

## Communications

### Mechanism of Olefin Hydrogenation Catalyzed by RuHCl(L)(PR<sub>3</sub>)<sub>2</sub> Complexes (L = CO, PR<sub>3</sub>): A DFT Study

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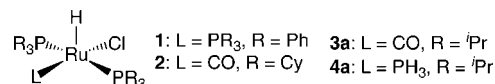
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**Summary:** A DFT study of the full catalytic cycle for H<sub>2</sub>-hydrogenation of ethylene by RuHCl(CO)(PR<sub>3</sub>)<sub>2</sub> (**3a**) and RuHCl(PH<sub>3</sub>)(PR<sub>3</sub>)<sub>2</sub> (**4a**) (R = <sup>i</sup>Pr) catalysts indicates that H<sub>2</sub> binding precedes and stabilizes ethylene insertion, and ethane loss proceeds through a readily accessible Ru(IV) dihydride intermediate. A comparison of the CO and PH<sub>3</sub> reaction coordinates also reveals that the latter is systematically more stable.

Hydrogenation of unsaturated bonds by homogeneous transition-metal catalysts offers tremendous potential to specify regio-, chemo-, and stereoselectivity, as well as overall system productivity.<sup>1</sup> While many metal complexes catalyze hydrogenation reactions, the late metals of groups 8–10 are most active.<sup>1,2</sup> Ruthenium catalysts of the general class RuHCl(L)(PR<sub>3</sub>)<sub>2</sub> (e.g., **1–3**) are of particular interest for their relatively low cost, their versatility, and their efficiency in reduction of challenging

substrates, including unsaturated polymers<sup>3</sup> (a capacity recently exploited in tandem metathesis–hydrogenation catalysis).<sup>4</sup>



Hydridoruthenium catalysts have been the subject of extensive development and study since Wilkinson's original report<sup>5</sup> of H<sub>2</sub>-hydrogenation of terminal alkenes by **1**. Early kinetic experiments on **1** established that the reaction is zero to first order in [olefin], first order in [H<sub>2</sub>], first order in [Ru], and inversely dependent on [PR<sub>3</sub>].<sup>2c</sup> Related Ru–monohydride catalysts, including **2**, obey the same rate law.<sup>3,6</sup> The accepted mechanism based on these data involves formation of the active

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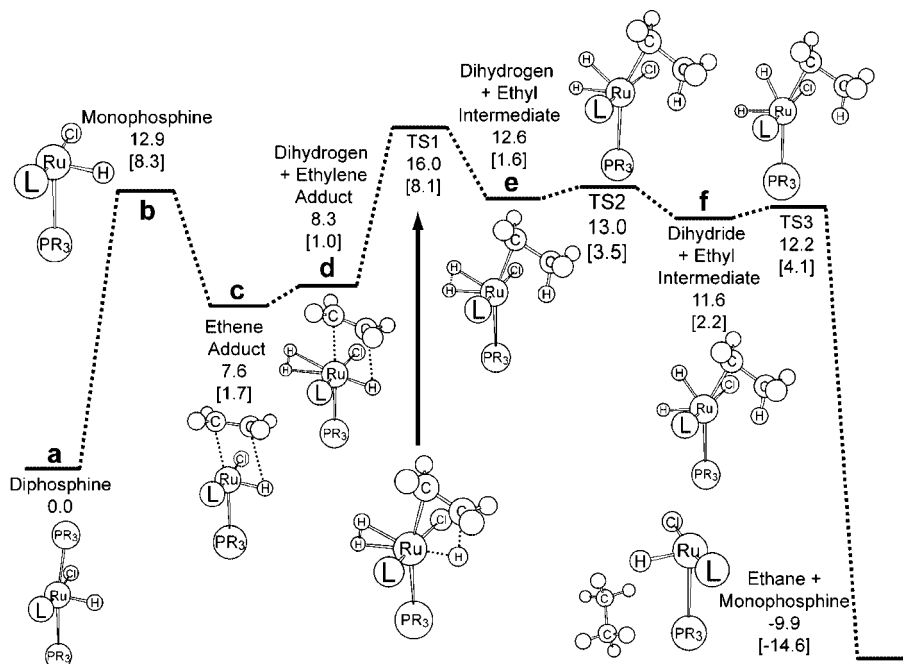
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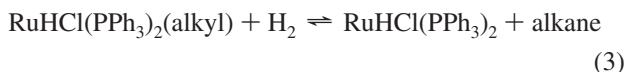
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**Figure 1.** Gibbs free energy reaction profile ( $R = {}^i\text{Pr}$ ): (top numbers)  $L = \text{CO}$ , **3**; (bottom numbers, in brackets):  $L = \text{PH}_3$ , **4**. All values are in  $\text{kcal mol}^{-1}$ .

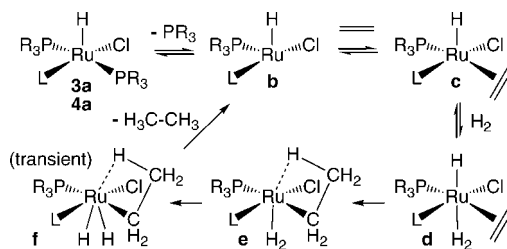
catalyst by loss of a phosphine ligand (eq 1), olefin coordination and insertion to form the putative square-planar metal–alkyl intermediate (eq 2), and finally addition of  $\text{H}_2$ , which triggers elimination of alkane (eq 3).



Previous quantum-chemical investigations on ruthenium hydride complexes have studied the effect of hydride orientation,<sup>7</sup> olefin insertion into  $\text{Ru}-\text{H}$  bonds,<sup>8</sup> and  $\text{Ru}-\text{H}$  and  $\text{Ru}-\text{H}_2$  interactions,<sup>9</sup> but no computational study of the full catalytic cycle of olefin hydrogenation has been reported.

Understanding the role and effect of ancillary ligands in the catalytic cycle can aid catalyst design. In the present context, we were intrigued by the effect associated with the  $\pi$ -acid ligand  $\text{CO}$ , which attenuates hydrogenation activity in arylphosphine complexes of  $\text{Ir}$ ,  $\text{Rh}$ , and  $\text{Ru}^2$  but which in  $\text{Ru}$  systems containing electron-rich donors can give rise to highly active catalysts.<sup>3,6,10</sup>

In this study, we identified the intermediates and transition states for hydrogenation of the model substrate ethylene by coordinatively unsaturated  $\text{Ru}$  hydrogenation catalysts, using B3LYP/LACV3P+\*\*.<sup>11,12</sup> Additionally, we investigated the



**Figure 2.** Proposed catalytic cycle for olefin hydrogenation.

effect of the carbonyl group as an ancillary ligand. Two truncated systems were chosen as models to simplify the calculations. The first,  $\text{CO}$  complex **3a**, itself an effective hydrogenation catalyst,<sup>10</sup> also serves as an analogue of the benchmark catalyst **2** and related alkylphosphine systems.<sup>3,6</sup> The second model catalyst, **4a**, permits us to isolate the effect of the electron-withdrawing  $\text{CO}$  ligand by replacing it with an electron-donating ligand of similarly low steric demand. Our reaction coordinate is shown in Figure 1, with a revised catalytic cycle in Figure 2.

The precatalysts **3a/4a** are square pyramidal, with the hydride ligand occupying the apical site. Our proposed mechanism begins with loss of one  $\text{P}^i\text{Pr}_3$  ligand to give **b**, in keeping with the accepted scheme.<sup>12</sup>  $\eta^2$ -Coordination of ethylene takes up the vacant site trans to the remaining  $\text{P}^i\text{Pr}_3$  ligand (see **c**), the high trans influence of hydride disfavoring the site trans to hydride. While insertion of alkene into the  $\text{Ru}-\text{H}$  bond and then coordination of  $\text{H}_2$  are generally considered the next steps, attempts to optimize the  $\text{Ru}$ -ethyl intermediate regenerate the ethylene adduct **c**. On reversing the order of these steps, with  $\text{H}_2$  bound trans to the hydride, an ethyl intermediate was successfully found.<sup>13</sup>

To better understand this behavior, we calculated the potential energy surface for the ethylene insertion step (**d** and **e**), both

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(12) See the Supporting Information for full computational details and alternative mechanisms.

(13)  $\text{H}_2$  binding is rather weak in **d**, with the  $\text{H}-\text{H}$  distance increasing by only 0.03 Å in **3d** and 0.04 Å in **4d**, relative to free  $\text{H}_2$ .

with and without H<sub>2</sub> coordinated.<sup>12</sup> A minimum is found in the first case: when the site trans to hydride is vacant, this is absent, and the ethyl structures are destabilized relative to the ethylene adduct by ~20 kcal mol<sup>-1</sup>. We therefore propose that ethylene insertion occurs only *after* coordination of H<sub>2</sub>. The transition-state structure (TS1; Figure 1) is similar to that found for other such insertion reactions,<sup>8</sup> with a coplanar Ru–C–H segment. A strong  $\sigma$ -agostic interaction between Ru and the methyl group is found in **e** (Ru–H<sub>ag</sub> = 1.89 Å (**3e**), 1.91 Å (**4e**); C–H<sub>ag</sub> = 1.19 Å (**3e**), 1.17 Å (**4e**)), and the donor character of the trans-bound H<sub>2</sub> increases significantly (H–H bond length 0.90 Å (**3e**), 0.98 Å (**4e**)).

Following insertion, the ethyl–H<sub>2</sub> intermediate **e** eliminates ethane through two steps with small energy barriers. Coordinated H<sub>2</sub> first cleaves to form the seven-coordinate Ru(IV) dihydride intermediate **f**, a distorted capped trigonal prism. The H–H distance for **3f** (1.61 Å) is within the range ( $d_{\text{HH}} > 1.6$  Å) that can be unequivocally designated as a dihydride,<sup>14</sup> although a slightly lower value of 1.57 Å is found for **4f**. An electron localization function (ELF)<sup>15</sup> map of the Ru–H–H plane in the CO system (P<sup>i</sup>Pr<sub>3</sub> truncated to PH<sub>3</sub>) shows distinct hydride ligands, consistent with H<sub>2</sub> being cleaved.<sup>12</sup>

Formation of Ru(IV) dihydride intermediates by oxidative addition of H<sub>2</sub> to a Ru(II) precursor was originally postulated in hydrogenation via **1**, by analogy to the Rh(I)/Rh(III) couple.<sup>2c</sup> Oxidative addition of H<sub>2</sub> was later found to be unfavorable in some cases,<sup>14</sup> the instability of the Ru(IV) dihydrides necessitating heterolytic cleavage of H<sub>2</sub> and retention of the +2 oxidation state. While much current evidence favors Ru(II) over Ru(IV) intermediates, unless small electron-donating ligands are present,<sup>1c</sup> this remains the subject of debate.<sup>1d</sup> For **3/4**, we find that the ethyl–H<sub>2</sub> (**e**) and ethyl–dihydride (**f**) intermediates are isoenergetic, and oxidative addition is facile. This presumably reflects stabilization of the Ru(IV) species by the basic alkylphosphine ligand.<sup>1c,16,17,18</sup> Examples of stable Ru(IV) dihydrides are now well established, where strong donors are present.<sup>17</sup>

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(16) Interestingly, the agostic interaction does not increase on oxidative addition (**3e**, 1.17 Å; **3f**, 1.14 Å; **4e**, 1.18 Å; **4f**, 1.15 Å), implying that it contributes minimally to stabilization of the Ru(IV) intermediate.

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In the final step of the catalytic cycle, a hydride ligand is transferred to the methylene carbon of the cis-ethyl group, elimination of ethane ensues, and the active catalyst is regenerated. As the barriers for TS2 and TS3 are very small (<1 kcal mol<sup>-1</sup>), the potential energy surface between olefin insertion and elimination is essentially flat; thus, elimination of ethane likely occurs immediately after olefin insertion (TS1), with no significant lifetime for the intervening intermediates.

Comparison of the calculated reaction profiles for the L = PH<sub>3</sub> and L = CO systems shows that the former is systematically more stable, beginning with phosphine dissociation, becoming more pronounced following olefin insertion. We attribute this to the  $\sigma$ -donor ability of the PH<sub>3</sub> ligand. The lower stability of the L = CO pathway suggests that the electron-withdrawing character of the  $\pi$ -acid carbonyl ligand should attenuate hydrogenation activity. A parallel experimental study of L = H<sub>2</sub> vs L = CO in PCy<sub>3</sub> systems confirms, however, that **2** exhibits higher activity in olefin hydrogenation.<sup>18</sup> This study rules out a purely steric origin for the activating effect of the CO ligand.

These findings update the long-standing mechanism for olefin hydrogenation via RuHCl(L)(PR<sub>3</sub>)<sub>2</sub> catalysts in two significant aspects. First, the ethyl intermediate formed by olefin insertion utilizes a pre-installed “ancillary” H<sub>2</sub> ligand to stabilize the ruthenium center through  $\sigma$ -bond donation, where the classic model invoked ethylene insertion prior to H<sub>2</sub> binding. Second, activation of H<sub>2</sub> and elimination of alkane involve an oxidative addition–reductive elimination sequence in these alkylphosphine systems (i.e., a Ru(IV) dihydride intermediate), rather than heterolytic cleavage of H<sub>2</sub> within Ru(II) species. We note that these revisions remain consistent with the experimentally determined rate law. Finally, in comparing RuHCl(CO)(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub> and RuHCl(PH<sub>3</sub>)(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub> catalysts, we find no electronic basis for the activating effect of the CO ligand. Evaluation of the origin of this effect is the focus of current work.

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**Supporting Information Available:** Text, figures, and tables giving computational details, details of alternative mechanisms explored, 2D PES of insertion reactions, coordinates of species, and ELF plots. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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