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Heterolytic Activation of Hydrogen as a Trigger for Iridium Complex Promoted Activation of Carbon–Fluorine Bonds

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The cationic iridium(III) complex $[IrCF_3(CO)(dppe)(DIB)][BARF]_2$ where DIB = *o*-diiodobenzene, dppe = 1,2-bis(diphenylphosphino)ethane, and BARF = $B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$ undergoes reaction in the presence of dihydrogen to form $[IrH_2(CO)_2(dppe)]^+$ as the major product. Through labeling studies and ^1H and $^{31}P\{^1H\}$ NMR spectroscopies including parahydrogen measurements, it is shown that the reaction involves conversion of the coordinated CF_3 ligand into carbonyl. In this reaction sequence, the initial step is the heterolytic activation of dihydrogen, leading to proton generation which promotes α-C–F bond cleavage. Polarization occurs in the final $[IrH_2(CO)_2(dppe)]^+$ product by the reaction of H_2 with the Ir(I) species $[Ir(CO)_2(dppe)]^+$ that is generated in the course of the $CF_3 \rightarrow CO$ conversion.

The activation of carbon−fluorine bonds has attracted considerable attention in the past decade, in part because of the challenge that such a stable entity represents for facile activation and in part because of interest in rendering inert fluorocarbons more reactive. Reports have described that fluoroalkyls, once coordinated to a metal ion, are subject to α-F electrophilic attack by strong Lewis acids with consequent fluorocarbene generation.[1−9] In a recent study by Caulton and co-workers, the metal center of an electrophilic trifluoromethyl complex with a labile or vacant coordination site was shown to function in this capacity for intramolecular fluoride transfer.[2,3] The use of protons as the electrophile for attack on α-F from either coordinated water or added mineral acid has also been documented,[4−8] and in a number of examples, trifluoromethyl groups have been converted to carbonyl ligands. In the present study, we describe a similar transformation in which heterolytic activation of dihydrogen serves as the trigger for the conversion.[17] The reaction derives from ongoing interest in the chemistry of cationic iridium(III) complexes having labile ligands. In this regard, we recently reported $[IrCF_3(CO)(dppe)(DIB)][BARF]_2$ (**1**) and its methyl analogue, where DIB = *o*-diiodobenzene, dppe = 1,2-bis(diphenylphosphino)ethane, and BARF = $B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$.[10] The weakly chelating DIB was found to be labile enough for facile substitution and stable enough for isolation and storage of the complex. Both complex **1** and its methyl analogue were also determined to function as cationic initiators for polymerization of different olefins.

Complex **1** reacts slowly with dihydrogen over several hours at room temperature forming one major product. ^1H and $^{31}P\{^1H\}$ NMR spectra at the end of the reaction, Figure 1, reveal a complex with inequivalent phosphine donors (δ 28.9 and 24.3, $J_{P-P} = 2.7$ Hz) and two hydride ligands observable at δ −9.83 (ddd, $J_{P-H} = 108$ and 13.6 Hz, $J_{H-H} = 4.4$ Hz) and −10.84 (td, $J_{P-H} = 14.8$ Hz). The coupling pattern of the δ −9.83 resonance indicates both trans and cis orientations relative to the two phosphine donors of dppe, while the coupling of the δ −10.84 resonance shows that it is cis to both phosphine donors. The hydride coupling patterns are thus similar to those previously reported for $IrH_2(CO)(dppe)X$ complexes,[11,12] but the nature of X was uncertain based on the absence of any observable $^1H-^{19}F$ coupling or ^{19}F resonance corresponding to a metal-bound CF_3 or CF_2 ligand.

An electrospray MS analysis of the product solution showed a parent ion peak corresponding to 26 mass units more than $IrH_2(CO)(dppe)$. Since H_2 reductive elimination

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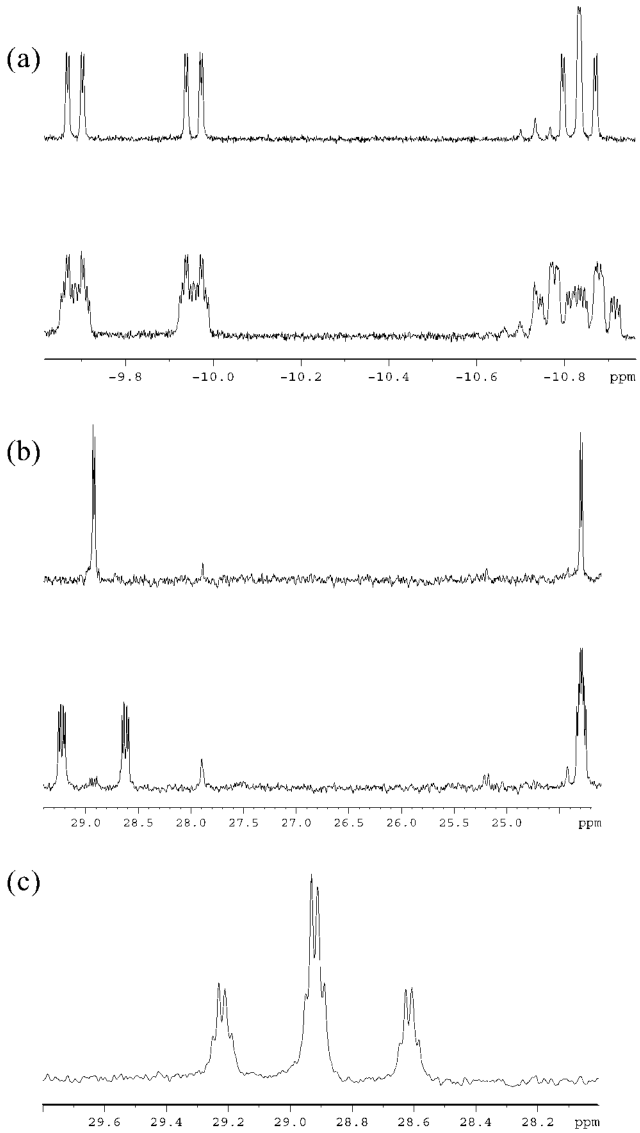

Figure 1. ^1H (hydride region) and $^{31}P\{^1H\}$ NMR spectra from reaction of **1** with H_2. (a) Hydride region before (top trace) and after (bottom trace) addition of ^{13}CO to **2**: hydrides at δ −9.83 ($J_{C-H} = 5.2$ Hz, trans to ^{31}P) and −10.84 ($J_{C-H} = 40$ and 6 Hz, trans to ^{13}CO). (b) ^{31}P NMR spectra before (top trace) and after (bottom trace) addition of ^{13}CO to **2**: dppe phosphines at δ 28.92 (ddd, $J_{C-P} = 98$ and 7.2 Hz, trans to ^{13}CO) and 24.28 (m). (c) The δ 28.92 resonance in the $^{31}P\{^1H\}$ spectrum obtained from reaction using **1-^{13}CO** with H_2: the coupling pattern indicates scrambling of the ^{12}CO and ^{13}CO ligands of **2**.

from the dihydride product occurs readily based on parahydrogen induced polarization results described below and since the ESMS experiment proceeds under conditions strongly favoring reductive elimination,[13] the observed ion corresponds to a dehydrogenated species and the remaining ligand has a mass of 28. An FT-IR spectrum of the product obtained using D_2 to eliminate M−H stretches revealed two bands at 2122 and 2088 cm^{-1}, thereby establishing CO as the undetermined ligand. Definitive confirmation of the major product as $IrH_2(CO)_2(dppe)^+$ (**2**) was achieved by exchange of ^{13}CO into the product, yielding the ^1H and ^{31}P NMR spectra shown in Figure 1 with increased complexity of ^1H and ^{31}P resonances due to coupling of hydride and phosphine ligands to *two* ^{13}CO ligands (see Figure 1 caption for coupling constants).

The reaction of **1** with H_2 was investigated using parahydrogen induced polarization (PHIP)[14] to shed light on H_2 activation in the reaction and possibly observe reaction intermediates. The PHIP-enhanced spectrum (see Supporting Information) is observed after heating a dichloromethane solution of **1** to 45 °C in the NMR spectrometer. The major polarized resonances are those of final product **2**, which would result from H_2 oxidative addition to $Ir(CO)_2(dppe)^+$. A second set of polarized resonances is also seen at δ −8.44 (ddd, $J_{H-H} = 4.4$ Hz, $J_{P-H} = 112$ and 16 Hz) and −17.40 (ddd, $J_{H-H} = 4.4$ Hz, $J_{P-H} = 11$ and 15 Hz), but the lack of additional coupling to CF_3 or CF_2 ligands indicates that these resonances do not result from an initial H_2 addition product. In fact, when the reaction is rerun with a different sample of **1**, these resonances are only seen *after* the formation of **2**.[15] The PHIP experiments thus do not give evidence of any *initial* species formed from H_2 addition to **1** such as an Ir(V) dihydride, which would suggest that initial dihydrogen activation proceeds via heterolytic splitting of H_2. The reaction of **1** with H_2 may proceed via a dihydrogen complex, and it is well-known that cationic dihydrogen complexes readily dissociate H^+.[16] This conclusion means that transformation of **1** including reduction of Ir(III) takes place *prior* to the PHIP-producing dihydrogen addition. The observation of PHIP in **2** indicates that H_2 addition to the metal center is pairwise and that the cycle of H_2 addition and elimination occurs readily for this system. Another species identified in the PHIP spectrum is the monohydride complex [IrH(CO)(DIB)(dppe)][BARF]$_2$ that has been prepared independently from $IrH(CO)(dppe)(OTf)_2$ + DIB + Na$^+$BARF$^-$; this species does not show polarization and is not on the path to producing **2**.

The fate of the CF_3 group in **1** and the origin of the second carbonyl were explored by carrying out the reaction of H_2 with ^{13}CO-labeled **1**. Prior experiments had failed to give any evidence of CHF_3 (a possible reductive elimination product) or any other readily discernible organo−fluorine compound originating from the trifluoromethyl ligand despite ^{19}F NMR spectral analysis at −94 °C (bp CF_3H = −84 °C) or GC/MS analysis of the reaction mixtures. From the reaction between **1-^{13}CO** (93% ^{13}CO enriched) and H_2, it was established that unlabeled CO is generated, leading to a mixture of ca. 50% labeled isotopomers of **2**. This is shown definitively by the $^{31}P\{^1H\}$ NMR resonance at δ 28.9 in

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[13] The electrospray MS analyzed for the iridium(I) complex $Ir(CO)_2(dppe)^+$. Under the conditions of the analysis, the sample is injected into a nitrogen stream at 300 °C leading to facile H_2 reductive elimination.

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[15] The second set of polarized resonances may be due to $IrH_2Cl(CO)(dppe)$ based on the chemical shift of the upfield hydride resonance.

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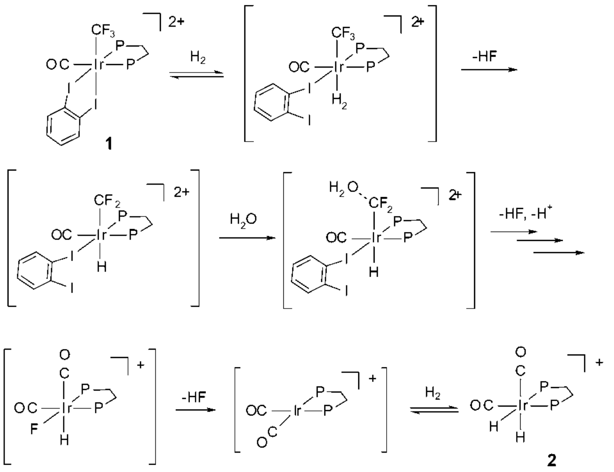
Figure 1c, which provides evidence of the phosphine being trans *and* cis to ~1:1 mixtures of labeled and unlabeled carbonyl ligands. The labeling experiment, the ^{19}F NMR analysis of reaction solutions, and the dominance of **2** as the final metal complex product give compelling support to the notion that the second carbonyl results from the CF_3 ligand.

In previously reported studies,[1,4–9] the conversion of coordinated CF_3 to CO has been promoted by electrophilic attack of strong Lewis acids or mineral acids on an α-F atom followed by addition of H_2O to the resulting difluorocarbene ligand. In the present study, weak ligation by DIB allows H_2 coordination and heterolytic activation to yield H^+ for α-F attack.[17] It is possible that η^1-DIB facilitates this proton transfer process. The elimination of HF then initiates a sequence that includes CF_2 hydration from adventitious water, proton loss, and two additional HF eliminations leading to the Ir(I) species $Ir(CO)_2(dppe)^+$. Scheme 1 illustrates some of the key steps and intermediates in this conversion. Indirect support for the importance of H^+ generation in promoting this sequence is given by the fact that while facile substitution of MeCN into **1** proceeds by generation of the labile species $[Ir(CF_3)(CO)(MeCN)(\eta^1\text{-}DIB)(dppe)]^{2+}$, a similar conversion of CF_3 into CO is not observed.[10] While this η^1-DIB species is capable of functioning as an internal Lewis acid for α-F abstraction, it does not do so rapidly enough to initiate the conversion relative to completing the substitution to give $[Ir(CF_3)(CO)(MeCN)_2(dppe)]^{2+}$.

The described reactivity of **1** with dihydrogen illustrates the Lewis acidic behavior of the Ir(III) metal center, leading to heterolytic activation of H_2, a reactivity mode often seen with Ru(II) but rarely with Ir(III). The resultant H^+ generation and the lability of the Ir(III) center derived from **1** promote the facile cleavage of C−F bonds and the unusual conversion of trifluoromethyl to coordinated CO.

Scheme 1



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Note Added after ASAP: Reference 17, which involves hydrogen addition for the activation of α-C−F bonds, was inadvertently omitted from the version of this communication posted ASAP on March 21, 2002. It is included in the version posted on April 15, 2002.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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