# Elimination of R−H from Iridium Acyl Hydrides without Loss of CO: Evidence for the Intervention of Metal Cation/Carbanion Pairs

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Fluoroalkyl ($M-C_nF_m$) and alkyl hydride (M(H)(R)) complexes have played a central role in the history of organometallic chemistry.[1−3] The former were among the first complexes prepared with stable late transition metal−carbon single bonds, and studies of the latter have helped to understand the thermodynamics and mechanisms of reactions such as hydroformylation and carbon−hydrogen bond activation. Therefore, when we recently found that our new method for synthesizing iridium acyl hydrides[4] could be applied to the preparation of fluoroacyl complexes such as Cp*(PMe₃)Ir-(H)[C(O)CF₃] (**1**, Cp* = η^5-C₅Me₅), we were intrigued by the possibility of investigating such systems. This interest was further stimulated by the fact that methods for delivering fluoroalkyl groups to metal centers are still not very general, the classic technique being the decarbonylation of their fluoroacyl relatives.[5,6] In contrast to this behavior, heating a C₆D₆ solution of **1** in a sealed tube at 105 °C gave an unusual result: CF₃H and the iridium(I) carbonyl Cp*(PMe₃)Ir(CO) **2** were generated in quantitative yield ($t_{1/2}$ = 2.3 h) (eq 1).[7] In this communication we report a study of the mechanism of this reaction, which has led us to the conclusion that fluoroalkyl carbanion/iridium cation pairs are involved as intermediates.[8]


(1)
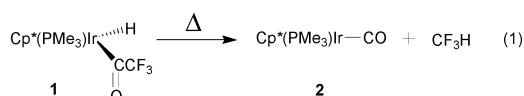
Scheme 1 shows four likely mechanisms for the α-fluoroalkyl elimination reaction: (A) concerted transition state **TS-1**, (B) intermediate ion-pair **4**, (C) intermediate **5** (perhaps with a simultaneous Cp* ring slip; one might also expect this intermediate to be capable of CO elimination to give Cp*(PMe₃)Ir(H)(CF₃) (**3**)), and (D) intermediate radical-pair **6**.

The rate of disappearance of **1** and formation of **2** exhibited clean first-order kinetics in all solvents and temperatures monitored.[9] Rate constants were determined in C₆D₆, DMSO-d_6, DMF-d_7, CD₃CN, and CD₃OD over a wide range of temperatures.[10] At 94.3 °C, the reaction proceeded approximately 32 times faster in CD₃OD and 180 times faster in DMSO-d_6 than in C₆D₆. The activation parameters for the reaction in C₆D₆ and DMSO-d_6 were found to be: C₆D₆ $\Delta H^{\ddagger}$ = 25.7 kcal/mol and $\Delta S^{\ddagger}$ = −14.0 kcal/mol; DMSO-d_6 $\Delta H^{\ddagger}$ = 24.3 kcal/mol and $\Delta S^{\ddagger}$ = −6.5 kcal/mol.[11] This dramatic solvent effect−quite unusual for a seemingly simple organometallic elimination reaction−was our first indication that an ionic intermediate such as that illustrated in path B could be involved. Further evidence for a stepwise mechanism was provided by substituting deuterium for the hydride in **1**. Rate studies on this compound showed *no* kinetic isotope effect in either C₆D₆ or DMSO-d_6 (k_H/k_D = 1.01 in C₆D₆ and 0.994 in DMSO-d_6). The negligible isotope effect requires that the first step is rate-determining in path B.

Additional evidence for the CF₃⁻ ionization mechanism came from isotope tracer studies. When the reaction was carried out in CD₃OD, the product of the elimination reaction was not CF₃H, but

Scheme 1. Possible Mechanisms for Observed Reaction
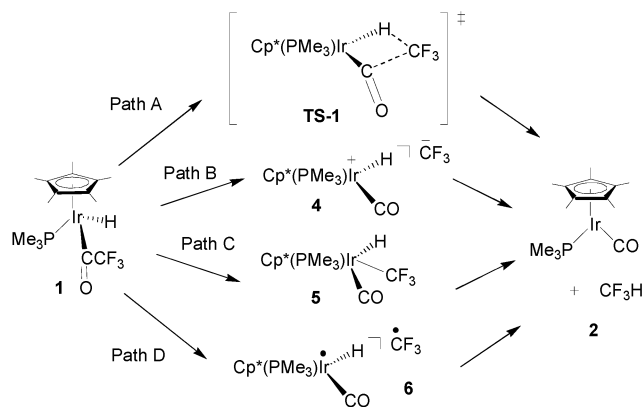
CF₃D. Heating **1** in CD₃OD at temperatures required to eliminate CF₃H did not result in deuterium incorporation into **1** before CF₃D was observed. In a second control experiment, heating **2** and CF₃H in CD₃OD in a sealed NMR tube at elevated temperatures did not result in any H/D exchange into the trifluoromethane. In CD₃CN or DMSO-d_6, solvents substantially less acidic than methanol, both CF₃H and CF₃D were generated in approximately 1:1.9 and 1:0.9 ratios. In the less acidic solvents, C₆D₆, THF-d_8, or DMF-d_7, only **2** and CF₃H were generated; no CF₃D was observed. Although the strong solvent effect argues against a radical version of the ionization mechanism (B), the radical alternative was ruled out conclusively by repeating the reaction in CH₃OD, which still led to CF₃-D.[12] A CF₃ radical should abstract the more weakly bound methyl hydrogen atom (BDE = 96.1 ± 0.2 kcal/mol) in preference to the more strongly bound hydroxyl-deuterium atom (104.6 ± 0.7 kcal/mol).[13]

Another indication that an organic group is able to undergo ionization from an iridium-bound acyl was gained by replacing the hydride in **1** with either a methyl group (**12**), or a chloride ligand (**13**). When **12** or **13** was heated in CD₃OD, CF₃D and the corresponding cationic-iridium methyl (**14**) and deuterido (**15**) carbonyl complexes were generated (eq 2).[14] The rate of elimination of CF₃⁻ from methyl complex **12** was 4 times faster than from **1**, while the elimination from chloride **13** was 51 times slower than from **1**. These data support the generation of an intermediate cation that is formed less favorably with an electron-withdrawing chloride on the metal center and more favorably with an electron-donating methyl group.[11] In aprotic solvents such as C₆D₆ or DMF-d_7, decomposition of **12** and **13** were observed upon heating.

(2)
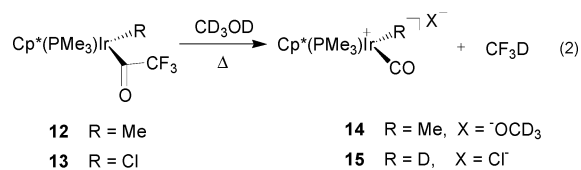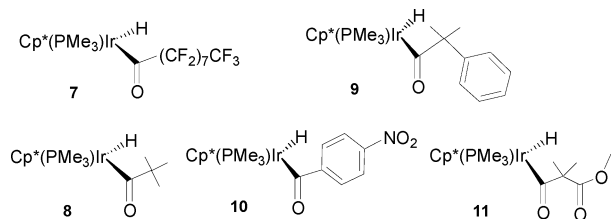
Figure 1. Other iridium acyl groups screened for elimination reaction.

To explore the generality of the elimination reaction, several other iridium acyl hydrides were examined (Figure 1). The perfluorononanoyl hydride (**7**) underwent clean elimination of 1-protioperfluorooctane in less than 20 min at 105 °C. In contrast, the *tert*-butyl- (**8**)- and 4-nitrophenyl (**10**)-substituted iridium acyl compounds were unreactive upon heating in C_6D_6 or DMSO-d_6 until 135 °C, at which time complete decomposition occurred. The dimethylbenzyl compound **9** underwent elimination slowly compared to **1** ($t_{1/2}$ = 13.3 h at 135.8 °C in C_6D_6), to give **2** and 2-phenylpropane. Compound **11** decomposed to **2** in low yield and unidentifiable organic products at a considerably longer reaction time compared to **1** ($t_{1/2}$ = 24 min at 135 °C in DMSO-d_6 and $t_{1/2}$ = 45 h at 135 °C C_6D_6). Unlike the conversion of **1** to **2**, the decomposition of **11** to **2** showed that upon prolonged heating, **2** also began to decompose. The decomposition reaction of **11**, possibly arising from ketene formation from the anionic ester, prevented further investigation.

The direct elimination of CF_3H from **1** (path A) and the CF_3 migration to iridium (path C) mechanisms were modeled using gas-phase DFT calculations.[15] Attempts to model the ion-pair (path B) have been challenging because of the high energetic cost of generating ions with substantial separation in the absence of a stabilizing solvent. The reaction leading to the observed products [**2** + CF_3H] was predicted to be highly exothermic (−19.6 kcal/mol). The formation of [**3** + CO] was also predicted to be slightly exothermic (−5.5 kcal/mol), although this product was not observed experimentally. Transition state **TS-1**, for the direct elimination of CF_3H from **1** to give the observed product [**2** + CF_3H], was predicted to lie 43.4 kcal/mol above **1**.[16] Comparing **TS-1** to **1**, calculations predict the C−CF_3 bond length of the acyl group to increase from 1.568 to 2.742 Å while the Ir−C bond length decreases from 2.010 to 1.896 Å (decreasing to 1.834 Å in **2**). There is negligible change (0.016 Å) in the Ir−H bond length upon going from **1** to **TS-1**. These changes indicate that the C−CF_3 bond undergoes substantial bond-breaking early in the reaction, leading to a transition state with considerable [Ir]C(O)−CF_3 bond cleavage before there is very much movement of the hydride ligand toward the CF_3 group. NBO analyses show that in **TS-1** the CF_3 fragment has a −0.719 charge build-up, while the remaining iridium fragment is positively charged. This represents a 0.619 increase of negative charge on the CF_3 fragment.[17] The calculated transition state is thus best described as an ion-pair with strong hydrogen bonding between the CF_3 and Ir−H. The lack of significant Ir−H bond-length change in the transition state is also consistent with the absence of an experimentally observed KIE.

The calculations of pathway C predict that migration of CF_3 to iridium should occur simultaneously with a Cp* ring slip via **TS-**

2, requiring a high energy cost of 49.0 kcal/mol. While intermediate **5** lies only 3.7 kcal/mol above **1**, compounds of this type are not common. Reductive elimination of CF_3H from **5** to give [**3** + CF_3H] proceeds via **TS-3**, with a barrier of 41.7 kcal/mol. Numerous attempts to model the conversion of **5** to [**3** + CO] all resulted in an almost barrierless elimination of CO. This computational result suggests that if intermediate **5** were formed, CO loss would rapidly generate **3**. The failure to observe **3** experimentally provides additional support for the absence of **5** in this reaction.

In summary, the thermal conversion of **1** to **2** constitutes a new type of elimination reaction occurring with organometallic fluoroacyl hydrides. We have presented strong evidence for the formation of a carbanion/metal cation pair intermediate in this reaction. Further calculations modeling the ion-pair path with solvent in the molecular environment are underway. Additional experiments to trap the intermediate ions are being explored.

Supporting Information Available: Characterization of all new compounds, kinetic procedures, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, California, 1987; Chapter 12.
(6) For an example of the addition of CF_3I to (COD)$PtMe_2$, see Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411. Group 12 bis-perfluoroalkyl complexes of Zn, Cd, and Hg have also been used as a source of perfluoroalkyl anions (Burton, D. J.; Wiemers, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 5014 and Eujen, R.; Hoge, B. *J. Organomet. Chem.* **1995**, *503*, C51).
(7) Early work in this group reported on the loss of H_2 from a related iridium formyl hydride complex under mild conditions. A preliminary experiment on the α-elimination of Cp*(PMe_3)Ir[C(O)C_3F_7](H) was also briefly mentioned. See Peterson, T. H.; Golden, J. T.; Bergman, R. G. *Organometallics* **1999**, *18*, 2005.
(8) A fluoroalkyl carbanion/metal cation pair has been reported in W and Mo chemistry. See Hughes, R. P.; Maddock, S. M.; Guzei, I. A.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **2001**, *123*, 3279.
(9) Addition of 5 eq of PMe_3 did not affect the observed rate of reaction.
(10) No aldehyde elimination was ever observed. Classical reductive elimination reactions of Ir(III) alkyl or aryl hydride compounds typically require much higher reaction temperatures. See Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537.
(11) See Supporting Information for details.
(12) For related experiments, see ref 8 and references therein.
(13) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255.
(14) See Supporting Information for details on the formation of **15**.
(15) Energies are reported relative to **1** and include zero-point vibrational energies (ZPE) and Gibbs free energy corrections at 298.15 K and 1 atm in the gas phase. See the Supporting Information and Figure S-2 for computational details.
(16) Although the gas-phase calculated energy of **TS-1** is high, it is a reasonable activation energy for a heterolytic bond-breaking process in the absence of solvent. Preliminary solvent-inclusive DFT calculations indicate that **TS-1** is significantly lowered in energy relative to **TS-2** or **TS-3**.
(17) *NBO*, 5.0; Theoretical Chemistry Institute, University of Wisconsin, Madison, Wisconsin, 2001.

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