Facile Intermolecular Activation of C–H Bonds in Methane and Other Hydrocarbons and Si–H Bonds in Silanes with the Ir(III) Complex $Cp^*(PMe_3)Ir(CH_3)(OTf)$

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The activation of compounds containing aliphatic C–H bonds and the transformation of these materials into functionalized organic compounds are major goals of organometallic and catalytic chemistry.[1-3] Late transition metals typically react with hydrocarbons by oxidative addition of C–H bonds to low-valent, electron-rich metal centers, such as the reactive Ir(I) species Cp*IrL (Cp* = (η^5-C_5Me_5); L = tertiary phosphine).[4] We now report that the more electron-deficient iridium(III) center in the trifluoromethanesulfonate (triflate) complex $Cp^*(PMe_3)Ir(CH_3)(OTf)$ (**1**, OTf = OSO_2CF_3) reacts with several types of aliphatic C–H bonds, including that in methane, as well as with the Si–H bonds in silanes.

Complex **1** was prepared in 80% yield by the reaction of $Cp^*(PMe_3)IrMe_2$[5] with $Cp^*(PMe_3)Ir(OTf)_2$[6] or by protonation of $Cp^*(PMe_3)IrMe_2$ with HOTf (also 80%). The structure of **1** was determined by X-ray diffraction; an ORTEP diagram is included in Scheme I, and structural data are provided as supplementary material. In the course of initiating a study of the triflate-replacement chemistry of **1**, we found that dissolution of this material in benzene at room temperature led to quantitative conversion to the corresponding phenyl triflate complex $Cp^*(PMe_3)Ir(C_6H_5)OTf$ (**2**)[7] and methane (Scheme I).

Charge-neutral iridium(III) and ruthenium(II) complexes are among the few late transition-metal complexes that have been shown to undergo intermolecular σ-bond methathesis-type exchange reactions with arenes (the relatively activated C–H bonds in metallocenes and aldehydes also react).[8-14] However, we felt that the greater electrophilicity of **1** (and the cation that would be derived from it by ionization of the triflate ion) might make its chemistry more similar to that observed with early metals, lanthanides, and actinides.[15-22] This led us to examine the reaction of **1** with methane. Figure 1a illustrates the ^1H NMR spectrum of **1** in CD_2Cl_2 under 2 atm of $^{13}CH_4$ immediately after being mixed at room temperature. As can be seen by inspection of Figure 1b, *after 6 h at 45 °C, incorporation of ^{13}C-labeled methane into 1 to give $Cp^*(PMe_3)Ir(^{13}CH_3)(OTf)$ and CH_4 had occurred to an extent of 50%.*

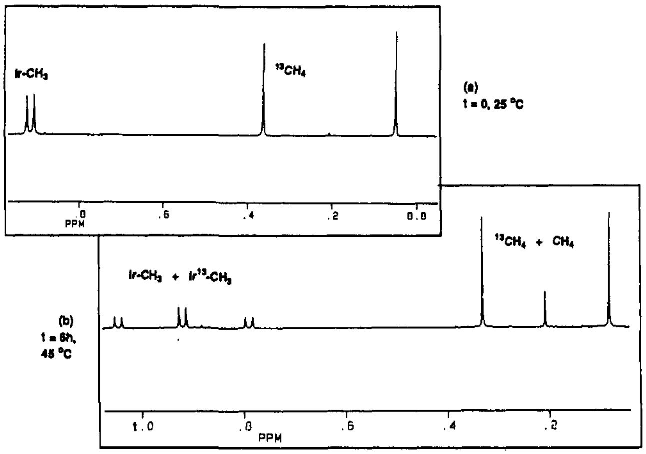
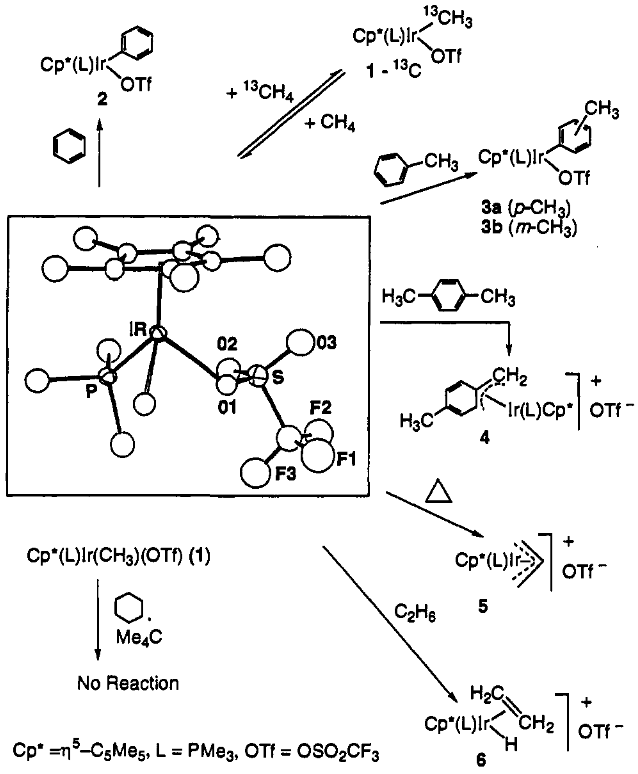


Figure 1. (a) High-field region of the ^1H NMR spectrum of a solution of (η^5-C_5Me_5)$(PMe_3)Ir(CH_3)(OSO_2CF_3)$ (**1**) in CD_2Cl_2 solution under 2 atm of $^{13}CH_4$ immediately after mixing of the solution at 25 °C. (b) High-field region of the ^1H NMR spectrum of the mixture described in a after heating of the mixture for 6 h at 45 °C.

Scheme I



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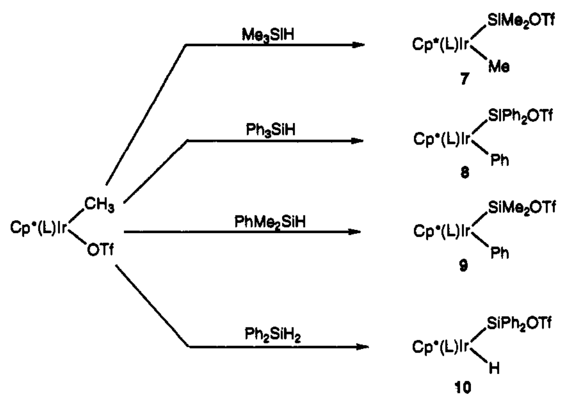
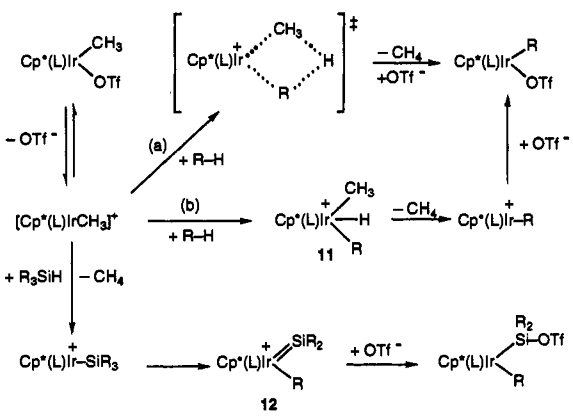
Scheme II



Triflate **1** reacts with certain other hydrocarbons, albeit with rearrangement of the apparently generated initial product. The products of these reactions are illustrated in Scheme I.[23] In contrast to the behavior of the photochemically or thermally induced C–H activation via the transient Cp*IrPMe$_3$,[24] however, there appear to be significant steric restrictions on the Ir(III) C–H activation process. This is exemplified by the fact that neither cyclohexane nor neopentane undergoes the C–H activation reaction (only slow decomposition of the triflate was observed in CD$_2$Cl$_2$ after 24 h at 45 °C). Steric control also plays a role in the competition of aryl and benzyl C–H bonds for the iridium center in **1**. Toluene's reactivity is similar to that of benzene; the reaction with **1** leads to aromatic rather than benzylic hydrogen substitution. However, only attack at the para and meta C–H bonds, leading to **3a** and **3b**, is observed (1.25:1 ratio, statistically corrected).[25] In contrast, *p*-xylene undergoes selective attack at its benzylic C–H bonds, giving compound **4**. The lack of ortho substitution in toluene and *p*-xylene is presumably a result of steric shielding of the proximate C–H bonds by the methyl groups. Reaction of **1** with cyclopropane leads to the cationic allyl complex **5**, and ethane gives the hydrido(ethylene) complex **6**. The structure of **6** was determined by X-ray diffraction (the hydride was not located) from the independently synthesized BF$_4^-$ complex **6a**; details are provided as supplementary material. We believe that these materials arise by initial formation of the cyclopropyl and ethyl triflate complexes followed by ring-opening and β-elimination, respectively.

The methyl triflate **1** also reacts efficiently with silanes, but once again rearrangement of the (presumed) initial Si–H activation products is observed. Trimethylsilane, for example, produces methane but does not give the expected (trimethylsilyl)-iridium complex. Instead, the methyliridium dimethylsilyl triflate Cp*(L)Ir(Me)(SiMe$_2$OTf) (**7**) is obtained in 88% yield (Scheme II).[26] Similarly, triphenylsilane leads to a 93% yield of the silyl triflate Cp*(L)Ir(Ph)(SiPh$_2$OTf) (**8**). We have carried out preliminary NMR experiments with silanes having different substituents to obtain an idea of the relative silicon-to-iridium migratory aptitude of the initially Si-bound substituents. We observed that phenyldimethylsilane leads exclusively (97%) to the phenyl migration product Cp*(L)Ir(Ph)(SiMe$_2$OTf) (**9**) and that diphenylsilane gives only the hydride-migration product Cp*(L)Ir(H)(SiPh$_2$OTf) (**10**) (89%).

Scheme III



The facile Ir(III) C–H and Si–H bond activations reported here raise a number of intriguing mechanistic questions. Cp*(PMe$_3$)Ir(Me)(Cl) is completely unreactive toward benzene up to 100 °C, demonstrating that the presence of the triflate group is critical to the efficiency of these reactions. Conductivity experiments suggest that **1** is slightly dissociated under the reaction conditions and more highly dissociated at lower initial concentrations (see supplementary material). We therefore propose that the first step of the reaction involves ionization of **1** to Cp*(PMe$_3$)Ir(CH$_3$)$^+$ and OTf$^-$ (and/or the corresponding ion pair), and then the C–H and Si–H bonds react at the cationic iridium center (Scheme III). A second issue concerns whether the activation step takes place by a concerted σ-bond metathesis transition state (path a in Scheme III) or by oxidative addition to an Ir(V) intermediate (**11**) followed by reductive elimination of methane (path b). Kinetic and isotope effect experiments designed to distinguish between these alternatives are currently underway. In the silane reactions, it is possible that cationic silylene intermediates **12** may be involved; experiments with silicon substituents designed to stabilize tricoordinate silicon are also in progress. Finally, preliminary evidence that other types of C–H bonds, such as those in ethers and other functionalized organic compounds, also react with **1** is being pursued. The results of these experiments will be reported in due course.

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Supplementary Material Available: Spectroscopic and analytical data for complexes **1-10**, X-ray diffraction data (ORTEP diagrams, crystal and data collection parameters, positional parameters, and intramolecular distances and angles) for **1** and **6a**, and a plot of the concentration dependent molar conductivity of **1** in methylene chloride (14 pages). This material is provided with the archival edition of the journal, available in many libraries. Alternatively, ordering information is given on any current masthead page.

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[23] Additional information on the reactions illustrated in Scheme I: (a) ^{13}CH$_4$, 2 atm, 45 °C, CD$_2$Cl$_2$, 6 h, 50% conversion; (b) benzene, 15 equiv, 25 °C, 6 h, CH$_2$Cl$_2$, 99%. (c) *p*-xylene, 20 equiv, 45 °C, 18 h, CH$_2$Cl$_2$, 90%, compound **4** is fluxional; metathetic reaction with LiCl afforded the corresponding (chloro)(η^1-benzyl)iridium complex **4a**, which possesses a static structure; (d) toluene, 15 equiv, 25 °C, 6 h, CH$_2$Cl$_2$, 92%; the yield was estimated by conversion to the corresponding (chloro)(tolyl) complexes **3c** with LiCl; (e) cyclopropane, 20 equiv, 25 °C, 8 h, CH$_2$Cl$_2$, 95%; (f) ethane, 2 atm, 45 °C, CD$_2$Cl$_2$, 40% conversion; the identity of this product was confirmed by independent synthesis of the corresponding BF$_4^-$ salt **6a**, for which satisfactory analytical data and an X-ray crystal structure were obtained (see supplementary material).

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[25] Reaction of **1** with α,α,α-trideuteriotoluene (CD$_3$C$_6$H$_5$) produced, within NMR detection limits, exclusively CH$_4$, suggesting that the aryliridium products do not arise by initial attack at the benzylic C–H group followed by a second exchange reaction.

[26] Additional information on the reactions illustrated in Scheme II: (a) SiMe$_3$H, 1.7 equiv, 25 °C, 10 min, CH$_2$Cl$_2$, 88%; (b) SiPh$_3$H, 1.15 equiv, 25 °C, 40 min, CH$_2$Cl$_2$, 93%; (c) SiMe$_2$PhH, 1.5 equiv, 25 °C, 45 min, CH$_2$Cl$_2$, 97%; (d) SiPh$_2$H$_2$, 1.3 equiv, 25 °C, 20 min, CH$_2$Cl$_2$, 89%.