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Water, water, everywhere.† Synthesis and structures of perfluoroalkyl rhodium and iridium(III) compounds containing water ligands

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The aqua complexes $[M(\eta^5\text{-}C_5Me_5)(PMe_3)(R_F)(H_2O)]^+[X]^-$, {M = Rh, Ir; $R_F = CF(CF_3)_2$; X = BF_4; M = Ir; $R_F = CF_2CF_3$, $CF_2CF_2CF_3$; X = CF_3SO_3; M = Rh; $R_F = CF_2CF_2CF_3$; X = CF_3SO_3} have been prepared and their molecular structures determined by single crystal X-ray diffraction studies. In addition, the aqua complexes $[M(\eta^5\text{-}C_5Me_5)(PR_3)(R_F)(H_2O)]^+[X]^-\cdot 0.5H_2O$ {M = Ir; R = CH_3; $R_F = CF(CF_3)_2$; X = $B(Ar_F)_4$; M = Ir; R = C_6H_5; $R_F = CF_2CF_2CF_3$; X = BF_4} containing both inner and outer sphere water molecules have been prepared and crystallographically characterized. The complexes exhibit hydrogen bonding networks in the solid state involving the aqua ligand and the BF_4^- or $CF_3SO_3^-$ anions, and in one case, to the BF_4^- anion and an outer sphere water molecule. In the presence of a non-coordinating anion, such as $B(Ar_F)_4$, hydrogen bonding to an outer sphere water molecule is still observed. A number of close contacts between the coordinated water molecule and α- and/or β-fluorines of the fluoroalkyl ligands are observed and discussed.

Introduction

While water is a ubiquitous ligand in classical inorganic coordination chemistry, far fewer examples of organometallic complexes containing aqua ligands are known. Following a useful compilation of some crystallographically characterized organometallic complexes containing water ligands, and a discussion of hydrogen bonding to counterions,[2] some more recent references have appeared.[3] Coordinating water to a metal, particularly in a cationic complex, increases its acidity. Thus, deprotonation of the aqua ligand is possible to give hydroxo complexes,[4,5] which may be further transformed to give oxo species.[6–8] The aqua ligand may also hydrolyze the counterion[9,10] or ancillary ligands on the complex, as has been illustrated in some fluoroalkyl(aqua) complexes of rhodium (*vide infra*).[11]

Aqua complexes of the late second and third row transition metals are also often less stable due to their relatively unfavorable hard–soft interactions. Consequently, the water ligand can often be displaced by better donor ligands. In addition, the rate of exchange of free and ligated water is often facile in such systems and has been determined for $[Rh(C_5Me_5)(OH_2)_3{}^{2+}][OTf^-]_2$ ($OTf^- = CF_3SO_3^-$) to be 8150 s^{-1}.[4] Other factors which affect the rate of exchange of water depend on the ancillary ligands and their ability to act as σ-donors and π-acceptors.[12] Ligands such as C_6H_6 and $C_5H_5^-$ have been found to increase the lability of an aqua ligand.[12] For example, $[Ru(\eta^6\text{-}C_6H_6)(H_2O)_3]^{2+}$ exchanges water 640 times faster than $[Ru(H_2O)_6]^{2+}$.[12] The rate of exchange of water is decreased by a factor of 2 when two aqua ligands in $[Rh(\eta^5\text{-}C_5Me_5)(H_2O)_3]^{2+}$ are replaced by 2,2′-bipyridine to give $[Rh(\eta^5\text{-}C_5Me_5)(bpy)(H_2O)]^{2+}$.[12] Steric effects can also result in changes in lability, with dissociation of an aqua ligand from a crowded metal center being more favorable. For example, $[Co(CH_3NH_2)_5(H_2O)]^{3+}$ exchanges water 123 times faster than $[Co(NH_3)_5(H_2O)]^{3+}$.[12]

Hydrogen bonding appears to be an important factor in stabilizing many coordinated aqua ligands. In the solid state, hydrogen bonding of the aqua ligand to counterions or oxygen-donor solvent molecules is often observed. While hydrogen bonding may also occur with other ligands on the metal or even on adjacent molecules,[13] the majority of the aqua complexes reported are cationic species which contain weakly coordinating anions, such as BF_4^-,[10,14] PF_6^-,[15] or $CF_3SO_3^-$ (OTf^-),[16] hydrogen bonded to the coordinated water ligand. This type of interaction is considered to represent a hydrogen bond if the distance between the two heavy atoms is less than 3.0 Å.[17]

In a preliminary communication, we described the reaction of the rhodium fluoroalkyl complexes **1a**,**b** with $AgBF_4$ to give the crystallographically characterized aqua complexes **2a**,**b**.[11] Complexes **2a**,**b** underwent facile hydrolysis of the α-CF_2 of the perfluoropropyl and perfluorobenzyl ligands by the coordinated water, a reaction whose facility was greatly increased by changing the counterion from BF_4^- to $B(Ar_F)_4^-$ [Ar_F = 3,5-bis(trifluoromethyl)phenyl].[11] Removing the ability to hydrogen bond to a counterion apparently increased the reactivity of the aqua ligands in these compounds, presumably by increasing its acidity. Here we describe the synthesis and crystallographic characterization of a further series of fluoroalkyl(aqua) complexes of rhodium and iridium that participate in various hydrogen bonding networks in their solid state structures.[11] These aqua compounds are also useful precursors to hydrido(fluoroalkyl) complexes and have been shown to activate molecular H_2, leading to eventual hydrogenolysis of the iridium–carbon and carbon–fluorine bonds.[18]

Results

Syntheses and characterization

As observed in the synthesis of other rhodium analogues,[11] treating the perfluoro-iso-propyl iodo complexes **3a**,**b** with $AgBF_4$ in CH_2Cl_2 solvent in the presence of added water gives

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† See ref. 1.

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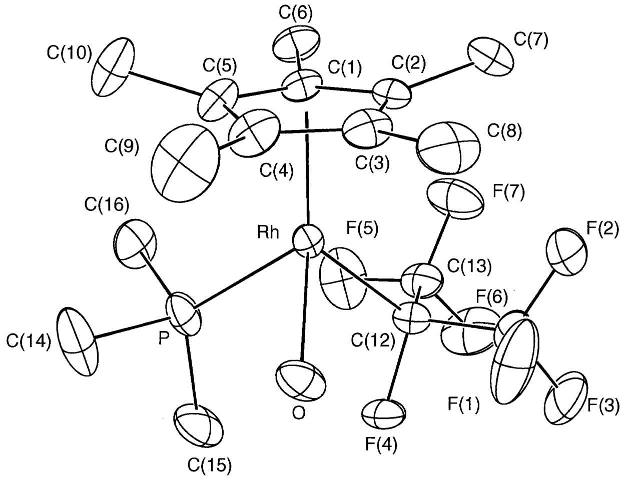
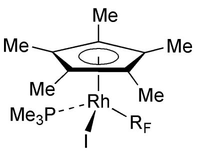
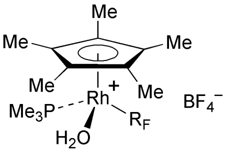


Fig. 1 ORTEP diagram and atom numbering scheme of **4a** with thermal ellipsoids at 30% probability. Hydrogen atoms and the BF_4^- anion are omitted for clarity.

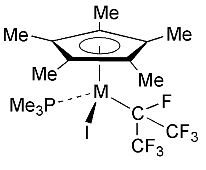


1a $R_F = CF_2CF_2CF_3$
b $R_F = CF_2C_6F_5$

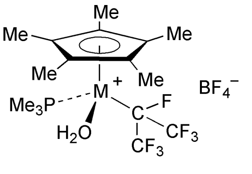


2a $R_F = CF_2CF_2CF_3$
b $R_F = CF_2C_6F_5$

the corresponding aqua complexes **4a**,**b** in good yield. When these reactions are carried out on a small scale in the absence of added water, compounds **4** are still formed, implying that the intermediate cations $[M(\eta^5\text{-}C_5Me_5)(PMe_3)(CF(CF_3)_2]^+$ are voracious scavengers of adventitious moisture, even from glass surfaces. In all these reactions, it is important to add a solution of the metal complex slowly to a slurry of the silver salt, otherwise the reaction is not clean. We speculate that on addition in the inverse sense there may be competition between water and the terminal iodide of unreacted starting material **3** for the vacant site on the intermediate cation $[M(\eta^5\text{-}C_5Me_5)(PMe_3)(R_F)]^+$, to give a bridging iodo species whose iodide ligand is far less easily removed by Ag^+. We have not attempted to isolate such bridging iodo complexes. Unlike their analogues **2a**,**b** containing an α-CF_2 group,[11] the aqua complexes **4a**,**b** appear to be stable towards any hydrolysis chemistry.



3a M = Rh
b M = Ir



4a M = Rh
b M = Ir

The structures of **4a**,**b** were determined by single crystal X-ray diffraction studies. They are isomorphous, and ORTEP diagrams of the cationic part of each molecule are shown in Fig. 1 and 2. Details of the crystallographic determinations are presented in Table 1, and some characteristic bond lengths and angles are provided in Table 2. Because of the differing atom numbering schemes in the various crystallographically determined structures described herein, a common system used in all comparisons of metric parameters is described in Fig. 3.

Each structure adopts the arrangement in the crystal previously described for **2a**,**b**, in which two cationic subunits are bridged by two BF_4^- anions, hydrogen bonded to the aqua ligands.[11] The two halves of the dimer are related by a two-fold rotational axis. Similar hydrogen bonded dimers have been observed in other aqua complexes,[10] and a similar arrangement is depicted more fully later in this paper for some analogous triflate complexes. Each structure includes a half-equivalent of CH_2Cl_2, which is not shown. Despite the presence of a bulky perfluoro-*i*-propyl group in **4a** the interligand bond angles are surprisingly similar to those in its perfluoro-n-propyl relative **2a**.[11] However, while the Rh–O bond distances for **2a** [2.219(5) Å][11] and **4a** [2.203(3) Å] are identical within experimental error, and are both significantly longer than that for the benzyl complex **2b** [2.164(7) Å].[11] they are well within the range for typical Rh–O distances shown in Table 3. On the other hand all three Rh–C_α bond lengths are the same within experimental error [2.086(7) (**2a**), 2.113(9) (**2b**), 2.113(4) Å (**4a**)]. The angles within the perfluoro-*i*-propyl ligand of **4a** [C(45)–C(46)–C(47) = 108.4(4) and Rh–C(46)–F(6) = 110.3 (3)°] do not deviate significantly from a tetrahedral geometry. The metric parameters for the iridium analogue **4b** do not differ significantly, except for a slightly longer M–O distance of 2.252(7) Å.

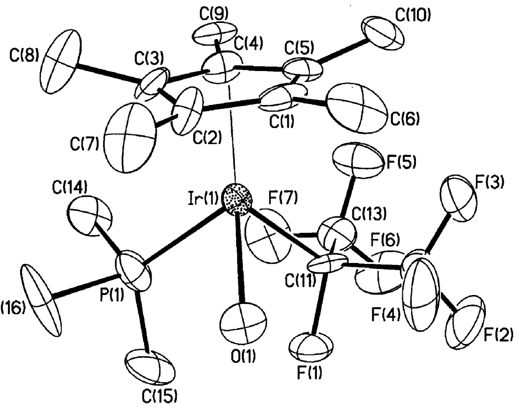
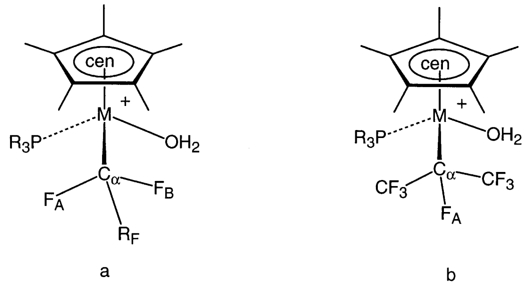


Fig. 2 ORTEP diagram and atom numbering scheme of **4b** with thermal ellipsoids at 30% probability. Hydrogen atoms and the BF_4^- anion are omitted for clarity.



a b

Fig. 3 Labeling schemes used in discussing structures with (a) perfluoro-n-alkyl ligands **5c**,**d**,**e** and **8** and (b) perfluoro-*i*-propyl ligands **4a**,**b** and **6**.

There are several close H···F contacts in **4a** and **4b** as shown in Fig. 4. For the Rh complex **4a**, the α-fluorine [F(4)], a CF_3 β-fluorine [F(1)], and two positions of the disordered BF_4 anion are in close contact with the aqua ligand [O···F(4) = 2.914, O···F(1) = 2.834, O···F(10) = 2.805, O···F(10′) = 2.815 Å]. These distances are within the sum of the van der Waals' radii of fluorine (1.55 Å as listed by Bondi;[19] 1.47 Å as listed by Smart[20]) and oxygen (1.50 Å),[19] strongly suggestive of hydrogen bonding. Clearly, some close H···F interactions may be unavoidable due to steric congestion, but it seems more likely that those involving the aqua ligand are a result of hydrogen bonding. In fact, the α-F(4)···O interaction shown in Fig. 4A is conformationally analogous to that observed in 2-fluoroethanol, and which has been found to stabilize the *gauche* conformation of that molecule.[21] Analogous contacts are observed in the iridium analogue **4b**, with O···F(1) = 2.898, O···F(4) = 2.792, O···F(12) = 2.694, and O···F(13′) = 2.886 Å.

Table 1 Summary of X-ray crystallographic data collection, solution, and refinement parameters

Compound	**4a**	**4b**	**5c**	**5d**	**5e**	**6**	**8**
Formula	$C_{16.5}H_{27}BClF_{11}OPRh$	$C_{16.5}H_{27}BClF_{11}IrOP$	$C_{16}H_{26}F_8IrO_4PS$	$C_{17}H_{26}F_{10}IrO_4PS$	$C_{17}H_{26}F_{10}O_4PRhS$	$C_{49}H_{41}BCl_2F_{31}IrO_{1.5}P$	$C_{31}H_{34}BF_{11}IrO_2P$
M	630.52	719.81	689.60	739.61	650.32	1547.70	881.56
Space group	$P4_12_12$	$P4_12_12$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a/Å	13.70290(10)	13.7267(6)	17.8926(2)	8.7018(2)	7.9856(2)	12.9162(3)	9.3292(2)
b/Å	13.70290(10)	13.7267(6)	8.4162(2)	11.1491(2)	10.2371(2)	34.8748(6)	35.4589(7)
c/Å	25.88380(10)	26.1103(18)	32.0068(2)	13.5780(2)	15.1273(4)	13.2920(3)	10.4739(2)
a/°	90	90	90	80.5213(5)	83.2160(10)	90	90
β/°	90	90	99.5855(5)	76.3566(5)	85.286(2)	98.6911(3)	107.0288(7)
γ/°	90	90	90	81.7157(7)	82.0550(10)	90	90
V/Å^3	4860.19(5)	4919.7(9)	4752.50(8)	1255.02(3)	1213.47(6)	5918.6(3)	3312.90(13)
Z	8	8	8	2	2	4	4
Crystal color, habit	orange block	yellow block	yellow plate	yellow plate	orange plate	orange plate	yellow plate
D(calc)/g cm^{-3}	1.723	1.944	1.928	1.928	1.780	1.737	1.767
μ/cm^{-1}	9.70	56.91	58.55	55.61	9.54	25.08	41.65
T/K	218(2)	198(2)	173(2)	173(2)	173(2)	173(2)	173(2)
Total data	29356	15639	20916	8600	7315	27462	13618
Unique data, R_{int}	5929, 0.0795	3861, 0.1174	8861, 0.0407	4388, 0.0320	5461, 0.0215	10390, 0.0450	4988, 0.0435
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0426, 0.0737	0.0519, 0.0871	0.0523, 0.1679	0.0714, 0.2745	0.0454, 0.1122	0.0877, 0.2404	0.0378, 0.1221
(all data)	0.0641, 0.0806	0.0885, 0.1006	0.0618, 0.1781	0.0741, 0.2764	0.0464, 0.1130	0.1155, 0.2607	0.0415, 0.1273

Table 2 Selected bond lengths (Å) and angles (°) of the crystallographically studied complexes. The labeling scheme is shown in Fig. 3

	4a	**4b**	**5c**	**5d**	**5e**	**6**	**8**
M—O	2.203(3)	2.252(7)	2.205(6)	2.184(14)	2.175(3)	2.258(9)	2.200(4)
M—P	2.3406(10)	2.333(4)	2.350(2)	2.300(4)	2.3151(10)	2.363(4)	2.3568(13)
M—C_α	2.113(4)	2.09(2)	2.090(9)	2.13(2)	2.078(4)	2.160(11)	2.116(5)
M—cen	1.844(11)	1.890(13)	1.880(8)	1.849(14)	1.857(9)	1.924(6)	1.876(6)
C_α—F_A	1.409(4)	1.389(14)	1.420(10)	1.37(3)	1.376(4)	1.456(14)	1.377(6)
C_α—F_B	—	—	1.407(10)	1.58(4)	1.400(5)	—	1.416(6)
C_α—M—P	91.93(12)	91.3(5)	87.3(2)	84.5(6)	93.82(12)	92.6(4)	92.03(15)
C_α—M—O	86.9(2)	83.9(5)	85.6(3)	88.2(8)	83.42(13)	83.6(4)	88.88(18)
O—M—P	85.90(12)	85.9(3)	87.16(16)	86.1(4)	88.00(9)	85.7(4)	88.58(11)
M—C_α—F_A	110.3(3)	114.5(11)	114.8(5)	125.1(16)	112.6(2)	109.1(7)	116.0(3)
M—C_α—F_B	—	—	112.6(6)	118.6(17)	107.5(2)	—	110.6(4)

Table 3 Rh–O bond distances in some aqua complexes

Compound	Rh–O distance/Å	Ref.
$[Rh(\eta^5\text{-}C_5Me_5)(CF_2C_6F_5)(OH_2)(PMe_3)][BF_4]$ **2b**	2.164(7)	11
$[Rh(\eta^5\text{-}C_5Me_5)(n\text{-}C_3F_7)(OH_2)(PMe_3)][BF_4]$ **2a**	2.219(5)	11
$[RhCl\{C_4(CF_3)_4\}(AsMe_3)_2(H_2O)]$	2.243(11)	28
$[RhCl(C_4O_2Cl_2)(PMe_2Ph)_2(H_2O)]$	2.280(6)	29
$[RhCl_2(PPh_3)\{ONN(C_6H_4Me\text{-}p)O\}(H_2O)]$	2.202(3)	30
$[Rh(PPh_3)_2(CO)(H_2O)][BF_4]\cdot 0.5H_2O$	2.115(5)	31
$[Rh(PPh_3)_2(CO)(H_2O)][CF_3SO_3]$	2.316(12)	32
$[Rh(PP')(CO)(H_2O)][PF_6]^a$	2.107(6)	33
$Rh(triphos)(C_2H_4)(H_2O)][BF_4]^b$	2.215(5)	14
$[Rh(\eta^5\text{-}C_5Me_5)(H_2O)_3][CF_3SO_3]_2$	2.213(8), 2.137(8), 2.131(8)	4

[a] PP′ = 1,11-bis(diphenylphosphino)-3,6,9-trioxaundecane-*P*,*P*′. [b] triphos = $MeC[(CH_2)PPH_2)]_3$.

The spectroscopic data for **4a** and **4b** are consistent with their solid state structures. Their IR spectra show broad bands centered at 3425 cm^{-1} with a shoulder at 3280 cm^{-1} due to the antisymmetric and symmetric O–H stretching modes, and the HOH bend at 1655 cm^{-1}.[2] The coordinated water in these complexes does not give a sharp signal in the ^{1}H NMR spectrum, but rather a broad concentration-dependent peak between δ 2–4. Their ^{19}F NMR spectra show only one signal for the CF_3 groups at room temperature. This result suggests that the compounds are fluxional in solution, with dissociation of water, inversion at the metal *via* a planar intermediate or transition state, and recoordination of water being fast on the NMR timescale. Variable temperature NMR studies showed the CF_3 resonances became non-equivalent only below −60 °C. Since the resonances could not be fully separated, the rate of the exchange process was not determined. These results are in contrast to analogous aqua compounds containing perfluoro-n-alkyl ligands described below, and elsewhere,[18] in which such exchange is apparently much slower. Since the perfluoroisopropyl ligand clearly has the largest steric requirement as evidenced by cone angle measurements,[22] and that steric crowding is known to accelerate dissociative exchange of water ligands,[12] it seems reasonable that compounds **4** would have the most labile aqua ligands since nearly all other factors in the system are identical.

Analogous iridium complexes **5a**,**b** containing perfluoro-n-alkyl ligands were also prepared by treatment of the iodo precursors with $AgBF_4$, and were characterized by IR and NMR spectroscopy and by elemental analysis. The IR spectrum of **5a** shows a broad band centered at 3422 cm^{-1} while that of **5b** shows a broad band centered at 3340 cm^{-1}, presumably due to the two overlapping O–H stretching absorptions. Once again, the coordinated water does not give a sharp signal in the ^{1}H NMR spectrum of either complex. The two fluorines of

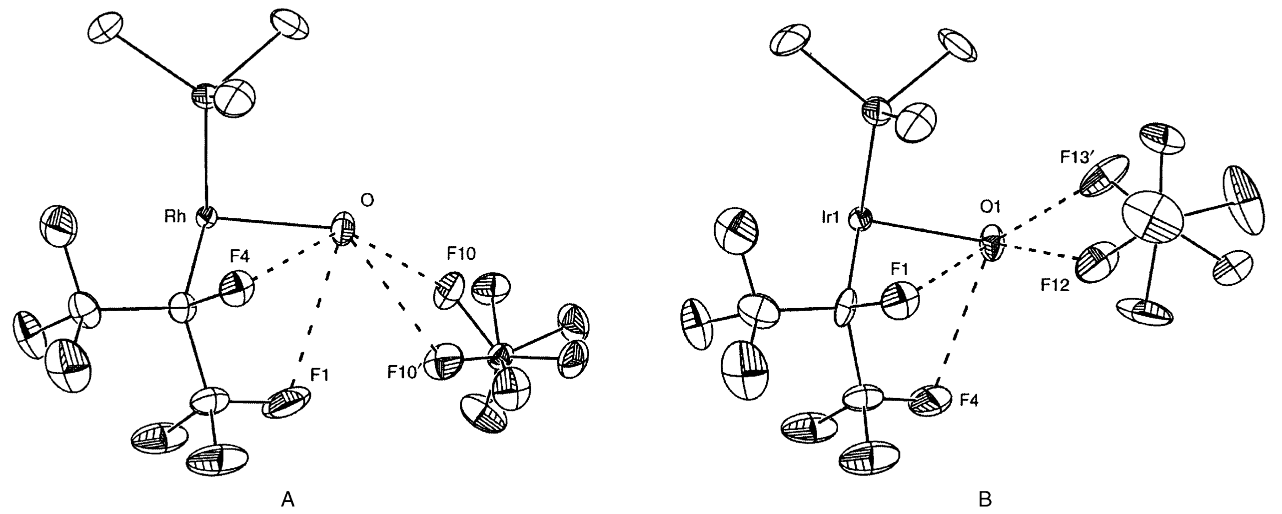
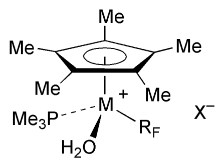


Fig. 4 ORTEP diagram of the cores of **4a** (A) and **4b** (B) with thermal ellipsoids at 30% probability. Dotted lines indicate those contacts closer than 3 Å between the oxygen atom of the aqua ligand and neighboring F atoms.

the α-CF_2 group are diastereotopic, and appear as a strongly coupled AX spin system, indicative of coordination to an asymmetric metal center. Thus, in contrast to the perfluoroisopropyl complexes **4**, the rate of water dissociation coupled with inversion at iridium appears to be relatively slow on the NMR timescale. These compounds also appear to be more stable towards subsequent hydrolysis of the α-CF_2 group than do their rhodium analogues.[11]



5a M = Ir; $R_F = CF_2CF_3$; X = BF_4
b M = Ir; $R_F = CF_2CF_2CF_3$; X = BF_4
c M = Ir; $R_F = CF_2CF_3$; X = CF_3SO_3
d M = Ir; $R_F = CF_2CF_2CF_3$; X = CF_3SO_3
e M = Rh; $R_F = CF_2CF_2CF_3$; X = CF_3SO_3

Analogous iridium and rhodium triflate complexes **5c**,**d**,**e** were prepared by treatment of the corresponding iodo precursors with AgOTf in CH_2Cl_2, and were also characterized by X-ray crystallographic analysis. The ORTEP diagrams are shown in Fig. 5–7, with relevant bond lengths and angles shown in Table 2. Complex **5d** (Fig. 6) exhibits some disorder in the perfluoro-n-propyl ligand; only the major occupancy structure is shown; the middle carbon atom resides in two locations separated by 0.68 Å causing the presence of a rotationally disordered terminal CF_3 group. The F atoms on the central CF_2 also occur in two locations; one of the positions was unresolvably close to another and it was modeled as a diffuse single atom.

Like their analogues with the BF_4^- counterion described above, and elsewhere,[11] all three complexes form a dimeric structure in the solid state, held together by a hydrogen bonding network involving the aqua ligands and the triflate counterions. Fig. 8 illustrates this using **5c** as an example. In the perfluoroethyl complex **5c**, which contains two crystallographically independent molecules in the asymmetric unit related by a pseudo inversion center. The two molecules are chemically very similar; the major difference is that in one the fluoroalkyl group is staggered with regard to the Cp* ring, and eclipsed in the other. Close OH···O contacts between the coordinated water and the triflate counterion are observed as shown, all of which are within the sum of the van der Waals' radii of the two oxygen atoms [O(1)···O(3) = 2.724, O(1)···O(2′) = 2.756, O(1′)···O(3′) = 2.751, O(1′)···O(2) = 2.693 Å].[19] There are also two close OH···F contacts between the aqua and the β-CF_2 fluorines of the perfluoroalkyl ligand [O(1)···F(5) = 2.849, O(1′)···F(3′) = 2.955 Å], as shown in Fig. 8. Comparable OH···O contacts are observed for **5d** and

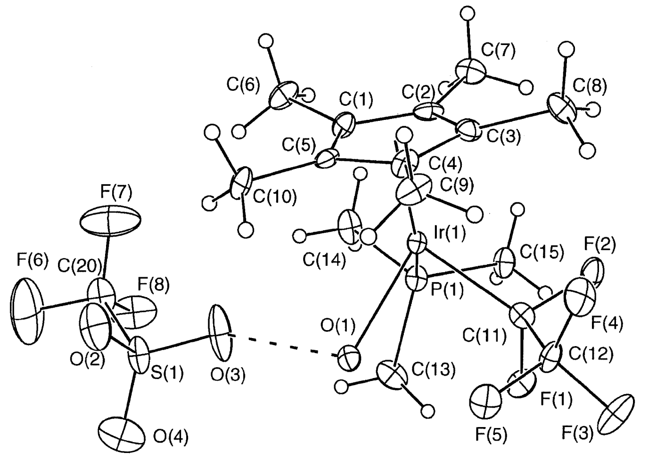


Fig. 5 ORTEP diagram and atom numbering scheme of **5c** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

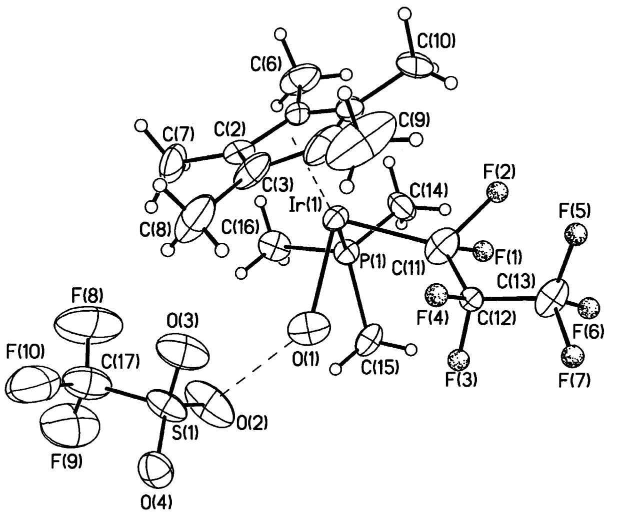


Fig. 6 ORTEP diagram and atom numbering scheme of **5d** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity. Fluorines on the perfluoropropyl ligand are disordered and only the major occupancy structure is shown.

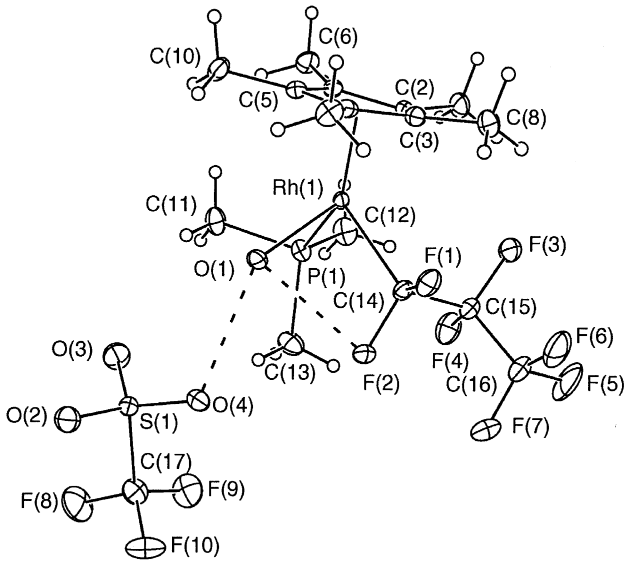


Fig. 7 ORTEP diagram and atom numbering scheme of **5e** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

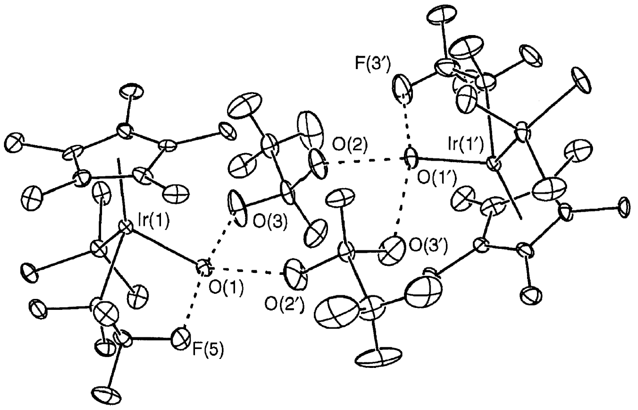


Fig. 8 ORTEP diagram and atom numbering scheme of **5c** with thermal ellipsoids at 30% probability, showing the dimeric bridged structure. Hydrogen atoms are omitted for clarity. Dotted lines indicate those contacts closer than 3 Å between the oxygen atom of the aqua ligand and neighboring O or F atoms.

5e but the O–F contacts are different. Whereas it is a β-F that is in close contact with the aqua ligand in perfluoroethyl complex **5c**, the perfluoro-n-propyl analogue **5e** adopts a different conformation that brings an α-fluorine F(2) to within 2.688 Å of O(1). The disorder in the fluoropropyl ligand of **5d** precludes a meaningful comparison for this complex.

An example of an aqua complex containing an anion incapable of hydrogen bonding was also isolated. Treatment of the perfluoroisopropyl complex **4b** with NaB(Ar$_F$) results in clean anion metathesis to give the analogous aqua complex **6**, which has been characterized spectroscopically and by crystallography. The solid state IR and solution NMR spectral data of the cation are very similar to that of the tetrafluoroborate complex **4b**. Since hydrogen bonding to the anion appears to be improbable in this compound, an X-ray crystallographic study of this complex was undertaken, and revealed a second molecule of water in the structure. The ORTEP is shown in Fig. 9, along with relevant bond lengths and angles in Table 2. The crystal structure reveals a close contact with the outer sphere water molecule and the aqua ligand, with an O(1) · · · O(2) distance of 2.518 Å, well within the sum of the van der Waals' radii of the two oxygen atoms. There also close contacts between O(1) · · · F(1) of 2.804 and O(1) · · · F(5) of 2.805 Å between the aqua ligand two fluorine atoms of the perfluoroisopropyl ligand similar to those observed in the cation of **4b**. The observation of three such interactions may indicate that the two fluorine interactions with O(5) may involve a bifurcated hydrogen bond. There are no close contacts from fluorines to the outer sphere water molecule. So the aqua ligand is still stabilized by hydrogen bonding, not to the counterion but to an additional piggybacked water molecule. The different counterion appears to have an insignificant effect on the structure of the cationic portion of the molecule compared to **4b**.

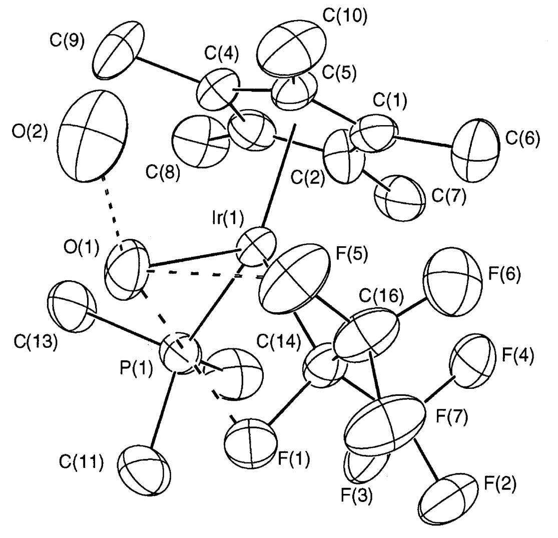
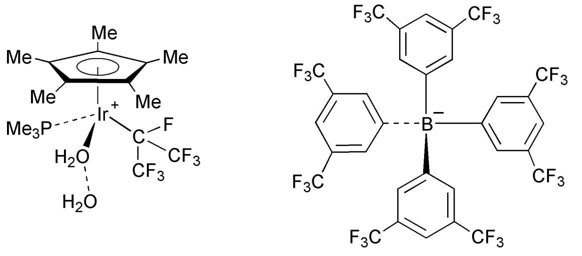


Fig. 9 ORTEP diagram and atom numbering scheme of the cation of **6** with thermal ellipsoids at 30% probability, showing the shared outer-sphere water molecule. Hydrogen atoms and the tetraarylborate anion are omitted for clarity. Dotted lines indicate those contacts closer than 3 Å between the oxygen atom of the aqua ligand and neighboring O or F atoms.



6

Finally, the ease in forming aqua complexes does not appear to be dependent on using PMe$_3$ as the phosphine. If the triphenylphosphine complex **7** is treated with AgBF$_4$ in the presence of water, the aqua complex **8** is formed. The spectral data for this complex is similar to that of the trimethylphosphine analogue **5b**. The complex was characterized crystallographically and exhibited the same kind of outer sphere water molecule as observed in **6**; the ORTEP diagram is shown in Fig. 10, with pertinent bond lengths and angles in Table 2. As shown in Fig. 11, this complex exhibits a more extensive hydrogen-bonding network than any of the other complexes, involving the aqua ligand, the outer sphere water molecule and the BF$_4^-$ counterion. The O(1) · · · O(2) distance of 2.679 Å is slightly longer than that observed in **6**, and the bound water exhibits interactions with two fluorines in the disordered BF$_4^-$ counterion, with O(1) · · · F(13) = 2.769 and O(1) · · · F(13′) = 2.642 Å. The perfluoro-n-propyl group adopts a conformation such that both the β-fluorine atoms are within hydrogen bonding distance to the aqua ligand with O(1) · · · F(3) = 2.851 and O(1) · · · F(4) = 2.739 Å. The outer sphere water molecule lies outside the range of H-bonding interactions with the counterion or the fluoroalkyl ligand.

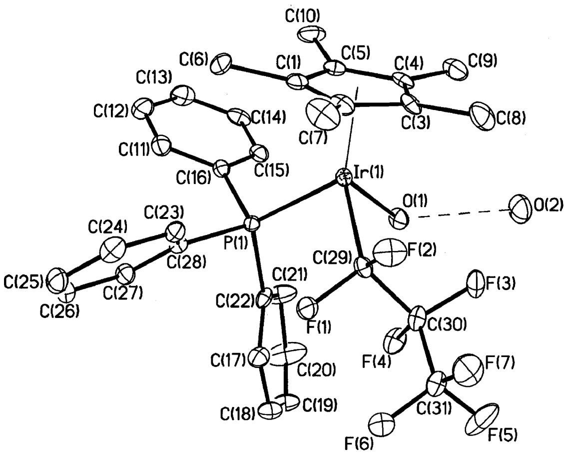


Fig. 10 ORTEP diagram and atom numbering scheme of the cation of **8** with thermal ellipsoids at 30% probability, showing the shared outer-sphere water molecule. Hydrogen atoms and the tetrafluoroborate anion are omitted for clarity.

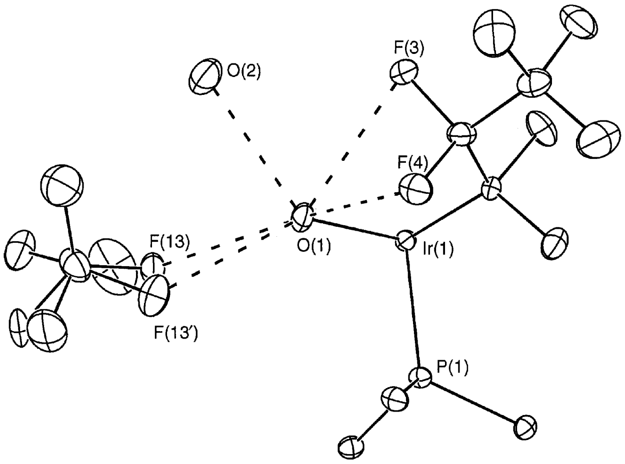
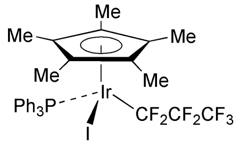


Fig. 11 ORTEP diagram of the core of **8** with thermal ellipsoids at 30% probability. Dotted lines indicate those contacts closer than 3 Å between the oxygen atom of the aqua ligand and neighboring O or F atoms.



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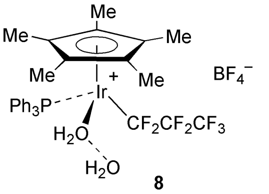

8

Conclusions

Rhodium(III) and iridium(III) cations containing fluoroalkyl and aqua ligands are readily prepared from the corresponding iodides. Even in the absence of water, the complexes are easily formed, suggesting that these d^6 M(III) perfluoroalkyl cations are very hydrophilic, perhaps due to the relative hardness of the metal center induced by the perfluoroalkyl ligand.

The tendency of these complexes to form hydrogen bonds to counterions or to additional outer sphere water molecules dominates the solid state structures of these compounds. It also seems clear that close contacts between fluorines on the fluoroalkyl group and the coordinated water molecule can play a role in determining the solid state conformation of the perfluoroalkyl ligand. Whether these intramolecular contacts are truly examples of hydrogen bonding, or whether they are dictated by the steric requirements of all the ligands, cannot be distinguished.

Experimental

General Procedures

All reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen, which had been deoxygenated over BASF catalyst and dried over molecular sieves, or in a Braun drybox. Solvents were deoxygenated and dried over activated alumina using an apparatus modified from that described in the literature.[23] ^{1}H (300 MHz), ^{19}F (282 MHz) and ^{31}P (121.4 MHz) NMR spectra were recorded on a Varian Unity-300 Spectrometer at 25 °C. Chemical shifts are reported as ppm downfield of TMS (^{1}H, referenced to solvent) or internal $CFCl_3$ (^{19}F) and external 85% H_3PO_4 (^{31}P). Coupling constants are reported in Hz. IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer. Elemental analyses were performed by Schwartzkopf (Woodside, NY)

Perfluoroalkyl iodides were purchased from PCR and used without further purification. Trimethylphosphine was obtained from Aldrich, silver tetrafluoroborate from ACROS, and silver trifluoromethanesulfonate from Johnson Matthey/Alfa Aesar. The complexes $[Rh(\eta^5\text{-}C_5Me_5)(CO)_2]$,[24,25] $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$, $[Ir(\eta^5\text{-}C_5Me_5)(CO)(CF_2CF_2CF_3)I]$,[22] $[Ir(\eta^5\text{-}C_5Me_5)(PMe_3)(R_F)I]$ $\{R_F = CF_2CF_3,\ CF_2CF_2CF_3,\ CF(CF_3)_2\}$,[22] $[Rh(\eta^5\text{-}C_5Me_5)(PMe_3)(CF_2CF_2CF_3)I]$[11] and $Na[B\{3,5\text{-}(CF_3)C_6H_3\}_4]$,[26] were prepared as previously reported.

Syntheses

$[Rh(\eta^5\text{-}C_5Me_5)\{CF(CF_3)_2\}I(CO)]$. $Rh(\eta^5\text{-}C_5Me_5)(CO)_2$ (250 mg, 0.850 mmol) was dissolved in benzene (12 mL) to give a pale orange colored solution. Then *i*-C_3F_7I (327 mg, 1.1 mmol) was added as a solution in benzene in two 1.5 mL portions. Immediately, the reaction mixture became darker red in color and effervesced. The reaction mixture was stirred at room temperature for 2 h, and the volatiles were removed under vacuum affording a red solid (357 mg, 75%). Analytically pure samples were obtained by dissolving the product in methylene chloride and allowing hexanes to diffuse slowly into the methylene chloride layer at −20 °C. Mp: >200 °C. ^{1}H NMR ($CDCl_3$): δ 2.03 (15H, C_5Me_5); (C_6D_6): δ 1.41 (15H, C_5Me_5). 19F NMR ($CDCl_3$): δ −66.5 (m, 3F, CF_3), −69.0 (m, 3F, CF3), −165.4 (s, 1F, CF); (C_6D_6): δ −65.2 (m, 3F, CF_3), −68.3 (m, 3F, CF_3), −166.2 (s, 1F, CF). IR (C_6H_6): $\nu_{CO} = 2065$ cm^{-1}. Anal. calc. for $C_{14}H_{15}F_7IORh$: C, 29.92; H, 2.64; found: C, 29.93; H, 2.61%.

$[Rh(\eta^5\text{-}C_5Me_5)\{CF(CF_3)_2\}I(PMe_3)]$ (3a). $[Rh(\eta^5\text{-}C_5Me_5)\{CF(CF_3)_2\}I(CO)]$ (200 mg, 0.356 mmol) was dissolved in benzene (5 mL) and PMe_3 (37 mL, 0.356 mmol) was added. The reaction was monitored by IR until the terminal carbonyl band disappeared (*ca.* 2 h). The volatiles were removed under vacuum to give an orange powder, which was washed with hexanes and dried, again under vacuum, affording the product, (911 mg, 91%). Mp: 185–189 °C. ^{1}H NMR ($CDCl_3$): δ 1.82 (d, $J_{HRh} = 2.9$, 15H, C_5Me_5), 1.68 (d, $J_{HP} = 10.5$, 9H, PMe_3); (C_6D_6): δ 1.40 (d, $J_{HRh} = 3.2$, 15H, C_5Me_5), 1.28 (d, $J_{HP} = 10.5$, $J_{HRh} = 1.7$, 9H, PMe_3). ^{19}F NMR ($CDCl_3$): δ −62.2 (m, CF_3), −69.5 (m, CF_3), −161.8 (m, CF); (C_6D_6): δ −61.2 (m, CF_3), −68.8 (m, CF_3), −160.9 (m, CF). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 1.8 (dm, $J_{PRh} = 151$, PMe_2Ph); (C_6D_6): δ 1.3 (dm, $J_{PRh} = 150$, PMe_3). Anal. calc. for $C_{16}H_{24}F_7IPRh$: C, 31.50; H, 3.97; found: C, 31.45; H, 4.08%.

$[Rh(\eta^5\text{-}C_5Me_5)\{CF(CF_3)_2\}(OH_2)(PMe_3)][BF_4]$ (4a). $[Rh(\eta^5\text{-}C_5Me_5)(n\text{-}C_3F_7)I(PMe_3)]$ **(3a)** (300 mg, 0.492 mmol) was dissolved in CH_2Cl_2 (10 mL) to give an orange colored solution and distilled H_2O (9 μL, 0.492 mmol) was added. Another flask was charged with $AgBF_4$ (115 mg, 0.590 mmol) and CH_2Cl_2 (10 mL) was added. As the rhodium–water solution was cannula transferred (slowly over about 10 min) to the stirring slurry of the silver salt, a fluffy pale yellow precipitate formed and the solution became more yellow. *It is important to carry out the addition in this manner*. The reaction mixture was stirred for 20 min after which it was filtered *via* cannula. The filtrate was concentrated to about half the original volume and hexanes (10 mL) were added to precipitate the product. The last step was repeated twice more and after concentrating the last time, the supernatant was removed. The yellow–orange solid was dried under vacuum giving a fluffy yellow, analytically pure, solid yield: 61–77%. Mp: decomposes up to 155 °C. ^{1}H NMR (CD_2Cl_2, −49 °C): δ 3.36 (br s, H_2O_{bound}), 2.16 (br s, H_2O_{free}), 1.55 (d, J_{HRh} = 3.3, 15H, C_5Me_5), 1.53 (dd, J_{HP} = 12.9, $J_{HRh,\ HF}$ = 2.7, 9H, PMe_3); (CD_2Cl_2, 21 °C): δ 2.87 (br s, H_2O_{bound}), 1.60 (d, J_{HRh} = 3.4, 15H, C_5Me_5), 1.59 (dd, J_{HP} = 10.7, $J_{HRh,\ HF}$ = 2.4, 9H, PMe_3); ($CDCl_3$): δ 2.96 (s, 2H, H_2O), 1.62 (d, J_{HRh} = 3.4, 15H, C_5Me_5), 1.61 (dd, J_{HP} = 10.5, $J_{HRh,\ HF}$ = 2.2, 9H, PMe_3). ^{19}F NMR (CD_2Cl_2, −49 °C): δ −68.8 (s, 3F, CF_3), −69.0 (s, 3F, CF_3), −149.0 (s, 4F, BF_4), −186.6 (s, 1F, CF); (CD_2Cl_2, 21 °C): δ −68.9 (s, 6F, CF_3), −149.9 (s, 4F, BF_4), −185.6 (s, 1F, CF); ($CDCl_3$): δ −69.2 (s, 6F, $2CF_3$), −150.2 (s, BF_4), −185.5 (s, 1F, CF). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −49 °C): δ 6.5 (ddm, J_{PRh} = 154, J_{PF} = 26, J_{PF} = 8, PMe_3); (CD_2Cl_2, 21 °C): δ 4.9 (dm, J_{PRh} = 149, PMe_3); ($CDCl_3$): δ 4.9 (br d, J_{PRh} = 151, PMe_3). IR (CH_2Cl_2) ν_{HO} = 3602, 3355 cm^{-1}. Anal. calc. for $C_{16}H_{26}BF_{11}OPRh$: C, 32.68; H, 4.46; found: C, 32.35; H, 4.19%.

[Ir(η^5-C_5Me_5)(PMe_3)$\{CF(CF_3)_2\}$(H_2O)][BF_4] (4b). A solution of [Ir(η^5-C_5Me_5)(PMe_3)$\{CF(CF_3)_2\}$I] (500 mg, 715 µmol) in CH_2Cl_2 (10 mL) with added distilled water (1 mL) was added *via* a cannula to a slurry of $AgBF_4$ (300 mg, 1.54 µmol) in CH_2Cl_2 (10 mL). There was immediate formation of a light colored precipitate. *It is important to carry out the addition in this manner*. The reaction was stirred at room temperature for 1 h, by which time the precipitate had turned black. Excess water was removed by addition of $MgSO_4$, and the resultant slurry filtered to give a yellow solution. The solvent was removed *in vacuo* to give a yellow powder, which was washed with hexanes and dried under vacuum. (467 mg, 99%). ^{1}H NMR (CD_2Cl_2): δ 1.66 (dd, J_{PH} = 11, J_{HH} = 2, 9H, PMe_3); 1.61 (d, J_{PH} = 2, 15H, C_5Me_5); ^{19}F NMR (CD_2Cl_2): δ −69.91 (s, 6F, CF_3), −149.56 (s, 4F, BF_4), −180.06 (s, 1F, CF). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −69.90 (br s, PMe_3). IR (KBr): ν_{OH} = 3442 cm^{-1} (br). Anal. calc. for $C_{16}H_{27}BF_{11}IrOP$: (677.35) C, 28.37; H, 3.87; found: C, 28.57; H, 3.98%.

[Ir(η^5-C_5Me_5)(PMe_3)(CF_2CF_3)(H_2O)][BF_4] (5a). A solution of [Ir(η^5-C_5Me_5)(PMe_3)(CF_2CF_3)I] (800 mg, 1.23 mmol) in CH_2Cl_2 (10 mL) with added distilled water (1 mL) was added *via* a cannula to a slurry of $AgBF_4$ (264 mg, 135 mmol) in CH_2Cl_2 (10 ml). *It is important to carry out the addition in this manner*. There was immediate formation of a light colored precipitate. The reaction was stirred at room temperature for 1 h, by which time the precipitate had turned black. Excess water was removed by addition of $MgSO_4$, and the resultant slurry filtered to give a yellow solution. The solvent was removed *in vacuo* to give a yellow powder, which was washed with hexanes and dried under vacuum. Crystallization from CH_2Cl_2–hexane afforded the product (644 mg, 84%). ^{1}H NMR ($CDCl_3$): δ 1.70 (s, 15H, C_5Me_5), 1.68 (d, J_{PH} = 11, 9H, PMe_3). ^{19}F NMR ($CDCl_3$): δ −82.29 (s, 3F, CF_3); −82.22 (d, J_{AB} = 303, 1F, $C_\alpha F_A$), −90.10 (d, J_{AB} = 303, 1F, $C_\alpha F_B$), −150.33 (s, 4F, BF_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −23.48 (dd, J_{PF} = 16.0, J_{PF} = 8.0, PMe_3). IR (KBr): ν_{OH} = 3422 cm^{-1} (br). Anal. calc. for $C_{15}H_{26}BF_9IrOP$ (627.34): C, 28.72; H, 4.18; found: C, 28.96; H, 4.43%.

[Ir(η^5-C_5Me_5)(PMe_3)($CF_2CF_2CF_3$)(H_2O)][BF_4] (5b). A solution of [Ir(η^5-C_5Me_5)(PMe_3)($CF_2CF_2CF_3$)I] (300 mg, 429 µmol) in CH_2Cl_2 (10 mL) with added distilled water (1 mL) was added *via* a cannula to a slurry of $AgBF_4$ (92 mg, 471 µmol) in CH_2Cl_2 (10 mL). *It is important to carry out the addition in this manner*. There was immediate formation of a light colored precipitate. The reaction was stirred at room temperature for 1 h, by which time the precipitate had turned black. Excess water was removed by addition of $MgSO_4$, and the resultant slurry filtered to give a yellow solution. The solvent was removed *in vacuo* to give a yellow powder, which was washed with hexanes and dried under vacuum. Crystallization from CH_2Cl_2–hexane afforded the product (231 mg, 77%). ^{1}H NMR ($CDCl_3$): δ 1.71 (d, J_{HH} = 2, 15H, C_5Me_5), 1.70 (d, J_{PH} = 11, 9H, PMe_3). ^{19}F NMR (CD_2Cl_2): δ −79.32 (t, J_{FF} = 12, 3F, CF_3); −71.96 (m, J_{AB} = 261, 1F, $C_\alpha F_A$), −94.96 (m, J_{AB} = 261, 1F, $C_\alpha F_B$), −116.40 (m, 2F, $C_\beta F_2$), −149.67 (s, 4F, BF_4). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −21.71 (br s, PMe_3). IR (KBr): ν_{OH} = 3340 cm^{-1} (br). Anal. calc. for $C_{16}H_{27}BF_{11}IrOP$ (677.35): C, 28.37; H, 3.87; found: 28.46; H, 3.79%.

[Ir(η-C_5Me_5)(PMe_3)(CF_2CF_3)(H_2O)][OSO_2CF_3] (5c). A yellow solution of [Ir(η^5-C_5Me_5)(PMe_3)(CF_2CF_3)I] (400 mg, 616 µmol) in CH_2Cl_2 (10 mL) was slowly added to a slurry of AgOTf (175 mg, 616 µmol) in CH_2Cl_2 (5 mL). *It is important to carry out the addition in this manner.* The color of the solution faded with the formation of a white precipitate. The reaction mixture was stirred overnight, and the solvent removed by vacuum pumping. The residue was extracted with CH_2Cl_2 and filtered to give a yellow solution. Yellow crystals were obtained by slow evaporation (335 mg, 79%). ^{1}H NMR (CD_2Cl_2): δ 1.70 (s, 15H, C_5Me_5), 1.66 (d, J_{PH} = 10.5, 9H, PMe_3). ^{19}F NMR (CD_2Cl_2): δ −76.40 (d, J_{AB} = 251, 1F, $C_\alpha F_A$), −79.18 (s, 3F, OSO_2CF_3), −82.54 (s, 3F, CF_3), −90.87 (d, J_{AB} = 251, 1F, $C_\alpha F_B$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −24.0 (m, PMe_3). Anal. calc. for $C_{16}H_{26}F_8O_4IrPS$ (689.60): C, 27.87; H, 3.80; found: C, 28.42; H, 3.96%.

[Ir(η^5-C_5Me_5)(PMe_3)($CF_2CF_2CF_3$)(H_2O)][OSO_2CF_3] (5d). A solution of [Ir(η^5-C_5Me_5)(PMe_3)$\{CF(CF_3)_2\}$I] (200 mg, 286 µmol) in CH_2Cl_2 (5 mL) was slowly added to a slurry of AgOTf (81 mg, 315 µmol) in CH_2Cl_2 (5 mL). *It is important to carry out the addition in this manner.* There was immediate formation of a white precipitate. After 30 min, the solution was filtered *via* a cannula to give a yellow solution. The solvent was removed by vacuum pumping to give a yellow solid (124 mg, 59%). ^{1}H NMR (CD_2Cl_2): δ 1.69 (s, 15H, C_5Me_5), 1.68 (d, J_{PH} = 11.7, 9H, PMe_3), 1.68 (d, J_{PH} = 1.8, 15H, C_5Me_5). ^{19}F (CD_2Cl_2): δ −78.67 (d, J_{AB} = 281, 1F, $C_\alpha F_A$), −78.99 (s, 3F, OSO_2CF_3), −79.86 (br s, 3F, CF_3), −87.87 (d, J_{AB} = 281, 1F, $C_\alpha F_B$), −115.95 (d, J_{AB} = 284, 1F, $C_\beta F_A$), −118.41 (d, J_{AB} = 284, 1F, $C_\beta F_B$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ − 20.92 (br s, PMe_3). IR (KBr): ν_{OH} = 3346, 3238 cm^{-1}. Anal. calc. for $C_{17}H_{26}F_{10}IrO_4PS$ (739.61): C, 27.61; H, 3.54; found: C, 27.57; H, 3.18%.

[Rh(η^5-C_5Me_5)($CF_2CF_2CF_3$)(H_2O)][OSO_2CF_3] (5e). [Rh(η^5-C_5Me_5)(n-C_3F_7)(I)(PMe_3)] (250 mg, 0.410 mmol) was dissolved in CH_2Cl_2 (5 mL) to give a red–orange colored solution. Then, $AgSO_3CF_3$ (105 mg, 0.410 mmol) was added to a different Schlenk flask and CH_2Cl_2 (12 mL) was added. The rhodium solution was cannula transferred to the silver triflate mixture, dropwise. *It is important to carry out the addition in this manner.* Additional CH_2Cl_2 (3 mL) was added to the rhodium flask and the contents were transferred to the reaction mixture *via* cannula. The reaction mixture was stirred for 30 min over which time a white precipitate was formed. The solution was dried over $MgSO_4$. The mixture was then filtered and washed with CH_2Cl_2 several times. The yellow solution was concentrated and hexane was added to precipitate the product as an orange powder in 94% yield (241 mg). Mp: 172–173 °C. ^{1}H NMR ($CDCl_3$): δ 1.69 (d, J_{HRh} = 2.7, C_5Me_5), 1.63 (d, J_{HP} = 11.2, PMe_3). ^{19}F NMR ($CDCl_3$): δ −78.4 (d, J_{AB} = 271, 1F, $C_\alpha F_A$), −78.6 (s, 3F, OTf), −79.9 (t, J_{FF} = 11, 3F, CF_3), −85.4 (d,

$J_{AB} = 271$, 1F, $C_{\alpha}F_B$), −115.6 (d, $J_{AB} = 288$, 1F, $C_{\beta}F_A$), −118.7 (d, $J_{AB} = 288$, 1F, $C_{\beta}F_B$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 7.6 (dm, $J_{PRh} = 151$, PMe_3); (C_6D_6): δ 7.6 (ddm, $J_{PRh} = 155$, $J_{PF} = 35$, PMe_3). Anal. calcd. for $C_{17}H_{24}F_{10}O_3PRhS$: C, 31.40; H, 4.03; found: C, 31.99; H, 3.81%.

[Ir(η^5-C_5Me_5)(PMe_3){CF(CF_3)$_2$}(H_2O)][B{3,5-(CF_3)$_2C_6H_{34}$]·0.5H_2O·CH_2Cl_2 (6). To a yellow solution of [Ir(η^5-C_5Me_5)(PMe_3){CF(CF_3)$_2$}(H_2O)][BF_4] (20 mg, 30 μmol) in CH_2Cl_2 (5 mL) was added a solution of Na[B{3,5-(CF_3)$_2C_6H_3$}$_4$] (29 mg, 32 μmol) in CH_2Cl_2 (5 mL). The reaction mixture darkened a little, and was stirred at room temperature for 30 min, and filtered to give a yellow solution. The solvent was removed by rotary evaporation, and the residue dissolved in a minimum of diethyl ether. Hexanes (*ca.* 20 mL) was added to form a yellow precipitate. The solvent was evaporated down to *ca.* 10 mL, the yellow solid filtered and dried *in vacuo* (35 mg, 80%).^1H NMR (CD_2Cl_2): δ 7.72 (s, 8H, *o*-H), 7.57 (s, 4H, *p*-H), 2.42 (br s, 2H, OH_2), 1.66 (dd, $J_{PH} = 10.5$, 9H, PMe_3), 1.53 (d, $J_{PH} = 1.8$, 15H, C_5Me_5). ^{19}F NMR (CD_2Cl_2): δ −63.24 (s, 24F, CF_3), −69.90 (br s, 6F, CF_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −18.7 (br s, PMe_3). IR (KBr): $\nu_{OH} = 3690$, 3629 cm^{-1}. Anal. calc. for $C_{46}H_{40}BF_{31}IrO_2P$·0.5$CH_2Cl_2$ (1490.23): C, 37.48; H, 2.77; found: C, 38.73; H, 2.81%.

[Ir(η^5-C_5Me_5)(PPh_3)($CF_2CF_2CF_3$)I] (7). [Ir(η^5-C_5Me_5)(CO)($CF_2CF_2CF_3$)I] (100 mg, 154 μmol) and PPh_3 (44 mg, 169 μmol) were dissolved in toluene (10 ml) to give a yellow solution which was heated to reflux and monitored by IR spectroscopy. On completion, as evidenced by disappearance of the CO band (24 h), the volatiles were removed by vacuum pumping. The resultant yellow powder was crystallized from CH_2Cl_2–heptane to give the product (75 mg, 55%). ^1H NMR (CD_2Cl_2): δ 7.49–7.20 (m, 15H, PPh_3), 1.52 (d, $J_{PH} = 1.8$, 15H, C_5Me_5). ^{19}F NMR (CD_2Cl_2): δ −59.03 (dd, $J_{AB} = 285.8$, $J_{PF} = 38.7$, 1F, $C_{\alpha}F_A$), −63.14 (d, $J_{AB} = 274.9$, 1F, $C_{\alpha}F_B$), −80.28 (t, $J_{FF} =$, 3F, CF_3), −111.28 (d, $J_{AB} = 279.7$, 1F, $C_{\beta}F_A$), −112.21 (d, $J_{AB} = 277.1$, 1F, $C_{\beta}F_B$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −0.06 (d, $J_{PF} = 38.7$). Anal. calc. for $C_{31}H_{30}F_7IrIP$ (885.62): C, 42.04; H, 3.41; found C, 41.92; H 3.68%.

[Ir(η-$^5C_5Me_5$)(PPh_3)($CF_2CF_2CF_3$)(H_2O)][BF_4]·H_2O (8). [Ir(η^5-C_5Me_5)(PPh_3)($CF_2CF_2CF_3$)I] (75 mg, 85 μmol) in CH_2Cl_2 (10 ml) with distilled water (1 ml) was added slowly to a slurry of $AgBF_4CH_2Cl_2$ (10 ml). A yellow slurry/solution formed. After 1 h, $MgSO_4$ was added, and the mixture filtered to give a yellow solution. The solvent was removed by rotary evaporation to give a yellow solid (38 mg, 51%). ^1H NMR (CD_2Cl_2): δ 7.50 [br s, 15H, P(C_6H_5)$_3$], 1.39 (d, $J_{PH} = 1.2$, 15H, C_5Me_5). ^{19}F NMR (CD_2Cl_2): δ −71.0 (br s, 2F, α-CF_2), −80.23 (s, 3F, CF_3), −114.8 (br s, 2F, β-CF_2), −150.25 (s, 4F, BF_4). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 14.5 (br s, PPh_3). Anal. calc. for $C_{31}H_{32}BF_{11}IrOP$·H_2O (881.57): C, 42.23; H, 3.97; found: C, 41.92; H, 3.50%.

Crystal structure analyses

All crystals were grown by crystallization from slowly cooled CH_2Cl_2–hexane solutions. Crystal data collection, and refinement parameters are given in Table 1. The data were collected on a Siemens P4 diffractometer equipped with a SMART CCD detector. The systematic absences in the diffraction data are uniquely consistent for the reported space group for **4b**, **5d**, **5e**, **6** and **8**. For **5d** and **5e**, no evidence of symmetry higher than triclinic was observed in the diffraction data, and the centrosymmetric space group option, $P\bar{1}$, was chosen, which yielded chemically reasonable and computationally stable results of refinement. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. Empirical DIFABS[27] absorption corrections were applied to the data sets of **5c** and **5d**.

The asymmetric unit of **5c** contains two cationic iridium complexes and two triflate counterions. The atoms C(12), and F(3) to F(7) of PrF/OTf are equally disordered over two positions. All non-hydrogen atoms, except C(12), C(12′) and the fluorine atoms of the n-C_3F_7 group for **5d** were refined with anisotropic coefficients. The hydrogen atoms of the ligated water molecule for **5c** and **5d** were ignored for both structures and all other hydrogen atoms were treated as idealized contributions.

For **4a** and **4b** the systematic absences in the diffraction data are uniquely consistent for the tetragonal space groups $P4_12_12$ or $P4_32_12$. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. Semi-empirical absorption corrections were applied to the data sets. Structure refinement indicated that the correct space group was $P4_12_12$, which was verified by refinement of the Flack parameter [−0.03(3) for **4a**; 0.009(2) for **4b**]. The asymmetric unit contains one ion pair and one-half of a solvent molecule of dichloromethane, which is located on a two-fold axis. Three fluorine atoms in the tetrafluoroborate counterion are rotationally disordered around the fourth boron–fluorine axis in two orientations with a 60 : 40 distribution. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms on the aqua ligand were located from the difference map and refined. All other hydrogen atoms were treated as idealized contributions.

For **6** the phenyl rings and the pentamethylcyclopentadienyl rings were fixed as rigid planar groups to conserve data. The fluorine atoms of the $B(Ar_F)_4$ counterion F(24)–F(26), F(31)–F(33), F(44)–F(46), F(51)–F(53) were disordered over two positions, 60 : 40 and F(34)–F(36), F(41)–F(43), F(54)–F(56) were equally disordered over two positions. The fluorine atoms, F(54)–F(56) and F(54′)–F(56′) were refined isotropically. The carbon atom of the dichloromethane solvent molecule, C(61) was disordered over two positions, 60 : 40. A water solvent molecule was located from the difference map, and its occupancy was refined to 50%. All other non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms on both the solvent water molecule and the coordinated water molecule could not be located from the difference map and were ignored. All other hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXTL (5.1) program library.

CCDC reference numbers 164768–164774.

See http://www.rsc.org/suppdata/dt/b1/b102482p/ for crystallographic data in CIF or other electronic format.

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