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Registry No. 1, 105282-83-5; **2,** 105282-78-8; **3,** 105282-79-9; **4,** 105282-80-2; **5,** 105282-81-3; **6,** 105282-82-4; 1,1-dimethyl-2-tetralone, 20027-76-3; 3-bromo-1,1-dimethyl-2-naphthalenone, 105282-76-6; 3-bromo-2-chloro-1,1-dimethyl-1,2-dihydronaphthalene, 105282-77-7; 1,3-diphenylisobenzofuran, 5471-63-6; 4,4-dimethyl-2-tetralone, 83810-57-5.

Methylidene Migratory Insertion into an Ru-H Bond

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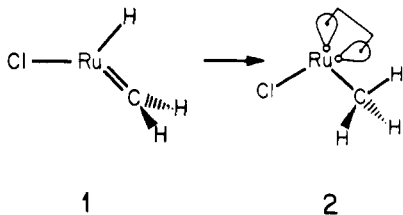
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The migratory insertions of CH_x fragments into transition-metal-hydrogen and transition-metal-alkyl bonds have long been proposed as chain initiation and propagation steps in the Fischer-Tropsch synthesis of hydrocarbons.¹ Particularly for ruthenium, 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-CH₃ 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



where **1** is a model for 18-electron complexes such as $(\text{C}_5\text{H}_5)_-$

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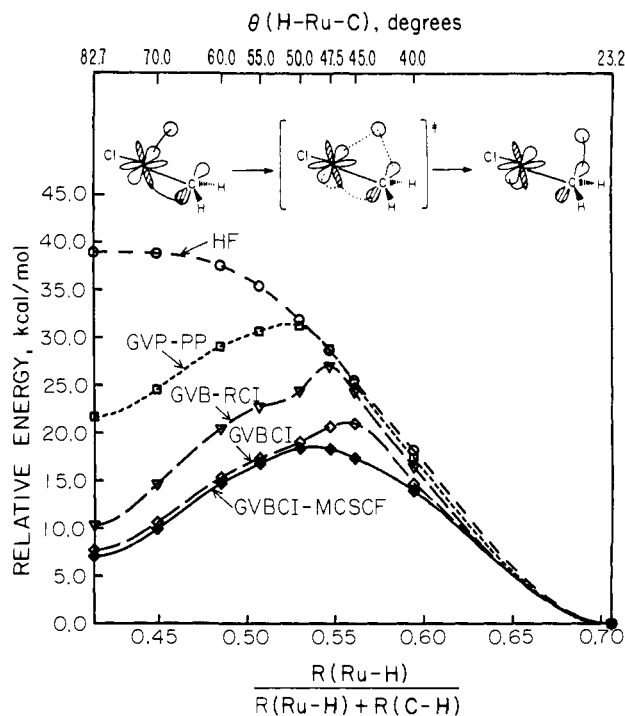
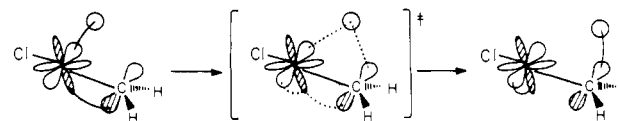


Figure 1. Reaction coordinate for the insertion of CH_2 into Ru-H in **1** to form $\text{ClRu}(\text{CH}_3)$ (**2**) at the HF, GVB-PP(3/6), GVB-RCI(3/6), GVB CI(3/6), and GVB CI(3/6)-MCSCF levels. Energy (kcal/mol) is plotted relative to the total energy for **2** vs. $R(\text{Ru-H})/[R(\text{Ru-H}) + R(\text{C-H})]$ (normalized reaction coordinate). Also shown at the top are the corresponding H-Ru-C angles (deg). The full GVB CI-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 transition 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.

$(\text{PPh}_3)_2\text{Ru}(\text{R})(\text{CH}_2)$ (**3**) or $[(\text{C}_6\text{Me}_6)(\text{PPh}_3)_2\text{Ru}(\text{CH}_3)(\text{CH}_2)]^+$ (**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 affinities¹⁰ such as Cp ($\eta^5\text{-C}_5\text{H}_5$) 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 -bond¹¹ 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.

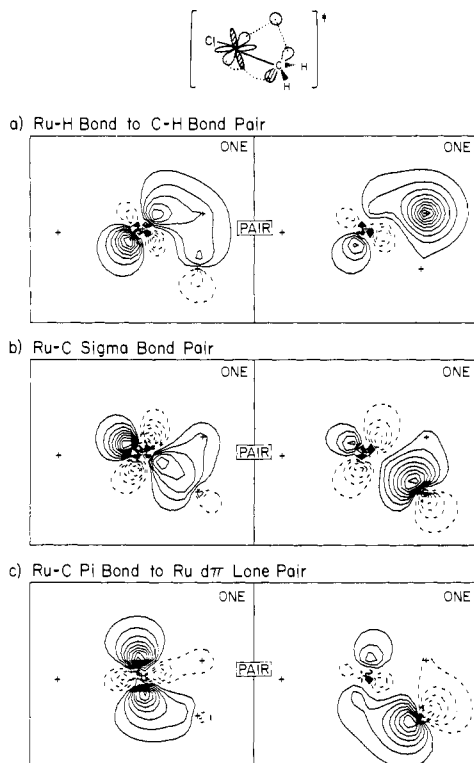


Figure 2. GVB(3/6)PP one-electron orbitals near the transition state ($\Theta(\text{H-Ru-C}) = 50.0^\circ$). (a) Orbital pair describing the Ru-H bond of the reactant **1** and the C-H bond of the product **2**; (b) orbital pair describing the Ru-C σ -bond for both **1** and **2**; (c) orbital pair describing the Ru-C π -bond of **1** and the Ru $d\pi$ 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 [$\Theta(\text{H-Ru-C}) = 50^\circ$]. 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

(12) By the point at which $\Theta(\text{H-Ru-C}) = 40.0^\circ$, 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).

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 calculations¹⁶ on various dissociation processes involving these species¹³ 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 Eisenstein.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., $[(\text{W}\equiv\text{CPh})\text{Br}(\text{CO})_4]$ (**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

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