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# Fluoro-Ligand Promotion of C−H Activation

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*Summary: Ethylene dehydrogenates $Ir(H)_2FL_2$ ($L = P^tBu_2Ph$) to give the metalated species* **1** *and* **2**. *These metalated species catalyze the exchange of deuterium from $C_6D_6$ to ethylene, and to ${}^tBu$ and ortho phenyl sites of coordinated L. This exchange is proposed to benefit from π-donation from F to Ir.*

Fluoride is a ligand which has been only modestly explored in organometallic and catalytic chemistry.[1] In particular, in addition to its σ-withdrawing (electronegative) effect, we have presented evidence[2] that the π-donating effect of fluoride is also maximal among the halide group (as it is among $BX_3$ analogs). This means that fluoride might be very influential in "operational unsaturation",[3] and in accelerating ligand dissociation steps (eq 1) and giving higher steady-state concentrations of "unsaturated" intermediates, all by F→M π-donation.

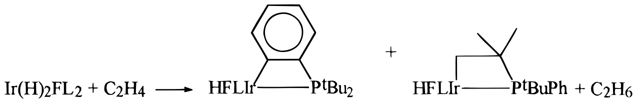
$$L_nM\overline{X} \rightleftharpoons L_{n-1}M\overset{\leftarrow}{=}X + L \qquad (1)$$

This greater π-donation by the most electronegative halide is not paradoxical but depends on the short M−F distance leading to optimal π-overlap. We report here some observations which extend our understanding of the influence of fluoride in the context of molecular reaction chemistry, where the M−F bond is retained throughout.

Halide metathesis with $Ir(H)_2ClL_2$ ($L = P^tBu_2Ph$) proceeds rapidly (10 min) at 25 °C in THF in the presence of excess anhydrous $[NMe_4]F$ to give complete conversion to $Ir(H)_2FL_2$.[4] The presence of one fluoride in the product is indicated by doublet structure in the hydride ($J_{F-H} = 42$ Hz) and ${}^{31}P\{{}^1H\}$ ($J_{P-F} = 6$ Hz) NMR signals, as well as by a ${}^{19}F$ NMR triplet. An X-ray structure determination of the non-hydrogen atoms of $Ir(H)_2FL_2$ has shown a T-shaped $IrFP_2$ unit.[5]

The Brønsted basicity of coordinated fluoride, as well as the unsaturation of $Ir(H)_2FL_2$, contributes to its rapid (time of mixing) reaction with $H_2$ (1 atm) in benzene at 25 °C to give complete conversion to $Ir(H)_5L_2$. The occurrence of this reaction is influenced by the strong bond in the coproduct, HF. No Ir−X bond cleavage occurs when $Ir(H)_2XL_2$ (X = Cl, Br, I, $O_3SCF_3$) is treated with $H_2$; only weak adduct formation is observed: $Ir(H)_2X(H_2)L_2$.[6]

If $Ir(H)_2FL_2$ is held at 50 °C for 12 h in toluene under an excess of ethylene, it is dehydrogenated to produce ethane and the following three products (**2** is found as two diastereomers, due to the chirality at both Ir and P):[7]



**1** **2**

Compounds **1** and **2** show AX ${}^{31}P\{{}^1H\}$ NMR patterns due to the large displacement of phosphorus chemical shift resulting from incorporation into a four-membered ring.[8] All show large ${}^2J(P-P)$ values (340−350 Hz), indicative of transoid location of the two phosphorus nuclei. These products are all the result of irreversible ethylene "scavenging" of hydride ligands from Ir and rapid trapping of highly unsaturated intermediates by intramolecular C−H oxidative addition. Ethylene and also ${}^tBuCHCH_2$ are particularly effective olefins for dehydrogenation of $Ir(H)_2FL_2$, apparently because they cannot be competitively isomerized to a (less reactive) internal (i.e., disubstituted) olefin. Thus, reaction of $Ir(H)_2FL_2$ with an excess of a substituted terminal olefin

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(1) Doherty, N. M.; Hoffman, N. W. *Chem. Rev.* **1991**, *91*, 553.

(2) Poulton, J. T.; Sigalas, M. P.; Folting, K.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 1476.

(3) Johnson, T. J.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1992**, *114*, 2725.

(4) **$Ir(H)_2F(P^tBu_2Ph)_2$.** To a flask containing anhydrous tetramethylammonium fluoride (1.2 g, 12.9 mmol) was added a solution of $Ir(H)_2Cl(P^tBu_2Ph)_2$ (1.0 g, 1.5 mmol) in 35 mL of THF. This heterogeneous yellow solution was stirred for 20 min at room temperature and filtered. The insoluble ammonium salts were washed with THF (2 × 3 mL) and the THF solutions combined. Removal of the THF *in vacuo* yielded a yellow-orange precipitate. This solid was washed with pentane (3 × 5 mL) to remove dark orange impurities. Recrystallization by layering of a saturated THF solution with pentane gave very large dark yellow crystals (695 mg, 71%). Anal. Calcd for $C_{28}H_{48}IrFP_2$: C, 51.12; H, 7.35. Found: C, 51.02; H, 7.5. ${}^1H$ NMR ($C_6D_6$, 25 °C): δ 8.35 (m), 7.2−7.06 (overlapping m), 1.50 (vt, $J_{PH} = 6.6$ Hz), −32.0 (dt, $J_{HF} = 42$ Hz, $J_{PH} = 12$ Hz). ${}^{31}P\{{}^1H\}$ NMR ($C_6D_6$, 25 °C): δ 62.0 (d, $J_{PF} = 6.0$ Hz). ${}^{19}F$ NMR ($C_6D_6$, 25 °C): δ −205 (tt, $J_{HF} = 42$ Hz, $J_{PF} = 6$ Hz). ${}^{13}C\{{}^1H\}$ NMR ($C_6D_6$, 25 °C): δ 137.2 (s), 134.0 (t, $J_{PC} = 18.9$ Hz), 129.7 (s), 127.3 (t, $J_{PC} = 4.4$ Hz), 36.4 (t, $J_{PC} = 11.1$ Hz), 30.8 (s).

(5) Crystallographic data (−171 °C): $a = 15.277(2)$ Å, $b = 16.424(2)$ Å, $c = 11.357(1)$ Å, $Z = 4$, space group $P2_12_12_1$; $R(F) = 0.0361$. There is a 70:30 disorder of two Ir and two F sites, and the hydrides were therefore not detected. Ir−F = 2.045(9) Å, and Ir−P = 2.325(3) and 2.323(3) Å; P−Ir−P = 176.6(3)°; and P−Ir−F = 93.3(3) and 89.2(3)°.

(6) Hauger, B. E.; Gusev, D.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 208.

(7) **Generation of $IrH(\eta^2\text{-}C_6H_4P^tBu_2)(F)(P^tBu_2Ph)$ and $IrH(\eta^2\text{-}CH_2CMe_2P^tBuPh)F(P^tBu_2Ph)$ Isomers.** In a 100-mL glass flask with a Teflon valve was placed a solution of $Ir(H)_2(F)(P^tBu_2Ph)_2$ (100 mg, 0.15 mmol) in 5 mL of toluene. This solution was degassed three times (freeze−pump−thaw) and 1 atm of ethylene introduced. The valve was closed tightly and the flask heated to 50 °C for 12 h with continuous stirring of the solution. During this time, the color of the solution changed from light orange to dark orange. the toluene was removed *in vacuo* and the resulting red oil extracted with pentane (3 × 5 mL). The pentane solution was evaporated to dryness *in vacuo* to yield a dark red solid. ${}^{31}P\{{}^1H\}$ NMR ($C_6D_6$, 25 °C): δ 53.3 [d, $J_{PP} = 340$ Hz, $IrH(\eta^2\text{-}C_6H_4P^tBu_2)(F)(P^tBu_2Ph)$ isomer], 52.6 [d, $J_{PP} = 346$ Hz, major diastereomer of $IrH(\eta^2\text{-}CH_2CMe_2P^tBuPh)F(P^tBu_2Ph)$], 45.7 [d, $J_{PP} = 348$ Hz, minor diastereomer of $IrH(\eta^2\text{-}CH_2CMe_2P^tBuPh)F(P^tBu_2Ph)$], 4.4 (d, $J_{PP} = 347$ Hz), −11.4 (d, $J_{PP} = 340$ Hz), −38.4 (d, $J_{PP'} = 348$ Hz). ${}^1H$ NMR ($C_6D_6$, 25 °C, hydride resonances only): δ −34.0 [br s, $IrH(\eta^2\text{-}CH_2CMe_2P^tBuPh)F(P^tBu_2Ph)$ diastereomers], −41.4 [apparent t, $J_{PH} = 11.4$ Hz, $IrH(\eta^2\text{-}C_6H_4P^tBu_2)(F)(P'Bu_tPh)$ isomer]. ${}^{19}F$ NMR ($C_6D_6$, 25 °C): δ −242.2 [m, $IrH(\eta^2\text{-}C_6H_4P^tBu_2)(F)(P^tBu_2Ph)$ isomer], −243.6 [m, minor diastereomer of $IrH(\eta^2\text{-}CH_2CMe_2P^tBuPh)F(P^tBu_2Ph)$], −243.9 [m, major diastereomer of $IrH(\eta^2\text{-}CH_2CMe_2P^tBuPh)F(P^tBu_2Ph)$].

(8) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

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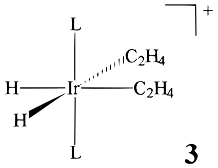
(1-hexene or 3-phenylpropene) at 75 °C causes complete isomerization to more highly substituted olefins (2- and 3-hexene and $\beta$-methylstyrene, respectively) within 4 h, with only very little (<5%) dehydrogenation of the Ir complex. Extended heating increases the yield of metalated complexes, but the dehydrogenation proceeds at a very slow rate (e.g., 35 equiv of 1-hexene causes only 50% conversion of $Ir(H)_2FL_2$ to **1** and **2** after 48 h at 75 °C). It is also significant that the distribution of products in the dehydrogenation of $Ir(H)_2FL_2$ is dependent on the olefin employed. This suggests kinetic control, and under conditions which do not subsequently reach equilibrium among the species **1** and **2**.

This dehydrogenation of $Ir(H)_2XL_2$ by olefins occurs only when X = F. Exposure of the chloride and iodide analogs to ethylene or 1-hexene under equivalent or more rigorous conditions (in triglyme up to 200 °C in a sealed tube) causes no dehydrogenation of the metal complex.

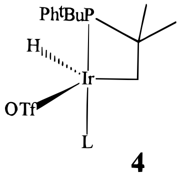
If the reaction of $Ir(H)_2FL_2$ with excess ethylene is monitored in $C_6D_6$ by $^1H$ NMR, one observes, only and cleanly, the equilibration of deuterium from benzene into the Ir−H, the $^tBu$, the ortho phenyl hydrogens of **1** and **2**, *and* the ethylene sites; the proton signal of benzene grows proportionately.[9] This same H/D exchange occurs if a preformed mixture of protio isomers of **1** and **2** is heated in $C_6D_6$ under $C_2H_4$, indicating that the exchange is not simply a property of $Ir(H)_2FL_2$ itself under ethylene (i.e., a more hydrogen-rich system than **1** and **2**).

We have established independently that mixtures of the all-protio metalated species **1** and **2** effect H/D exchange when heated in $C_6D_6$ in the absence of ethylene, so that ethylene only functions to *form* the reactive species but plays no essential role in the attack on benzene. Particularly because **1** and **2** are Ir(III) compounds, but are unsaturated, these H/D exchange reactions could occur by benzene (a) oxidative addition (implicating Ir(V)), (b) $\sigma$-bond metathesis on Ir(III), or (c) oxidative addition to $Ir^IFL_2$ (see below). In contrast, thermolysis of $IrH(\eta^2\text{-}P(C_6H_4)^tBu_2)(X)(P^tBu_2Ph)$ (X = Cl, Br, I) in $C_6D_6$ fails to show any H/D exchange under comparable conditions.

The triflate ($CF_3SO_3^-$) analog of $Ir(H)_2FL_2$ behaves very differently.[10] If $Ir(H)_2(OTf)L_2$ is treated with ethylene (1 atm, 25 °C) in $C_6D_6$, there is immediate formation of $[Ir(H)_2(C_2H_4)_2L_2]OTf$ (**3**), which quickly precipitates from this solution. While triflate thus behaves as a good leaving group, heating a slurry of this salt in $C_6D_6$ under 1 atm of ethylene for 2 h at 80 °C gives conversion to ethane and only one diastereomer of the molecular (i.e., OTf is coordinated) product **4**, where a $^tBu$ C−H bond has oxidatively added to Ir.



**3**



**4**

Moreover, in comparison to the fluoro analog under comparable conditions, this product is much less deuterated (growth of $C_6D_5H$ is observed), indicating a slower rate for H/D exchange with **4** and also establishing that OTf and F must be present in the catalytically active species to influence the rate. Since triflate and fluoride are at opposite extremes in $(\sigma + \pi)$ donor ability, as judged by $\nu$(CO) values of $L_nM(CO)X$ (X = F, OTf) species,[2,11] we suggest that the rate differences observed here are influenced by the better donor ability of fluoride, perhaps in stabilizing a phosphine-loss species of a metalated phosphine, $IrHX(\eta^2\text{-}C{\sim}P)$, which then reacts with $C_6D_6$ (or with olefin).

It was reported recently[12] that $Cp^*Ir(PMe_3)(aryl)F$ shows "surprisingly easy Ir−F ionization". The four-electron destabilization which results from repulsion between fluorine lone pairs and filled $d_\pi$ orbitals in this or any *saturated* metal complex promotes such ionic loss of $F^-$.[13] The molecules we report here, because they are unsaturated, lack this propensity, and thus fluoride actively participates both before and after the adduct is formed with substrate. These thus represent two conceptually distinct ways to manipulate reactivity by incorporation of the lightest halide. Finally, it might have been generally thought that ortho metalation of a pendant phenyl ring is a nuisance side reaction. This is *not* the case, at least in $IrHF(\eta^2\text{-}C_6H_4P^tBu_2)(P^tBu_2Ph)$, since the strain in the small ring represents latent reactivity that can be triggered by an attacking arene C−H bond.[14] Strain provides a facile route to unsaturated Ir(I), *via* the reductive elimination of the metalated C−H bond, which is absent in the parent $Ir(H)_2F(P^tBu_2Ph)_2$ species.

Whatever the detailed formula of the transient(s) involved here, its high reactivity is implicated by its lack of selectivity: it reacts with aliphatic, olefinic, and aryl C−H bonds. We have independent experimental observations for equilibria 2 and 3.[15,16] Moreover, phosphine loss occurs at a much higher rate (>$10^3$) for the metalated species than for $Ir(H)_2XL_2$, thus implicating eq 3 in the $IrH/C_6D_6$ exchange observed here. Reductive elimination of Ir−C and Ir−D bonds in equilibrium 2[17] provides a mechanism for deuteration of $^tBu$ and ortho

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[9] **H/D Exchange in $C_6D_6$ Solutions of $Ir(H)_2F(P^tBu_2Ph)_2$ and $C_2H_4$.** A solution of $Ir(H)_2F(P^tBu_2Ph)_2$ (15 mg, 0.02 mmol) in 0.6 mL of $C_6D_6$ was placed in an NMR tube. This solution was degassed three times (freeze−pump−thaw) and 700 Torr of ethylene introduced before flame-sealing of the tube. The solution was mixed thoroughly for 1 h at room temperature before $^1H$ assay. The $^1H$ NMR spectrum shows very little (*ca.* 2%) conversion to metalated species after this time. The sample was then heated to 75 °C for 6 h, during which time the color changed from yellow to light brown. $^{31}P\{^1H\}$ NMR ($C_6D_6$, 25 °C): $\delta$ 52.6 [d, $J_{PP}$ = 347 Hz, major diastereomer of $IrH(\eta^2\text{-}CH_2CMe_2P^tBuPh)F(P^tBu_2Ph)$], 45.7 [d, $J_{PP'}$ = 348 Hz, minor diastereomer of $IrH(\eta^2\text{-}CH_2CMe_2P^tBuPh)(P^tBu_2Ph)$], 4.4 (d, $J_{PP'}$ = 347 Hz), −38.4 (d, $J_{PP'}$ = 348 Hz). $^1H$ NMR ($C_6D_6$, 25 °C): $\delta$ 7.15 (s, $C_6D_5H$), 0.80 (s, $C_2H_6$); Ir−H, $^tBu$, and ortho Ph peaks were absent.

[10] Cooper, A. C.; Huffman, J. C.; Caulton, K. G. Manuscript in preparation.

[11] Vaska, L.; Peone, J. *J. Chem. Soc. D* **1971**, 418. Merrifield, J. A.; Fernandez, J. M.; Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022.

[12] Veltheer, J. E.; Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 12478.

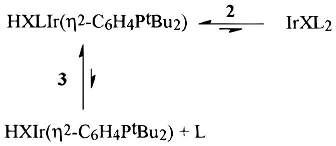
[13] Caulton, K. G. *New J. Chem.* **1994**, *18*, 25.

[14] Belli, J.; Jensen, C. M. *Organometallics* **1996**, *15*, 1532.

[15] Cooper, A. C.; Caulton, K. G. *Inorg. Chim. Acta* **1996**, *251*, 41.

[16] Cooper, A. C.; Huffman, J. C.; Caulton, K. G. *Organometallics*, submitted for publication.

[17] Demonstrated for X = Cl[15] and for X = CCPh.[16]



phenyl sites. Work is currently underway to further specify the mechanism of these several C−H activation processes and the special role played by “hard” ligands such as fluoride and triflate.

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**Supporting Information Available:** Text giving details of the syntheses and characterization data for the compounds in this paper and details of the X-ray crystal structure determination of Ir(H)$_2$F(P$^t$Bu$_2$Ph)$_2$ (3 pages). Ordering information is given on any current masthead page.

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