $^3J_{PH}$ = 11.4, 3H), 2.47 (s, 3H). ^{13}C NMR (CD_2Cl_2, 100 MHz): 147.3 (*p*-tolyl), 143.3, 141.0, 135.1, 134.6, 133.6, 133.2, 131.9, 131.8, 131.7, 131.4, 130.6, 129.7, 129.3, 129.1, 128.7, 128.3, 128.0, 127.7, 114.7, 112.0, 109.4, 106.6 (ipso-tolyl), 103.7, 93.1, 85.9, 52.3 (O-*C*H_3), 51.0 (O-*C*H_3), 22.1 (*C*H_3). ^{19}F NMR (CD_2Cl_2, 376 MHz): −79.28. ^{31}P NMR (CD_2Cl_2, 162 MHz): 78.3 (br), 61.7 (d, $^2J_{PP}$ = 60.2). MS (FAB): 766.3 (M^+), 649.2 (M − *p*-tolunitrile), 539.1 (RuBiNap − PPh_2, 100%). Anal. Calcd for $C_{43}H_{36}F_3NO_6P_2RuS\cdot 3H_2O$: C: 53.30, H, 4.37; N, 1.45. Found: C, 53.49; H, 4.14; N, 1.57. (We do observe H_2O in the spectrum.)

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Supporting Information Available: Text giving experimental details and a full listing of crystallographic data for compound **6** including tables of positional and isotropic equivalent displacement parameters, calculated positions of the hydrogen atoms, anisotropic displacement parameters, bond distances and angles, and an ORTEP figure showing the full numbering scheme. This material is available free of charge via the Internet at http://pubs.acs.org.

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