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DFT Mechanistic Study of the Selective Terminal C-H Activation of n-Pentane with a Tungsten Allyl Nitrosyl Complex

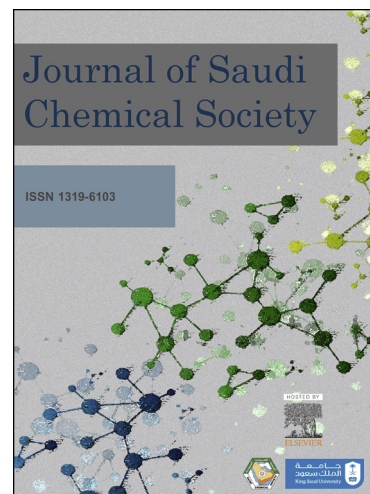Richmond Lee,[1] Davin Tan,[1] Chaoli Liu,[1,2] Huaifeng Li,[1] Hao Guo,[2] Jing-Jong Shyue[3] and Kuo-Wei Huang[1*]

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Abstract   Mechanistic insights into the selective C-H terminal activation of n-pentane with tungsten allyl nitrosyl complex reported by Legzdins were gained by employing density functional theory with B3LYP hybrid functional. Using Bader's atom in molecules (AIM) analysis on the elementary steps of the hydrogen transfer process, **TS1** and **TS2**, it was observed that the calculated H-transfer models were closely similar to Hall's metal-assisted σ-bond metathesis through bond critical point (BCP) comparisons. One distinguishable feature was the fact that the formal oxidation state of the W changed in the concerted H-transfer process. To better differentiate, we term these processes as 'Formal Reductive Hydrogen Transfer' (FRHT) for **TS1** and 'Formal Oxidative Hydrogen Transfer' (FOHT) for **TS2**.

1. Introduction

The selective functionalization of sp^3 C-H bonds confers a facile and direct conversion of abundant hydrocarbon from petroleum sources to higher-valued products[1-5]. Several theoretical studies have been undertaken in order to understand these elementary steps for sp^3 C-H bond activation[6-21]. Legzdins and co-workers have reported the synthesis of a tungsten methylallyl nitrosyl complex **1** which possesses intriguing C-H bond activating properties that selectively activates the terminal C-H bond of linear n-pentane (Scheme 1) [22,23]. The product as a stable tungsten pentyl methylallyl complex (**4**) was isolated and fully characterized by X-ray crystallography. Further studies by the same group to activate branched alkanes, olefins, aromatics and heteroatoms with the same system have demonstrated its versatility and selectivity[24,25].

It was proposed that a 16e intermediate **2a** was formed from the extrusion of neopentane, corroborated by a trapping experiment with PMe$_3$. When n-pentane-d_{12} was used, it was observed that deuterium was incorporated at the terminal C of the methyl allyl moiety, suggesting that the hydrogen migration originated from n-pentane. The current interpretation of hydrogen atom transfer mediated by transition metals can be classified as a two-step or concerted process (Scheme 2) [5,26-30]. Two-step processes involve an oxidative addition step (A), the formation of an M^{n+2} intermediate, followed by a subsequent reductive elimination (B)[31-33], while concerted σ-bond metathesis pathways proceed via an "oxidative" (C) or four-center transition state (D)[18]. Herein, we attempted to correlate current understanding of σ-bond metathesis process to elucidate this C-H activation mechanism[34]. Although the hydrogen migration pathway has been reported by Legzdins and co-workers[22,23], the detailed mechanistic description for this process was not available. In this study, we focused on the

analysis of the H-transfer processes on the basis of Bader's AIM description and two new terms (FRHT and FOHT) describing the processes were proposed.

2. Computational Details

Density functional theory (DFT) calculations were performed by employing the Gaussian 03 program[35]. The Becke three-parameter functional with the nonlocal Lee-Yang-Parr correlation functional (B3LYP) theory was applied[36,37], LANL2DZ basis set including double-ξ valence basis set with the Hay and Wadt effective core potential (ECP) was used for the W atom[38-40], and 6-31G(d) Pople basis set for the rest of atoms[41-43]. Please see supporting information for a summary of Cartesian coordinates and thermodynamic data. For atoms in molecules quantum theory (AIM), the wavefunction was generated with Gaussian 09 package[44]. B3LYP theory was applied, all electron Well-tempered basis set (WTBS) was used for W[45,46], and 6-31G(d) Pople basis set was used for the rest of atoms. The wavefunction output was analyzed with the AIM2000 software for topological interpretation. WTBS was obtained from the EMSL basis set library[47].

3. Results and Discussions

The initial steps can be described as allylic isomerization, involving the change in the coordination mode of the methylallyl moiety. The resulting orientation (**1c**) is fundamentally important for the terminal hydrogen transfer as the C-H bond must be close to the neopentyl group and the tungsten metal center [30]. The hydrogen migration from the terminal methyl group of the methylallyl ligand to the neopentyl group proceeds through transition state **TS1**[22,23] with an overall activation barrier of 26.5 kcal/mol. As the formal

oxidation state of W changes from +2 to 0, we termed this process as a 'formal reductive hydrogen transfer' (FRHT) route.[48] The neopentane molecule then dissociates from the resulting 18e intermediate **2a** to **2**, which later σ-coordinate with pentane to give the σ-complex **3**. Subsequently, **3** undergoes 'formal oxidative hydrogen transfer' (FOHT; W is formally oxidized from 0 to +2) through transition state **TS2** by hydrogen migration from the n-pentane to the coordinated olefin moiety overcoming an activation barrier of 23.2 kcal/mol (relative to **1**). This process is similar in retrospect to σ-complex assisted metathesis[49-54], whereby the incoming n-pentane forms a σ-complex with the metal center. The H-transferred 16e intermediate **4a** is unstable and prefers to form η^3 coordination with the allylic ligand to **4b**. Subsequent allylic isomerization through **4c** forms the observed product **4**.

A study on the various models of hydrogen transfer process by Vastine and Hall concisely categorized and summarized the various reaction models in literature according to Bader's atoms in molecules (AIM) analysis[55,56]. The electron density of the transition states and intermediates during the hydrogen transfer process provided valuable information about bond and ring critical points (BCP and RCP) that could be described using the AIM2000 software that analyzes electron density, gradient field and Laplacian of atoms according to AIM theory[57]. These critical points are therefore pertinent in categorizing and characterizing the nature of hydrogen transfer during bond metathesis processes. Using AIM2000 analysis on **TS1** and **TS2**, we are able to identify the geometrical similarities of the critical points with Hall's metal-assisted σ-bond metathesis type. For both optimized transition states **TS1** and **TS2**, the W-H bond lengths are both about 1.8 Å, which is similar to the neutron diffraction W-H bond length of 1.73Å[58]. The key BCP (Figure 2, BCP is red dot) between W

and the transferring H was identified, suggesting that the transfer of H is mediated by the transient oxidative-added W metal center. Although the critical point features closely resemble Hall's metal-assisted σ-bond metathesis, it is dissimilar in that our model involves changes in formal oxidation state from substrate to the hydrogen-transferred product.

Using Mayer's bond order analysis of the transition state, we are able to further analyze the existence of bonding between the involved atoms in the transition state.[59-62], In accordance to the principle of conservation of bond order, the sum of bond orders for forming and breaking a bond in a reaction must be close to unity[63]. The sum of bond order of the terminal pentane C to both W and H is calculated to be 0.93, The hydrogen bond order between H-W, H-$C_{pentane}$ and H-$C_{1,allyl}$ is computed to be 0.916, indicating that the hydrogen transfer proceeds through W with a significant W-H bond character. Summation of all the W-ligand bond forming or breaking orders, W-$C_{pentane}$ (0.617), W-$C_{1,allyl}$ (0.558), W-H (0.351) and W-$C_{2,allyl}$ (0.729) give a total bond order of 2.225, corresponding to the two newly formed W-C σ-bonds of intermediate **4** (Figure 3).

Furthermore, our calculations on W activation of internal C2 of n-pentane reveal that this pathway incurs an additional 3.4 kcal/mol higher than that of **TS2** (**TS2-int** 26.6 kcal/mol, relative to **1**), which can be attributed to the more sterically demanding internal C-H environment. These observations confirm the experimental results that only the terminal C-H of pentane is preferentially activated but not the internal C-H bond. The activation entropies $\Delta S^{\ddagger}$, for both FRHT and FOHT routes leading to the transition states are -4.9 and -9.2 e.u., respectively, supporting the concerted mechanism model as the reaction proceeded through the more highly ordered transition states.

4. Conclusion

Our results suggest that the W-mediated C-H activation process proceed via methyl allyl ligand isomerization and a series of hydrogen transfer reactions. Computations reveal that the terminal C-H bond of the pentane is more easily accessible than the internal C-H bonds of the molecule and hence the preference for activation at the terminal site as conforming to experiments. The type of H transfer mechanism was validated through AIM analysis and new unique features of 5-centered concerted hydrogen migratory process were identified as FRHT and FOHT, which both involve a change in the formal oxidation of the metal center in the elementary step.

Acknowledgments

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Captions for schemes

**Scheme 1:** C-H bond activation by **1.**

Scheme 2: Processes in σ-bond metathesis. Two-step process: A = oxidative addition; B = reductive elimination. Concerted process: C = "oxidative" transition state; D = four-center transition state.

Captions for figures

Figure 1: Reaction profile in relative energy, E (values are in italics). Dotted line for internal C-H activation.

Figure 2: AIM analysis diagram and display of critical points of **TS1** (top) and **TS2** (bottom). Inset illustrates the whole 2D representation of molecule with zoom-in-area highlighted. BCPs are red dots with bond path passing through while RCPs are yellow. H_t refers to the transferring H and NO ligands are omitted for viewing clarity.
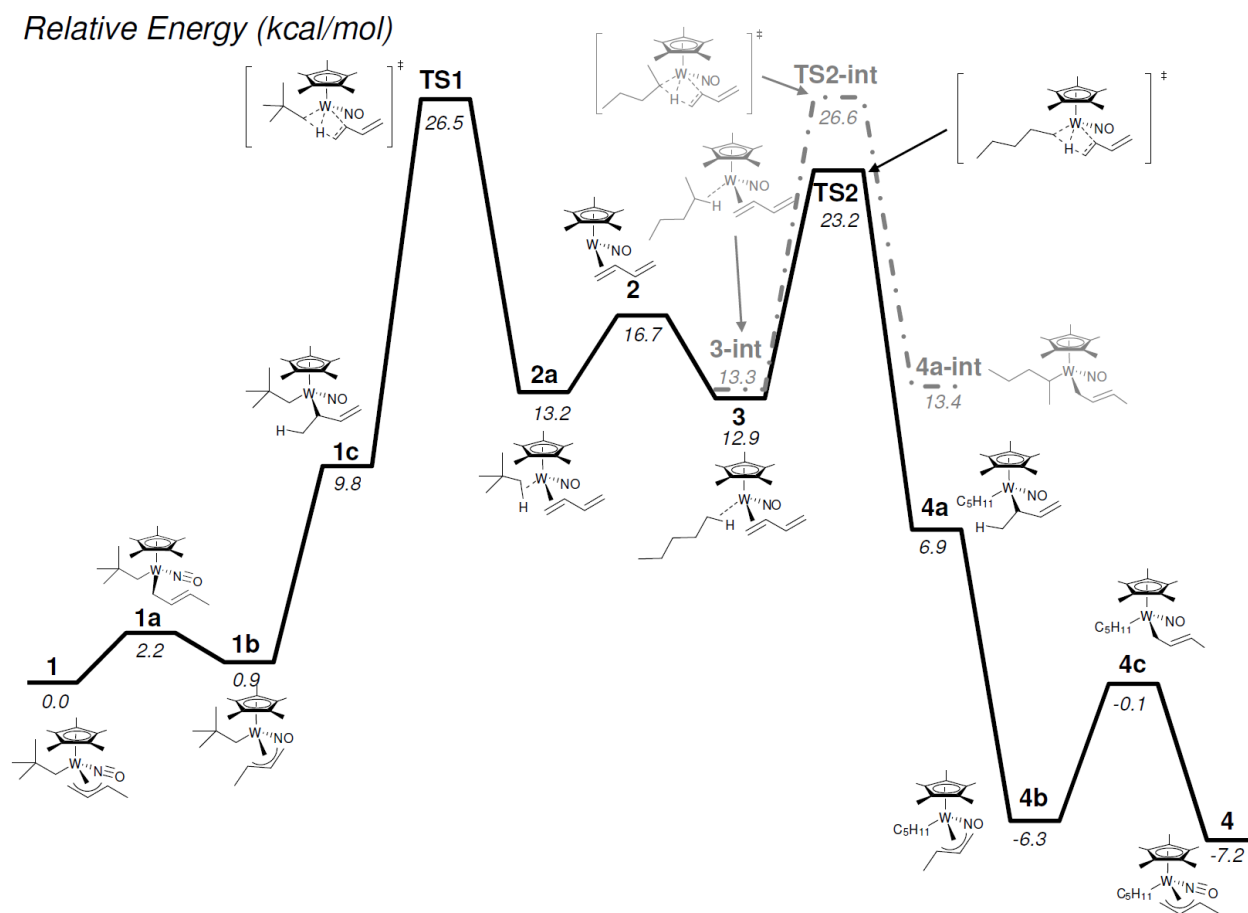
Figure 3: Bond order analysis of **TS2.**
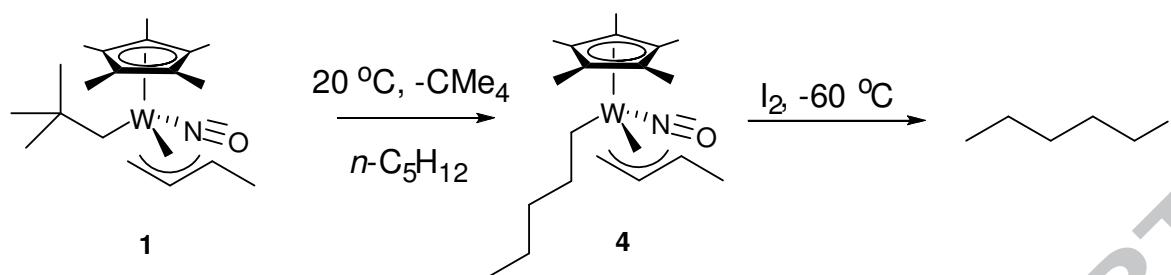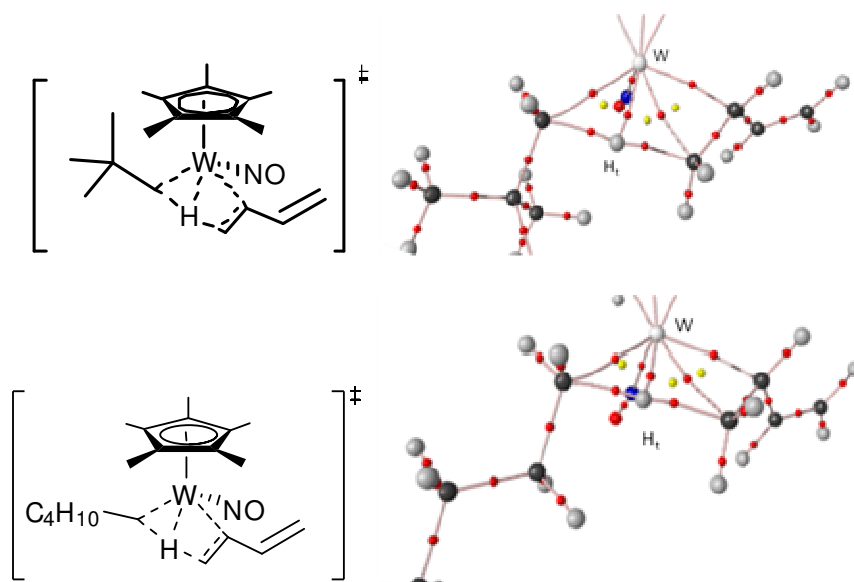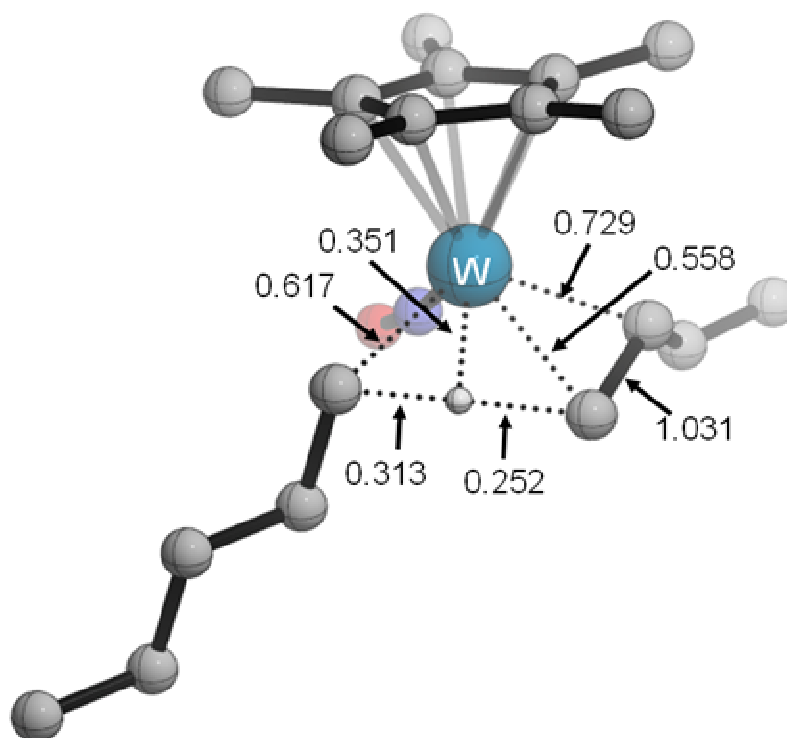
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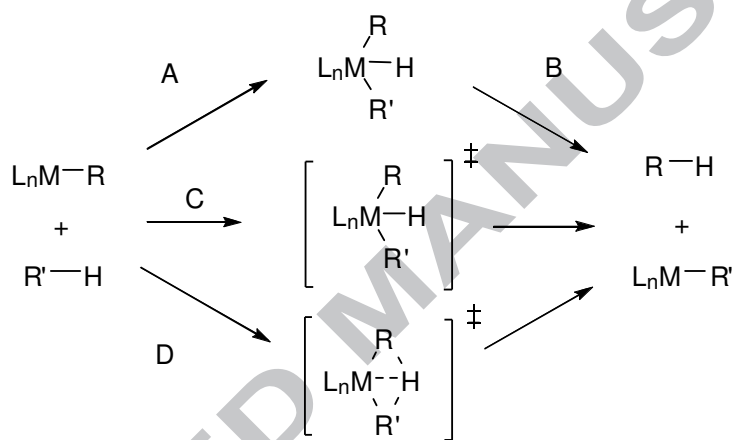
Scheme 2

Figure 1.

Figure 2

Figure 3