Organometallics **1999,** *18,* 4068−4074

Synthesis and Structures of Organometallic Aqua Complexes of Ruthenium(II)

Mary F. Mahon,† Michael K. Whittlesey,*,† and Paul T. Wood‡

Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, U.K., and School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K.

Received June 1, 1999

Treatment of *all-cis*-Ru(dppe)$(CO)_2Cl_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with 2 equiv of $AgOSO_2CF_3$ yields the bis(triflate) complex Ru(dppe)$(CO)_2(OSO_2CF_3)_2$ (**1**), which has been characterized by NMR spectroscopy and X-ray crystallography. Exposure of solid **1** to atmospheric moisture gives the carbonyl aqua complex Ru(dppe)(CO)$(H_2O)(OSO_2CF_3)_2$ (**2**). The X-ray structure of **2** shows both intra- and intermolecular hydrogen bonding between the coordinated water and triflates. The ^{19}F NMR spectra of **1** and **2** display coupling between the triflate groups; $^{19}F-^{19}F$ NOESY suggests that this arises from both through-bond and through-space coupling. The reaction of **1** with 10 equiv of water results in the rapid formation of a species assigned as the cationic diaqua complex [Ru(dppe)(CO)$(H_2O)_2(OSO_2CF_3)$][OSO_2CF_3] (**3**). Over a longer period of time, further reaction occurs to form the triaqua carbonyl complex [Ru(dppe)(CO)$(H_2O)_3$][OSO_2CF_3]$_2$ (**4**), which has also been characterized by X-ray crystallography. The structure of **4** indicates that all three water ligands participate in hydrogen bonding. Complex **4** is unstable in the absence of water, re-forming a mixture of **1** and **2**.

Introduction

While water is regarded as a very common ligand in coordination chemistry, far fewer examples are known of organometallic aqua complexes, since a metal center wants to be either "hard" or "soft", but not usually both at the same time.[1] It is precisely this contradiction that makes organometallic aqua complexes of special interest in terms of their reactivity. The coordinated water can undergo chemical transformation to hydroxy[2] or oxo[3] ligands, act as a supporting ligand for bond activation reactions,[4] or simply be displaced to yield a coordinatively unsaturated metal fragment. This last area has received the most attention because of the potential applications in organic synthesis and catalysis. Rhodium(III) aqua complexes have been reported to catalyze alkene polymerization,[5] while aqua complexes of ruthenium(II) have proved effective for the ring-opening metathesis polymerization (ROMP) of functionalized norbornenes[6] and the isomerization of allylic alcohols and ethers.[7] Recent studies of organometallic rhenium and technetium aqua complexes have focused on their potential applications in nuclear medicine.[8]

It has been proposed that the ruthenium(II) oxidation state is particularly suited for bonding conventional organometallic ligands such as CO and, at the same time, binding to water.[1a] In this respect, we now wish to report the synthesis, structural characterization, and preliminary reactivity studies of two new ruthenium(II) carbonyl aqua complexes containing a dppe ligand (dppe = $Ph_2PCH_2CH_2PPh_2$). The complexes can be readily prepared by reactions of the new triflate complex Ru(dppe)$(CO)_2(OSO_2CF_3)_2$ with water either in the solid state or in solution. Weakly coordinating anionic ligands such as triflate are recognized as facile leaving groups that can be readily displaced under mild conditions.[9] When the incoming ligand is water, the free triflate anion also serves a secondary role in stabilizing the low-valent aqua complexes through hydrogen-bonding interactions.[10]

---

* To whom correspondence should be addressed. E-mail: chsmkw@bath.ac.uk.

† University of Bath.

‡ University of East Anglia.

[1] Selected references: (a) Kölle, U. *Coord. Chem. Rev.* **1994**, *135/136*, 623. (b) Eisen, M. S.; Haskel, A.; Chen, H.; Olmstead, M. H.; Smith, D. P.; Maestre, M. F.; Fish, R. H. *Organometallics* **1995**, *14*, 2806. (c) Stebler-Röthlisberger, M.; Hummel, W.; Pittet, P.-A.; Bürgi, H.-B.; Ludi, A.; Merbach, A. E. *Inorg. Chem.* **1988**, *27*, 1358. (d) Kölle, U.; Flunkert, G.; Görissen, R.; Schmidt, M. U.; Englert, U. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 440. (e) Ganja, E. A.; Rauchfuss, T. B.; Stern, C. L. *Organometallics* **1991**, *10*, 270.

[2] (a) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163. (b) Burn, M. J.; Fickes, M. G.; Hartwig, J. F.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 5875.

[3] Nugent, W. A.; Mayer, J. M. *Metal Ligand Multiple Bonds*; Wiley: New York, 1988.

[4] Johansson, L.; Ryan, O. B.; Tilset, M. *J. Am. Chem. Soc.* **1999**, *121*, 1974.

[5] Wang, L.; Lu, R. S.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1993**, *115*, 6999.

[6] (a) McGrath, D. V.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 3611. (b) Hillmyer, M. A.; Lepetit, C.; McGrath, D. V.; Novak, B. M.; Grubbs, R. H. *Macromolecules* **1992**, *25*, 3345.

[7] McGrath, D. V.; Grubbs, R. H. *Organometallics* **1994**, *13*, 224.

[8] (a) Alberto, R.; Egli, A.; Abram, U.; Hegetschweiler, K.; Gramlich, V.; Schubiger, P. A. *J. Chem. Soc., Dalton Trans.* **1984**, 2815. (b) Egli, A.; Hegetschweiler, K.; Alberto, R.; Abram, U.; Schibli, R.; Hedinger, R.; Gramlich, V.; Kissner, R.; Schubiger, P. A. *Organometallics* **1997**, *17*, 11833. (c) Alberto, R.; Schibli, R.; Egli, A.; Schubiger, A. P.; Abram, U.; Kaden, T. A. *J. Am. Chem. Soc.* **1998**, *120*, 7987.

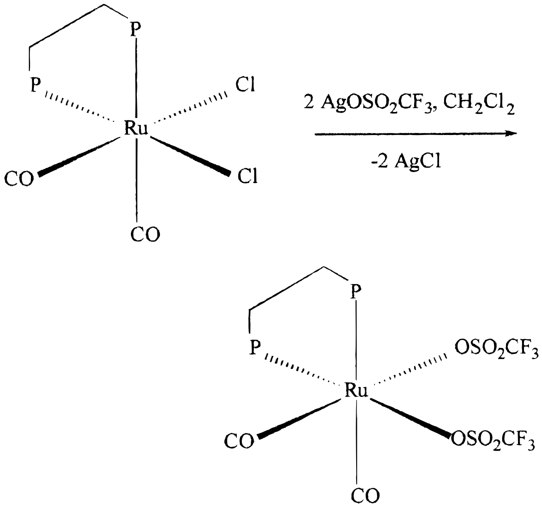
[9] Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405.

[10] (a) Harding, P. A.; Preece, M.; Robinson, S. D.; Henrick, K. *Inorg. Chim. Acta* **1986**, *11*, L31. (b) Takahashi, Y.; Akita, M.; Hikichi, S.; Moro-oka, Y. *Inorg. Chem.* **1998**, *37*, 3186.

10.1021/om990411s CCC: $15.00

Results and Discussion

Synthesis and Characterization of Ru(dppe)$(CO)_2(OSO_2CF_3)_2$ (1). Treatment of a dichloromethane solution of *all-cis*-Ru(dppe)$(CO)_2Cl_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with 2.2 equiv of $AgOSO_2CF_3$ gives a pale yellow solution from which the complex Ru(dppe)$(CO)_2(OSO_2CF_3)_2$ (**1**) may be isolated in reasonable yield. The spectroscopic data are consistent with the structure shown in eq 1.[11]



(1)

1

The IR spectrum displays two carbonyl bands at 2106 and 2030 cm^{-1} of equal intensity consistent with a *cis* geometry. These peaks are shifted 26−27 cm^{-1} to higher frequency relative to the dichloride precursor (2079 and 2004 cm^{-1}), which reflects the weaker π-donor ability of triflate compared to chloride. Bands associated with coordinated triflate (v(SO) at 1013 and 1329 cm^{-1}, v(CF_3) at 1199 and 1232 cm^{-1}) are observed at lower frequency.[12] The $^{31}P\{^1H\}$ NMR spectrum of **1** in $CDCl_3$ shows two doublet resonances for the dppe ligand. The $^{13}C\{^1H\}$ NMR spectrum exhibits two carbonyl resonances with coupling constants indicating a geometry in which the carbons are *cis* to one phosphorus atom and *trans* to the other. The room-temperature ^{19}F NMR spectrum shows two quartet resonances at δ −76.91 (J = 3.45 Hz) and δ −77.66 (J = 3.45 Hz) for the two inequivalent triflate ligands; $^{19}F-^{19}F$ COSY shows beyond doubt that this splitting arises from coupling of the CF_3 groups. No changes are observed in either the ^{19}F or $^{31}P\{^1H\}$ NMR spectra of **1** in CD_2Cl_2 between 30 °C and −80 °C, suggesting (i) that the orientations of the triflate groups do not change with respect to each other with temperature and (ii) that there is no fluxionality involving triflate dissociation as seen in other Ru−OSO_2R complexes (R = CH_3, CF_3).[13]

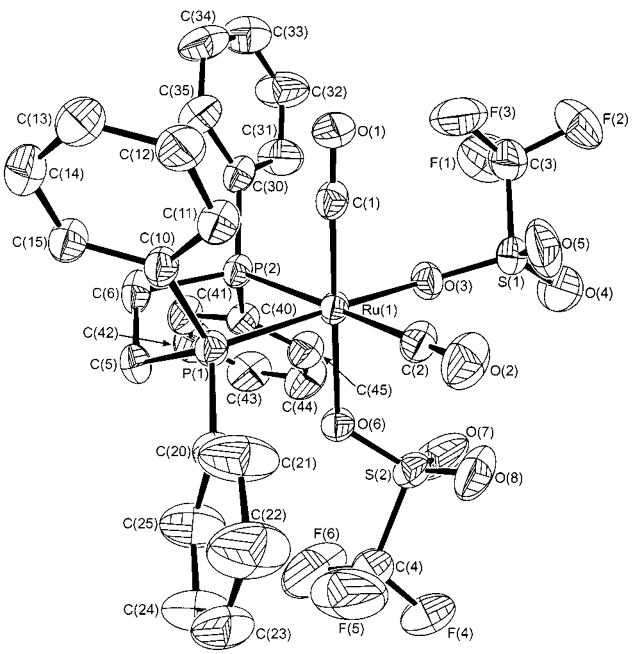


Figure 1. ORTEX diagram of Ru(dppe)$(CO)_2(OSO_2CF_3)_2$ (**1**). Thermal ellipsoids are shown at the 30% level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Ru(dppe)$(CO)_2(OSO_2CF_3)_2$ (1)

Ru(1)−C(1)	1.859(7)	C(3)−F(3)	1.326(10)
Ru(1)−C(2)	1.992(7)	C(3)−F(2)	1.329(10)
Ru(1)−O(6)	2.182(4)	S(2)−O(8)	1.407(5)
Ru(1)−O(3)	2.197(4)	S(2)−O(7)	1.417(6)
Ru(1)−P(1)	2.324(2)	S(2)−O(6)	1.488(4)
Ru(1)−P(2)	2.418(2)	S(2)−C(4)	1.818(11)
S(1)−O(4)	1.396(6)	C(4)−F(6)	1.225(13)
S(1)−O(5)	1.441(7)	C(4)−F(4)	1.287(10)
S(1)−O(3)	1.480(4)	C(4)−F(5)	1.32(2)
S(1)−C(3)	1.803(11)	C(1)−O(1)	1.152(7)
C(3)−F(1)	1.288(12)	C(2)−O(2)	1.126(8)
C(1)−Ru(1)−C(2)	90.0(3)	P(1)−Ru(1)−P(2)	84.30(6)
C(1)−Ru(1)−O(3)	92.8(2)	O(4)−S(1)−O(5)	118.5(5)
C(2)−Ru(1)−O(3)	95.8(2)	O(4)−S(1)−O(3)	114.0(4)
O(6)−Ru(1)−O(3)	85.8(2)	O(5)−S(1)−O(3)	113.2(3)
C(1)−Ru(1)−P(1)	93.0(2)	O(4)−S(1)−C(3)	102.0(5)
C(2)−Ru(1)−P(1)	91.9(2)	O(5)−S(1)−C(3)	103.8(5)
O(6)−Ru(1)−P(1)	88.34(12)	O(3)−S(1)−C(3)	102.6(4)
O(3)−Ru(1)−P(1)	170.41(12)	O(8)−S(2)−O(7)	115.2(5)
C(1)−Ru(1)−P(2)	88.6(2)	O(8)−S(2)−O(6)	114.9(3)
C(2)−Ru(1)−P(2)	175.9(2)	O(7)−S(2)−O(6)	113.8(3)
O(6)−Ru(1)−P(2)	90.77(12)	O(8)−S(2)−C(4)	104.8(6)
O(3)−Ru(1)−P(2)	88.16(13)	O(7)−S(2)−C(4)	103.9(6)

Crystal Structure of Ru(dppe)$(CO)_2(OSO_2CF_3)_2$ (1). Colorless crystals of **1** suitable for X-ray crystallography were grown from CH_2Cl_2/hexane. The ORTEX[14] diagram of **1** (Figure 1) shows the expected octahedral coordination geometry about the ruthenium center with the dppe ligand *trans* to one carbonyl and one triflate. Selected bond distances and angles are given in Table 1. The bite angle for the phosphine of 84.30(6)° is comparable to that in related ruthenium complexes.[15] There are relatively few structurally characterized ruthenium triflate complexes.[16] The Ru−O bond distances of 2.197(4) Å for Ru−O(3) and 2.182(4) Å for Ru−O(6) are shorter than those in the bis(triflate) phosphine complex Ru(Cyttp)(CO)$(OSO_2CF_3)_2$ (Cyttp = $PhP(CH_2CH_2CH_2PCy_2)_2$; distances of 2.221(3) and 2.233-

---

[11] The analogous ruthenium amine triflate complexes Ru(N−N)$(CO)_2(OSO_2CF_3)_2$ (N−N = bpy, phen) have been reported by Deacon and co-workers: (a) Black, D. St. C.; Deacon, G. B.; Thomas, N. C. *Aust. J. Chem.* **1982**, *35*, 2445. (b) Black, D. St. C.; Deacon, G. B.; Thomas, N. C. *Polyhedron* **1983**, *2*, 409.

[12] Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.

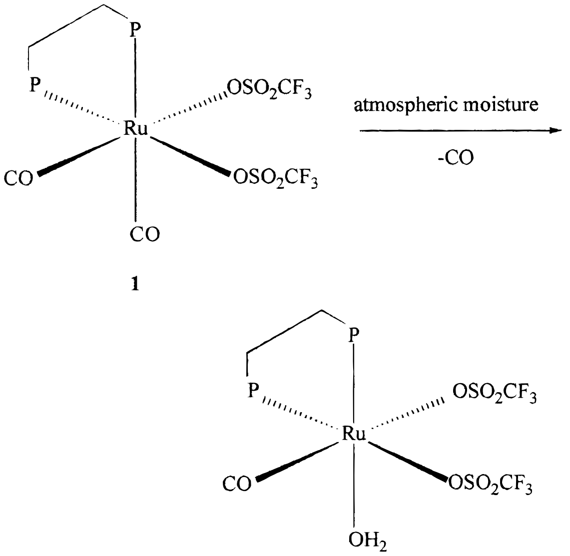
[13] (a) Bailey, O. H.; Ludi, A. *Inorg. Chem.* **1985**, *24*, 2582. (b) Harding, P. A.; Robinson, S. D.; Henrick, K. *J. Chem. Soc., Dalton Trans.* **1988**, 415.

[14] McArdle, P. *J. Appl. Crystallogr.* **1994**, *27*, 438.

[15] (a) Gargaluk, J. D.; Berry, A. J.; Noirot, M. D.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1992**, *114*, 8933. (b) Gargulak, J. D.; Gladfelter, W. L. *Inorg. Chem.* **1994**, *33*, 253.

(3) Å)[16a] but significantly longer than those in the more electrophilic half-sandwich complex (η^5-$C_5(CH_3)_5$)Ru(NO)(OSO_2CF_3)$_2$ (Ru−O distances of 2.125(5) and 2.133(5) Å).[16b] The triflate groups in **1** clearly point away from one another in the crystal structure with the closest intramolecular F−F interaction of 8.54 Å. There is a significant difference in the Ru−CO bond distances (Ru−C(1) = 1.859(7) Å and Ru−C(2) = 1.992(7) Å), reflecting the different *trans* effects of the phosphine and triflate ligands.

Preparation and X-ray Structure of Ru(dppe)(CO)(H_2O)(OSO_2CF_3)$_2$ (2). During the synthesis of **1**, we noted on occasions in the IR spectrum the appearance of a second product **2** as a single carbonyl band at 2001 cm^{-1}. This peak is more intense if the glassware is not rigorously flame-dried prior to use, suggesting that this species arises from reaction with water. We assign this as the carbonyl aqua complex Ru(dppe)(CO)(H_2O)(OSO_2CF_3)$_2$ (**2**) (eq 2). Exposure of a solid sample of **1** to atmospheric moisture for 3 weeks gives **2** in almost quantitative yield.



1

2

(2)

The ^{1}H NMR spectrum of **2** in $CDCl_3$ shows a singlet at δ 5.85 for the coordinated water, while two doublet resonances in the $^{31}P\{^1H\}$ NMR spectrum indicates that the two ends of the dppe ligand are in different environments. The $^{13}C\{^1H\}$ NMR spectrum contains a single carbonyl resonance at δ 197.1 with coupling to two *cis* phosphorus nuclei (J = 17.7 Hz). The ^{19}F NMR spectrum of **2** is similar to that of **1** and shows two quartet resonances for the coordinated triflate ligands, although the $^{19}F-^{19}F$ coupling is marginally larger (3.84 Hz) than that seen in **1**. Both the ^{19}F and $^{31}P\{^1H\}$ NMR spectra are unchanged between 25 and −60 °C.

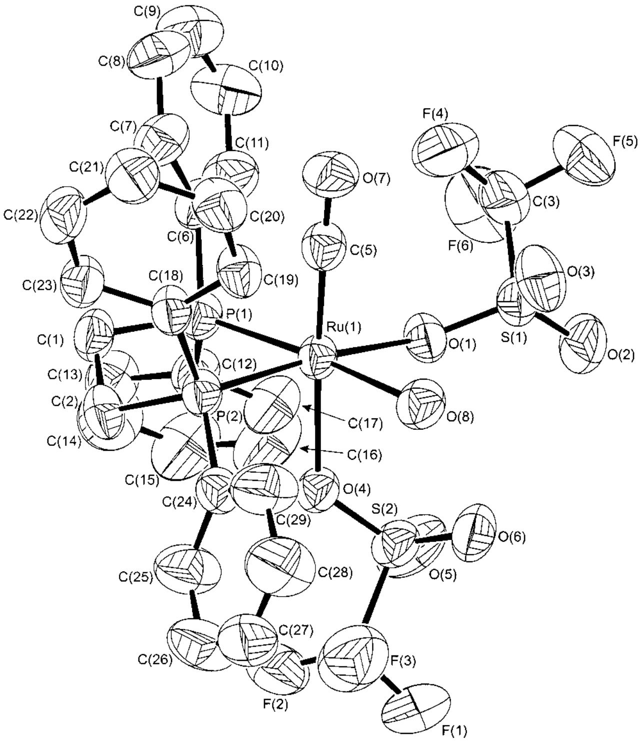


Figure 2. ORTEX diagram of Ru(dppe)(CO)(H_2O)(OSO_2CF_3)$_2$ (**2**). Thermal ellipsoids are shown at the 30% level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Ru(dppe)(CO)(H_2O)(OSO_2CF_3)$_2$ (2)

Ru(1)−C(5)	1.817(8)	F(6)−C(3)	1.255(11)
Ru(1)−O(4)	2.187(4)	S(1)−O(2)	1.395(5)
Ru(1)−O(8)	2.198(5)	S(1)−O(3)	1.428(5)
Ru(1)−O(1)	2.199(4)	S(1)−O(1)	1.472(4)
Ru(1)−P(2)	2.300(2)	S(1)−C(3)	1.827(11)
Ru(1)−P(1)	2.331(2)	S(2)−O(5)	1.407(6)
F(1)−C(4)	1.354(11)	S(2)−O(6)	1.430(5)
F(2)−C(4)	1.250(11)	S(2)−O(4)	1.473(4)
F(3)−C(4)	1.311(12)	S(2)−C(4)	1.814(12)
F(4)−C(3)	1.308(10)	O(7)−C(5)	1.163(8)
F(5)−C(3)	1.347(10)		
C(5)−Ru(1)−O(4)	177.0(2)	O(2)−S(1)−O(3)	117.1(4)
C(5)−Ru(1)−O(8)	94.4(2)	O(2)−S(1)−O(1)	114.5(3)
O(4)−Ru(1)−O(8)	83.8(2)	O(3)−S(1)−O(1)	113.4(3)
C(5)−Ru(1)−O(1)	93.5(3)	O(2)−S(1)−C(3)	103.6(5)
O(4)−Ru(1)−O(1)	84.0(2)	O(3)−S(1)−C(3)	104.2(5)
O(8)−Ru(1)−O(1)	88.8(2)	O(1)−S(1)−C(3)	101.5(4)
C(5)−Ru(1)−P(2)	93.5(2)	O(5)−S(2)−O(6)	116.7(4)
O(4)−Ru(1)−P(2)	89.03(12)	O(5)−S(2)−O(4)	113.4(3)
O(8)−Ru(1)−P(2)	91.86(14)	O(6)−S(2)−O(4)	114.0(3)
O(1)−Ru(1)−P(2)	172.90(12)	O(5)−S(2)−C(4)	105.9(5)
C(5)−Ru(1)−P(1)	89.0(2)	O(6)−S(2)−C(4)	103.5(5)
O(4)−Ru(1)−P(1)	92.92(12)	O(4)−S(2)−C(4)	101.1(4)
O(8)−Ru(1)−P(1)	175.33(13)	S(1)−O(1)−Ru(1)	131.2(3)
O(1)−Ru(1)−P(1)	94.16(13)	S(2)−O(4)−Ru(1)	128.8(3)
P(2)−Ru(1)−P(1)	84.73(7)	O(7)−C(5)−Ru(1)	177.5(6)

The solid-state structure of **2** was established by X-ray crystallography, as shown in Figure 2. The triflate groups adopt an orientation very similar to that found in the structure of **1**. The water ligand is located *trans* to P(1) with a Ru−O(8) distance of 2.198(5) Å (Table 2). This distance is close to that found in the related ruthenium(II) complex Ru(PPh_3)$_2$(CO)(H_2O)(OSO_2 p-$C_6H_4CH_3$)$_2$ (Ru−O = 2.202(6) Å)[13b] but substantially longer than the sum of the Pauling covalent radii (1.99 Å) for ruthenium and oxygen, demonstrating the weak nature of the Ru−O bond.[17] There are close contacts between the coordinated water ligand and the two

---

(16) (a) Blosser, P. W.; Gallucci, J. D.; Wojcicki, A. *Inorg. Chem.* **1992**, *31*, 2376. (b) Svetlanova-Larsen, A.; Zoch, C. R.; Hubbard, J. L. *Organometallics* **1996**, *15*, 3076. (c) Sutter, J.-P.; James, S. L.; Steenwinkel, P.; Karlen, T.; Grove, D. M.; Veldman, N.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1996**, *15*, 941. (d) Germel, C.; Kalt, D.; Mereiter, K.; Sapunov, V. N.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *16*, 427. (e) Abbenhuis, R. A. T. M.; del Rio, I.; Bergshoef, M. M.; Boersma, J.; Veldman, N.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1998**, *37*, 1749. (f) Fong, T. P.; Lough, A. J.; Morris, R. H.; Mezzetti, A.; Rocchini, E.; Rigo, P. *J. Chem. Soc., Dalton Trans.* **1998**, 2111.

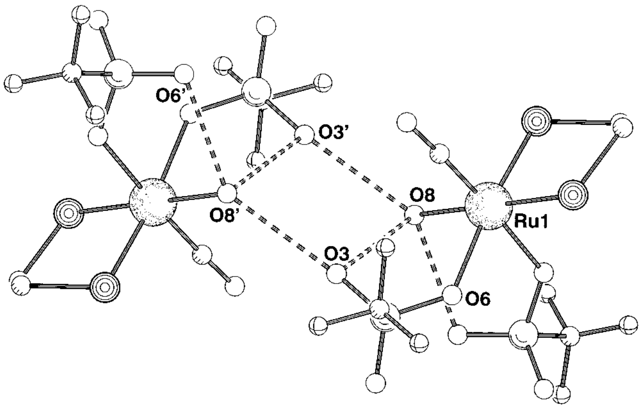


Figure 3. Intra- and intermolecular hydrogen-bonding interactions in **2**.

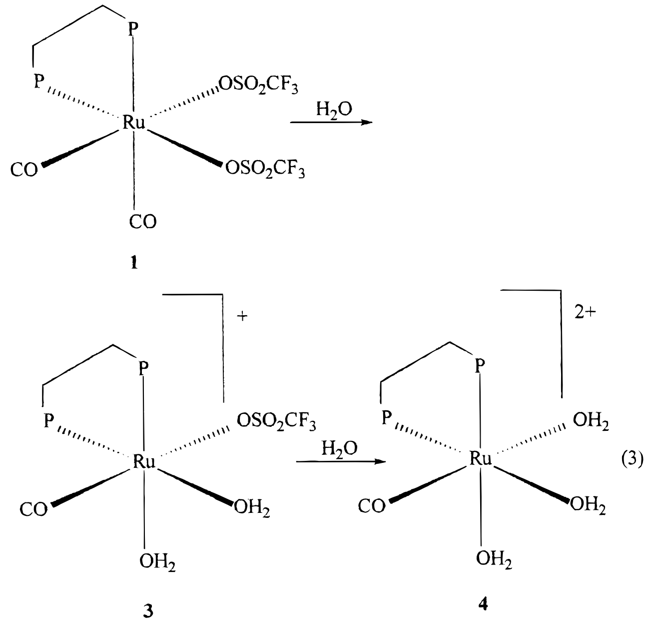
triflate groups in the asymmetric unit as presented (O(8)−H···O(6) = 2.723(7) Å, O(8)−H···O(3) = 2.835(7) Å), supporting intramolecular hydrogen bonding (Figure 3). The ligated water also exhibits a close contact with a triflate in an adjacent molecule (O(8)−H···O(3A) = 3.006(8) Å) generated by the symmetry operation −*x*, −*y*, −*z*, suggesting the presence of intermolecular hydrogen bonding.

The weakly coordinated water ligand in Ru(dppe)(CO)(H_2O)(OSO_2CF_3)$_2$ proves to be substitutionally labile. Exposure of a dichloromethane solution of **2** to CO for 10 min results in quantitative conversion back to **1**.

^{19}F−^{19}F NOESY Studies of 1 and 2. At first sight, the coupling between the triflate groups seen in the ^{19}F NMR spectra of both **1** and **2** appears to be too large for through-bond coupling (the fluorines are separated by eight bonds) and suggests through-space coupling, which is well-established in organofluorine compounds.[18] From a recently published correlation[19] of coupling constant (J_{FF}) with distance (d_{FF}) based on a series of difluorocyclophanes with rigidly constrained geometries, a ^{19}F−^{19}F coupling constant of 3.45 Hz in **1** yields a distance of 3.51 Å between fluorine atoms. The X-ray structure gives the closest intramolecular interaction at 8.54 Å; while the solution and solid-state structures must not necessarily be the same, we have attempted to establish through-space interactions of the triflates in solution by ^{19}F−^{19}F NOESY.

A ^{19}F−^{19}F NOESY spectrum of a $CDCl_3$ solution containing a mixture of **1** and **2** (and also a small amount of free triflate) was recorded at 300 K with a mixing time (τ_m) of 400 ms. The spectrum shows that the two triflate groups in **1** exchange with each other and also with free triflate. Intra- and intermolecular exchange (with free triflate) is also observed for **2**. When the temperature is lowered to 255 K, these exchange processes are halted and weak NOE cross-peaks (ca. 1%) are observed between the two CF_3 groups in **1** and between the CF_3 groups in **2**. The observation of only a weak NOE effect appears to indicate that, while there is some through-space F−F coupling in **1** and **2**, there must also be a contribution from through-bond coupling.

Reaction of Ru(dppe)(CO)$_2$(OSO$_2$CF$_3$)$_2$ with Water in Solution. The surprisingly facile displacement of a carbonyl ligand in **1** by water in the solid state prompted us to investigate the reactivity with water in solution. Hubbard and co-workers have reported quite different behavior for the reactions of water with the triflate complexes Cp′Ru(NO)(OSO_2CF_3)$_2$ (Cp′ = η^5-$C_5(CH_3)_5$, η^5-$C_5(CH_3)_4(CH_2CH_3)$) and Rh(PPh_3)$_2$(CO)(OSO_2CF_3).[16b,20] Addition of 10 equiv of water to a solution of **1** in $CDCl_3$ results in an immediate reaction, as shown by $^{31}P\{^1H\}$ NMR spectroscopy, which indicates the formation of at least six dppe-containing products, none of which correspond to **2**. After 12 h at room temperature the ^{31}P NMR spectrum contains only one product, a singlet at δ 66.1. The ^{19}F NMR spectrum shows two resonances, a sharp singlet at δ −77.66 and a broader singlet at δ −77.72, while the solution IR spectrum contains a single carbonyl band at 1997 cm^{-1}. We tentatively assign this species as the cationic diaqua complex [Ru(dppe)(CO)(H_2O)$_2$(OSO_2CF_3)][OSO_2CF_3] (**3**), which is formed upon displacement of a carbonyl group and a triflate group from the bis(triflate) complex **1** by water. The two water ligands must be located *trans* to the bidentate dppe ligand to account for the single peak in the ^{31}P NMR spectrum (eq 3). We have been unable to characterize this species further due to its reactivity in solution. Removal of the water/$CDCl_3$ in vacuo and redissolution of the residue in dry $CDCl_3$ regenerates complexes **1** and **2**, in a 2:1 ratio, as shown by $^{31}P\{^1H\}$ NMR spectroscopy.



(3)

Similarly, when **1** is left in a $CDCl_3$/water solution for 1 day, the signal arising from **3** disappears and a new singlet resonance grows in at δ 51.9 in the $^{31}P\{^1H\}$ NMR spectrum. We have isolated this complex and identified it as the dicationic triaqua carbonyl complex [Ru(dppe)(CO)(H_2O)$_3$][OSO_2CF_3]$_2$ (**4**) by NMR, IR, and X-ray crystallography (eq 3).

---

[17] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

[18] (a) Günther, H. *NMR Spectroscopy*, 2nd ed.; Wiley: Chichester, U.K., 1995. (b) Mallory, F. B.; Mallory, C. W.; Ricker, W. M. *J. Am. Chem. Soc.* **1975**, *97*, 4770.

[19] Ernst, L.; Ibrom, K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1881.

[20] Svetlanova-Larsen, A.; Hubbard, J. L. *Inorg. Chem.* **1996**, *35*, 3073.

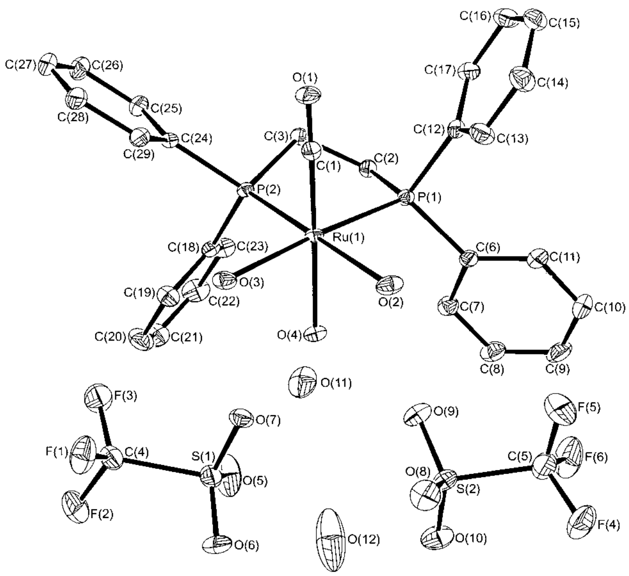


Figure 4. ORTEX diagram of $[Ru(dppe)(CO)(H_2O)_3][OSO_2CF_3]_2$ (**4**). Thermal ellipsoids are shown at the 30% level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Ru(dppe)(CO)(H_2O)_3][OSO_2CF_3]_2$ (4)

Ru(1)−C(1)	1.833(3)	S(2)−O(8)	1.435(2)
Ru(1)−O(4)	2.157(2)	S(2)−O(9)	1.446(2)
Ru(1)−O(3)	2.170(2)	S(2)−C(5)	1.813(4)
Ru(1)−O(2)	2.180(2)	O(1)−C(1)	1.145(3)
Ru(1)−P(2)	2.2654(7)	C(4)−F(3)	1.317(4)
Ru(1)−P(1)	2.2876(7)	C(4)−F(2)	1.320(4)
S(1)−O(5)	1.420(3)	C(4)−F(1)	1.325(4)
S(1)−O(6)	1.432(3)	C(5)−F(5)	1.309(4)
S(1)−O(7)	1.450(2)	C(5)−F(6)	1.322(4)
S(1)−C(4)	1.822(3)	C(5)−F(4)	1.333(4)
S(2)−O(10)	1.431(2)		

C(1)−Ru(1)−O(4)	176.53(10)	P(2)−Ru(1)−P(1)	85.44(3)
C(1)−Ru(1)−O(3)	95.47(10)	O(5)−S(1)−O(6)	116.5(2)
O(4)−Ru(1)−O(3)	81.40(8)	O(5)−S(1)−O(7)	115.1(2)
C(1)−Ru(1)−O(2)	96.19(10)	O(6)−S(1)−O(7)	112.87(14)
O(4)−Ru(1)−O(2)	82.17(8)	O(5)−S(1)−C(4)	103.5(2)
O(3)−Ru(1)−O(2)	86.80(8)	O(6)−S(1)−C(4)	104.0(2)
C(1)−Ru(1)−P(2)	86.05(8)	O(7)−S(1)−C(4)	102.64(14)
O(4)−Ru(1)−P(2)	95.70(6)	O(10)−S(2)−O(8)	114.4(2)
O(3)−Ru(1)−P(2)	95.09(6)	O(10)−S(2)−O(9)	114.75(14)
O(2)−Ru(1)−P(2)	176.92(6)	O(8)−S(2)−O(9)	114.96(14)
C(1)−Ru(1)−P(1)	88.31(8)	O(10)−S(2)−C(5)	104.8(2)
O(4)−Ru(1)−P(1)	94.81(6)	O(8)−S(2)−C(5)	103.0(2)
O(3)−Ru(1)−P(1)	176.21(6)	O(9)−S(2)−C(5)	102.8(2)
O(2)−Ru(1)−P(1)	92.51(6)	O(1)−C(1)−Ru(1)	77.4(2)

The ^{19}F NMR spectrum of **4** shows a single, sharp resonance at δ −78.63, which we assign to the uncoordinated triflate groups. The ^1H NMR spectrum shows a very broad resonance for the coordinated water ligands at δ 4.94; the resonance for free water at δ 1.73 is also broad, suggesting exchange between bound and free water. The IR spectrum of **4** in KBr contains a single carbonyl band at 1990 cm^{-1} and a band associated with uncoordinated triflate at 1232 cm^{-1}.

Isolation of $[Ru(dppe)(CO)(H_2O)_3][OSO_2CF_3]_2$ (4). The triaqua complex crystallizes slowly from $CDCl_3$/water solution as pale yellow cubes, which prove to be suitable for a structural determination. An ORTEX diagram[14] of the structure of **4** is shown in Figure 4. Selected bond lengths and angles are given in Table 3. The asymmetric unit contains the octahedral ruthenium dicationic complex, two free triflate anions, and 1.8 molecules of free water. Two of the aqua ligands are located *trans* to the dppe ligand, and one is *trans* to CO. The Ru−O bond lengths for the two equivalent waters are of comparable length (Ru−O(2) = 2.180(2) Å, Ru−O(3) = 2.170(2) Å), while the Ru−O distance *trans* to CO is slightly shorter (Ru−O(4) = 2.157(2) Å). Analysis of the supramolecular array reveals that the gross structure is dominated by hydrogen-bonding chains parallel to the *c* axis of the unit cell and that these are propagated by two sets of alternating interactions (Figure 5). Each dicationic center is hydrogen-bonded to the lattice neighbor (generated as a consequence of the inversion center) closest to its ligated waters. In particular, the two protons attached to both O(2) and O(3), along with one of the protons attached to O(4), interact with the oxygen atoms of the triflate counterions from the same asymmetric unit along with those generated by the inversion center. These units are then "cemented" further along *c* by interaction of the remaining proton on O(4) and a lattice water molecule (O(12)). This cementing is consolidated by interaction of O(12) with O(5) of a triflate ion.

Initial studies have shown that **4** readily dissociates in the absence of water. Although **4** is not soluble in D_2O, the $^{31}P\{^1H\}$ NMR spectrum recorded immediately upon dissolution of crystalline material in dry $CDCl_3$ or CD_2Cl_2 shows large resonances for **1** and **2**, a smaller signal for **4**, and a singlet resonance for a fourth, unidentified species at δ 67.7. After 1 week in solution, this last complex is the only remaining product. Addition of excess water to the solution results in the reformation of **4** in quantitative yield. We are currently investigating this solution reactivity in greater detail to determine the identity of this singlet product. The interconversion of **1**, **2**, **3**, and **4** is summarized in Scheme 1.

Conclusions

We have prepared and fully characterized two new organometallic aqua complexes of ruthenium(II) by facile substitution of carbonyl and triflate groups in $Ru(dppe)(CO)_2(OSO_2CF_3)_2$. Preliminary studies indicate that the coordinated water ligands in $Ru(dppe)(CO)(H_2O)(OSO_2CF_3)_2$ (**2**) and $[Ru(dppe)(CO)(H_2O)_3]^{2+}$ (**4**) are labile, which may offer a route to coordinatively unsaturated metal complexes with applications in organic synthesis. We are currently investigating the reactivity of **4** with this aim in mind, as well as studying more fundamental properties such as ease of deprotonation of the coordinated water ligands and the kinetics of intra- and intermolecular exchange. The paucity of studies in this area[1b,c,21] suggests that our studies should reveal important new information about organometallic aqua complexes.

Experimental Section

General Comments. The compounds were synthesized and handled under argon using standard Schlenk and high-vacuum techniques. Ether and hexanes were distilled from purple solutions of sodium dispersion/benzophenone, and CH_2Cl_2 was distilled from either CaH_2 or P_2O_5. Water was doubly distilled. $CDCl_3$ and CD_2Cl_2 (Apollo Scientific Ltd.) were

---

[21] Aebischer, N.; Churlaud, R.; Dolci, L.; Frey, U.; Merbach, A. E. *Inorg. Chem.* **1998**, *37*, 5915.

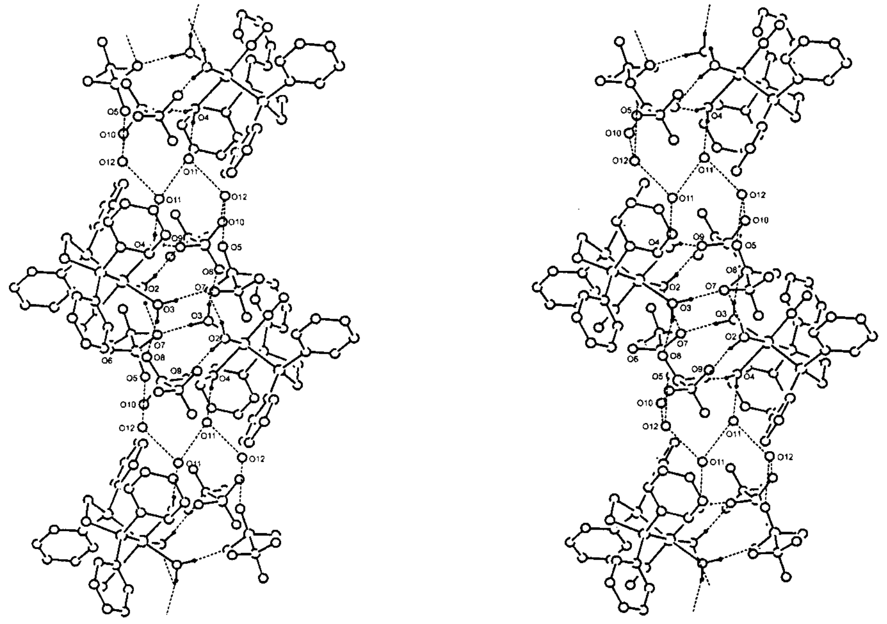
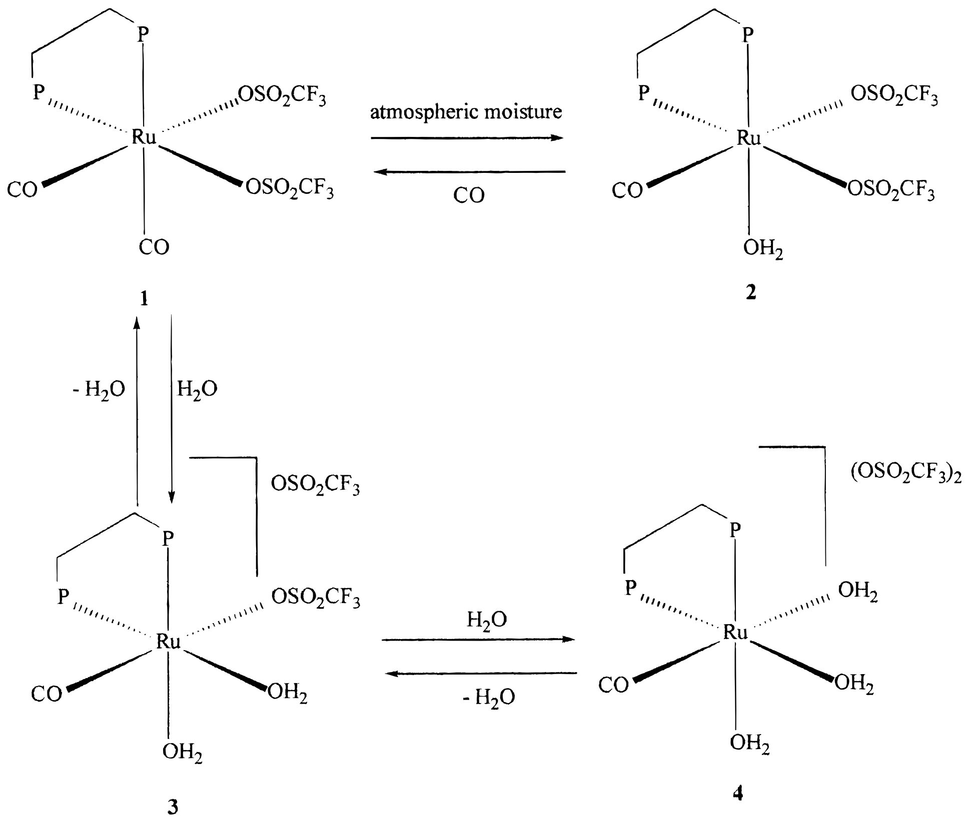


Figure 5. Stereoplot illustrating the hydrogen-bonding interactions in the crystal lattice of **4**.

Scheme 1



vacuum-transferred from CaH_2. Silver triflate was purchased from Lancaster Synthesis and used as received. *all-cis*-Ru(dppe)$(CO)_2Cl_2$ was prepared according to the method of Barnard.[22] Spectroscopic data for this compound have already been reported in the literature.[17a] NMR spectra were recorded on a JEOL EX 270 NMR spectrometer. The $^{19}F-^{19}F$ NOESY experiments were carried out on a Bruker AMX 500 NMR spectrometer at the University of York. ^1H NMR spectra were referenced to residual $CHCl_3$ at δ 7.27. ^{19}F NMR spectra were referenced to external $CFCl_3$ (δ 0.00). ^{13}C NMR spectra were referenced to $CDCl_3$ at δ 77.0. ^{31}P NMR chemical shifts were referenced externally to 85% H_3PO_4 (δ 0.0). IR spectra were recorded as KBr disks or in either $CDCl_3$ or CH_2Cl_2 solution on Nicolet Protégé 460 or Impact 410 FTIR spectrometers. Elemental analyses were performed at the Universities of East Anglia and Bath.

Ru(dppe)$(CO)_2(OSO_2CF_3)_2$ (1). Silver triflate (272 mg, 1.06 mmol) was added to a Schlenk tube containing a stirred solution of *cis*-Ru(dppe)$(CO)_2Cl_2$ (302 mg, 0.48 mmol) in CH_2Cl_2 (10 mL). The solution was stirred at room temperature for

---

[22] Barnard, C. F. J. D. Phil. Thesis, The University of York, York, U.K., 1978.

Table 4. Experimental Data for the X-ray Diffraction Studies of Compounds 1, 2, and 4

	1	**2**	**4**
empirical formula	$C_{30}H_{24}FO_8P_2RuS_2{\cdot}1.2H_2O$	$C_{29}H_{28}F_6O_8P_2RuS_2$	$C_{29}H_{30}F_6O_{10}P_2RuS_2{\cdot}1.8H_2O$
fw	875.24	845.64	912.09
T/K	293(2)	293(2)	198(2)
λ	0.710 73	0.710 73	0.710 69
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a/Å	11.637(6)	11.603(2)	11.719(1)
b/Å	18.452(2)	18.396(4)	23.365(3)
c/Å	17.227(3)	16.840(1)	13.851(2)
β/deg	100.72(3)	100.03(1)	102.54(1)
U/Å^3	3635(2)	3539.5(10)	3702.1(8)
Z	4	4	4
D_{calcd}/g cm^{-3}	1.600	1.587	1.636
μ/mm^{-1}	0.715	0.728	0.710
F_{000}	1760	1704	1848
cryst dimens/mm	0.09 × 0.10 × 0.10	0.08 × 0.10 × 0.10	0.15 × 0.15 × 0.15
θ range/deg	1.63 → 24.58	2.10 → 25.46	2.24 → 25.00
index ranges	$-13 \le h \le 13$; $-21 \le k \le 21$; $-20 \le l \le 20$	$-13 \le h \le 13$; $-22 \le k \le 22$; $-20 \le l \le 20$	$0 \le h \le 13$; $0 \le k \le 27$; $-16 \le l \le 16$
no. of rflns collected	11 878	11 981	7045
no. of indep rflns	6091 (R(int) = 0.0481)	6362 (R(int) = 0.0424)	6495 (R(int) = 0.0106)
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
no. of data/restraints/ params	6086/0/447	6357/0/436	6488/6/494
goodness of fit on F^2	0.970	0.942	0.981
R1, wR2 ($I > 2\sigma(I)$)	0.0590, 0.1606	0.0580, 0.1531	0.0302, 0.0731
R1, wR2 (all data)	0.0953, 0.1885	0.1101, 0.1900	0.0369, 0.0835
largest diff peak and hole, e Å^{-3}	1.087 and −0.570	0.765 and −0.654	0.701 and −0.538
weighting scheme/w	$1/[\sigma^2(F_o^2) + (0.1102P)^2 + 0.0000P]$; $P = (F_o^2 + 2F_c^2)/3$	$1/[\sigma^2(F_o^2) + (0.1027P)^2 + 0.0000P]$; $P = (F_o^2 + 2F_c^2)/3$	$1/[\sigma^2(F_o^2) + (0.0358P)^2 + 6.4816P]$; $P = (F_o^2 + 2F_c^2)/3$
extinction coefficient			0.00039(11)
extinction expression			$F_c^* = kF_c[1 + 0.001F_c^2\lambda^3/(\sin 2\theta)]^{-1/4}$

1 h and then filtered under argon. The filtrate was concentrated to 5 mL, and diethyl ether (20 mL) was added with vigorous stirring to bring about the precipitation of a white solid. The volume of the solution was then reduced by 50% to maximize precipitation. The residual solvent was removed by cannula to leave a white solid, which was washed with 5 mL of diethyl ether and then dried under vacuum (186 mg, 0.22 mmol). Yield: 50%. ^{1}H NMR ($CDCl_3$, 270 MHz, 293 K): δ 2.75 (m, 2H, PCH_2), 3.06 (m, 2H, PCH_2), 7.35−7.85 (br, 20H, PC_6H_5). $^{31}P\{^1H\}$ NMR: δ 44.5 (d, J_{PP} = 16.2 Hz), 66.3 (d, J_{PP} = 16.2 Hz). ^{19}F NMR: δ −76.91 (q, J_{FF} = 3.45 Hz, CF_3), −77.66 (q, J_{FF} = 3.45 Hz, CF_3). $^{13}C\{^1H\}$ NMR: δ 186.0 (dd, J_{PC} = 108.0 Hz, J_{PC} = 9.9 Hz), 193.6 (t, J_{PC} = 14.9 Hz). IR (CH_2Cl_2, cm^{-1}): 2106 (ν(CO)), 2030 (ν(CO)). Anal. Found (calcd) for $RuC_{30}H_{24}P_2O_8S_2F_6{\cdot}1.2H_2O$: C, 41.76 (42.21); H, 2.90 (2.83).

Ru(dppe)(CO)(H_2O)(OSO_2CF_3)$_2$ (2). In a typical experiment, a solid sample of **1** (40 mg, 0.047 mmol) was left in the air at room temperature for 3 weeks. The sample, which slowly changed color from white to brown, was periodically checked by IR spectroscopy until only a single band for ν(CO) at 2001 cm^{-1} was seen. Recrystallization from CH_2Cl_2/hexane afforded colorless crystals of **2** suitable for X-ray diffraction (26 mg, 0.031 mol, 66% yield). ^{1}H NMR ($CDCl_3$, 270 MHz, 293 K): δ 2.50 (m, 2H, PCH_2), 2.95 (m, 2H, PCH_2), 5.85 (s, 2H, H_2O), 7.38−7.95 (br, 20H, PC_6H_5). $^{31}P\{^1H\}$ NMR: δ 65.0 (d, J_{PP} = 19.3 Hz), 67.0 (d, J_{PP} = 19.3 Hz). ^{19}F NMR: δ −77.63 (q, J_{FF} = 3.84 Hz, CF_3), −78.19 (q, J_{FF} = 3.84 Hz, CF_3). $^{13}C\{^1H\}$ NMR: δ 197.0 (t, J_{PC} = 17.7 Hz). IR ($CDCl_3$, cm^{-1}): 2001 (ν(CO)). Anal. Found (calcd) for $RuC_{29}H_{26}P_2O_8S_2F_6$: C, 40.41 (40.80); H, 3.09 (3.11).

[Ru(dppe)(CO)(H_2O)$_3$][OSO_2CF_3]$_2$ (4). A sample of **1** (13 mg, 0.015 mmol) was placed in a J. Youngs resealable NMR tube and $CDCl_3$ condensed in. Water (3 μL, 0.17 mmol) was added by syringe, and the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. Complete conversion to **4** was observed in 1 day. Crystals of **4** slowly precipitated from solution. ^{1}H NMR ($CDCl_3/H_2O$, 270 MHz, 293 K): δ 4.94 (br, 6H, H_2O). $^{31}P\{^1H\}$ NMR: δ 51.9 (s). ^{19}F NMR: δ − 78.63 (s). IR (KBr, cm^{-1}): 3306 br, 1990 vs, 1653 br, 1468 w, 1437 m, 1417 w, 1308 s, 1232 s, 1213 s, 1172 s, 1101 m, 1028 s, 816 w, 747 m, 717 m, 692 m, 636 s, 581 m, 529 m, 496 w. Anal. Found (calcd) for $RuC_{29}H_{34}P_2O_{12}S_2F_6{\cdot}1.8H_2O$: C, 38.56 (38.19); H, 3.57 (3.71).

X-ray Experimental Data. Crystal structure details for **1**, **2**, and **4** are summarized in Table 4. X-ray data for **1** and **2** were recorded on a Rigaku RAXIS II image plate, while the data for **4** were collected on an Enraf-Nonius CAD 4 diffractometer. Crystals were mounted on glass fibers with epoxy resin. In all cases, no absorption corrections were applied. The structures were solved by direct methods using SHELXS[23] and all non-hydrogen atoms refined anisotropically using full-matrix least squares (SHELXL-93)[24] on F^2.

Acknowledgment. M.K.W. wishes to thank Dr. S. B. Duckett (University of York, York, U.K.) for help with the $^{19}F-^{19}F$ NOESY experiments and discussions. We acknowledge Johnson Matthey plc for the loan of ruthenium trichloride hydrate and the Universities of East Anglia and Bath for financial support.

Supporting Information Available: X-ray crystallographic data, including tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and U_{eq} values and packing diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990411S

---

[23] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *467−473*, A46.

[24] Sheldrick, G. M. University of Göttingen, Göttingen, Germany, 1993.