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# X-ray Diffraction and NMR Studies on a Series of Binap-Based Ru(II) Hydroxyphosphine $\pi$-Arene Complexes

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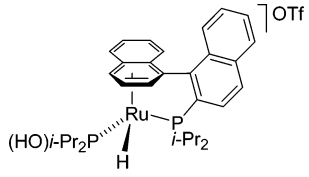
A series of new Ru(II) arene phosphine complexes derived from Binap have been prepared. Specifically, reaction of $Ru(OAc)_2$(Binap) with 3,5-$(CF_3)_2C_6H_3)_4B$ (BArF)·$H(OEt_2)_2$, is shown to afford new mono- and dinuclear Ru(II) hydroxyphosphine $\pi$-arene complexes via a series of P–C bond cleavage reactions. The dinuclear Ru(II) $\pi$-arene complexes contain bridging $P(O)(OH)_2$ ligands. Crystal structures of five new complexes are reported and suggest an $\eta^4$-arene rather than an $\eta^6$-arene coordination mode. However, in solution, their $^{13}C$ NMR data are more consistent with a strongly distorted $\eta^6$-coordination mode. PGSE $^1H$ and $^{19}F$ diffusion measurements on the dinuclear complexes suggest hydrogen bonding of the triflate anion and ion-pairing of the $BArF^-$ anion.

## Introduction

Ruthenium is at present among the most prevalent metals in catalytic organometallic chemistry. This is due to its excellent performance as catalyst in metathesis[1] and enantioselective hydrogenation chemistry,[2] combined with the relative insensitivity of Ru(II) compounds toward air and moisture.

We have recently[3−5] been exploring the organometallic chemistry of the hydrogenation catalyst precursors $Ru(OAc)_2$-(Binap or MeO-Biphep) in the presence of strong acids. The ability of these atropisomeric phosphine ligands to coordinate Ru(II) is somewhat more flexible than originally thought in that these ligands can act as 6 and 8 electron donors.[4,5] Moreover, reaction of $Ru(OAc)_2$(Binap), **1**, with triflic acid in the absence of additional suitable ligands causes a stereospecific P−C bond scission to afford complex **2** (see Scheme 1).[4e] The triflate ligand in **2** is easily solvolyzed in simple alcohols leading to **3a** via a stereospecific migration of a P-phenyl group to the ruthenium.[5a,c] If **2** is kept in a water/THF mixture, the ultimate product is **4a** which represents the first example of a metal complex bearing a $P(OH)_2R$ ligand.[5b] Analogous experiments using alkyl Binap analogues of **2**, e.g., (*iso*-propyl)$_2$-Binap or (cyclohexyl)$_2$-Binap, with triflic acid reveal that these alkyl phosphine compounds are stable with respect to multiple P−C bond scission, but they instead react with the solvent methanol via $\beta$-hydrogen elimination to afford the corresponding 18-electron hydride complexes, e.g., **5**.[5e]




**5**

The $P(OH)_2$ fragment in **4a** represents an interesting acid which might be utilized to bind other substrates. However, from preliminary experiments it appears that the $CF_3SO_3^-$ counterion binds to both OH groups of the $P(OH)_2$ moiety, thus preventing utilization of these functional groups. Therefore, we sought a preparative route which circumvents

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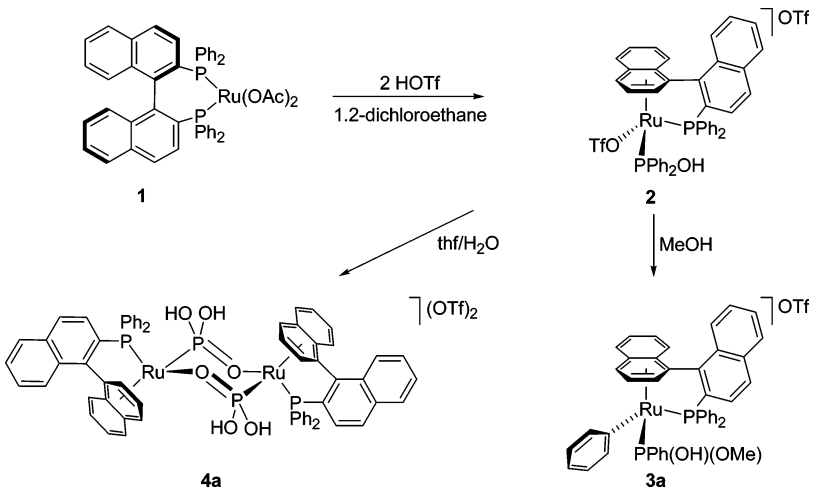
**Scheme 1.** P−C Bond Splitting Reactions

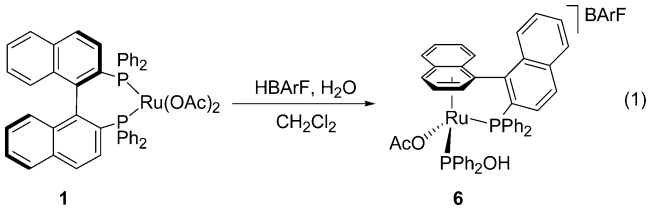



the presence of coordinating and/or H-bonding anions and considered a triflate-free approach based on the noncoordinating acid $(3,5\text{-}(CF_3)_2C_6H_3)_4B{\cdot}H(OEt_2)_2$ (=HBArF, BArF = tetrakis [3,5bis(trifluoromethyl)phenyl]borate). We report here on the preparation of a set of new hydroxyphosphine $\pi$-arene complexes and show that the distorted $\pi$-arene−Ru interaction in our new compounds adopts one structure in the solid state, but a different structure in solution.

## Results and Discussion

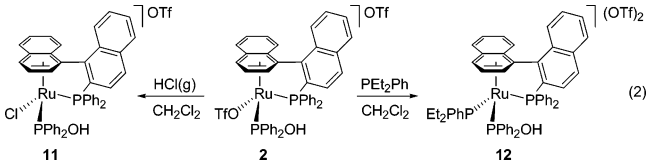
**Preparative Chemistry.** Scheme 2 shows the syntheses of the new dinuclear ruthenium(II) complexes. Treatment of a dichloromethane solution of the bis-acetate compound, **1**, with 1 equiv of HBArF and subsequent reaction with water quantitatively affords the acetate complex **6**, see eq 1. Clearly, $CF_3SO_3H$, is not necessary for P−C bond cleavage.

The observation of a single diastereomer in the NMR spectra of **6** (or **2** and **11**) is thought to be due to kinetic control of the P−C bond splitting. Starting from the complexed racemic Binap in $Ru(OAc)_2$(Binap), the P-donor complexes a proximate double bond from the naphthyl moiety when 1 equiv of HOAc is lost.[4a−c,f] This olefin complexation directs the subsequent P−C cleavage such that the P-ligand moves to the stereogenic Ru-atom in a selective manner.



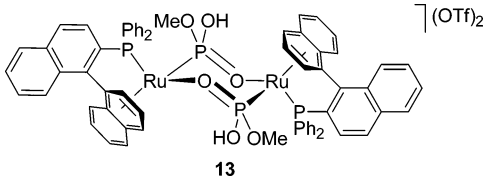

The acetate ligand in **6** is readily solvolyzed in methanol to afford **3b** (see Scheme 2). Compound **3b** was not isolated but appears as the only reaction product, and its structure has been confirmed by NMR studies. Complex **6** is easily converted to the dinuclear complex **4b** upon stirring a water/THF mixture overnight. Interestingly, the main species present in the reaction solution (via NMR) is not dimer **4b**, but a complex which, in accordance with its characteristic low-frequency $^{31}P$ NMR resonances, $\delta = 71.7$ and 57.6 ppm, was tentatively assigned to be monomer **7**. Presumably, this unprecedented mononuclear phosphorus acid complex is solvent-stabilized and converts to **4b** upon removal of the solvent during the workup procedure. In contrast to the poorly soluble triflate derivative **4a**, complex **4b** easily dissolves in ethers and chlorinated solvents but is insoluble in hydrocarbons and aromatic solvents.

The dimethoxy-analogue, **9**, of the postulated monomeric intermediate, **7**, was prepared by allowing **6** to react with methanol in the presence of HBArF. The synthesis proceeds in satisfactory yield, with complex **8** identified in situ as the only intermediate. Relative to **7**, complex **9** reacts slowly in dichloromethane solution to afford dinuclear **10**. The model mononuclear complexes, **11** and **12** (see eq 2), were also prepared when it became obvious that the arene bonding in **4a** was not trivial.



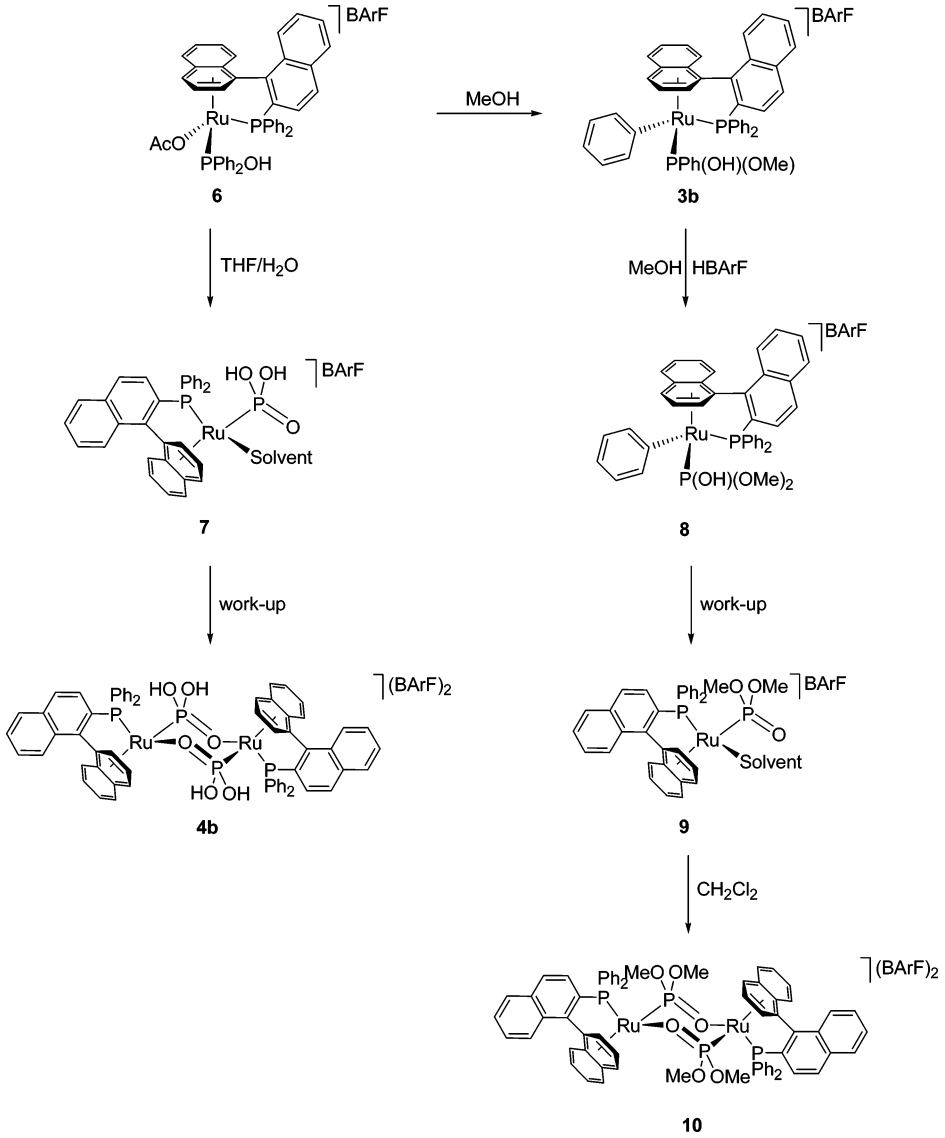

**X-ray Diffraction Studies.** X-ray data from the two model mononuclear compounds **11** and **12**, the dinuclear complexes, **4a** and **4b**, as $CF_3SO_3^-$ and $BArF^-$ salts, respectively, and the tetra-methoxy complex **10** are given in Table 1.

We have previously reported the structure of related dinuclear complex **13** which was accidentally obtained by keeping a solution of **3a** (the triflate analogue of **3b**) in wet THF.[5b]




Figures 1−5 show views of these new complexes. Crystals suitable for X-ray diffraction studies were obtained from slow

**Scheme 2.** Synthetic Route to the New Ru(II) Complexes




diffusion of either diethyl ether (**4a**, **11**, and **12**) or *n*-pentane (**4b** and **10**) into dichloromethane solutions. All of the structures, except that for the chloro-complex **11**, contain additional solvent molecules, which in some cases are highly disordered. Furthermore, some of the $CF_3$-groups of the $BArF^-$ and triflate anions are disordered over two positions in the solid state. Although this disorder affects the *R*-values, the bonding situation within the cationic part of the complexes is unambiguous. In the dinuclear structures, only half of the molecule is independent; the other half is generated via a symmetry operation. Details concerning the data collection and refinement are given in the Experimental Section and in Table 2. It is useful to discuss all six of these complexes as a group since they have many common features.

The coordination sphere of the metal consists of the strongly distorted $\pi$-arene plus three additional ligands. On the basis of the various coordination angles shown in Table 1, the three monodentate donor ligands are disposed in a facial arrangement, i.e., the (donor)−Ru−(donor) angles range from 89° to 101°. Consequently, the local geometry at ruthenium can be considered as strongly distorted tetrahedral.

**Table 1.** Selected Bond Lengths (Å) and Bond Angles (deg)

| | **4a** | **4b** | **10** | **13** | **11** | **12** |
|---|---|---|---|---|---|---|
| Ru−P1 | 2.307(2) | 2.308(1) | 2.318(2) | 2.255(2) | 2.288(2) | 2.348(4) |
| Ru−P2 | 2.244(2) | 2.236(1) | 2.242(2) | 2.315(2) | 2.302(3) | 2.276(4) |
| Ru−P3 | | | | | | 2.431(4) |
| Ru−O1 | 2.086(6) | 2.101(2) | 2.091(4) | 2.085(4) | | |
| Ru−Cl | | | | | 2.364(2) | |
| Ru−C1 | 2.127(8) | 2.146(3) | 2.138(6) | 2.138(7) | 2.163(5) | 2.18(1) |
| Ru−C2 | 2.503(9) | 2.510(3) | 2.483(6) | 2.514(7) | 2.373(5) | 2.53(1) |
| Ru−C3 | 2.46(1) | 2.524(4) | 2.483(6) | 2.511(7) | 2.434(5) | 2.53(1) |
| Ru−C4 | 2.298(9) | 2.305(4) | 2.299(7) | 2.300(7) | 2.298(5) | 2.29(1) |
| Ru−C5 | 2.27(1) | 2.270(4) | 2.286(6) | 2.278(7) | 2.233(5) | 2.26(1) |
| Ru−C6 | 2.137(9) | 2.154(4) | 2.146(6) | 2.146(6) | 2.196(5) | 2.20(1) |
| P2−O1 | 1.509(6) | 1.516(2) | 1.511(4) | 1. 517(4) | 1.582(4) | 1.576(7) |
| P2−O2 | 1.592(6) | 1.604(3) | 1.611(5) | 1.590(9) | | |
| P2−O3 | 1.581(6) | 1.580(3) | 1.598(5) | 1.581(8) | | |
| P1−Ru−P2 | 88.9(1) | 89.4(1) | 91.6(1) | 91.2(2) | 94.0(1) | 90.1(2) |
| O1−Ru−P1 | 99.5(2) | 99.7(1) | 98.3(1) | 100.5(1) | | |
| O1−Ru−P2 | 94.0(2) | 92.2(1) | 89.6(1) | 89.4(1) | | |
| Cl−Ru−P1 | | | | | 88.7(1) | |
| Cl−Ru−P2 | | | | | 93.4(1) | |
| P1−Ru−P3 | | | | | | 101.5(2) |
| P2−Ru−P3 | | | | | | 91.0(2) |

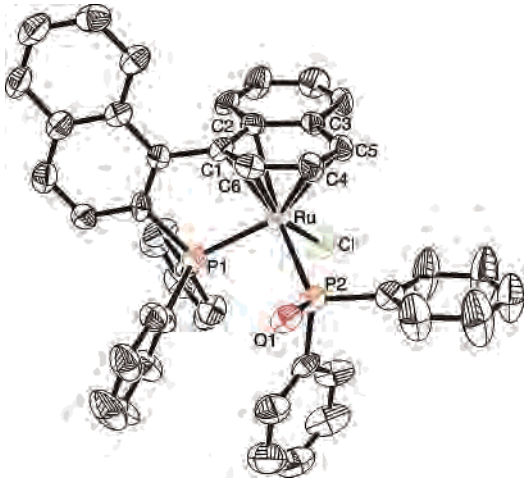



**Figure 1.** ORTEP plot of the Ru(II) complex **11**. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

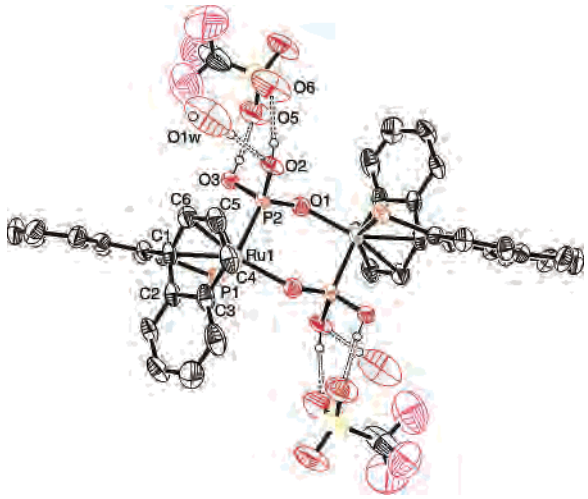



**Figure 2.** ORTEP plot of the dinuclear Ru(II) complex **4a** showing the hydrogen bonding between the triflate counteranion, the solvent water molecule, and the P−OH groups. Thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms (except for those noted above) and P-phenyl rings have been omitted for clarity (equivalent atoms generated by $-x + 2$, $-y + 1$, $-z + 1$).

The bonding from the arene to the ruthenium is highly asymmetric. Distances from the metal to carbon atoms C1 and C6, 2.12−2.20 Å are rather short, those to C4 and C5, 2.23−2.31 Å, relatively routine,[7−17] but those to the bridgehead carbons C2 and C3, ca. 2.37−2.53 Å are very long. Indeed, if one excludes chloro-complex **11**, the distances for Ru−C2 and Ru−C3 fall routinely in the range ca. 2.46−2.53Å, which values might well be considered as too long to be associated with a complexed double bond. Consequently, on the basis of these data, it is tempting to regard all of these compounds as having an $\eta^4$-arene rather than an $\eta^6$-arene coordination mode. Within this context, we find that the plane of the coordinated arene in **12** comprising the arene carbon atoms C1−C6 is distorted toward that of an $\eta^4$-butadiene-like structure, with the remaining naphthyl moiety folded upward (see Figure 5a,b). Coordinated nonplanar $\pi$-arenes have been observed previously, e.g., in complexes of the type $[RuCl_2(\eta\text{-arene})(PMePh_2)]$.[18]

Apart from the arene coordination, the various Ru−(donor atom) separations are fairly routine and correspond to literature expectations,[6] with the possible exception of the Ru−P distances in the tris phosphine complex, **12**. Here, we note that the ruthenium distance to the presumably best

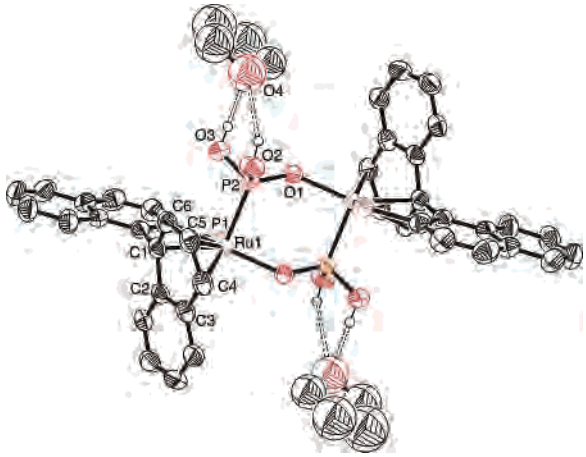



**Figure 3.** ORTEP plot of the cation of the dinuclear Ru(II) complex **4b** showing the hydrogen bonding between THF and the P−OH groups. Thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms (except for those noted above), P-phenyl rings, and the counterion ($BArF^-$) have been omitted for clarity (equivalent atoms generated by $-x + 2$, $-y + 1$, $-z + 1$).

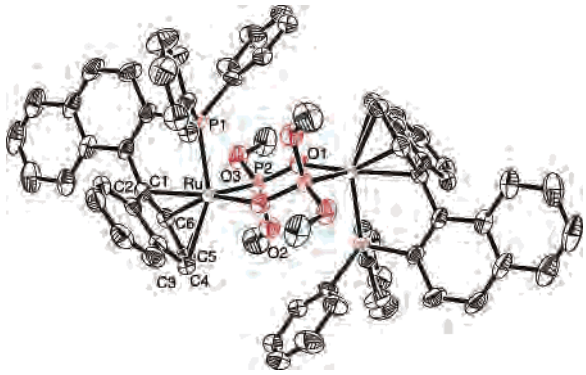



**Figure 4.** ORTEP plot of the cation of the Ru(II) dimethoxy-analogue, **10**. Thermal ellipsoids are drawn at the 40% probability level. The hydrogen atoms and the counterion ($BArF^-$) are omitted for clarity (equivalent atoms generated by $-x + 1$, $-y + 1$, $-z + 1$).

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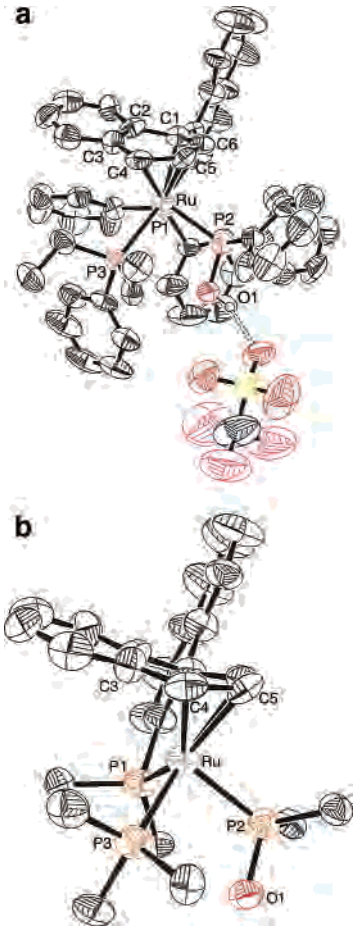


**Figure 5.** (a) ORTEP plot and numbering scheme for **12**, showing the interaction of the triflate anion with the hydroxy-group (···). Hydrogen atoms (except H1 located at O1) are omitted for clarity; thermal ellipsoids are drawn at the 40% probability level. (b) Partial view of tris phosphine Ru(II) complex **12** showing the distortion in the complexed arene toward an $\eta^4$-arene rather than an $\eta^6$-arene.

and smallest phosphorus donor, diethyl phenyl phosphine, P3, is the longest, 2.431(4) Å. We believe this to be a kinetic effect in that the larger donors, P1 and P2, were already complexed to the Ru(II) with the result that P3 cannot approach as closely as might be expected. In the four dinuclear compounds, **4a**, **4b**, **10**, and **13**, the bridging PO moieties are best considered as phosphine oxide donors. The observed P2−O1 bond separations of 1.509(6)−1.517(4) Å are consistent with P═O double bonds. For the P−O single bonds, the values lie between 1.58 and 1.61 Å.

In **4a**, there is pronounced hydrogen bonding from each of the triflate-oxygen atoms O5 and O6 to a set of geminal hydroxy-protons with an additional contact to the hydroxy-oxygen O2 from a water-molecule present. Distances between the OH···O-atoms of the hydrogen bridges range between 1.8 and 2.1 Å, and Figure 2 shows a view of the cation together with the interaction of the anion and water molecules.

As expected, the $BArF^-$ anion in **4b** does not interact with the P(OH)-groups; however, the latter hydrogen-bonds to solvent THF molecules as shown in Figure 3. The H-bonding is not symmetric, with the distance H(O3)−O4 (around 1.8 Å) being significantly shorter than H(O2)−O4 (around 3 Å). The presence of different anions and solvent molecules in the solid state is not reflected in the bonding parameters within the coordination sphere of the Ru(II). A comparison of the various Ru−(donor) bond lengths reveals these to be identical within experimental errors.

**NMR Studies.** Table 3 lists complexed arene $^{13}C$ and $^{31}P$ NMR chemical shifts for the complexes with the numbering as given in the X-ray figures. The $^{13}C$ data stem from a combination of one-bond and long-range $^{13}C$, $^1H$ correlation experiments (see Figure 6), with the latter measurements critical in terms of finding and assigning the fully substituted aromatic C1−C3 carbon signals.

Routine literature $^{13}C$ chemical shifts for the C−H signals of free Binap and for the Binap C−H resonances in the compounds not involved in the complexation are found at ca. 125−130 ppm, whereas those carbons which are $\pi$-complexed to Ru(II) often appear at ca. 70−100 ppm; [29−35] i.e., there are coordination chemical shifts, $\Delta\delta$, ranging from ca. 30 to 70 ppm. Our $^{13}C$ values for the carbon atoms C1 and C6, for which we observed the shortest Ru−C distances in the X-ray studies, as well as those for the carbon atoms C4

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**Table 2.** Crystallographic Parameters

| | 4a | 4b | 10 | 11 | 12 |
|---|---|---|---|---|---|
| formula | $C_{33}H_{26}F_3O_{6.5}P_2RuS$ | $C_{146}H_{114}B_2F_{48}O_8P_4Ru_2$ | $C_{67}H_{43}BCl_2F_{24}O_3P_2Ru$ | $C_{45}H_{34}ClF_3O_4P_2RuS$ | $C_{57}H_{49}Cl_2F_6O_8P_3RuS_2$ |
| *M* | 778.61 | 3256.04 | 1596.73 | 926.24 | 1304.96 |
| cryst syst | monoclinic | triclinic | monoclinic | triclinic | monoclinic |
| space group | $P2_1/n$ | $P\bar{1}$ | $P2_1/c$ | $P\bar{1}$ | $P2_1/c$ |
| *a*/Å | 14.422(3) | 14.154(4) | 12.839(1) | 10.632(6) | 11.55(1) |
| *b*/Å | 14.972(3) | 16.131(5) | 18.934(2) | 13.039(8) | 23.80(2) |
| *c*/Å | 14.869(3) | 16.602(5) | 27.128(3) | 15.48(2) | 21.78(3) |
| α/deg | 90 | 108.787(6) | 90 | 88.69(7) | 90 |
| *β*/deg | 95.92(3) | 92.473(6) | 90.614(2) | 79.52(6) | 104.33(9) |
| *γ*/deg | 90 | 102.810(6) | 90 | 72.74(5) | 90 |
| *V*/Å$^3$ | 3193.5(1) | 3472(2) | 6594(1) | 2014(3) | 5801(11) |
| *Z* | 4 | 1 | 4 | 2 | 4 |
| *d* [Mg/m$^3$] | 1.619 | 1.557 | 1.608 | 1.527 | 1.494 |
| *T*/K | RT | 233 | 200 | RT | RT |
| 2*θ* range/deg | $4.07 \le 2\theta \le 50.00$ | $2.76 \le 2\theta \le 52.74$ | $3.00 \le 2\theta \le 56.58$ | $3.28 \le 2\theta \le 40.08$ | $3.42 \le 2\theta \le 39.60$ |
| *μ*/mm$^{-1}$ | 0.610 | 0.386 | 0.610 | 0.645 | 0.589 |
| reflns measured | 3278 | 30974 | 67271 | 3990 | 5599 |
| unique reflns [$I > 2\sigma(I)$] | 2172 | 14185 ($R_{int} = 0.0486$) | 16355 ($R_{int} = 0.0358$) | 3798 | 5252 |
| final R1, wR2 [$I > 2\sigma(I)$] | 0.0474, 0.1290 | 0.0494, 0.1368 | 0.1165, 0.2530 | 0.0314, 0.0572 | 0.0649, 0.1609 |

**Table 3.** Selected $^{13}$C and $^{31}$P NMR Data for Complexes[a]

| | C1 | C2 | C3 | C4 | C5 | C6 | P1 | P2 |
|---|---|---|---|---|---|---|---|---|
| **3b**[b] | 116.2 | 109.9 | 115.5 | 92.7 | 100.4 | 92.1 | 61.7 | 140.3 |
| **4b**[c] | 101.3 | 117.8 | 112.9 | 99.7 | 104.2 | 76.8 | 56.6 | 105.2 |
| **6**[d] | 108.7 | 112.7 | 115.6 | 95.0 | 103.9 | 76.7 | 55.9 | 114.7 |
| **8**[e] | 115.7 | 110.6 | 115.4 | 92.5 | 98.0 | 92.7 | 61.0 | 125.1 |
| **9**[e] | 100.3 | 117.1 | 113.0 | 94.1 | 103.4 | 77.6 | 58.8 | 83.4 |
| **10**[d] | 108.5 | 112.6 | 110.9 | 92.9 | 103.7 | 74.0 | 55.3 | 119.3 |
| **11**[d] | 108.2 | 111.6 | 111.4 | 97.1 | 107.2 | 81.8 | 53.5 | 109.8 |

[a] See X-ray structures for numbering scheme. [b] $d_4$-MeOH, 400 MHz. [c] $CD_2Cl_2$, 400 MHz. [d] $CD_2Cl_2$, 500 MHz. [e] $d_4$-MeOH, 500 MHz. Chemical shifts are in ppm.

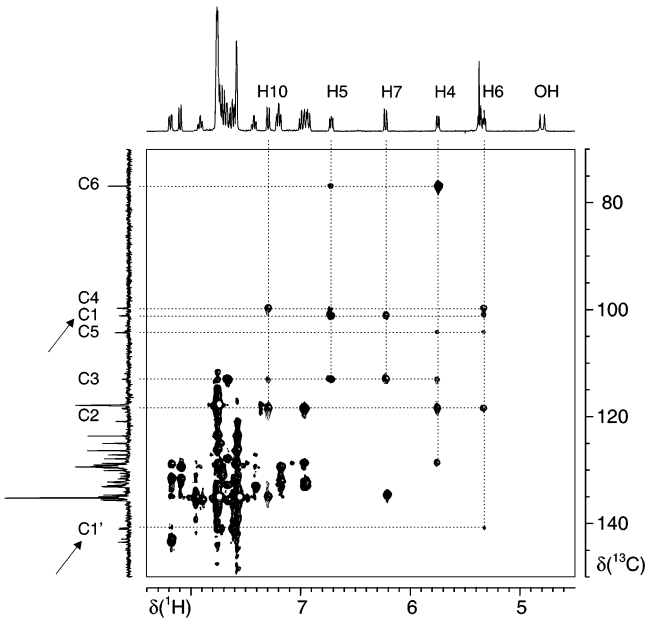
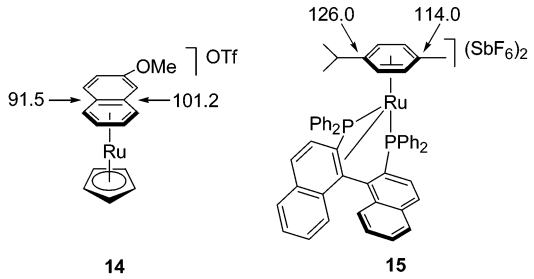



**Figure 6.** $^{13}$C,$^1$H-HMQC for **4b**, showing (among others) the low-frequency positions of the complexed C1 and noncomplexed C1′ (arrows). This pseudocoordination chemical shift difference indicates that C1 is indeed complexed. The chemical shift of C1′ is typical for a fully substituted aromatic Binap carbon resonance.

and C5, found at normal distances from the Ru-atom, are fully consistent with complexation of these atoms in a *π*-fashion.

For the fully substituted aromatic $^{13}$C signals, not involved in *π*-arene interactions, e.g., C1′−C3′, one expects and finds chemical shifts of the order of 130−140 ppm. For those fully substituted carbon atoms which are complexed to ruthenium, e.g., for the two model compounds, **14**[36] and **15**,[37] literature values of ca. 90−126 are found. If an $\eta^4$ bonding description




**14** **15**

(chemical shifts shown refer to fully substituted carbons only)

in solution were correct for C2 and C3 (the two carbon atoms with the rather large Ru−C separations), one would expect relatively small $\Delta\delta$ values for these fully substituted carbon resonances. Their observed $^{13}$C absorptions appear at ca. 110−118 ppm, so that their $\Delta\delta$ values are not trivial and amount to ca. 20−30 ppm. Further, these values are rather similar to those observed in **14** and **15** so that, on the basis of the $^{13}$C results, we conclude there is some interaction of these two carbon atoms with the Ru-atom. Undoubtedly, the *π*-complexation in our compounds is strongly distorted, but in solution, the data point to an $\eta^6$ bonding description; i.e., the arene bonding is simply different from that found in the solid state.

**Diffusion Measurements.** Given the various H-bonding interactions in the solid-state, we have measured the diffusion constant, *D*, for **4a** and **4b** via pulsed field gradient spin−echo (PGSE) methods.[19] This methodology, which allows one to relate rates of translation to chemical association (H-bonding or ion-pairing), is finding increasing application in coordination chemistry.[20−27] The diffusion constants, which result from these measurements, are given in Table 4 ($r$ = hydrodynamic radius, $D$ = diffusion constant, and $\eta$ =

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**Table 4.** Diffusion Data[a] for the Dinuclear Ru(II) Complexes **4a**, **4b**, and Model Complex **16**

| compd | | $D$ ($10^{-10}$ m$^2$ s$^{-1}$) | $r$ (Å) |
|---|---|---|---|
| **4a** ($CF_3SO_3$) | cation | 7.33 | 7.3 |
| | anion | 7.63 | 7.0 |
| **4b** (BArF) | cation | 5.27 | 10.2 |
| | anion | 6.56 | 8.2 |
| **16a** (X=$CF_3SO_3$) | cation | 7.73 | 6.9 |
| | anion | 10.46 | 5.1 |
| **16b** (X=BArF) | cation | 7.71 | 6.9 |
| | anion | 8.05 | 6.6 |

[a] $CD_2Cl_2$, concentration ≈ 2 mM.

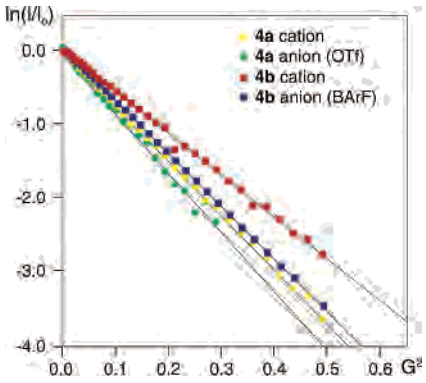
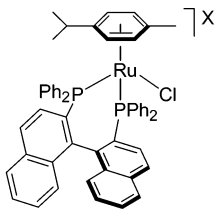



**Figure 7.** $^1$H PGSE NMR data for the cations of **4a** and **4b** with the corresponding $^{19}$F data, for the anions. The lines from the fluorine measurements have been corrected for the difference in gyromagnetic ratio. The much smaller slope for the cation of **4b** (red squares) is consistent with the relatively large average volume for this salt, due to the ion-pairing.

viscosity), and Figure 7 shows the $^1$H PGSE data for the cations of **4a** and **4b** together with the corresponding $^{19}$F derived data for the anions.

$$r_H = \frac{kT}{6\pi\eta D} \quad (3)$$

For dinuclear complex **4a**, the almost equivalent $D$ values for the cation, $7.33 \times 10^{-10}$ m$^2$ s$^{-1}$, and anion, $7.63 \times 10^{-10}$ m$^2$ s$^{-1}$, support significant (but not 100%) H-bonding of the $CF_3SO_3^-$ anion to the OH-groups of the cation. The observed 7.63 $D$-value (the units will now be omitted for clarity) for the $CF_3SO_3^-$ anion is relatively small and indicates much slower than normal translation. A typical $D$-value for this anion in dichloromethane for a 1:1 salt would be much larger, e.g., the 10.46 value given in Table 4 for model compound [RuCl(*p*-cymene)(Binap)]($CF_3SO_3$), **16a**.[28] It is known that




**16**

**a**, X = $CF_3SO_3^-$, **b**, X = $BArF^-$

dichloromethane promotes some ion pairing[27] in **16a**;[28] i.e., the hydrodynamic radius, 5.1 Å, derived from the 10.46 $D$-value is too large for an isolated triflate anion. The $D$-value for the cation in the $BArF^-$ salt, **4b**, 5.57, is very much smaller in magnitude than the 7.33 value given for the cation in **4a**. This slower rate of diffusion for the cation of **4b** with $BArF^-$ is again consistent with markedly reduced translation due to the ion-pairing of two relatively large $BArF^-$ anions. Since the 6.56 $D$-value for the $BArF^-$ (via $^{19}$F PGSE) is not identical to the value for the cation, 5.27, the ion pairing is not complete. For comparison we show the $D$-value, 8.05, for [RuCl(*p*-cymene)(Binap)](BArF), **16b**,[28] in Table 4, and note that the 6.56 value in **4b** is, indeed, much smaller.

**Summary.** A new set of Ru(II) arene hydroxy-phosphine complexes have been prepared and characterized. The P−C bond splitting reactions proceed smoothly in the presence of the $BArF^-$ anion. Interestingly, the $\pi$-arene bonding appears to be best described as $\eta^4$ in the solid state but changes to a distorted $\eta^6$-arene coordination mode in solution. For **4a** and **4b** diffusion measurements reveal that the $CF_3SO_3^-$ anion is H-bonded via hydrogen bridges to the hydroxyl-groups and that, in the $BArF^-$ salt, **4b**, the ion pairing is important, but not complete.

## Experimental Section

**Crystallography.** Data collection for the X-ray structure determinations were performed on Siemens CCD 1k (**4b**) or Bruker APEX (**13**) diffractometer systems, respectively, by using graphite-monochromated Mo $K_\alpha$ (0.71073 Å) radiation and a low-temperature device. Complex **4a** was measured on a Picker 4-circle, Stoe upgraded diffractometer (Cu $K_\alpha$ radiation), and **11** and **12** were measured on a Syntex P21 4-circle diffractometer (Mo $K_\alpha$ radiation), all at room temperature. Yellow crystals of **4a**, **11**, and **12**, suitable for X-ray diffraction, were obtained by slow diffusion of diethyl ether into a $CH_2Cl_2$ solution and are air stable. Orange crystals of **4b** and **10** were obtained upon slow diffusion of *n*-pentane into a $CH_2Cl_2$ solution and are sensitive to solvent-loss. Therefore, the single crystals were mounted in perfluoro ether oil on top of a glass fiber and then brought into the cold nitrogen stream of a low-temperature device so that the oil solidified. All calculations were performed on PCs by using the SHELX97[38] (**4b**, **10**) software package or the Unix version of the SHELX-93[39] (**4a**, **11**, **12**) programs. All structures were solved by Patterson methods and successive interpretation of the difference Fourier maps, followed by full-matrix least-squares refinement (against $F^2$). The collected intensities[40] were corrected for Lorentz and polarization factors, and an absorption correction[41] was applied.

All atoms, even the distorted solvent molecules in the crystals of **4b** (*n*-pentane) and **10** (dichloromethane), were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. The hydroxyl hydrogen atoms could be located in a Fourier difference density map but were restrained to ideal positions during refinement, using the implemented HFIX riding model for OH groups.

(38) Sheldrick, G. M. *SHELX-97. Structure Solution and Refinement Package*; Universität Göttingen: Göttingen, Germany, 1997.
(39) Sheldrick, G. M. *SHELX-93;* Universität Göttingen: Göttingen, Germany, 1993.
(40) *SAINT: SAX Area Detector Integration*; Siemens Analytical Instrumentation, Karlsruhe, 1996.
(41) Sheldrick, G. M. *SADABS*; Universität Göttingen: Göttingen, Germany, 1997.

Although cooled to 233 or 200 K, respectively, many of the $CF_3$ groups of the counteranions of **4b** and **10** were still rotating, and therefore, several fluorine atoms had to be split over two positions and were refined against each other using one free variable (FVAR) for each $CF_3$ group with occupation factors of roundabout 15−45% for the disordered positions. In **12**, one of the triflate anions was disordered and was refined using the rigid body approximation.

Upon convergence, the final Fourier difference map of the X-ray structures of **4a**, **4b**, and **11** showed no significant peaks. For **10**, some residual electron density was located close to the heavy atom ruthenium (∼0.8 Å) even when an absorption correction (SADABS)[41] was applied. In **12**, the final Fourier difference map showed significant residual peaks, which were assigned to a dichloromethane and a water molecule. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[42]

Relevant data concerning crystallographic data, data collection, and refinement details are compiled in Table 3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 211855−211859. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: (+44) 1223-336-033. E-mail: deposit@ccdc.cam.ac.uk. Internet: www.ccdc.cam.ac.uk/conts/retrieving.html.)

**Synthesis.** All organometallic manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Pentane and diethyl ether were distilled from sodium−potassium alloy, dichloromethane from $CaH_2$, and methanol from magnesium. $(3,5\text{-}(CF_3)_2C_6H_3)_4B{\cdot}H(OEt_2)_2$[43] and $[Ru(OAc)_2(Binap)]$[44] were prepared according to literature. All other chemicals were commercial products and were used as received. NMR spectra were recorded with Bruker Avance 400 and 500 spectrometers. Chemical shifts are given in ppm and coupling constants (*J*) in Hz. Elemental analyses and mass spectroscopic studies were performed at the ETHZ.

**In Situ Characterization of 3b.** A solution of **6** (10 mg, 0.006 mmol) in deuterated methanol (0.6 mL) was kept for 30 min at RT, resulting in quantitative conversion to **7**. $^1$H (400 MHz, $d_4$-MeOH): $\delta$ 8.10 (m, H$^{4'}$, H$^{10'}$), 7.94 (d, $^3J_{HH}$ = 8.6, H$^{10}$), 7.89 (d, $^3J_{HH}$ = 8.4, H$^{7'}$), 7.76 (m, H$^9$), 7.73−7.56 (m, 18H), 7.51 (m, 2H), 7.34 (m, 3H), 7.28 (m, 1H), 7.21 (m, 2H), 7.15 (dd, $^3J_{HH}$ = 7.9, $^3J_{HH}$ = 7.9, H$^8$), 7.03 (m, 2H), 6.88−6.73 (m, 6H), 6.62 (dd, $^3J_{HH}$ = 7.6, $^3J_{HH}$ = 7.6, 2H, H$^{13}$), 6.57 (d, $^3J_{HH}$ = 6.7, H$^4$), 6.37 (m, H,[6] H$^7$). $^{13}$C (100 MHz, $CD_2Cl_2$): $\delta$ 161.9 (q, $^1J_{CB}$ = 50, *ipso*-BArF), 150.2 (br, C$^{11}$), 148.5 (d, $^1J_{PC}$ = 51, C$^{6'}$), 147.8 (d, $^3J_{PC}$ = 5, C$^{12}$), 140.6 (d, $^2J_{PC}$ = 21, C$^{1'}$), 135.5 (d, $^2J_{BC}$ = 11, *ortho*-BArF), 134.8 (m), 133.6 (C$^9$), 131.5 (C$^8$), 131.1 (d, $^3J_{PC}$ = 3, C$^{2'}$), 130.9 (C$^{4'}$), 130.7, 129.8 (d, $J_{PC}$ = 10), 129.6 (m), 129.3 (*meta*-BArF), 128.9 (C,[7] C$^{9'}$), 128.6 (C$^{8'}$), 128.5 (C$^{10'}$), 128.3 (d, $J_{PC}$ = 11), 128.0 (m), 127.7 (d, $J_{PC}$ = 11), 126.4 (C$^{13}$), 125.4 (C$^{7'}$), 125.0 (q, $^1J_{CF}$ = 272, *C*F$_3$), 123.3 (C$^{14}$), 117.5 (m), 116.2 (br, C$^1$), 115.5 (br, C$^3$), 109.9 (d, $J_{PC}$ = 10, C$^2$), 100.4 (d, $J_{PC}$ = 5, C$^5$), 92.7 (d, $J_{PC}$ = 10, C$^4$), 92.1 (C$^6$). $^{31}$P (162 MHz, $d_4$-MeOH): $\delta$ 140.3 (d, $^2J_{PP}$ = 60), 61.7 (d, $^2J_{PP}$ = 62).

**Synthesis of 4b.** To an orange solution of **6** (50 mg, 0.030 mmol) in THF (10 mL) was added $H_2O$ (1 mL), which resulted in slow lightening of color. The solution was stirred at 313 K overnight. Pentane was added, resulting in the separation of an aqueous layer, which was removed with a syringe. The remaining organic solution was reduced in volume to almost complete dryness and then pentane added to precipitate the product which was collected via decanting the supernatant liquid. The residue was washed with pentane to afford **4b** as a yellow solid. At this stage, two isomers are observed, which arise from hydrogen bonding of either THF or $H_2O$ to the cation. Recrystallization from $CH_2Cl_2$/pentane affords one clean product (33 mg, 74%). $^1$H (400 MHz, $CD_2Cl_2$): $\delta$ 8.18 (dd, $^3J_{HH}$ = 8.6, $^4J_{PH}$ = 2.1, H$^{4'}$), 8.10 (d, $^3J_{HH}$ = 8.3, H$^{10'}$), 7.91 (m), 7.78−7.58 (m), 7.42 (m), 7.29 (d, $^3J_{HH}$ = 8.2, H$^{10}$), 7.20 (m, 2H), 6.99 (dd, $^3J_{HH}$ = 7.8, $^3J_{HH}$ = 7.8, H$^8$), 6.93 (m, 2H), 6.72 (m, H$^5$), 6.22 (d, $^3J_{HH}$ = 8.4 H$^7$), 5.75 (m, H$^4$), 5.37 (d, $^2J_{PH}$ = 10.7, O*H*), 5.32 (m, H$^6$), 4.80 (d, $^2J_{PH}$ = 16.5, O*H*). $^{13}$C (100 MHz, $CD_2Cl_2$): $\delta$ 162.1 (q, $^1J_{BC}$ = 50, *ipso*-BArF), 143.1 (d, $^1J_{PC}$ = 55, C$^{6'}$), 140.8 (C$^{1'}$), 135.5, 135.2 (*ortho*-BArF), 135.0 (C$^8$), 134.8 (C$^9$), 133.0 (d, $J_{PC}$ = 11), 132.9, 132.1 (C$^{4'}$), 131.6 (d, $^3J_{PC}$ = 5, C$^{2'}$), 131.4 (d, $^3J_{PC}$ = 3, C$^{3'}$), 130.6, 130.1, 129.4 (C$^{10'}$), 129.1 (*meta*-BArF), 128.7 (C$^{10}$), 127.9 (C$^7$), 127.1 (C$^{5'}$), 125.0 (q, $^1J_{CF}$ = 272, *C*F$_3$), 124.9 (C$^{7'}$), 117.8 (m, *para*-BArF), 112.9 (C$^3$), 104.2 (C$^5$), 101.3 (C$^1$), 99.7 (d, $J_{PC}$ = 9, C$^4$), 76.8 (C$^6$). $^{19}$F (282 MHz, $CD_2Cl_2$): $\delta$ −63.31 (s). $^{31}$P (162 MHz, $CD_2Cl_2$): $\delta$ 105.2 (d, $^2J_{PP}$ = 69), 56.6 (d, $^2J_{PP}$ = 69). MS-ESI (*m*/*z*): 1240.9 (M$^+$), 1222.1 (M$^+$ − $H_2O$), 620.9 (M$^{2+}$). Anal. Calcd for $C_{128}H_{74}B_2F_{48}O_6P_4Ru_2$: C, 51.81; H, 2.51. Found: C, 51.83; H, 2.76.

**Synthesis of 6.** HBArF·2$Et_2O$ (75 mg, 0.074 mmol) was added to a solution of **1** (60 mg, 0.071 mmol) in dichloromethane (15 mL) resulting in an orange solution, which, with time, lightens in color. The solution was stirred at RT overnight, then $H_2O$ (10 $\mu$L) was added, and stirring continued for another 3 h, resulting in quantitative conversion to the product. Most of the solvent was pumped off and pentane (35 mL) added to deposit the product as an oil, which was washed with pentane and dried to afford **6** as a yellow solid (99 mg, 84%). $^1$H (500 MHz, $CD_2Cl_2$): $\delta$ 8.18 (dd, $^4J_{PH}$ = 1.7, $^3J_{HH}$ = 8.8, H$^{4'}$), 8.14−8.12 (m, H,[9] H$^{10'}$), 7.90 (d, $^3J_{HH}$ = 8.3, H$^{10}$), 7.77 (m, 10H), 7.67−7.63 (m, 2H), 7.60 (m, 7H), 7.53 (m, 2H), 7.48−7.38 (m, 5H), 7.34 (dd, $^3J_{HH}$ = 7.7, $^3J_{HH}$ = 7.7, H$^8$), 7.25−7.21 (m, 4H), 7.17 (m, 1H), 7.07 (dd, $^3J_{HH}$ = 8.3, $^3J_{PH}$ = 12.0, 2H), 6.95 (dd, $^3J_{HH}$ = 8.3, $^3J_{PH}$ = 12.0, 2H), 6.87 (d, $^3J_{HH}$ = 6.8, H$^4$), 6.76 (dd, $^3J_{HH}$ = 7.9, $^3J_{PH}$ = 11.5, 2H), 6.63 (d, $^3J_{HH}$ = 8.3, H$^7$), 6.18 (m, H$^5$), 5.32 (m, H$^6$), 1.90 (s, C*H*$_3$, 3H). $^{13}$C (125 MHz, $CD_2Cl_2$): $\delta$ 187.0 (*C*═O), 162.1 (q, $^1J_{BC}$ = 50, *ipso*-BArF), 143.2 (d, $^1J_{PC}$ = 46, C$^{6'}$), 140.3 (d, $^2J_{PC}$ = 21, C$^{1'}$), 137.1 (C$^9$), 135.2 (*ortho*-BArF), 134.9 (C$^{3'}$), 134.7 (d, $J_{PC}$ = 11), 134.1 (C$^8$), 132.9 (d, $J_{PC}$ = 11), 132.4, 132.2 (d, $^3J_{PC}$ = 3, C$^{4'}$), 131.8, 130.9, 130.8 (C$^7$), 130.5 (d, $J_{PC}$ = 12), 130.1 (C$^{9'}$), 129.5 (C$^{8'}$), 129.4, 129.3, 129.2, 129.1 (*meta*-BArF), 129.0 (C$^{10'}$), 128.9, 128.8, 128.7, 127.9 (C$^{10}$), 127.8 (C$^{5'}$), 125.1 (C$^{7'}$), 125.0 (q, $^1J_{CF}$ = 272, *C*F$_3$) 117.8 (m, *para*-BArF), 115.6 (C$^3$), 112.7 (C$^2$), 108.7 (C$^1$), 103.9 (d, $J_{PC}$ = 5, C$^5$), 95.0 (d, $J_{PC}$ = 10, C$^4$), 76.7 (C$^6$), 25.4 (*C*H$_3$). $^{19}$F (282 MHz, $CD_2Cl_2$): $\delta$ −63.28 (s). $^{31}$P (162 MHz, $CD_2Cl_2$): $\delta$ 114.7 (br), 55.9 (d, $^2J_{PP}$ = 45). MS-ESI (*m*/*z*): 777.1 (M$^+$ − $CH_3$), 741.0 (M$^+$ − OAc, 100%). Anal. Calcd for $C_{78}H_{49}BF_{24}O_3P_2Ru$: C, 56.30; H, 2.97. Found: C, 55.85; H, 3.40.

**In Situ Characterization of 8.** A solution of **6** (10 mg, 0.006 mmol) in deuterated methanol (1 mL) was stirred for 30 min, then HBArF·2 $Et_2O$ (7 mg, 0.007 mmol) was added, and the solution was stirred for another 30 min, quantitatively affording **8**. $^1$H (500 MHz, $d_4$-MeOH): $\delta$ 8.08 (m, H$^{4'}$, H$^{10'}$), 8.03 (d, $^3J_{HH}$ = 8.5, H$^{10}$), 7.89 (d, $^3J_{HH}$ = 8.2, H$^{7'}$), 7.82 (m, 2H), 7.70 (dd, $^3J_{HH}$ = 7.5, $^3J_{HH}$ = 7.5, H$^{9'}$), 7.62 (m, 14H), 7.55−7.47 (m, 5H), 7.42 (d, $^3J_{HH}$ = 7.4, H$^{12}$), 7.28 (m, 1H), 7.20 (m, H,[4] H$^8$), 7.02 (m, 2H), 6.96 (m,

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$H^5$), 6.81−6.74 (m, 3H), 6.67 (m, 2H, $H^{13}$), 6.42 (d, $^3J_{HH}$ = 8.5, $H^7$), 6.22 (d, $^3J_{HH}$ = 5.1, $H^6$), 3.11 (d, $^3J_{PH}$ = 11.7, C$H_3$, 3H), 2.99 (d, $^3J_{PH}$ = 11.7, C$H_3$, 3H). $^{13}$C (125 MHz, $d_4$-MeOH): $\delta$ 161.8 (q, $^1J_{BC}$ = 50, *ipso*-BArF), 148.0 (d, $^1J_{PC}$ = 51, $C^{6'}$), 147.2 ($C^{11}$), 147.1 (d, $^3J_{PC}$ = 5, $C^{12}$), 140.7 ($C^{1'}$), 135.3 (d, $^2J_{BC}$ = 11, *ortho*-BArF), 134.8 (m), 134.3 (d, $J_{PC}$ = 10), 133.7 ($C^9$), 132.0 ($C^8$), 131.1 (d, $^3J_{PC}$ = 2, $C^{4'}$), 131.0 ($C^{2'}$), 129.6 (*meta*-BArF), 129.3 (m), 129.0, 128.8 ($C^7$), 128.5 ($C^{10'}$), 128.2 ($C^{10}$), 128.1, 126.6 ($C^{13}$), 125.4 ($C^{7'}$), 125.0 (q, $^1J_{CF}$ = 272, $CF_3$), 123.4 ($C^{14}$), 117.5 (m, *para*-BArF), 115.9 ($C^1$), 115.3 (d, $J_{PC}$ = 7, $C^3$), 110.6 ($C^2$), 98.0 (d, $J_{PC}$ = 5, $C^5$), 92.7 ($C^6$), 92.5 (d, $J_{PC}$ = 9, $C^4$), 51.7 (d, $^3J_{PC}$ = 10, $CH_3$). $^{19}$F (282 MHz, $CD_2Cl_2$): $\delta$ −63.25 (s). $^{31}$P (202 MHz, $d_4$-MeOH): $\delta$ 125.1 (d, $^2J_{PP}$ = 74), 61.0 (d, $^2J_{PP}$ = 75).

**Synthesis of 9.** A solution of **6** (30 mg, 0.018 mmol) in methanol (10 mL) was stirred for 15 min at RT. Addition of HBArF·2 $Et_2O$ (18 mg, 0.018 mmol) was followed by stirring for another 15 min. The solution was concentrated to almost complete dryness and the yellow oil washed twice with pentane to remove acetic acid. The remaining residue was briefly dried, then redissolved in methanol (5 mL) and the solution stirred at 50 °C for 10 min. The solvent was removed to almost complete dryness and the remaining oil washed again twice with pentane. The yellow residue was thoroughly dried to afford **9** as a yellow solid. Yield: 18 mg, 65%. $^1$H (500 MHz, $d_4$-MeOH): $\delta$ 8.23 (d, $^3J_{HH}$ = 8.6, $H^{4'}$), 8.14 (d, $^3J_{HH}$ = 8.3, $H^{10'}$), 8.06 (d, $^3J_{HH}$ = 7.9, $H^{10}$), 7.95 (dd, $^3J_{HH}$ = 7.5, $^3J_{HH}$ = 7.5, $H^9$), 7.89 (d, $^3J_{HH}$ = 8.8, $H^{7'}$), 7.84−7.73 (m, 3H), 7.63 (m, 13H), 7.56 (t, $^3J_{HH}$ = 6.6, 1H), 7.44 (m, 5 H), 7.35−7.20 (m, 5H), 7.01 (dd, $^3J_{HH}$ = 8.6, $^3J_{PH}$ = 11.1, 2H), 6.42 (d, $^3J_{HH}$ = 8.6, $H^7$), 5.44 (m, $H^6$), 3.48 (d, $^3J_{PH}$ = 11.5, C$H_3$, 3H), 3.13 (d, $^3J_{PH}$ = 11.5, C$H_3$, 3H). $^{13}$C (125 MHz, $CD_2Cl_2$): $\delta$ 161.8 (q, $^1J_{BC}$ = 50, *ipso*-BArF), 142.6 (d, $^1J_{PC}$ = 55, $C^{6'}$), 141.5 (d, $^2J_{PC}$ = 22, $C^{1'}$), 135.0 (d, $^2J_{BC}$ = 10, *ortho*-BArF), 134.8 (m), 134.6 ($C^9$), 133.9 ($C^8$), 133.3 (d, $J_{PC}$ = 12), 131.6 (d, $^3J_{PC}$ = 6, $C^{4'}$), 131.3 (d, $^3J_{PC}$ = 3, $C^{2'}$), 129.6 (*meta*-BArF), 129.3 ($C^{9'}$), 129.0 ($C^{8'}$), 128.9 (d, $J_{PC}$ = 11), 128.7 ($C^{10'}$), 128.0 (C,[7] $C^{10}$), 127.3 (d, $J_{PC}$ = 2), 125.1 ($C^{7'}$), 124.9 (q, $^1J_{CF}$ = 272, $CF_3$), 117.5 (m, *para*-BArF), 117.1 (d, $J_{PC}$ = 11, $C^2$), 113.0 (m, $C^3$), 103.4 (d, $J_{PC}$ = 5, $C^5$), 100.3 (d, $J_{PC}$ = 4, $C^1$), 94.1 (d, $J_{PC}$ = 9, $C^4$), 77.6 (d, $J_{PC}$ = 2, $C^6$), 51.5 (d, $^3J_{PC}$ = 9, $CH_3$), 50.7 (d, $^3J_{PC}$ = 10, $CH_3$). $^{19}$F (282 MHz, $CD_2Cl_2$): $\delta$ −63.23 (s). $^{31}$P (202 MHz, $d_4$-MeOH): $\delta$ 83.4 (d, $^2J_{PP}$ = 69), 58.8 (d, $^2J_{PP}$ = 68). MS-ESI (*m*/*z*): 648.9 ($M^+$, 100%).

**Synthesis of 10.** A solution of **9** (35 mg, 0.023 mmol) in dichloromethane (5 mL) was stirred for 30 min at 313 K and then concentrated and pentane (15 mL) added, resulting in the deposition of a yellow oil. The supernatant was discarded and the oil dried, affording **10** as yellow solid. Yield 30 mg, 88%. $^1$H (500 MHz, $CD_2Cl_2$): $\delta$ 8.28 (dd, $^3J_{HH}$ = 8.8, $^4J_{PH}$ = 2.4, $H^{4'}$), 8.19 (dd, $^3J_{HH}$ = 7.7, $^3J_{HH}$ = 7.7, $H^9$), 8.17 (d, $^3J_{HH}$ = 8.6, $H^{10'}$), 8.02 (d, $^3J_{HH}$ = 8.6, $H^{10}$), 7.85−7.81 (m, 2H), 7.76 (s, 8H), 7.74−7.69 (m, 2H), 7.60 (s, 4H), 7.56 (m, 1H), 7.46 (m, 1H), 7.40 (dd, $^3J_{HH}$ = 7.9, $^3J_{HH}$ = 7.9, $H^8$), 7.29 (m, 2H), 7.24 (m, 2H), 6.86 (m, 3H), 6.68 (m, H,[4] $H^7$), 6.63 (dd, $^3J_{HH}$ = 8.1, $^3J_{PH}$ = 11.8, 2H), 5.71 (m, $H^6$), 3.82 (d, $^3J_{PH}$ = 11.8, C$H_3$, 3H), 3.11 (d, $^3J_{PH}$ = 12.2, C$H_3$, 3H). $^{13}$C (125 MHz, $CD_2Cl_2$): $\delta$ 162.1 (q, $^1J_{BC}$ = 50, *ipso*-BArF), 140.8 (d, $^1J_{PC}$ = 49, $C^{6'}$), 140.7 (d, $^2J_{PC}$ = 27, $C^{1'}$), 138.0 ($C^9$), 135.3 ($C^8$), 135.2 (d, $^2J_{BC}$ = 10, *ortho*-BArF), 134.0 ($C^{3'}$), 133.8 (d, $J_{PC}$ = 11), 133.0 (d, $^3J_{PC}$ = 3, $C^{4'}$), 132.9, 132.6, 132.2 (d, $J_{PC}$ = 11), 131.4 ($C^{2'}$), 130.9 ($C^{9'}$), 130.7 ($C^{8'}$), 130.3 ($C^7$), 130.1 (d, $J_{PC}$ = 10), 130.0 ($C^{8'}$), 129.6 (*meta*-BArF), 129.3 ($C^{10'}$), 129.1 (d, $J_{PC}$ = 12), 128.1 ($C^{10}$), 127.6 ($C^{5'}$), 124.9 ($C^{7'}$), 124.9 (q, $^1J_{CF}$ = 272, $CF_3$), 117.8 (m, *para*-BArF), 112.6 ($C^2$), 110.8 ($C^3$), 108.5 ($C^1$), 103.7 (d, $J_{PC}$ = 5, $C^5$), 92.9 (d, $J_{PC}$ = 9, $C^4$), 74.0 ($C^6$), 55.3 (d, $^3J_{PC}$ = 11, $CH_3$), 55.1 (d, $^3J_{PC}$ = 11, $CH_3$). $^{19}$F (282 MHz, $CD_2Cl_2$): $\delta$ −63.41 (s). $^{31}$P (202 MHz, $CD_2Cl_2$): $\delta$ 119.3 (d, $^2J_{PP}$ = 64), 55.3 (d, $^2J_{PP}$ = 64). Anal. Calcd for $C_{132}H_{82}B_2F_{48}O_6P_4Ru_2$·$2CH_2Cl_2$: C, 50.39; H, 2.71. Found: C, 49.60; H, 2.90.

**Synthesis of 11.** A solution of **2** (75 mg, 0.071 mmol) in dichloromethane (10 mL) was stirred under an atmosphere of HCl for 4 h during which time the color changed from yellow to orange. The solution was concentrated to approximately 2 mL and the product precipitated via addition of diethyl ether. Filtration and washing with diethyl ether afforded **11** as an orange-red solid (63 mg, 96%). $^1$H (500 MHz, $CD_2Cl_2$): $\delta$ 8.99 (br, O$H$, 1H), 8.18 (dd, $^4J_{PH}$ = 1.8, $^3J_{HH}$ = 8.8, $H^{4'}$), 8.15 (d, $^3J_{HH}$ = 8.3, $H^{10'}$), 7.96−7.88 (m, 4H), 7.80 (m, 2H), 7.68 (m, $H^{8'}$), 7.61 (dd, $^3J_{PH}$ = 7.5, $^3J_{HH}$ = 8.8, $H^{5'}$), 7.53−7.44 (m, 5H), 7.37 (m, 1H), 7.25−7.14 (m, 7H), 7.09−6.98 (m, 5H), 6.66 (d, $^3J_{HH}$ = 6.8, $H^4$), 6.58 (d, $^3J_{HH}$ = 8.4, $H^7$), 6.22 (m, $H^6$), 6.03 (m, $H^5$). $^{13}$C (125 MHz, $CD_2Cl_2$): $\delta$ 144.5 (d, $^1J_{CP}$ = 52, $C^{6'}$), 141.0 (d, $^2J_{CP}$ = 21, $C^{1'}$), 135.8 ($C^9$), 135.1 ($C^{2'}$), 134.1 (d, $^2J_{CP}$ = 10), 134.0 (d, $^2J_{CP}$ = 11), 133.5 ($C^8$), 131.8 (d, $^3J_{CP}$ = 7, $C^{2'}$), 131.6 ($C^{4'}$), 131.4, 130.9 (d, $^2J_{CP}$ = 11) 130.6, 129.9 (d, $^2J_{CP}$ = 11), 129.7 ($C^{10'}$), 129.3, 129.2, 129.1 ($C^7$), 128.9 ($C^{8'}$), 128.7 (d, $^3J_{CP}$ = 11), 128.4, 128.3 (d, $^3J_{CP}$ = 12), 128.1 ($C^{10}$), 128.0 ($C^{9'}$), 125.5 ($C^{7'}$), 114.0 (br, $C^3$), 111.6 (br, $C^2$), 108.2 (br, $C^1$), 107.2 (d, $J_{CP}$ = 6, $C^5$), 97.0 (d, $J_{CP}$ = 10, $C^4$), 81.8 ($C^6$). $^{19}$F (282 MHz, $CD_2Cl_2$): $\delta$ −79.4. $^{31}$P (202 MHz, $CD_2Cl_2$): $\delta$ 109.8 (d, $^2J_{PP}$ = 55), 53.5 (d, $^2J_{PP}$ = 55). MS-FAB (*m*/*z*): 777.2 ($M^+$, 100%), 742.2 ($M^+$ − Cl), 539.2 ($M^+$ − $PPh_2OH$). Anal. Calcd for $C_{45}H_{34}ClF_3O_4P_2RuS$: C, 58.35; H, 3.70. Found: C, 58.46; H, 3.88.

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**Supporting Information Available:** ORTEP representations and full crystallographic data of all structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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