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Exceptionally Low-Temperature Carbon−Hydrogen/Carbon−Deuterium Exchange Reactions of Organic and Organometallic Compounds Catalyzed by the Cp*(PMe$_3$)IrH(ClCH$_2$Cl)$^+$ Cation

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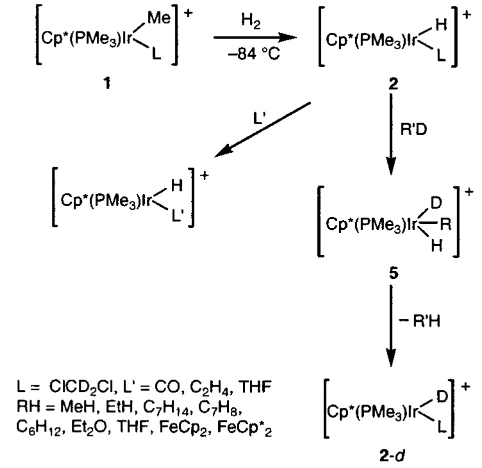
Because of the role that metal-mediated carbon−hydrogen bond activation could play in the conversion of saturated hydrocarbons to more useful, functionalized organic compounds, much effort has gone into developing mild methods for carrying out this transformation in solution.[1] Most of the classical methods for activating C−H bonds involve oxidative addition reactions with uncharged, electron-rich, coordinatively unsaturated metal centers (eq 1). Recently, however, several new C−H activation reactions have been discovered that take place at cationic "electrophilic" late transition metal centers, creating a resurgence of interest in this class of C−H activating reactions (eq 2).[2−8] Most of the reactions in this class require elevated temperatures. The precursors are nearly always metal alkyls or aryls: few late metal hydrides have been shown to promote these reactions. Herein, we report (a) the synthesis of a long-sought simple, monomeric cationic iridium hydride, (b) the demonstration that this material induces alkane C−H activation at an unexpectedly high rate and surprisingly low temperature, and (c) that this mode of C−H activation likely involves a dihydridoalkyl intermediate that undergoes reductive elimination of only alkane and not H$_2$.

$$\mathrm{M + R\text{-}H \longrightarrow R\text{-}M\text{-}H} \qquad (1)$$

$$\mathrm{[M\text{-}CH_3]^+ + R\text{-}H \longrightarrow [M\text{-}R]^+ + CH_4} \qquad (2)$$

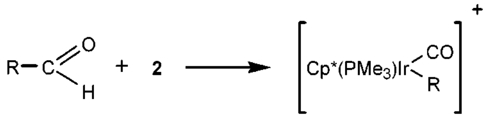
The cation system, [Cp*(PMe$_3$)IrMe(ClCH$_2$Cl)]$^+$[B(3,5-C$_6$H$_3$-(CF$_3$)$_2$)$_4$]$^-$,[3] is known for its ability to activate C−H bonds. For example, [Cp*(PMe$_3$)IrMe(ClCH$_2$Cl)]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (**1**) reacts with isotopically labeled methane at −10 °C to exchange the iridium-bound methyl group for a labeled one. We have been interested in synthesizing complexes such as [Cp*(PMe$_3$)IrH-(ClCH$_2$Cl)]$^+$X$^-$ (**2**) to compare them to the analogous methyliridium cation. Methods designed to provide this material led to salts of the trihydrides [Cp*(PMe$_3$)IrH$_3$]$^+$ (**3**)[9] and/or [Cp*(PMe$_3$)-HIr-H-IrH(PMe$_3$)Cp*]$^+$ (**4**),[10] by unknown mechanisms.

Scheme 1. Generation and Reactions of **2**



We found a solution to this vexing problem while developing a new method for generating methyl cation **1** that utilizes the ability of fluoroarylboranes to abstract a methyl group from charge-neutral metal centers.[11] Thus, addition of trispentafluorophenylborane[12] to Cp*(PMe$_3$)IrMe$_2$[13] in CD$_2$Cl$_2$ at −84 °C results in the quantitative formation of methyl cation **1**.[14] A slight excess of borane (1.2 equiv) is used to ensure complete conversion to the desired cationic methyliridium complex.

Addition of an atmosphere of dihydrogen at −84 °C to solutions of **1** in dichloromethane solvent results in the immediate loss of methane and the formation of **2**. The light yellow hydrido cation **2** is thermally unstable at temperatures above about −20 °C, where it decomposes to **3** and/or **4**; thus it cannot be isolated. The ^{1}H NMR spectrum at −75 °C reveals an iridium hydride resonance (coupled to phosphorus) at −12.1 ppm, a chemical shift farther downfield than that of most neutral iridium hydrides in this series. The methyl borate signal at 0.45 ppm indicates no direct interaction between the ions.[15,16] As shown in Scheme 1, hydrido complex **2** is easily trapped by treatment with ethylene (93% NMR),[17] CO (94%),[18] or tetrahydrofuran (THF) to produce the thermally robust adducts [Cp*(PMe$_3$)IrH(L′)]$^+$ (L′ = C$_2$H$_4$, CO, THF). Reaction with the aldehydes ethanal and benzaldehyde (eq 3) also produced the expected alkyl−carbonyl cationic



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products at −84 °C (94% and 92% NMR yields, respectively).[19] A small amount of the trihydrido cation **3** (ca. 3% to 10%) is formed during the synthesis of **2**. Complex **3** does not interfere with subsequent reactivity of the monohydrido cation **2**. The low solubility of dihydrogen in CD_2Cl_2 at −84 °C is likely responsible for preventing high conversion of **2** to **3** at −84 °C.

Interest in understanding the thermal decomposition of monohydride **2** to form trihydride **3** in the presence of alkanes[20] prompted us to carry out the decomposition of **2** in the presence of cyclohexane-d_{12}. This resulted in the exclusive production of **3**-d_3, indicating that the alkane is the source of the iridium-bound deuterium in the product. Monitoring the reaction at temperatures below −20 °C revealed that the iridium-bound hydrogen in **2** undergoes H/D exchange with cyclohexane-d_{12} *before* thermal decomposition produced **3**-d_3. To confirm this observation, the isotopically labeled complex $[Cp^*(PMe_3)IrD(ClCD_2Cl)]^+[MeB(C_6F_5)_3]^-$ (**2**-*d*) was prepared. Reaction of **2**-*d* with cyclohexane at −40 °C resulted in the formation of **2** and cyclohexane-*d*. Even faster exchange was observed between **2** and 4 equiv of benzene-d_6 in CD_2Cl_2 (100% apparent exchange into the hydride position after 1 h at −84 °C). To show that alkane substrates were the actual sources of hydrogen, reactions of **2**-*d* with several alkanes were performed. In each case, the resonance corresponding to the hydride of **2** grew in intensity and increasing deuteration of the hydrocarbon was evident. Dichloromethane-d_2 is not the source of deuterium in these exchanges, as no H/D exchange is noted when undeuterated hydrocarbons are treated with **2** in CD_2Cl_2.

Since the late 1960s, a few homogeneous metal systems have been found which thermally promote the exchange of hydrogen and deuterium between hydrocarbon substrates and a sacrificial deuterium donor.[21−26] However, these systems require temperatures substantially higher than those required for exchanges catalyzed by **2**.

Our experiments revealed that hydrido cation **2** could catalyze H/D exchange between molecules containing C−H bonds of differing bond strengths, acidities, and hybridizations. The results are summarized in Table 1. For example, all the isotopomers of methane are produced when a 1:1 mixture of CH_4 and CD_4 is treated with **2**. Using C_6D_6 as a deuterium source, hydrido cation **2** is a very active H/D exchange catalyst. Treatment of a solution

$$R-H \xrightarrow{2\ \text{mol}\ \%\ \mathbf{2}\ /\ C_6D_6} R-D \qquad (4)$$

of **2** in CD_2Cl_2 (0.75 mL) with C_6D_6 (0.5 mL) and an atmosphere of methane produced all the isotopomers of deuterated methane. The H/D exchange is observed as low as −60 °C, with a half-life of about 20 min at −30 °C. To our knowledge, this is the lowest temperature homogeneous "electrophilic" alkane C−H activation reaction that has been reported. We have observed no detectable deuterium incorporation into the Cp* or PMe_3 ligands of the catalyst at temperatures below −20 °C. Additionally, trihydrido cation **3** is unable to effect H/D exchange at these temperatures.

Table 1. H/D Exchange Catalyzed by **2** or **3**[27]

substrate	catalyst	% D inc.	*T* (°C)	time[a]
methane	**2**	96	−20	2 days
ethane	**2**	75	−20	2 days
C_6H_{12}	**2**	13	−30	120 min
$CH_3C_6H_{11}$	**2**	20	−30	65 min
toluene	**2**	40	−20	65 min
ferrocene	**2**	97	−20	600 min
$FeCp^*_2$	**2**	90	−30	180 min
Et_2O	**2**	61	−30	80 min
THF	**2**	49	−10	75 min

[a] See refs 23 and 24 for earlier routes to the deuterated ferrocenes. The times listed are those used to establish the maximum extent of deuteration that could be reached at a convenient reaction time and temperature; in some cases (e.g., the ferrocenes), these times are substantially longer than those required for extensive deuterium incorporation at lower temperatures.

Ferrocene and decamethylferrocene are the fastest reacting substrates in the group of materials examined, being deuterated rapidly at −84 °C. Toluene is also deuterated by action of **2**. In the case of toluene, the meta and para positions are deuterated rapidly and at low temperatures (−84 °C), but the ortho hydrogens resist deuteration even while the methyl group is deuterated at −20 °C.

Diethyl ether and THF exchange more slowly than the hydrocarbons and ferrocenes, requiring long reaction times at temperatures just below −10 °C to effect significant deuterium incorporation into the α and β positions, respectively.[28] Although ethers are successfully deuterated, more strongly binding ligands such as ethylene, pyridine, and phosphines poison the catalyst **2**, and no exchange occurs. Trimethylsilane acts analogously to H_2, producing $[Cp^*(PMe_3)IrH_2(SiMe_3)]^+[MeB(C_6F_5)_3]^-$.

Whether the exchange process involves oxidative addition or σ-bond metathesis is a fundamental question; at present, neither can be ruled out. On the basis of what we have learned about C−H activation reactions of **1**, the most likely mechanism begins with the oxidative addition of a C−H bond to the metal center of the hydride. This leads to a dihydridoalkyl Ir(V) intermediate **5** (Scheme 1) with an unusual property: it undergoes elimination of R−H easily, but H_2 less easily,[29] since we never observe the formation of alkyl complexes in these exchange reactions. Our present efforts are directed at understanding this selectivity and improving the scope and efficiency of the H/D exchange reactions.

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Supporting Information Available: Synthetic and spectroscopic details for new compounds and experimental details for the H/D exchanges (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) These products are similar to the known triflate salts, see ref 2.

(20) Warming the THF-solvated species $[Cp^*(PMe_3)IrH(THF)]^+[MeB(C_6F_5)_3]^-$ above −10 °C produced trihydrides **3** and **4** rather than the carbene complex $[Cp^*(PMe_3)Ir(H)C_4H_6O]^+[MeB(C_6F_5)_3]^-$ observed on reaction of methyl analogue **1** with THF.

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