Homogeneous Hydrogenation of Alkenes Catalyzed by the Ruthenium−Hydride Complex $(PCy_3)_2(CO)(Cl)RuH$: Spectroscopic Observation of the Ruthenium−Ethyl and Ruthenium−Ethylene−Hydride Intermediate Species

Chae S. Yi* and Do W. Lee

Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53201-1881

Received June 28, 1999

The ruthenium−hydride complex $(PCy_3)_2(CO)(Cl)RuH$ (**1a**) was found to catalyze the hydrogenation of terminal and cyclic alkenes. For example, the reaction of 1-hexene with 4 atm of H_2 in the presence of **1a** (1-hexene:**1a** = 8300:1) produced the hydrogenation product **2** (TON = 12 000 h^{-1}). The treatment of **1a** with excess ethylene led to the observation of both the ruthenium−ethyl and ruthenium−ethylene−hydride species **4a** and **5a**, respectively. The thermodynamic parameters for the equilibria among **1a**, **4a**, and **5a** were estimated from the VT NMR data. These results are consistent with a monohydride mechanistic pathway.

Introduction

The mechanism of olefin hydrogenation reactions catalyzed by Wilkinson's catalyst, $(PPh_3)_3RhCl$, has been well-known to occur via a so-called "dihydride" mechanism, in which a metal−dihydride species is formed from an oxidative addition of H_2 to the metal center.[1] In contrast, the mechanism of the hydrogenation reactions catalyzed by complexes of the type $(PPh_3)_3(CO)RhH$ and $(PPh_3)_3RuHCl$ has been commonly regarded to proceed via a "monohydride" pathway.[1a] The distinguishing features of the hydrogenation reaction catalyzed by monohydride metal complexes include (1) high activity and selectivity toward terminal alkenes, (2) a tendency to form isomerization products, and (3) the generation of metal−alkyl intermediate species from an insertion of olefin into a metal−hydride bond.[1,2] Despite experimental evidence of its existence, however, the metal−alkyl intermediate species has been rarely observed under catalytically viable conditions.[3] The need for a better mechanistic understanding of the monohydride pathway has also been exemplified by recent developments in metal-catalyzed asymmetric hydrogenation reactions, wherein the monohydride mechanistic pathway has been suggested in some cases.[2]

We recently described an effective synthesis of the previously inaccessible complex $(PCy_3)_2(CO)(Cl)RuH$ (**1a**).[4] Since carbonyl−hydride complexes of the type $(L)_2(CO)(Cl)MH$ (M = Ru, Os; L = PPr^i_3, PBu^t_2Me) have been shown to catalyze the hydrogenation and hydrosilylation reactions of alkenes and alkynes,[5] we decided to explore the catalytic activity of **1a** toward these reactions. Our initial hope was that the sterically demanding PCy_3-containing complex **1a** might lead to a higher activity and/or observation of reactive intermediate species. Herein, we wish to report that **1a** is an effective catalyst precursor for the homogeneous hydrogenation of terminal and cyclic alkenes. We further disclose a direct spectroscopic observation of the metal−alkyl and alkene−hydride species in the reaction of **1a** and ethylene.

(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Spencer, A. In *Comprehensive Coordination Chemistry*, Wilkinson, G., Ed.; Pergamon: New York, 1987; Vol. 6. (c) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley: New York, 1992. (d) Chalonger, P. A.; Esteruelas, M. A.; Joó, F.; Oro, L. A. *Homogeneous Hydrogenation*; Kluwer: Boston, 1994. (e) Bruner, H. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: New York, 1996; Vol. 1.

(2) (a) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994. (b) Takaya, H.; Noyori, R. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: New York, 1990; Vol. 8. (c) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97−102. (d) Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241−10254. (e) Burk, M. J.; Harper, T. G. P.; Kalberg, C. S. *J. Am. Chem. Soc.* **1995**, *117*, 4423−4424. (f) Ohkuma, T.; Ooka, H.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 10417−10418. (g) Wiles, J. A.; Bergens, S. H.; Young, V. G. *J. Am. Chem. Soc.* **1997**, *119*, 2940−2941. (h) Fehring, V.; Selke, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1827−1830. (i) Troutman, M. V.; Appella, D. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 4916−4917.

(3) (a) Baird, M. C.; Mague, J. T.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 1347−1359. (b) Jardine, F. H. *Prog. Inorg. Chem.* **1984**, *31*, 265−370 and references therein. (c) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sánchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431−7437. (d) Ashby, M. T.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 589−594. (e) Ashby, M. T.; Khan, M. A.; Halpern, J. *Organometallics* **1991**, *10*, 2011−2015.

(4) The synthesis of complex **1a** was first reported without complete characterization data and yields in: Mores, F. G.; Langhout, J. P. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 591−600. We recently reported a reliable synthesis and characterization of **1a** following a modified literature procedure:[5a,b] Yi, C. S.; Lee, D. W.; Chen, Y. *Organometallics* **1999**, *18*, 2043−2045.

(5) For the synthesis and reactions of **1b**, see: (a) Buil, M. L.; Elipe, S.; Esteruelas, M. A.; Oñate, E.; Peinado, E.; Ruiz, N. *Organometallics* **1997**, *16*, 5748−5755 and references therein. (b) Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221−231. For hydrogenation and hydrosilation reactions catalyzed by **1b** and related complexes, see: (c) Esteruelas, M. A.; Valero, C.; Oro, L. A.; Meyer, U.; Werner, H. *Inorg. Chem.* **1991**, *30*, 1159−1160. (d) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1992**, *11*, 3362−3369. (e) Esteruelas, M. A.; Herrero, J.; Oro, L. A. *Organometallics* **1993**, *12*, 2377−2379.

10.1021/om990493k CCC: $18.00
Publication on Web 11/02/1999

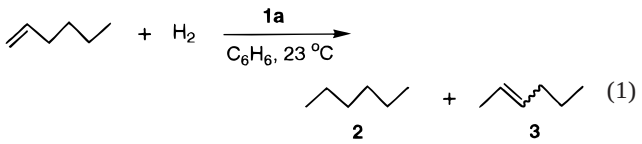
Table 1. Hydrogenation of Alkenes Catalyzed by 1a[a]

entry	alkene	product	amt of H_2 (atm)	turnover rate[b]
1	1-hexene	hexane	1.0	1200 (180)
2	1-hexene	hexane	4.0	12000 (150)[c]
3	allylbenzene	1-phenylpropane	2.0	2000 (390)
4	4-vinyl-1-cyclohexene	4-ethylcyclohexene	2.0	1300
5	cyclopentene	cyclopentane	1.0	960
6	cyclooctene	cyclooctane	1.0	940
7	cyclooctene	cyclooctane	2.0	2700
8	*trans*-4-phenyl-3-buten-2-one	4-phenyl-2-butanone	4.0	15[d]
9	cyclopentenone	cyclopentanone	4.0	70[d]

[a] Reaction conditions: 5.7 mmol of alkene (1.0 M); 0.69 μmol of the catalyst (0.12 mM; alkene:**1a** = 8300:1); 5 mL of C_6H_6; room temperature. [b] Turnover rate = (mol of product) (mol of catalyst)$^{-1}$ h^{-1}. The values in parentheses correspond to isomerization turnovers. [c] The turnover rate was estimated after 30 min of reaction time. [d] Reaction conditions: 2.0 mmol of alkene; 3.4 μmol of the catalyst (alkene:**1a** = 600:1); 55 °C.

Results and Discussion

We found that **1a** is an effective catalyst precursor for the hydrogenation of terminal and cyclic alkenes. For example, the treatment of 1-hexene (0.48 g, 5.7 mmol) with 1.0 atm of H_2 in the presence of **1a** (0.5 mg, 0.69 μmol) at room temperature produced the hydrogenation product *n*-hexane (**2**) along with the isomerization products, 2-hexenes (**3**; TON = 1200 h^{-1}; **2**:**3** = 6.7:1) (eq 1). The turnover number (TON) for the hydrogenation of 1-hexene reached 12 000 h^{-1} at 4.0 atm of H_2 with a virtually unchanged isomerization rate (Table 1, entry 2).[6] The activity of the PPr^i_3 analogue $(PPr^i_3)_2$(CO)(Cl)RuH (**1b**)[5a] was found to be considerably lower than that of **1a** under similar reaction conditions (TON = 700 h^{-1} for 1-hexene at 1.0 atm of H_2).



(1)

We next explored the catalytic activity of **1a** toward both terminal and cyclic alkenes. In general, high activity/selectivity toward the hydrogenation of terminal alkenes has been observed, as exemplified in the 4-vinyl-1-cyclohexene case (entry 4). The hydrogenation rate of strained cyclic alkenes was somewhat lower than that of terminal alkenes (entries 5 and 6), while the hydrogenation of internal alkenes was found to be very sluggish (entries 8 and 9).

In an attempt to better understand the mechanism of the reaction, reactions of complex **1a** with different alkenes were followed by NMR. The most noticeable change was observed in the reaction with ethylene. In a heavy-walled NMR tube, excess ethylene (2.0 mmol) was condensed into a CD_2Cl_2 solution containing complex **1a** (6 mg, 8.3 μmol), and the tube was flame-sealed at liquid-N_2 temperature. When the mixture was warmed to room temperature, the formation of a new species was detected by ^{31}P NMR (δ 26.1), and this new species was found to exist as an equilibrium mixture with **1a** (**1a**:(new complex) = 1:1.7). Since no other peaks could be assigned, due to the presence of PCy_3 signals, the structure of new species was established from an analogous reaction with ^{13}C-enriched ethylene. The ^{13}C NMR of the ^{13}C-enriched sample showed two new ethyl carbon resonances at δ 25.1 (qd, J_{CH} = 126.4, J_{CC} = 36.0 Hz) and 7.4 (ttd, J_{CH} = 126.4, J_{CC} = 36.0, J_{CP} = 6.9 Hz). The phosphorus signal at δ 26.1 turned into a doublet (J_{CP} = 6.9 Hz) due to the coupling with the α-^{13}C atom. All of these spectroscopic data are consistent with the ethyl complex **4a**. The addition of H_2 (1 atm) to this reaction mixture slowly produced ethane (TON ≈ 5 h^{-1}).

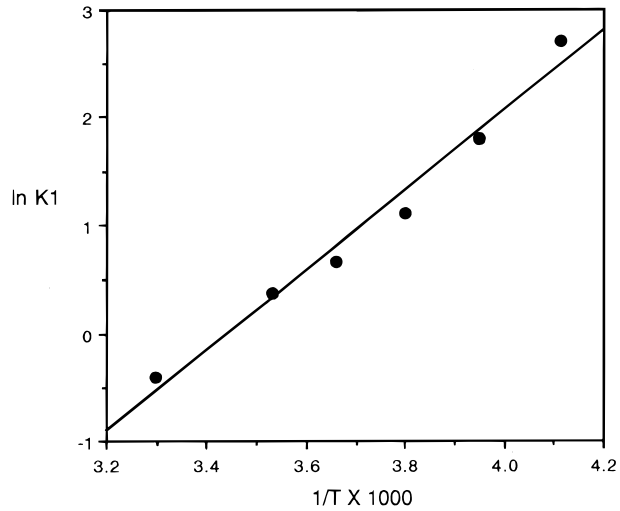
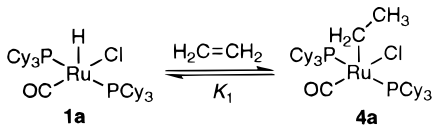


Figure 1. van't Hoff plot of ln K_1 vs 1/T.



ΔH_1° = -7.5 ± 1.0 kcal/mol
ΔS_1° = -27 ± 4 e.u.

The equilibrium constants between **1a** and **4a** were estimated from the VT NMR using the phosphorus integration for both complexes in the temperature range of −40 to +30 °C. The van't Hoff analysis of these data led to the thermodynamic parameters of ΔH_1° = −7.5 ± 1.0 kcal/mol and ΔS_1° = −27 ± 4 eu for this equilibrium reaction (Figure 1), which are comparable to those for recently reported late-metal-mediated olefin insertion reactions.[7] Examples of low-valent ruthenium−alkyl complexes having β-hydrogens are relatively rare,[8]

(6) Most of the isomerization reactions were found to occur during the first 20 min before adding H_2 (>90%).

(7) For selected examples on the energetics of late-metal-mediated olefin insertions, see: (a) Brookhart, M.; Hauptman, E.; Lincoln, D. M. *J. Am. Chem. Soc.* **1992**, *114*, 10394−10401. (b) Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 1137−1138. (c) Tanner, M. J.; Brookhart, M.; DeSimone, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 7617−7618.

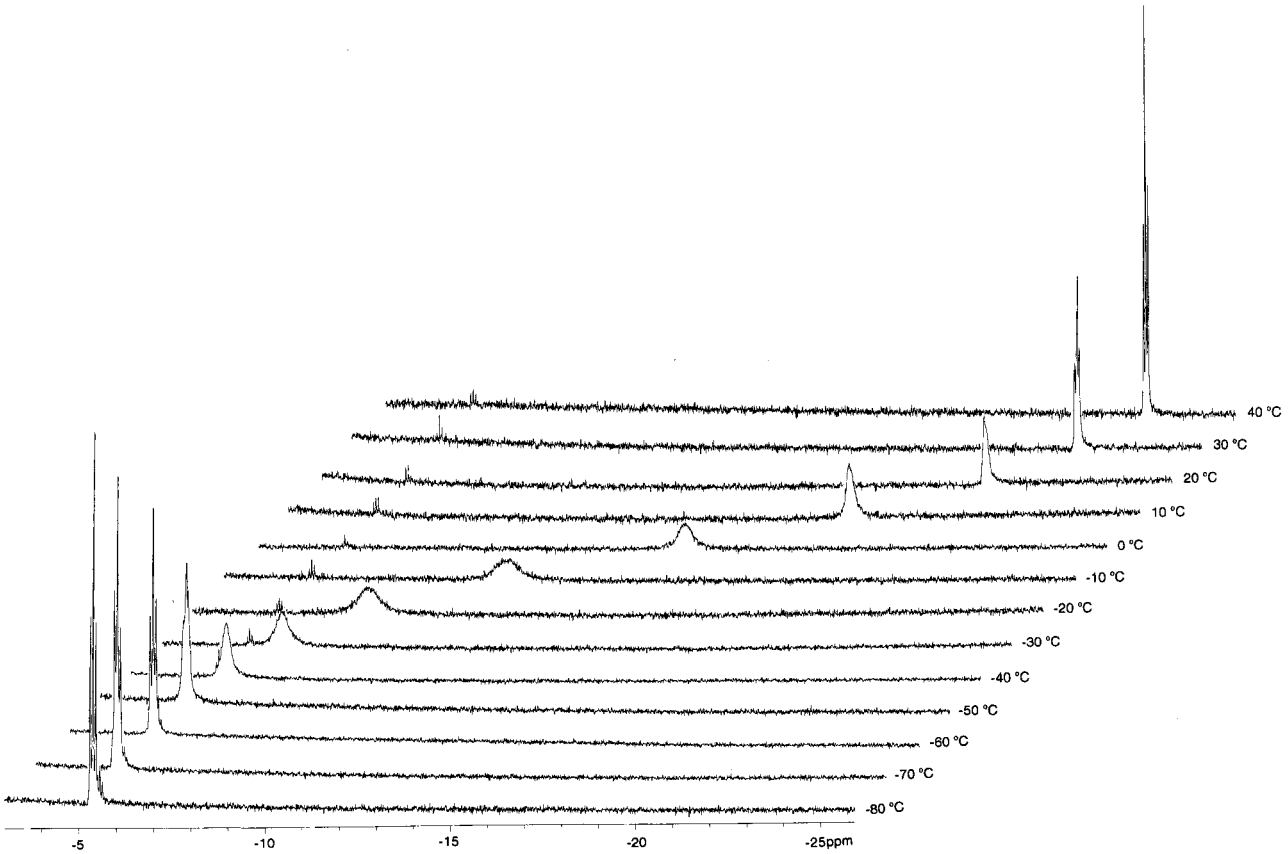
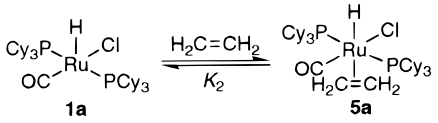


Figure 2. Metal−hydride region of the variable-temperature ^{1}H NMR (CD_2Cl_2, 300 MHz) spectra of **1a** and **5a** from −80 to +40 °C.

and to the best of our knowledge, this is the first example in which a ruthenium−alkyl species has been directly observed under catalytically relevant conditions.

Another ruthenium species was identified in the reaction of **1a** with ethylene at low temperatures. Thus, the new metal−hydride peak appeared at δ −5.20 (t, J_{HP} = 24.0 Hz) at −80 °C, the structure of which was established as the *trans*-ethylene−hydride species **5a** on the basis of the spectroscopic data. The hydride peak



ΔH_2° = -12.0 ± 0.3 kcal/mol

ΔS_2° = -45 ± 2 e.u.

of **5a** was found to undergo temperature-dependent chemical shift changes; the hydride peak of **5a** at δ −5.20 continuously moved toward the hydride peak of **1a** at δ −23.0 ppm upon warming to room temperature (Figure 2). The equilibrium constants (K_2) between **1a** and **5a** were determined by correlating the chemical shift of the hydride peak in the temperature range of −80 to +40 °C using a two-site chemical shift exchange

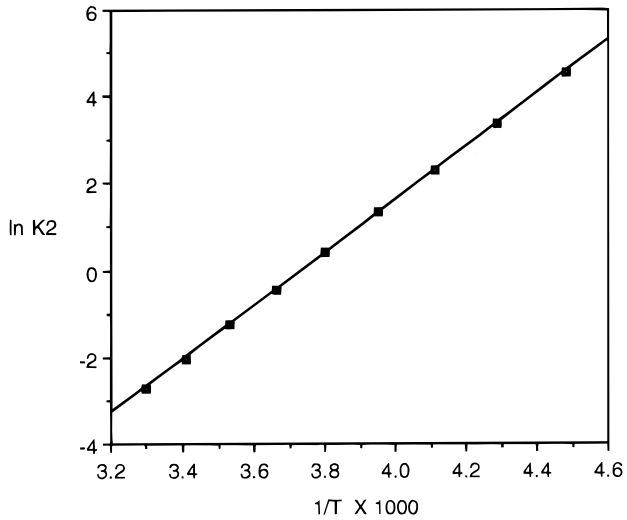


Figure 3. van't Hoff plot of ln K_2 vs 1/T.

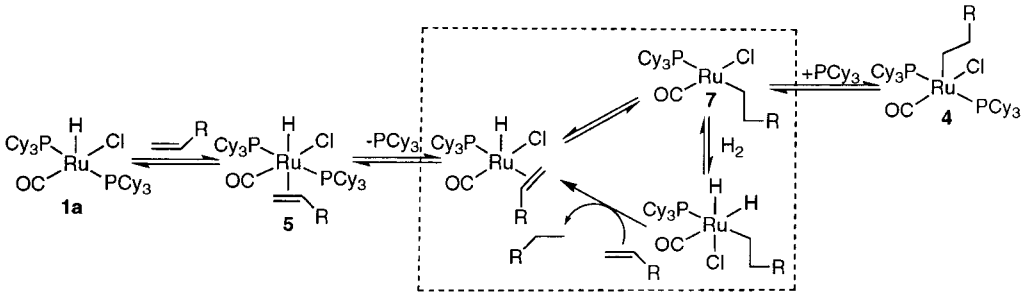
method.[9] The van't Hoff plot for this equilibrium reaction led to the thermodynamic parameters of ΔH_2° = −12.0 ± 0.3 kcal/mol and ΔS_2° = −45 ± 2 eu (Figure 3). In all of these measurements, ethylene concentration in the solution was found to be in excess and remained relatively constant throughout the temperature range (ethylene:**1a** ≥ 50:1; [ethylene] = 1.7 M).[10]

We found that the phosphine ligand strongly inhibits the catalytic reaction. For example, the addition of 0.7 mol % of PCy_3 to the reaction mixture led to a drastically

(8) (a) Hill, A. F. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1994; Vol. 12. (b) Fabre, S.; Kalck, P.; Lavigne, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1092−1095. (c) Faure, M.; Maurette, L.; Donnadieu, B.; Lavigne, G. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 518−522. (d) Edwards, A. J.; Elipe, S.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1997**, *16*, 3828−3836.

(9) Hauger, B. E.; Gusev, D.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 208−214.

Scheme 1



reduced catalytic activity for 1-hexene (TON = 20 h^{-1} at 1.0 atm of H_2). Furthermore, the rate of the hydrogenation reaction was found to be considerably lower if H_2 was added to a cooled solution before adding an alkene substrate (e.g., TON = 5100 h^{-1} with 4.0 atm of H_2), compared to the reaction mixture stirred for about 20 min in the presence of an alkene substrate prior to adding H_2. In a separate experiment, the treatment of **1a** with ca. 2 atm of H_2 led to the formation of the η^2-H_2 complex **6**, which was found to exist as a mixture with **1a** at low temperature. These results suggest that the formation of η^2-H_2 complex **6** might initially retard the rate of hydrogenation by preventing the alkene coordination to **1a**. Previously, small molecules, including H_2 and ethylene, have been shown to coordinate to similar ruthenium and osmium complexes.[11]

We observed an inverse isotope effect for the hydrogenation reaction. For example, the hydrogenation of cyclooctene with 2.0 atm of H_2/D_2 led to $k_H/k_D = 0.7$ at 23 ± 0.5 °C. We also found that the hydrogenation of allylbenzene using a 1:1 mixture of H_2 and D_2 (2 atm) produced a mixture of d_0, d_1, and d_2 hydrogenation products. The formation of both d_1 and d_2 products is consistent with the involvement of a monohydride species. While it is risky to draw any conclusions for a multistep catalytic reaction,[12] these data suggest that the C−H bond-forming process is the rate-determining step. Similar inverse equilibrium isotope effects have been commonly observed in metal-promoted hydrogen transfer and alkene insertion reactions.[13]

These results are consistent with the generally accepted monohydride mechanistic pathway for the hydrogenation reaction (Scheme 1). One plausible way to a catalytically active species is an alkene-induced dissociation of PCy_3 ligand from **1a**. The initial inhibition of the reaction by H_2 and the formation of **6** suggest that the coordination of an alkene substrate might facilitate the dissociation of a phosphine ligand from the metal center. The spectroscopic observation of **4a** also implies that the unsaturated alkyl species **7** could be formed from **4** via the dissociation of a phosphine ligand. The subsequent H_2 addition/reductive elimination sequences have been commonly proposed in the reactions catalyzed by monohydride metal complexes.[1,2]

In summary, the ruthenium−hydride **1a** was found to catalyze the hydrogenation reaction of terminal and cyclic alkenes. The spectroscopic observation of key intermediate species, **4a** and **5a**, and preliminary mechanistic studies suggest a monohydride mechanistic pathway for this reaction. Efforts to increase the catalytic activity of **1a** and to determine the kinetics of the hydrogenation reaction are currently underway.

Experimental Section

General Information. All reactions were carried out in an inert-atmosphere glovebox or by using standard high-vacuum and Schlenk-line techniques unless otherwise noted. Benzene, hexanes, and Et_2O were distilled from purple solutions of sodium and benzophenone immediately prior to use. CH_2Cl_2 was distilled from CaH_2. The NMR solvents were dried from activated molecular sieves (4 Å). All organic alkene substrates were vacuum-distilled from molecular sieves or sodium prior to use. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a GE GN-Omega 300 MHz FT-NMR spectrometer. Mass spectra were recorded from a Hewlett-Packard HP 5890 GC/MS spectrometer. Gas chromatographs were recorded from a Hewlett-Packard HP 6890 GC spectrometer.

General Procedure of the Catalytic Hydrogenation Reaction. In a glovebox, 1.0 mL of a predissolved 0.69 mM C_6H_6 solution of **1a** (0.5 mg, 0.69 μmol) was placed in a 100 mL Fisher-Porter pressure bottle equipped with a pressure gauge and a stirring bar. The solution was diluted with 4.0 mL of C_6H_6. Excess alkene (5.7 mmol) was added, and the bottle was attached to a vacuum line. The reaction bottle was evacuated while it was cooled in a liquid-N_2 bath. The reaction bottle was warmed to room temperature with stirring over a 20 min period. An appropriate amount of H_2 gas pressure was applied to the reaction bottle, and the reaction mixture was vigorously stirred at room temperature (22−23 °C) for 0.5−4 h. The product ratio was determined by GC.

VT NMR Study for the Reaction of 1a with Ethylene. The ruthenium−hydride complex **1a** (6 mg, 8.3 μmol) was dissolved in 0.3 mL of CD_2Cl_2 in a heavy-walled NMR tube. After three cycles of freeze−pump−thaw degassing, excess ethylene gas (125 mL at 300 Torr, 2.0 mmol) was condensed into the tube at liquid-N_2 temperature, after which the tube was flame-sealed. The tube was warmed to room temperature and the solution was allowed to equilibrate for 30 min before NMR analysis. The sample tube was inserted into the NMR probe, and the probe was cooled by a cold stream of N_2. The equilibrium constants K_1 were determined from the phospho-

(10) Ethylene concentration in the solution was found to vary ca. 20% in the temperature range −80 to +40 °C as measured against an internal standard. We treated ethylene as a constant in calculating equilibrium constants because ethylene concentration was sufficiently in excess (>50-fold) compared to the ruthenium complexes in all cases. An analogous measurement of equilibrium constants at a higher pressure of ethylene ([ethylene] = 2.2 M) was found to give virtually identical thermodynamic parameter values.

(11) (a) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Meyer, U.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1563−1564. (b) Gusev, D. G.; Vymenits, A. B.; Bakhmutov, V. I. *Inorg. Chem.* **1992**, *31*, 2−4. (c) Bakhmutov, V. I.; Bertrán, J.; Esteruelas, M. A.; Lledós, A.; Maseras, F.; Modrego, J.; Oro, L. A.; Sola, E. *Chem. Eur. J.* **1996**, *2*, 815−825. (d) Gusev, D. G.; Kuhlman, R. L.; Renkema, K. B.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 6775−6783. (e) Huang, D.; Huffman, J. C.; Bollinger, J. C.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 7398−7399.

(12) Halpern, J.; Okamoto, T.; Zakhariev, A. *J. Mol. Catal.* **1976**, *2*, 65−68.

(13) Bullock, R. M. In *Transition Metal Hydrides*, Dedieu, A., Ed.; VCH: New York, 1992.

rus integration of **1a** and **4a** by ^{31}P NMR in the temperature range −40 to +30 °C (10 °C intervals). Similarly, the equilibrium constants K_2 were determined by measuring the change in chemical shift of the metal−hydride between **1a** and **5a** from −80 to +40 °C (10 °C intervals). The sample was allowed to equilibrate for 10−15 min before the data acquisition at each temperature. The van't Hoff plots using Cricket Graph v. 1.3 led to the thermodynamic values listed in the main text (Figures 1 and 3). The stack plot of the variable-temperature ^1H NMR spectra of **1a** and **5a** in the metal−hydride region is shown in Figure 2. The ethylene concentration was assumed to be constant throughout the temperature range (ethylene: **1a** ≥ 50:1).

Selected spectroscopic data for **4a** taken from ^{13}C-enriched ethylene: ^{13}C NMR (CD_2Cl_2, 75.6 MHz) δ 25.1 (qd, J_{CH} = 126.4, J_{CC} = 36.0 Hz, RuCH_2CH_3), 7.4 (ttd, J_{CH} = 126.4, J_{CC} = 36.0, J_{CP} = 6.9 Hz, RuCH_2CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.6 MHz) δ 26.1 (d, J_{CP} = 6.9 Hz, PCy_3).

Selected spectroscopic data for **5a**: ^1H NMR (CD_2Cl_2, 300 MHz, −80 °C) δ −5.20 (t, J_{HP} = 24.0 Hz, Ru−H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.6 MHz, −80 °C) δ 57.0 (br s, CH_2═CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.6 MHz, −80 °C) δ 40.9 (br s, PCy_3).

Spectroscopic Characterization of 6. The ruthenium complex **1a** (6 mg, 8.3 μmol) was dissolved in 0.3 mL of CD_2Cl_2 in a heavy-walled NMR tube. After three cycles of freeze−pump−thaw degassing, excess H_2 gas (∼2 atm) was condensed into the tube at liquid-N_2 temperature, and the tube was flame-sealed. The tube was warmed to room temperature, and the solution was allowed to equilibrate for 30 min prior to the NMR analysis. The η^2-H_2 complex **6** was found to exist as a 30:70 equilibrium mixture with **1a** at −90 °C.

Selected spectroscopic data for **6**: ^1H NMR (CD_2Cl_2, 300 MHz, −90 °C) δ −8.97 (br s, Ru−H), η^2-H_2 peak was masked by PCy_3 signals; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.6 MHz, −90 °C) δ 38.3 (br s, PCy_3).

Acknowledgment. Financial support from the National Institutes of Health (Grant No. R15 GM55987) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

OM990493K