## Methylidene Migratory Insertion into an Ru–H Bond

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The migratory insertions of CH_x fragments into transition-metal–hydrogen and transition-metal–alkyl bonds have long been proposed as chain initiation and propagation steps in the Fischer–Tropsch synthesis of hydrocarbons.[1] Particularly for ruthenium, an effective heterogeneous catalyst for the production of high molecular weight polymethylenes,[2] there is strong indirect evidence that the chain growth mechanism involves methylidene insertion into growing alkyl chains.[1,3] Several experiments on homogeneous systems point to the facility of direct CH_2 insertions into both M–H and M–R bonds.[4] Thorn and Tulip[5a] proposed that acidification of a hydrido hydroxymethyliridium complex proceeds via a hydridomethyleneiridium intermediate which undergoes CH_2 insertion into the Ir–H bond to yield an iridium methyl complex. Upon hydrogen abstraction from mononuclear metal dimethyl complexes, Thorn and Tulip,[5b] as well as Cooper,[6] Maitlis,[7] and Werner,[8] have postulated the intermediacy of methyl methylidene metal complexes which insert CH_2 into M–CH_3 and then β-hydride eliminate en route to the formation of ethylene hydride complexes. Thus these studies suggest that both the chain initiation and propagation steps in Fischer–Tropsch synthesis may be facile even at a single metal center.

As a model for these important elementary reactions, we have used ab initio quantum mechanical techniques to investigate the migratory insertion of CH_2 into an adjacent Ru–H bond. To our knowledge, these calculations provide the first quantitative description of the energetics of such a reaction, including evaluations of both the activation barrier to insertion as well as the relative stabilities of the reactant and product. The reaction pathway is depicted below

1   **2**
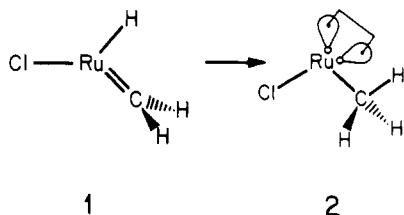
where **1** is a model for 18-electron complexes such as (C_5H_5)-

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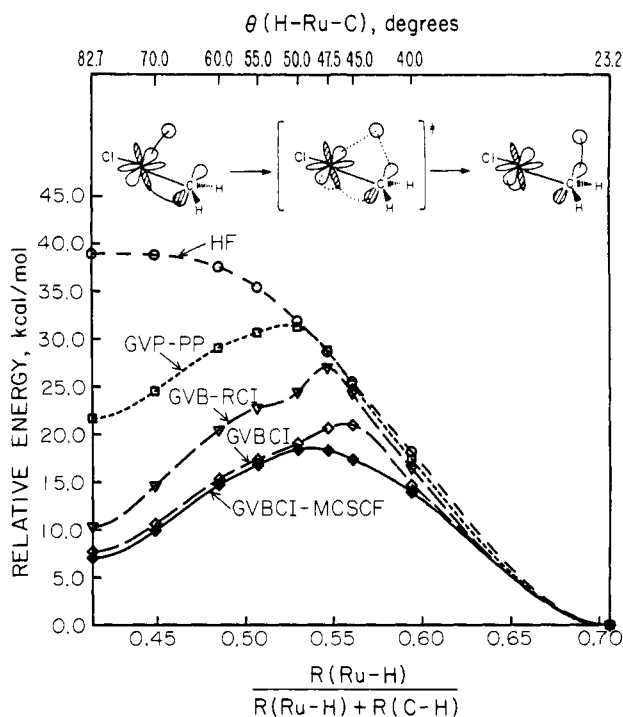
Figure 1. Reaction coordinate for the insertion of CH_2 into Ru–H in **1** to form $ClRu(CH_3)$ (**2**) at the HF, GVB-PP(3/6), GVB-RCI(3/6), GVBCI(3/6), and GVBCI(3/6)-MCSCF levels. Energy (kcal/mol) is plotted relative to the total energy for **2** vs. $R(Ru–H)/[R(Ru–H) + R(C–H)]$ (normalized reaction coordinate). Also shown at the top are the corresponding H–Ru–C angles (deg). The full GVBCI-MCSCF leads simultaneously to a proper description of both the reactant-like and product-like configurations important at the transition state and hence to a smooth potential curve. Some lower level calculations lead to a less smooth transition, the wave function being less capable of simultaneous description of both reactant and product channels.

$(PPh_3)Ru(R)(CH_2)$ (**3**) or $[(C_6Me_6)(PPh_3)Ru(CH_3)(CH_2)]^+$ (**4**), the intermediate postulated by Werner.[8] As discussed previously,[9] **1** conforms to the valence bond (VB) view of oxidation states in which electronegative ligands may remove no more than two units of charge from the metal (the easily ionized s-electrons), leaving the other ligands to form covalent bonds to unpaired d-electrons (or to form donor bonds into empty metal valence orbitals). Thus ligands with large electron affinities[10] such as Cp (η^5-C_5H_5) and Cl form rather ionic bonds with the metal valence electrons, while neutral π-donor ligands (e.g., π-aryls) and phosphines require empty metal valence orbitals. Finally, ligands with unpaired electrons (and small electron affinities, e.g., CH_2, CH_3, H, NO, etc.) require unpaired metal d-electrons with which to form covalent bonds. As a result, we believe the singlet state of **1** is a good model for **3** and **4**, since all three complexes have a metal VB oxidation state of +1. Ru(I) is d[7], with three unpaired d-electrons to form covalent bonds to R and CH_2 in **1**, **3**, and **4**.

Consider the process of inserting the CH_2 ligand into the Ru–H bond to form an Ru–CH_3 species. We begin with an Ru–H bond and two Ru–C in-plane bonds (one σ and one π) which are converted to a C–H bond, one Ru–C bond and an Ru d lone pair. Notice that the *presence of the in-plane π-bond*[11] suggests a
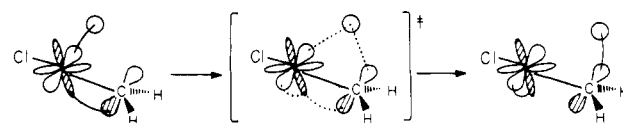
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(10) The electron affinities of Cp and Cl are 2.2 eV (Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977,** *6*, 736–772) and 3.62 eV (Hotop, H.; Lineberger, W. C. *J. Chem. Phys. Ref. Data* **1975,** *4*, 539–576), respectively.
(11) This conformation is the lowest energy orientation for **1**: Carter, E. A.; Goddard, W. A., III, manuscript in preparation.
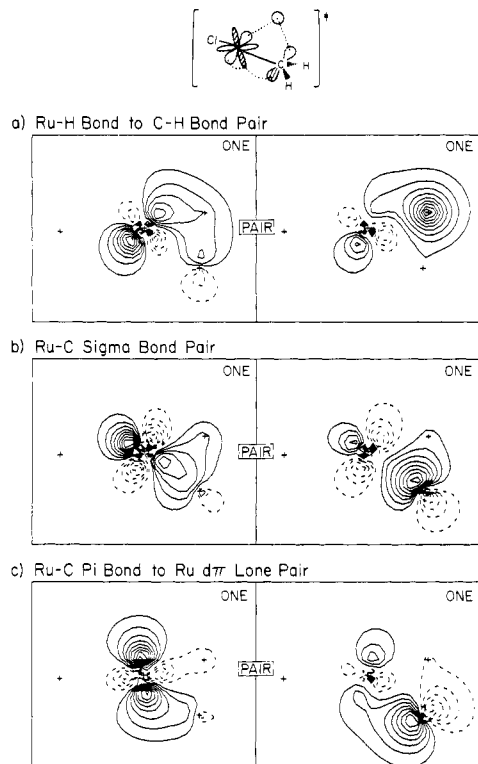
Figure 2. GVB(3/6)PP one-electron orbitals near the transition state (Θ(H–Ru–C) = 50.0°). (a) Orbital pair describing the Ru–H bond of the reactant 1 and the C–H bond of the product 2; (b) orbital pair describing the Ru–C σ-bond for both 1 and 2; (c) orbital pair describing the Ru–C π-bond of 1 and the Ru dπ lone pair of 2. Contours are shown at intervals of 0.05 au.

smooth transition from an Ru–H to a C–H bond may be possible, since the in-plane carbon p-orbital is oriented correctly for formation of the in-plane C–H bond. Indeed, at the highest level of theory examined, we find that the CH$_2$ insertion into Ru–H proceeds with a low activation barrier (11.5 kcal/mol) and is thermodynamically favorable, with an exothermicity of 7.1 kcal/mol, as displayed in the reaction coordinate of Figure 1. Notice that the transition state occurs approximately halfway between reactants and products, as expected for a reaction which is nearly thermoneutral (Hammond postulate).

Figure 2 shows the orbitals near the transition state [Θ(H–Ru–C) = 50°]. Here we see that the Ru–H bond smoothly converts into the C–H bond (Figure 2a), while the Ru–C σ-bond (Figure 2b) does not change significantly. At the transition state, the Ru–C π-bond (Figure 2c) has begun to move out of the way of the incipient C–H bond and already has substantial Ru d lone-pair character.[12] The Ru–C and Ru–H bonds at the transition state have lengthened significantly from their values in 1, increasing from 1.87 to 1.93 Å for Ru–C and from 1.65 to 1.77 Å for Ru–H.

The exothermicity, activation barrier, and transition-state geometry were calculated at five levels of theory, as shown in Figure 1.[13] The geometries along the reaction coordinate were predicted by analytic gradients of Hartree–Fock wave functions,[14] with all geometrical parameters optimized at each H–Ru–C angle.[15] In

the highest level of theory considered (the bottom curve of Figure 1), we optimize the six active orbitals (the orbitals actively involved in the insertion, namely, the Ru–H and the Ru–C σ- and π-bond pairs) self-consistently for a full six-electron CI within those six orbitals (all occupations of six electrons in six orbitals—the GVB(3/6)CI-MCSCF level). This level allows a balanced description of the three bond pairs changing during the reaction. Higher level, extended basis dissociation-consistent CI calculations[16] on various dissociation processes involving these species[13] suggest that the true exothermicity is 10.4 kcal/mol, in good agreement with our MCSCF calculations.

. In conclusion, we have shown that alkylidene migratory insertions can be quite facile, proceeding with a low activation barrier. These calculations provide the first quantitative evidence for the feasibility of this elementary reaction (previously postulated based on experimental results,[4-8] but never directly observed). These results suggest that for Ru, the reverse reaction of α-hydrogen elimination is subject to a barrier of 18.6 kcal/mol. This is consistent with the fact that α-H eliminations most often occur for the early transition metals. Work in progress on the related reaction of CH$_2$ insertion into an Ru–alkyl bond suggests an exothermicity of 4.9 kcal/mol. The activation barrier will probably be higher than that for H due to the necessary reorientation of the alkyl upon migration from Ru to CH$_2$.[17] The alkyl migration differs primarily from the hydride energetics because the incipient C–C bond is weaker than the incipient C–H bond. While our calculations suggest that late transition metals undergo CH$_2$ insertion with relative ease, early metal alkylidenes have been observed that do *not* insert into M–R bonds. We believe that this is due to the much greater strength of the M–C π-bond for the early transition metals.[18]

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Carbyne–Carbyne Ligand Coupling on a Single Tungsten Center

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The coupling of two carbyne ligands on a single transition-metal center has been analyzed theoretically by Hoffmann, Wilker, and Einsenstein.[1] These authors concluded that the reaction should be allowed for systems containing six electrons in the metal–ligand π-orbitals. In Fischer-type carbyne complexes, e.g., [(W≡CPh)Br(CO)$_4$] (1), there are six electrons in metal–ligand π-orbitals.[2] The carbyne complex 1 is derived from tungsten hexacarbonyl, itself a six-π-electron system, by transformation of a carbonyl ligand into a carbyne ligand. Since the number of π-electrons is not changed during this reaction, a second transformation of one of the remaining carbonyl ligands in 1 into a carbyne ligand should lead to a tungsten bis(carbyne) system with

(12) By the point at which Θ(H–Ru–C) = 40.0°, the Ru d lone pair is fully formed. (The equilibrium geometry of ClRuCH$_3$ has an H–Ru–C angle of 23.2°.)
(13) Full details to be published elsewhere. A valence double-ζ quality basis was used.
(14) Hartree–Fock (HF) calculations are known to predict accurate geometries. As a test, we optimized the geometry of 1 at both the HF and GVB-RCI(3/6) levels and found that the two geometries were very similar (e.g., all bond lengths and angles differed by at most 0.03 Å and 11.9°, respectively); see ref 11.
(15) The geometries of 1 and 2 were optimized with no restrictions except the retention of C$_s$ symmetry (lower symmetry cases were found to be higher in energy; ref 11).

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