Facile Activation of Carbon−Fluorine Bonds in Saturated Fluoroalkyl Ligands by Coordinated Water in Fluoroalkyl Aqua Complexes of Rhodium

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Activation of normally inert carbon−fluorine bonds in saturated fluorocarbons is a topic of considerable recent interest.[1] The methodology of choice usually involves strongly reducing conditions; the fate of the fluorine is usually fluoride ion, stabilized as an alkali metal salt. An alternative method for activation of CF_2 groups is hydrolysis, with strong H−F and C=O bonds providing driving force for the reaction. However, conditions necessary to hydrolyze a CF_2 group in saturated fluorocarbons often require a combination of strong bases or acids, heat, and long reaction times, depending on the position of the hydrolyzable group in the molecule.[2] Hydrolysis of CF_2 or CF_3 groups bound to transition metal centers is sometimes more facile, but initial activation of an α-C−F bond still requires a strong Lewis acid, such as BF_3,[3] SbF_5,[4] or $SiMe_3^+$,[5] although there are some indications that a proton can act as the initial fluoride acceptor.[6] We have reported remarkably facile hydrolysis of a Rh−CF_2 group in a coordinatively unsaturated perfluorometallacyclobutene complex by traces of moisture present on glassware surfaces; a coordinatively saturated analogue was inert, leading to the hypothesis that the vacant coordination site on the metal could bind and activate water in the hydrolysis mechanism.[7] Here, we describe the synthesis and structures of two cationic complexes containing adjacent fluoroalkyl and water ligands, both of which undergo hydrolysis of a CF_2 group, the facility of which depends strongly on the hydrogen-bonding ability of the counterion.

Addition of perfluorobenzyl complex **1**[8] or perfluoropropyl analogue **2**[9] to $AgBF_4$ in moist CH_2Cl_2 affords BF_4^- salts of the cationic aqua complexes **3** and **4**,[9] the structures of which were confirmed by X-ray crystallographic studies.[10] ORTEP diagrams for the two ion pairs, with selected bond distances and angles, are presented in Figures 1 and 2. Each molecule exhibits close hydrogen-bonding interactions of coordinated
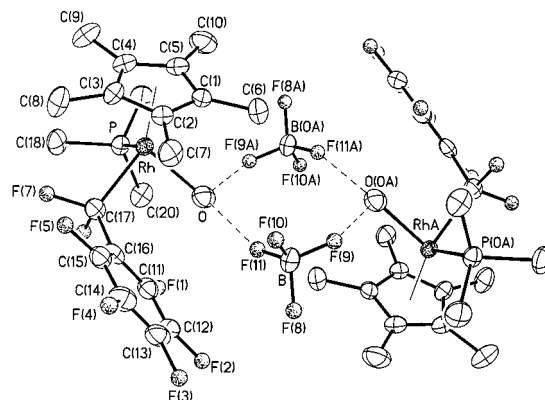

Figure 1. Molecular structure of **3**; fluorines are shown as spheres for clarity. A full ORTEP appears in the Supporting Information. Selected bond distances (Å) and angles (deg): Rh−O, 2.164(7); Rh−P, 2.338(2); Rh−C(17), 2.113(9); C(17)−F(7), 1.388(10); C(17)−F(6), 1.412(10); F(7)−C(17)−F(6), 101.8(6); C(17)−Rh−O, 89.5(3); O−Rh−P, 90.4(2); C(17)−Rh−P, 88.1(2).
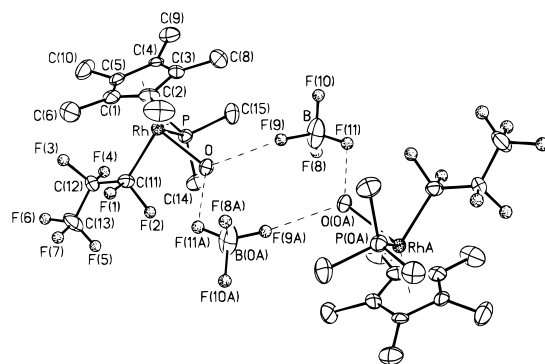

Figure 2. Molecular structure of **4**; fluorines are shown as spheres for clarity. A full ORTEP appears in the Supporting Information. Selected bond distances (Å) and angles (deg): Rh−O, 2.219(5); Rh−P, 2.319(2); Rh−C(11), 2.086(7); C(11)−F(1), 1.396(8); C(11)−F(2), 1.389(8); F(1)−C(11)−F(2), 102.1(6); C(11)−Rh−O, 85.2(3); O−Rh−P, 85.8(2); C(11)−Rh−P, 92.8(2).

water molecule with the tetrafluoroborate counterion, with O−F(9A) and O−F(11) distances of 2.640 and 2.855 Å in **3**, and 2.723 and 2.636 Å in **4**; such interactions are well precedented.[11] Close approaches of O−F(1) [2.749 Å] in **3** and O−F(2) [2.767 Å] in **4** are also well within potential hydrogen-bonding distance.

Solution spectra of **3** are consistent with the solid state structure. Asymmetric and symmetric stretches of coordinated

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(2) See: *Chemistry of Organic Fluorine Compounds II*; Hudlicky, M., Pavlath, A. E., Eds.; ACS Monograph 187; American Chemical Society: Washington, DC, 1995; Chapter 4. *Chemistry of Organic Fluorine Compounds,* 2nd ed.; Hudlicky, M., Ed.; John Wiley & Sons: New York, NY, 1976; Chapter 5. *Chemistry of Organic Fluorine Compounds*; Hudlicky, M., Ed.; Macmillan; New York, 1962.

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(9) Experimental details and spectroscopic data for this compound are provided in the Supporting Information.

(10) Crystal data for **3**: $C_{20}H_{26}BF_{11}OPRh$, red block, triclinic, $P\bar{1}$, $a =$ 8.682(3), $b =$ 11.033(2), and $c =$ 14.376(3) Å, $\alpha =$ 74.50(1), $\beta =$ 76.11-(3), and $\gamma =$ 73.02(3)°, $V =$ 1249.4(7) Å^3, $Z =$ 2, $D_x =$ 1.691 g cm^{-3}, $T =$ 298 K, $R(F) =$ 6.74%, $R(wF^2) =$ 19.49%. Crystal data for **4**: $C_{16}H_{26}$-$BF_{11}OPRh$, orange block, monoclinic, $P2_1/n$, $a =$ 10.115(1), $b =$ 16.270-(2), and $c =$ 14.070(2) Å, $\beta =$ 92.74(1)°, $V =$ 2312.7(7) Å^3, $Z =$ 4, $D_x =$ 1.689 g cm^{-3}, $T =$ 298 K, $R(F) =$ 4.81%, $R(wF^2) =$ 8.41%. Details of the crystallographic determinations are provided in the Supporting Information.

(11) For a compilation of some crystallographically characterized organometallic complexes containing water ligands and a discussion of hydrogen-bonding to counterions, see: Kubas, G. J.; Burns, C. J.; Khalsa, G. R. K.; Van Der Sluys, L. S.; Kess, G.; Hoff, C. D. *Organometallics* **1992,** *11,* 3390. For other more recent references, see: Veltheer, J. E.; Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1995,** *117,* 12478. Canty, A. J.; Jin, H.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1995,** *503,* C16. Bodige, S.; Porter, L. C. *J. Organomet. Chem.* **1995,** *487,* 1. Dadci, L.; Elias, H.; Frey, U.; Hörnig, A.; Koelle, U.; Merbach, A. E.; Paulus, H.; Schneider, J. S. *Inorg. Chem.* **1995,** *34,* 306. Carmona, D.; Cativiela, C.; García-Correas, R.; Lahoz, F. J.; Lamata, M. P.; López, J. A.; López-Ram de Víu, M. P.; Oro, L. A.; San José, E.; Viguri, F. *J. Chem. Soc., Chem. Commun.* **1996,** 1247. Fries, A.; Green, M.; Mahon, M. F.; McGrath, T. D.; Nation, C. B. M.; Walker, A. P.; Woolhouse, C. M. *J. Chem. Soc., Dalton Trans.* **1996,** 4517.

Scheme 1
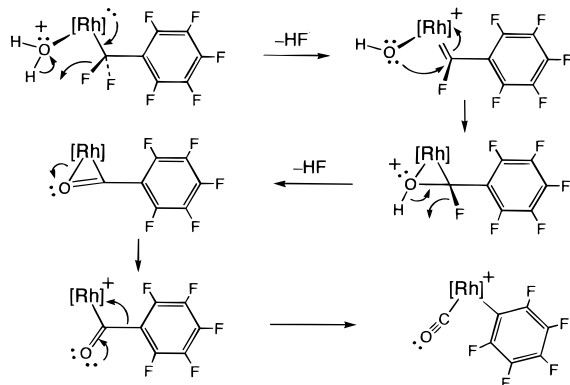
water are observed in the IR spectrum at 3630 and 3370 cm^{-1}.[12] ^{19}F NMR resonances for the diastereotopic fluorines of the CF$_2$ group are broad at room temperature, but sharpen when cooled to -50 °C to give a typical AX pattern. This temperature dependence may reflect dissociation of water[13] with inversion at rhodium, thereby equilibrating the CF$_2$ environments; ^{103}Rh coupling to ^{31}P is retained indicating that phosphine dissociation is not responsible for this phenomenon. In contrast, perfluoropropyl analogue 4[9] shows a sharp AX pattern for the α-CF$_2$ resonances at room temperature indicating that the molecule is not fluxional on the NMR time scale.

While perfluoropropyl complex 4 appears to be indefinitely stable on standing in solution at room temperature, perfluorobenzyl analogue 3 is cleanly transformed on standing overnight in CDCl$_3$ solution into pentafluorophenyl carbonyl complex 5;[9] the CO stretch is observed in the IR spectrum at 2074 cm^{-1}, and the pentafluorophenyl ligand exhibits five resonances in the ^{19}F NMR spectrum due to restricted rotation, as previously observed for other pentafluorophenyl rhodium complexes.[14] HF can be observed in the volatiles, after vacuum transfer, as previously noted.[8] A suggested mechanism is shown in Scheme 1; hydrolysis of the CF$_2$ group affords a coordinatively unsaturated pentafluorobenzoyl complex, which undergoes pentafluorophenyl migration into the vacant coordination site to afford 5. The initial step is suggested to involve a proton from coordinated water acting as a fluoride acceptor with loss of fluoride enhanced by resonance stabilization from Rh; presumably the difference in reactivity of the CF$_2$ groups toward hydrolysis in perfluorobenzyl complex 3 compared to perfluoropropyl analogue 4 rests in additional enhancement of the leaving group ability of the benzylic fluoride.

This transformation does not take place in acetone-d_6, which displaces water from the coordination sphere of 3,[13] suggesting that it is a reaction of coordinated water with the adjacent CF$_2$ group which is important; addition of more water to an acetone solution failed to accomplish hydrolysis. In addition, reaction of 1 with silver triflate affords the triflate complex 6;[9] the sharp AX pattern observed for the CF$_2$ group at room temperature indicates the triflate ligand is not labile. The triflate ligand is not displaced by water alone, and no hydrolysis of the CF$_2$ group is observed. Bergman has shown that addition of the sodium salt of weakly coordinating anion tetrakis{3,5-bis(trifluoromethyl)-phenyl}borate (B{Ar$_F$}$_4$) will displace triflate from iridium as sodium triflate;[15] however, attempts to prepare the B{Ar$_F$}$_4$$^-$

salt of cation 3 from 6 using this method in the presence of water afforded very rapid hydrolysis to give the B{Ar$_F$}$_4$$^-$ salt 7[9] with no signs of any intermediate water complex analogous to 3.

The inability to isolate the perfluorobenzyl aqua cation using the B{Ar$_F$}$_4$$^-$ counterion suggests that an anion incapable of either displacing water, or of hydrogen-bonding to it, might strongly enhance the ability of coordinated water to hydrolyze the adjacent CF$_2$ group. Loss of hydrogen bonding to the counterion will allow the proton of coordinated water a stronger interaction with the adjacent CF$_2$ group. In agreement with this hypothesis, the perfluoropropyl complex 2 reacts with silver triflate to afford 8;[9] treatment of 8 with NaB{Ar$_F$}$_4$ in the presence of water results in rapid hydrolysis to give the perfluoroethyl carbonyl complex 9.[9] The BF$_4$$^-$ analogue 10 was prepared unambiguously by the reaction of [Rh(η^5-C$_5$Me$_5$)-(C$_2$F$_5$)I(PMe$_3$)] with AgBF$_4$ in the presence of CO.
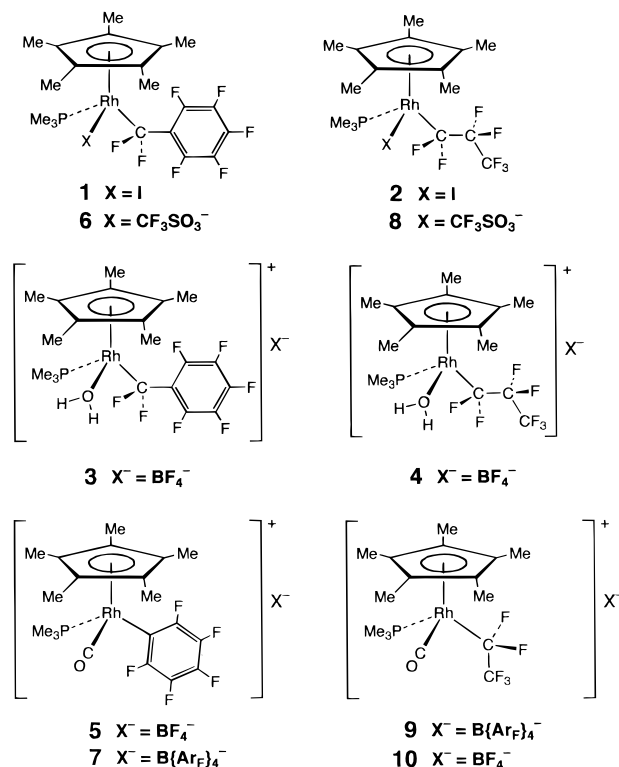
In summary, we provide evidence that the hydrolysis reaction of CF$_2$ groups in perfluoroalkyl aqua complexes is a reaction of coordinated water, which can be extremely facile if the counterion is incapable of hydrogen bonding. This represents an unusually mild activation of saturated C$-$F bonds and suggests that other reactions of water in the coordination sphere of transition metals, particularly those in which it acts as a protic acid, might also benefit from the presence of a non-hydrogen-bonding counterion.

Supporting Information Available: Details of syntheses and characterizations of complexes 2$-$9, and the X-ray structure determinations, tables of atomic coordinates and anisotropic thermal parameters, bond lengths and bond angles, anisotropic displacement parameters, and hydrogen atom coordinates for 3 and 4 (24 pages). See any current masthead page for ordering and Internet access instructions.

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(13) The water ligands in [Rh(C$_5$Me$_5$)(OH$_2$)$_3$$^{2+}$][OTf$^-$]$_2$ are labile to exchange and substitution: Eisen, M. S.; Haskel, A.; Chen, H.; Olmstead, M. M.; Smith, D. P.; Maestre, M. F.; Fish, R. H. *Organometallics* **1995**, *14*, 2806.

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