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Inter- and Intramolecular C−H Activation by a Cationic Iridium(III) Center via Oxidative-Addition Reductive-Elimination and *σ*-Bond Metathesis Pathways

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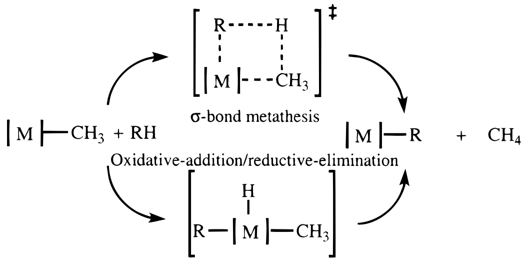
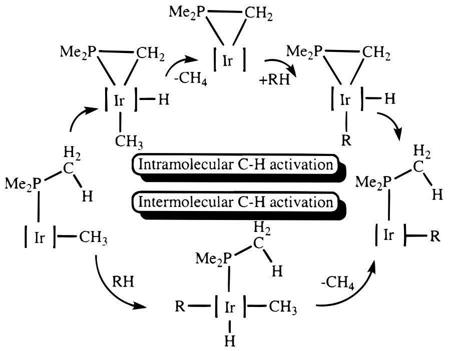
The C−H activation of alkanes by late-transition-metal complexes is an extremely active area of experimental and theoretical investigation.[1,2] Bergman and co-workers have reported an Ir(III) system, $Cp^*Ir(PMe_3)(CH_3)^+$ [$Cp^* = \eta^5$-$C_5(CH_3)_5$] (**1**), which thermally activates methane (**2**) and alkanes in the solution-phase at unprecedentedly low temperatures.[3] Two possible mechanisms are shown in Scheme 1. Recent calculations on a model for this system show that the oxidative-addition mechanism is the low-energy pathway and that the four-center *σ*-bond metathesis mechanism is doubtful even at higher energies.[4]

More recently, Hinderling et al. reported a combined gas-phase, solution-phase, and computational study on similar cationic iridium(III) complexes, $CpIr(PMe_3)(CH_3)^+$ [$Cp = \eta^5$-C_5H_5] (**3**) and $Cp^*Ir(PMe_3)(CH_3)^+$ (**1**).[5] They showed that intramolecular C−H activation through a cyclometalated intermediate operates in the gas phase and suggested that a similar reaction may operate in solution. Furthermore, after performing density functional theory (DFT) calculations on this system, they concluded that the C−H activation through the oxidative-addition/reductive-elimination mechanism was not operative because the calculated energy difference, 18 kcal/mol, between the reactant, **3**, and the oxidative-addition intermediate, $CpIr(\eta^2$-$PMe_2CH_2)(H)(CH_3)^+$ (**9**), was higher than the experimentally determined activation energy for the loss of methane from **3**. Hinderling et al. suggested that the system reacts through the four-center *σ*-bond metathesis mechanism. Following this report, Bergman and co-workers have shown that cyclometalation can take place with cationic iridium(III) complexes in solution, but this observation depends on the nature of the phosphine ligands.[6] With the trimethylphosphine system, they have shown that **1** does not undergo intramolecular C−H activation in solution via a cyclometalated intermediate. Using theoretical method, we explore here the inter- and intramolecular C−H activation in $CpIr(PMe_3)(CH_3)^+$ [$Cp = \eta^5$-C_5H_5] (**3**) via both oxidative-addition/reductive-elimination and *σ*-bond metathesis pathways. The theoretical results show that the intermolecular C−H activation is a lower-energy process and that both inter- and intramolecular C−H activation proceed only through an oxidative-addition mechanism (Scheme 2).

Scheme 1



Scheme 2



Theoretical calculations in this work have been performed using density functional theory (DFT) method,[7] specifically the Becke three-parameter hybrid exchange functional[8] and the Lee−Yang−Parr correlation functional (B3LYP).[9] The transition states (TS) were optimized by using a quasi-Newton method,[10] in which the final updated Hessian shows only one negative eigenvalue and were characterized by one and only one imaginary frequency for every unique TS in a separate calculation.[11] The basis set for Ir is a modified version of the Gaussian 94[12] LANL2DZ basis,[13] where the two outermost p functions have been replaced by a (41) split of the optimized Ir 6p function from Couty and Hall.[14] For carbon, hydrogen, and phosphorus atoms, two different basis sets were used, which are denoted as BS1 and BS2. BS1 represents the standard Gaussian 94/LANL2DZ basis sets for all of the ligand's atoms. BS2 results from BS1 by adding polarization functions[12] to the phosphorus, carbons, and hydrogen which are directly involved in the C−H activation process.

The B3LYP geometry optimizations have been carried out for reactants (**2** and **3**), intermediates (**5**, **7**, and **9**), transition states (**4**, **6**, and **8**), and products along both the inter- and intramolecular C−H activation processes. The stationary points and energy

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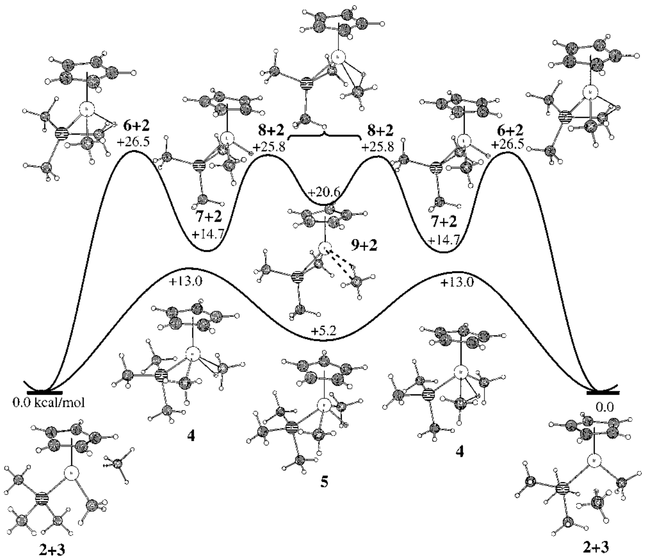

Figure 1. The lower curve shows energy profiles and geometries for the species involved in the intermolecular C−H activation process, from reactants **2** (methane) and **3**, through **4** and **5**, to products (**2** and **3**). The upper curve illustrates the intramolecular process, from reactants **2** and **3**, through **6**, **7**, and **9**, to products (**2** and **3**). The relative energy of the reactants (**2** and **3**) is zero.

Table 1. Relative Energies at the B3LYP/BS1 and BS2 Levels for Reactants, Intermediates, Transition States and Products for Both the Inter- and Intramolecular C−H Activation Processes (kcal/mol)

	BS1	BS2		BS1	BS2
2 + 3	0.00	0.00	**2 + 7**	14.67	10.95
4 (TS$_{3-5}$)	12.96	9.57	**2 + 8 (TS$_{7-9}$)**	25.77	22.47
5	5.23	3.44	**2 + 9**	20.58	17.38
2 + 6 (TS$_{3-7}$)	26.49	21.09			

profiles are shown in Figure 1, and the relative energies at the B3LYP/BS1 and BS2 levels are summarized in Table 1. Along the intermolecular C−H activation process (lower curve in Figure 1), from reactants, $CpIr(PMe_3)(CH_3)^+$ (**3**) and methane (**2**), to products, only a single oxidative-addition intermediate, **5**, is found at 5.2 kcal/mol above the reactants. The reaction barrier is only 13.0 kcal/mol at the B3LYP/BS1 level.

Along the intramolecular C−H activation process, both an oxidative-addition intermediate, **7**, and a cyclometalated reductive-elimination intermediate, **9**, are found. This result is similar to that reported by Hinderling et al.[5b] The reaction along the intramolecular oxidative-addition mechanism from reactant, **3**, to the intermediate, **7**, is endothermic by 14.7 kcal/mol with an activation barrier of 26.5 kcal/mol, while the reductive-elimination reaction from **7** to **9** is endothermic by 5.9 kcal/mol with a barrier of 11.1 kcal/mol at the B3LYP/BS1 level.

Since the calculated (B3LYP/BS1) intramolecular C−H activation barrier for the oxidative-addition mechanism is higher than the value determined experimentally by Hinderling et al.,[5b] we have examined the potential energy surface (PES) along the C−H coordinates ($r_1 = CH_3{-}H$ and $r_2 = P(H)_2CH_2{-}H$) to search for a lower-energy σ-bond metathesis pathway. It was a similarly high value for the energy of the oxidative-addition intermediate that led Hinderling et al. to postulate a σ-bond metathesis route. Despite a careful search for a σ-bond metathesis pathway for both the inter- and intramolecular C−H activation processes, none was found. The outcome of the intramolecular search is demonstrated in Figure 2 (results of the intermolecular search have been reported[4a]). Pathway 1 illustrates the oxidative-addition mechanism from reactant **3** through TS **6** to intermediate **7** then through TS **8** to intermediate **9**. If a σ-bond metathesis pathway, as found in early-transition-metal systems, had existed in this system, a transition state (TS) would be observed along pathway 2 as illustrated in Figure 2a. For the model system $CpIr(PH_2Me)(CH_3)^+$, we set r_1 and r_2 equal and optimized the remaining geometric parameters. If a TS existed along pathway 2, a "minimum" would appear in the potential energy curve along this $r_1 = r_2$ coordinate. However, as shown in Figure 2b, the energy increases rapidly along this coordinate. Thus, pathway 2, the σ-bond metathesis mechanism, does not exist for this system.

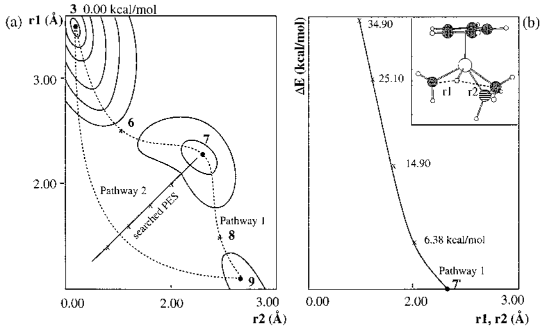

Figure 2. (a) The illustrated potential energy surface (PES) of the reaction for the intramolecular C−H activation process. Pathway 1 is the oxidative-addition/reductive-elimination pathway, and pathway 2 is hypothetical σ-bond metathesis pathway. (b) The searched PES along the C−H coordinates ($r_1 = CH_3{-}H$ and $r_2 = P(H)_2CH_2{-}H$) from pathway 1 to 2.

To obtain more quantitative results, we reoptimized the geometries of the reactants, intermediates, transition states, and products for both the intra- and intermolecular C−H activation processes at the B3LYP/BS2 level (Table 1). The calculations show that the intramolecular oxidative-addition barrier from **3** to **7** is reduced to 21.1 kcal/mol at the B3LYP/BS2 level. After the zero-point energy (ZPE) corrections, it is further reduced to 18.4 kcal/mol,[15] a value which compares favorably with the experimental value of 13.6 ± 2 to 16.6 ± 2 kcal/mol at 0 K.[5b,16] Our larger basis set and ZPE correction have brought the theoretical barrier for oxidative addition into the experimental range.

Combined with our previous work,[4a,c] it is reasonably certain that only an oxidative-addition/reductive-elimination mechanism exists for both the inter- and intramolecular C−H activation processes. Although it may be difficult in some case to distinguish between oxidative addition and σ-bond metathesis, here the intermediates (**5** and **7**) have fully formed Ir−H bonds and nonbonding C···H distances. Compared to the intramolecular C−H activation process, the intermolecular C−H activation process is a lower-energy process. A cyclometalated intermediate for the ligand PMe_3 will be observed under reaction conditions without added hydrocarbon because CH_4 loss in **3** leads to an equilibrium favoring the cyclometalated complex. However, in the presence of added hydrocarbon, an intermolecular C−H activation process is favored over an intramolecular one because of its lower activation barrier. The lower barrier for orthometalation of PPh_3,[17] as compared to PMe_3, results in the cyclometalated product being observed in this case.[6] More detailed studies of reaction mechanisms, electronic structural features, and energy correlation effects are in progress.

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(15) We performed the geometry optimization and ZPE calculations for the transformations $Ir(Cl)(CH_3)(PH_2CH_3)^+ \rightarrow$ TS for $Ir(Cl)(CH_3)(H)(\eta^2\text{-}PH_2CH_2)^+$ reaction and $Ir(Cl)(CH_3)(PH_2CH_3)^+ + CH_4 \rightarrow$ TS for $Ir(Cl)(CH_3)_2(H)(PH_2CH_3)^+$ reaction and found the ZPE corrections to be −2.38 and −0.02 kcal/mol for the reaction barriers.

(16) Accoording to Hinderling et al.,[5b] the value of 13.6 kcal/mol was obtained assuming that the PMe_3 and the methyl ligands are free rotors. If their motions are treated as harmonic vibrations instead, one obtains 16.6 kcal/mol for the 0 K barrier. Thus, the "true" barrier may be somewhat larger than 13.6 kcal/mol as the PMe_3 group may not be freely rotating.

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