Methylidene Migratory Insertion into an Ru–H Bond

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The migratory insertions of CH$_2$ fragments into transition-metal–hydrogen and transition-metal–alloy bonds have long been proposed as chain initiation and propagation steps in the Fischer–Tropsch synthesis of hydrocarbons. Particularly for ruthenium, an effective heterogeneous catalyst for the production of high molecular weight polymethylenes, there is strong indirect evidence that the chain growth mechanism involves methylidene insertion into growing alkyl chains. Several experiments on homogeneous systems point to the facility of direct CH$_2$ insertions into both M–H and M–R bonds. Thorn and Tulip proposed that acidification of a hydrido hydroxymethylidiridium complex proceeds via a hydridomethylidiridium 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, as well as Cooper, Maitlis, and Werner, have postulated the intermediacy of 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 an ab initio quantum mechanical technique 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:

![Reaction Pathway](image)

where 1 is a model for 18-electron complexes such as (C$_3$H$_4$)$_2$-

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(4) The first observation of general alkylidene insertions into M–R bonds was by: Sharp, P. R.; Schrock, R. R. J. Organomet. Chem. 1979, 171, 43.
(11) This conformation is the lowest energy orientation for 1: Carter, E. A.; Goddard, W. A., III, manuscript in preparation.

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Figure 1. Reaction coordinate for the insertion of CH$_2$ into Ru–H in 1 to form CIRu(C$_3$H$_4$)$_2$ (2) at the HF, GVB-PP(3/6), GVB-RCI(3/6), GVBCI(3/6), and GVBCLI(3/6)-MCSCF levels. Energy (kcal/mol) is plotted relative to the total energy for 2 vs. R(Ru-H)/R(C-Ru) + R(C-H) (normalized reaction coordinate). Also shown at the top are the corresponding H-Ru-C angles (deg). The full GVBCLI-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.
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 thermodinamically 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 \( \theta(\text{H-Ru-C}) \approx 50^\circ \). Here we see that the Ru-H bond smoothly converts into the C-H bond (Figure 2a), while the Ru-C $\pi$-bond (Figure 2b) does not change significantly. At the transition state, the Ru-C $\pi$-bond (Figure 2c) has begun to move out of the way for the incipient C-H bond and already has substantial Ru d lone-pair character. 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 geometries were calculated at several levels of theory, as shown in Figure 1. The geometries along the reaction coordinate were predicted with analytic gradients of Hartree-Fock wave functions, with all bond lengths and angles differed by at most 0.03 Å and 11.5°, respectively; see 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 $\pi$- and $\sigma$-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 on various dissociation processes involving these species suggest that the true exothermicity is 10.4 kcal/mol, in good agreement with our MCSCF calculations.

In conclusion, we have shown that alkyldine 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, but never directly observed).

These results suggest that for Ru, the reverse reaction of $\alpha$-hydrogen elimination is subject to a barrier of 18.6 kcal/mol. This is consistent with the fact that $\alpha$-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$_2$. 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 alkyldines 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 $\pi$-bond for the early transition metals.

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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 Hofmann, Wilker, and Eisenstein. These authors concluded that the reaction should be allowed for systems containing six electrons in the metal–ligand $\pi$-orbitals. In Fischer-type carbyne complexes, e.g., \([W(\text{Cp})\text{Br(CO)}_3])\), there are six electrons in metal–ligand $\pi$-orbitals. The carbyne complex I is derived from tungsten hexacarbonyl, itself a six-$\pi$-electron system, by transformation of a carbonyl ligand into a carbyne ligand. Since the number of $\pi$-electrons is not changed during this reaction, a second transformation of one of the remaining carbonyl ligands in I into a carbyne ligand should lead to a tungsten bis(carbyne) system with