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Activation of Arene C−H Bonds by a Cationic Hafnium Silyl Complex Possessing an α-Agostic Si−H Interaction

Aaron D. Sadow and T. Don Tilley*

Department of Chemistry, University of California, Berkeley, Berkeley, California 94720-1460

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σ-Bond metathesis via four-center transition states is a fundamental mechanism for the cleavage of C−H bonds.[1−4] Such reactions are associated with highly electrophilic d^0 or $f^n d^0$ transition metal complexes possessing reactive M−H or M−C σ-bonds, which can activate hydrocarbons such as methane[3] and benzene.[4] Early transition metal and f-metal silyl complexes have been observed to react with the Si−H bonds of hydrosilanes via a related mechanism which is the basis for the catalytic dehydropolymerization of silanes to polysilanes.[5] However, catalytic hydrocarbon functionalizations via the σ-bond metathesis of unactivated C−H bonds have not been demonstrated.[6] A likely limitation in the development of such catalytic cycles is the apparent restriction that carbon cannot adopt the β-position of a four-centered transition state.[7]

A potential catalytic cycle for the functionalization of hydrocarbons via σ-bond metathesis involves the dehydrogenative coupling of C−H and Si−H bonds to produce a C−Si-bonded product. This process could involve various fundamental steps, one of which would be the activation of a C−H bond by a d^0 M−Si bond.[8] However, this transformation requires more reactive M−Si σ-bonds, as known examples do not react directly with C−H bonds. A possible strategy for the generation of more reactive d^0 M−Si bonds is suggested by recent results which show that cationic hafnocene alkyl and hydride complexes are highly reactive in σ-bond metathesis reactions.[9] Here we describe a reactive cationic silyl complex that possesses an α-agostic Si−H bond. The Hf−Si bond of this complex reacts with the C−H bonds of arenes, apparently by a concerted, σ-bond metathesis process.

The hafnium silyl complex $Cp_2Hf(SiHMes_2)Me$ (**1**, Mes = 2,4,6-trimethylphenyl) was readily prepared by the reaction of $Cp_2HfMeCl$ with $(THF)_{2.5}LiSiHMes_2$[10] in diethyl ether at −78 °C. The ^{29}Si NMR spectrum of **1** contains a singlet at 8.24 ppm. The low $^1J_{SiH}$ coupling constant (145 Hz) and ν(SiH)-stretching frequency (2077 cm^{-1}) are consistent with bonding of the $-SiHMes_2$ group to an electropositive element.[8a,10]

Addition of $B(C_6F_5)_3$ to a benzene-d_6 solution of **1** quantitatively produces a dark red solution of the zwitterionic complex $Cp_2Hf(\eta^2\text{-}SiHMes_2)(\mu\text{-}Me)B(C_6F_5)_3$ (**2**), which reacts with the solvent (vide infra) at room temperature. However, this complex is stable for >8 h below −40 °C in toluene-d_8. Various ^{11}B NMR experiments established the presence of a $B-CH_3$ bond, and significant ion-pairing in **2** (see Supporting Information).[11] The most interesting feature of **2** is the agostic Si−H group. The SiH hydrogen gives rise to a highly upfield-shifted resonance at 1.80 ppm (toluene-d_8, −47 °C). A $^1H-^{29}Si$ HMQC experiment revealed coupling between this SiH resonance and the surprisingly downfield-shifted ^{29}Si NMR resonance at 158 ppm. The low $^1J_{SiH}$ coupling constant (57 Hz) and ν_{SiH}-stretching frequency (1414 cm^{-1}; $\nu_{SiD} = 1015$ cm^{-1}) for **2** suggest a significant weakening of the Si−H bond. The gas-phase structure of $Cp_2HfSiH_3^+$ was calculated using DFT methods.[12] The energy-minimized structure possesses a strong interaction between an Si−H bond and the Hf center, and the calculated Si−H stretching frequency (1475 cm^{-1}) is close to the experimentally observed value.

Previously reported complexes with agostic Si−H bonds exhibit spectroscopic features which are consistent with those observed for **2**. Coordination of a β-Si−H bond to the d^0 centers in $Cp_2Zr[N(SiHMe_2)^tBu]X$ (X = H, halide) results in upfield ^1H NMR shifts for the silicon hydride at 1.21−2.94 ppm, low $^1J_{SiH}$ coupling constants of 113−135 Hz, and reduced values for the ν_{SiH}-stretching frequency (1912−1998 cm^{-1}).[13] Similarly, $Me_2Si(\eta^5\text{-}C_9H_5\text{-}2\text{-}Me)_2Y[\kappa^2\text{-}N(SiHMe_2)_2]$, exhibits a ^1H NMR shift of 2.97 ppm, a $^1J_{SiH}$ value of 142 Hz, and a ν_{SiH}-stretching frequency of 1804 cm^{-1}.[14] These comparisons suggest a strong donation of electron density from the Si−H bond to the electrophilic hafnium center of **2**. Harrod has isolated and spectroscopically characterized dimeric, dicationic zirconocene hydridosilyl complexes formulated as $[Cp'_2Zr(\mu\text{-}H)(SiHR)]_2^{2+}$ (R = Ph, CH_2Ph; Cp′ = Cp, Cp*, C_5H_4Me), which do not possess Zr−H−Si interactions.[15]

The presence of the α-agostic SiH-interaction suggests that the Hf−Si bond might be unusually reactive toward cleavage reactions that pass through four-center, electrocyclic transition states, since a related effect has been proposed for transition states of alkene insertions into M−C bonds.[16] The participation of an α-agostic element-hydrogen bond in σ-bond metathesis has not been documented experimentally, but several computational studies describe such an effect.[16] In fact, at room temperature in benzene-d_6, compound **2** rapidly converts ($t_{1/2} = 54$ min) to $Cp_2Hf(Ph\text{-}d_5)(\mu\text{-}Me)B(C_6F_5)_3$ (**3**-d_5), with elimination of Mes_2SiHD (identified by its characteristic SiH triplet resonance in the ^1H NMR spectrum, with $^2J_{HD} = 3.6$ Hz). The characterization of **3**-d_5 was aided by the independent preparation of **3**, via reaction of $Cp_2HfPhMe$ with $B(C_6F_5)_3$ (Scheme 1).

In neat toluene-d_8, **2** reacts with the solvent (over ca. 2.5 h at room temperature) to give all of the possible products of C−D bond activation, $Cp_2Hf(o\text{-}tolyl\text{-}d_7)(\mu\text{-}Me)B(C_6F_5)_3$ (**4**-d_7), $Cp_2Hf(p\text{-}tolyl\text{-}d_7)(\mu\text{-}Me)B(C_6F_5)_3$ (**5**-d_7) (together, 45%), $Cp_2Hf(m\text{-}tolyl\text{-}d_7)(\mu\text{-}Me)B(C_6F_5)_3$ (**6**-d_7, 32%), and $Cp_2Hf(benzyl\text{-}d_7)(\mu\text{-}Me)B(C_6F_5)_3$ (**7**-d_7, 23%). The identity of each product was confirmed by its independent synthesis from the appropriate $Cp_2Hf(tolyl)Me$ derivative.

Kinetic studies of the C−H activation of benzene provide mechanistic insight into the nature of this transformation. For the reaction of **2** with benzene, linear plots of ln[**2**] versus time established first-order dependence on the hafnium complex. It proved possible to vary the concentration of benzene by the addition

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* To whom correspondence should be addressed. E-mail: tdtilley@socrates.berkeley.edu.

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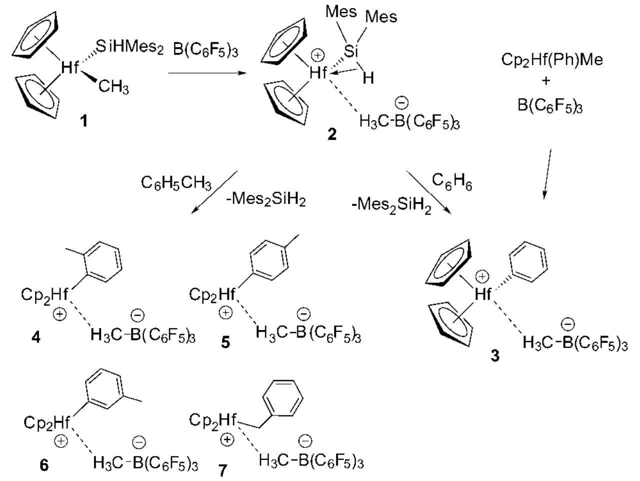
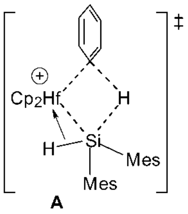
Scheme 1



of small amounts of hexafluorobenzene (ca. 7−13%), demonstrating first-order dependence in benzene and a rate law of $k[\mathbf{2}][C_6D_6]$ ($k = 5.0 \times 10^{-6}$ M^{-1} s^{-1}, 13.5 °C). A large primary kinetic isotope effect [$k_H/k_D = 6.9(7)$] confirmed that benzene is involved in the rate-determining step. Furthermore, the magnitude of this isotope effect is consistent with transfer of hydrogen from carbon to silicon in the β-position of a concerted transition state.[18] An Eyring plot provided activation parameters of $\Delta H^‡ = 19(1)$ kcal/mol and $\Delta S^‡ = -17(3)$ eu, which imply an ordered transition state.

To investigate the possible role of the $MeB(C_6F_5)_3^-$ anion in the C−H bond activation process, reaction rates were determined for benzene activations in the presence of 10 and 20 equiv of $[N(CH_2Ph)Bu_3][MeB(C_6F_5)_3]$. These rates were identical to those observed in the absence of excess borate anion; therefore, we conclude that the dissociation of $MeB(C_6F_5)_3^-$ is not involved in the rate-determining step for C−H activation.[19] A negligible secondary isotope effect of $k_H/k_D = 1.1$ (1), determined by measuring the rate of benzene-d_6 activation by $Cp_2Hf(\eta^2\text{-SiDMes}_2)(\mu\text{-Me})B(C_6F_5)_3$ (**2**-*d*), suggests that the agostic interaction is not disrupted in the transition state for C−H bond activation. Also, a related cationic hafnocene silyl complex lacking an α Si−H moiety, $Cp_2Hf[Si(SiMe_3)_3](\mu\text{-Me})B(C_6F_5)_3$, does not react with benzene.[20] On the basis of these observations, we propose that the reactive form of the complex possesses significant cationic character and that the α-agostic Si−H interaction plays an important role in the transition state for σ-bond metathesis (**A**).



A

Although d^0 metal hydride and alkyl complexes have been observed to activate benzene,[1−4] the reaction reported here represents the first intermolecular C−H bond activation by a d^0 metal−silicon bond. Interestingly, the cation-like hydride $CpCp^*HfH(\mu\text{-H})B(C_6F_5)_3$ does not react with benzene,[9] although $[Cp^*_2MH][HB(C_6F_5)_3]$ (M = Zr, Hf) undergoes H/D exchange with benzene-d_6 at room temperature[21] and $Cp^*_2HfH_2$ metalates benzene at high temperatures.[4c] Whereas the d^2 tantalum complex $Cp_2Ta(SiH^tBu_2)(PMe_3)$ activates benzene in a net process similar to that of Scheme 1, it does so via oxidative addition of a C−H bond followed by reductive elimination of a silane.[22] The unusual reactivity observed for **2** constitutes further evidence that cation-like derivatives of d^0 complexes are more reactive than analogous neutral species toward σ-bond metathesis.[9] Perhaps more importantly, the observation of C−H bond activations by a d^0 M−Si bond should expand the scope of strategies for catalytic hydrocarbon functionalization. We are currently pursuing the incorporation of this step into catalytic cycles.

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Supporting Information Available: Procedures for the synthesis and characterization of new complexes, experimental details for the kinetics runs, and representative kinetics data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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