

**LETTERS****Concerted Hydrogen Rearrangement in Nickelocenium Cation and the Formation of NiH<sub>2</sub><sup>+</sup>****Thalappil Pradeep,<sup>†</sup> Jeffrey S. Patrick, Bingbing Feng, Scott A. Miller, Teodor Ast,<sup>‡</sup> and R. Graham Cooks\****Department of Chemistry, Purdue University, West Lafayette, Indiana 47907-1393**Received: August 1, 1994; In Final Form: January 18, 1995<sup>⊗</sup>*

The first experimental observation of the NiH<sub>2</sub><sup>+</sup> ion is described. Concerted hydrogen rearrangement upon mild collisional activation of the nickelocene molecular ion in either ion/surface or gas-phase ion/molecule collisions yields NiH<sub>2</sub><sup>+</sup>. Changes in the intensity of NiH<sub>2</sub><sup>+</sup> with variation of collision and electron impact energies suggest that the mechanism involves the excitation of a low-energy vibrational mode of the molecular ion, resulting in cyclopentadienyl ring fusion to form C<sub>10</sub>H<sub>8</sub> with the simultaneous transfer of two hydrogen atoms to Ni<sup>+</sup>. Attempts at the formation of NiH<sub>2</sub><sup>+</sup> by direct insertion of Ni<sup>+</sup> into hydrogen gas or by dehydrogenation of an alkane were unsuccessful; however, oxidative addition of H<sub>2</sub> to NiCp<sup>+</sup> was observed. Gas-phase reactions between NiCp<sub>n</sub><sup>+</sup> (*n* = 0–2) and 1,3- or 1,4-cyclohexadiene (CHD) show the production of ionic Ni complexes which involve dehydrogenation processes. These products include Ni(C<sub>6</sub>H<sub>6</sub>)<sup>+</sup>, NiCpH<sub>2</sub><sup>+</sup>, and polyligated complexes with benzene, CHD, and cyclopentadiene. These dehydrogenation reactions suggest that the dihydride might be important in the hydrogenation/dehydrogenation chemistry of nickel.

The chemistry of Ni, Pd, and Pt varies significantly from that of other group VIII elements. Hydrogenation and dehydrogenation of hydrocarbons are frequently catalyzed over these metals with Raney nickel being especially important as an enantio-differentiating catalyst.<sup>1</sup> The economic advantage of using enhanced surface area materials has caused interest in the use of cluster catalysts,<sup>2</sup> and hydrogenation of alkenes has been carried out with cluster catalysts<sup>3</sup> such as H<sub>3</sub>Ni<sub>4</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>4</sub>. An understanding of metal–hydrogen chemistry is important in addressing fundamental issues concerning oxidative addition and reductive elimination reactions which are central to catalytic

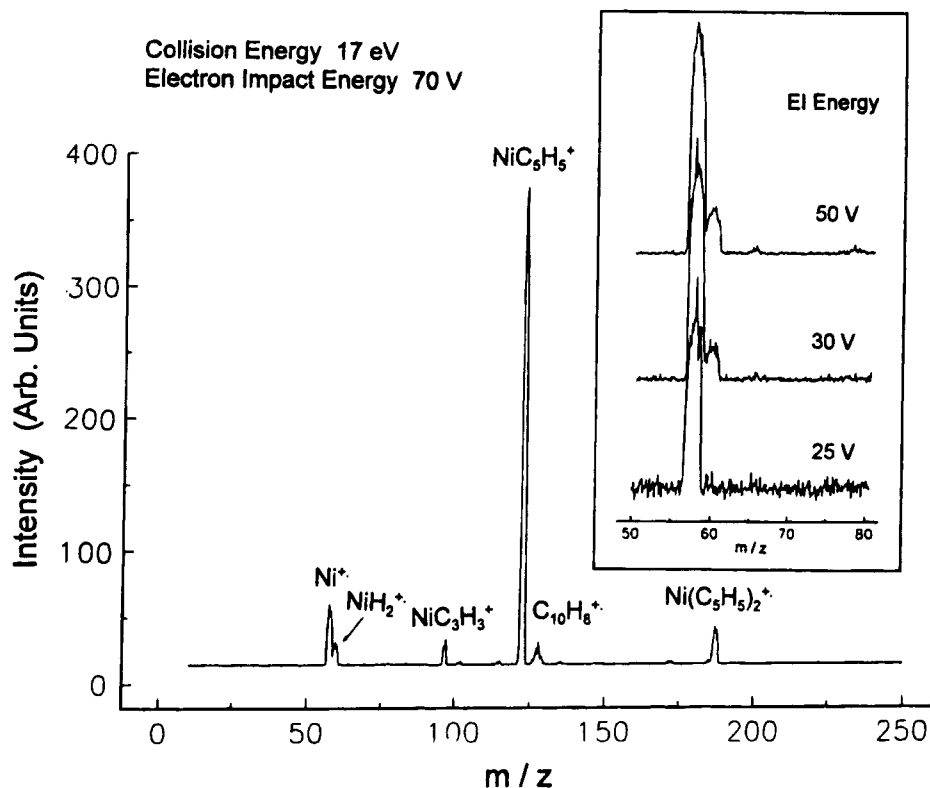
processes.<sup>4</sup> An important step in catalytic hydrogenation is believed to be the insertion of the metal atom into the H–H bond. To understand the metal–hydrogen interaction, a number of investigators have probed metal ion/hydrogen chemistry; however, most studies pertain to simple monohydrides.<sup>5</sup> Although direct insertion of Ni<sup>+</sup> in its <sup>2</sup>D state into hydrogen to form the dihydride ion has been predicted by theory,<sup>6</sup> no experimental evidence for this reaction exists. A number of theoretical studies exist on the neutral mono- and dihydrides;<sup>7–11</sup> PdH<sub>2</sub><sup>+</sup> has also been investigated by theory.<sup>11</sup> High-quality calculations predict NiH<sub>2</sub><sup>+</sup> to be bent, with a bond angle of 28.2° and a dissociation energy (to yield Ni<sup>+</sup> and H<sub>2</sub>) of 22 kcal/mol.<sup>6</sup> In the following, we describe the first experimental observation of the NiH<sub>2</sub><sup>+</sup> ion, formed by hydrogen rearrangement in nickelocenium molecular ion. Possible implications of this finding to catalysis are assessed by studying gas-phase ion/molecule reactions.

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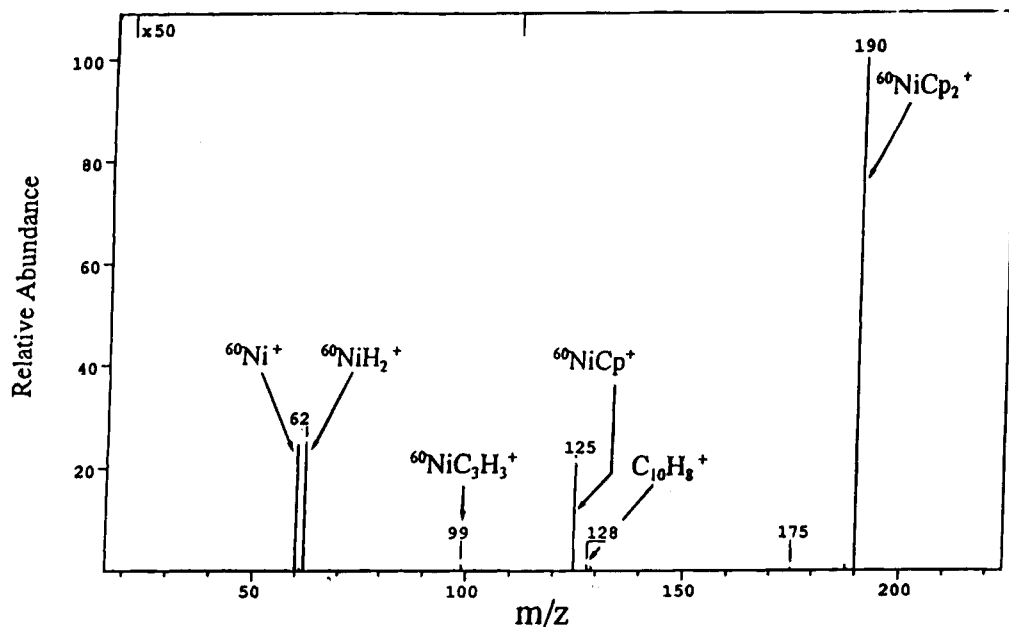
**Figure 1.** Scattered ion mass spectrum obtained upon 17 eV collisions of nickelocene molecular ions ( $\text{NiCp}_2^{2+}$ ) with a fluorinated self assembled monolayer surface. Note the peak at  $m/z$  60 due to  $\text{NiH}_2^{2+}$ . In the insert, mass spectra in the range of  $m/z$  50–80 recorded for three different electron impact energies are shown. The peak at  $m/z$  60 due to  $\text{NiH}_2^{2+}$  disappears at 25 eV electron impact energy.

In the course of investigating excited state effects in low-energy ion/surface reactions using a custom-built tandem mass spectrometer of BEEQ configuration<sup>12</sup> (B = magnetic sector, E = electric sector, Q = quadrupole mass filter), a decision was made to probe the reactions of nickelocenium cation  $\text{NiCp}_2^{2+}$  (Cp =  $\text{C}_5\text{H}_5$ ) upon collision with a fluorinated self-assembled monolayer (SAM) surface.<sup>13</sup> The scattered ion mass spectrum obtained upon 20 eV collisions of the isotopically selected  $^{58}\text{NiCp}_2^{2+}$  projectile ( $m/z$  188) exhibits a peak at  $m/z$  60, corresponding to  $\text{NiH}_2^{2+}$ . This assignment was verified by an experiment using the nickelocenium projectile containing the  $^{60}\text{Ni}$  isotope. On the basis of theoretical predictions<sup>6</sup> of the stability of this species, we believe that  $\text{NiH}_2^{2+}$  represents a true molecular ion rather than a loose ion–molecule complex. Studies employing a perdeuterated SAM surface<sup>14</sup> failed to generate any  $\text{NiD}_2^{2+}$  but yielded again  $\text{NiH}_2^{2+}$ , confirming that the product obtained is not due to an ion/surface reaction.<sup>15</sup>

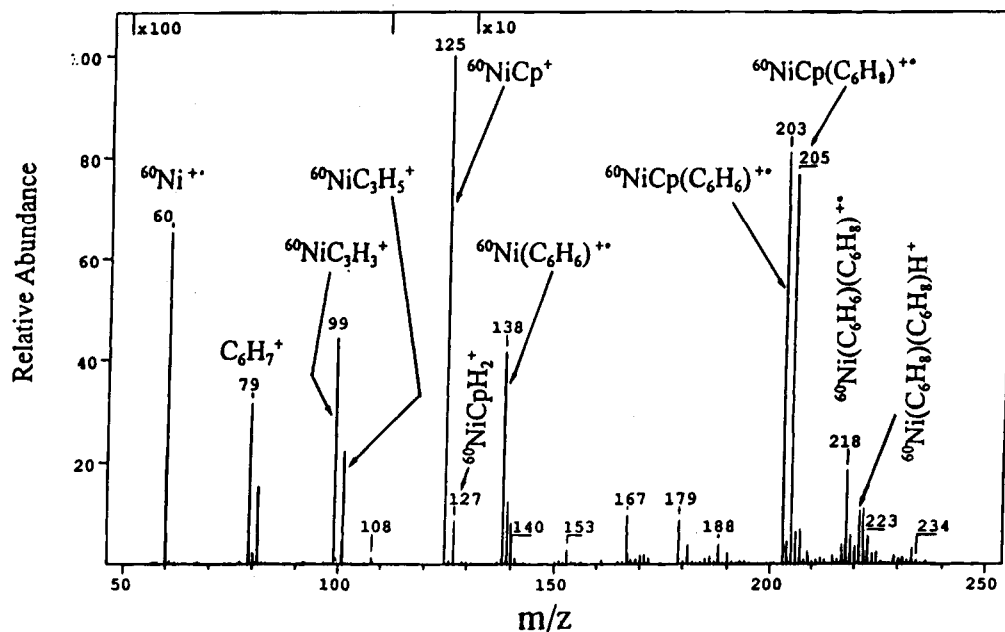
The scattered ion mass spectrum obtained upon 17 eV collisions of the nickelocene molecular ion ( $m/z$  188) on a fluorocarbon SAM surface is shown in Figure 1. Prominent peaks in the mass spectrum occur at  $m/z$  188, 128, 123, 97, and 58 and are due to  $\text{NiC}_{10}\text{H}_{10}^{2+}$ ,  $\text{C}_{10}\text{H}_8^{2+}$ ,  $\text{NiC}_5\text{H}_5^{2+}$ ,  $\text{NiC}_3\text{H}_3^{2+}$ , and  $\text{Ni}^{2+}$ , respectively. Except for the intact projectile, these ions are the products of surface induced dissociation.<sup>16</sup> As the collision energy is increased, other peaks appear in the mass spectrum, due either to ion/surface reactions<sup>17</sup> ( $\text{NiF}^+$ ,  $\text{C}_5\text{H}_5\text{F}^+$ ), or to chemical sputtering<sup>18</sup> ( $\text{CF}^+$ ,  $\text{CF}_2^{2+}$ ,  $\text{C}_2\text{F}_5^+$ , etc.). The peak at  $m/z$  60 is due to  $\text{NiH}_2^{2+}$ . This peak appears at a collision energy as low as 10 eV; as the collision energy is increased, it decreases in intensity relative to  $\text{Ni}^+$  ( $m/z$  58) and finally disappears at 30 eV. At a fixed collision energy, a decrease in electron impact energy results in disappearance of the peak at  $m/z$  60 below 25 eV (see the insert of Figure 1). The occurrence of this product at low collision energies is indicative of a

rearrangement reaction.<sup>19</sup> Collectively, the above results suggest that excitation of a low-energy vibrational mode of  $\text{Ni}(\text{Cp})_2^{2+}$  may be a primary cause of the reaction. In experiments using cobaltocene or ferrocene, collision of either the intact molecular ion or a fragment with the fluorinated surface shows no evidence of metallodihydride ( $\text{MH}_2^{2+}$ ) formation. The other fragment ions observed were, however, analogous to those seen for nickelocene. In a further attempt to form the  $\text{NiH}_2^{2+}$  ion from  $\text{Ni}^{2+}$  and a hydrogen-containing species,  $^{58}\text{Ni}^+$  and  $\text{C}_3\text{H}_8\text{N}^+$  (chosen because they are isobaric) were simultaneously mass-selected and allowed to collide at a fluorocarbon surface. No ions at  $m/z$  60 could be detected over a range of collision energies from 10 to 30 eV, nor were  $\text{NiH}_2^{2+}$  ions generated by collisions of  $\text{NiCp}^+$ .

Behavior similar to that of the nickelocene molecular ion in ion/surface collisions was observed in gas-phase ion/molecule collision experiments<sup>20</sup> performed using  $\text{C}_6\text{F}_{14}$  or Xe as collision targets in a triple quadrupole mass spectrometer (Figure 2). The formation of  $^{60}\text{NiH}_2^{2+}$  occurs efficiently in collisions of  $^{60}\text{NiCp}_2^{2+}$  at low energies (below 10 eV), and the intensity of  $^{60}\text{NiH}_2^{2+}$  decreases sharply relative to  $^{60}\text{Ni}^{2+}$  with increasing collision energy. This is illustrated by the  $m/z$  60/62 ratio, which ranges from 0.75 at 4 eV to about 10 at 49 eV collision energy. The same effect is seen with a decrease in the electron impact energy. As in the case of the ion/surface collisions, the relative intensity of the  $\text{C}_{10}\text{H}_8^{2+}$  ion ( $m/z$  128) varies directly with that of  $\text{NiH}_2^{2+}$ . Neither  $\text{Ni}(\text{Cp})^+$  nor  $\text{Ni}^{2+}$  projectiles show the formation of  $\text{NiH}_2^{2+}$ ; the former exhibits the expected simple fragmentation by ligand loss. Fragmentation of the cyclopentadienyl ring is also observed ( $^{60}\text{NiC}_3\text{H}_3^{2+}$  and  $^{60}\text{NiC}_3\text{H}_5^{2+}$  at  $m/z$  99 and 101, respectively), and this may itself be a metal-catalyzed reaction.<sup>21</sup> Most importantly, however, the 70 eV electron impact mass spectrum of  $\text{Ni}(\text{Cp})_2^{2+}$  shows no detectable signal due to  $\text{NiH}_2^{2+}$ . This is consistent with the mechanistic suggestion that a low-energy, intramolecular rearrangement is



**Figure 2.** Product ion mass spectra obtained as a result of 9 eV collision-induced dissociation of nickelocene molecular ion ( $m/z$  190) with Xe at 0.5 mTorr.



**Figure 3.** Products of 2 eV reactive collisions of cyclopentadienyl- $\text{Ni}^+$  ( $m/z$  125) with 1,4-cyclohexadiene at 1 mTorr.

responsible for the  $\text{NiH}_2^{2+}$  production; the vibrational frequency required is not available from electronic excitation.

Gas-phase collisions of ferrocene and cobaltocene molecular ions as well as their respective fragments were also investigated. Experiments in which a Xe target at 1 mTorr and 1–10 eV collision energy was employed failed to generate any  $\text{MH}_2^{2+}$  ions although  $(\text{MCP}_2-\text{H}_2)^{2+}$  ions were observed. These results are consistent with observations from the corresponding surface experiments.

In an effort to examine the ability of nickelocene and related ions to abstract hydrogen atoms from noncomplexed, neutral organics,  $^{60}\text{NiCp}_n^+$  ( $n = 0-2$ ) ions were collided with 1,3-cyclohexadiene, 1,4-cyclohexadiene, and 1,4-dihydronaphthalene at nominal 2 eV collision energy and 1 mTorr pressure. The resulting product ion spectra were recorded, and that for collision of  $\text{NiCp}^+$  with 1,4-cyclohexadiene (CHD) is shown in Figure 3. Numerous reaction products are generated including  $(\text{CHD}+\text{H})^+$ ,  $(\text{CHD}-\text{H})^+$ ,  $\text{Ni}(\text{CHD})^+$ ,  $\text{Ni}(\text{CHD}-\text{H})^+$ ,

$\text{NiC}_6\text{H}_6^+$ ,  $\text{Ni}(\text{C}_6\text{H}_6)(\text{CHD})^+$ , and  $\text{Ni}(\text{CHD})_2^{2+}$  at  $m/z$  values of 81, 79, 140, 139, 138, 218, and 220, respectively. These ions were formed for each of the  $\text{Ni}(\text{Cp})_n^+$  projectiles and are similar to the metal complexed organic dehydrogenation products observed previously by Muller and Goll<sup>22</sup> in studies of ion/molecule reactions of  $\text{CpNiNO}^+$  with organics in the ion source. However, when  $^{60}\text{NiCp}^+$  ( $m/z$  125) is used as the projectile, an additional ion is seen at  $m/z$  127 (Figure 3) which corresponds to  $\text{NiCpH}_2^+$ . This ion was not reported as an ion/molecule reaction product in the reaction of  $\text{CpNiNO}^+$  with similar alkanes in the ion source.<sup>22</sup> It is likely that  $\text{NiCpH}_2^+$  arises from the decomposition of  $^{60}\text{NiCp}(\text{CHD})^+$ , observed at  $m/z$  205. Alternate channels for the decomposition of this complex include the formation of  $^{60}\text{NiCp}(\text{C}_6\text{H}_6)^+$  ( $m/z$  203), which is also seen in the product ion spectrum. Other ions are also observed, such as  $\text{Ni}(\text{C}_6\text{H}_6)(\text{CHD})^+$  ( $m/z$  218) and  $\text{Ni}(\text{CHD})_2\text{H}^+$  ( $m/z$  221), which may be intermediates in the decomposition of ionic complexes of CHD with  $\text{Ni}^+$ . (While not addressed in the

current study, it is possible that at least a portion of the ions corresponding to  $\text{NiCHD}^+/\text{NiCpCHD}^{2+}$  actually have the structure  $\text{Ni}(\text{C}_6\text{H}_6)\text{H}_2^+/\text{NiCp}(\text{C}_6\text{H}_6)\text{H}_2^+$ . Reaction of  $\text{Ni}^+$  with CHD produced  $\text{Ni}(\text{C}_6\text{H}_6)^+$  and  $\text{NiH}^+$ . These ions provide support for the identification of  $m/z$  127 as  $^{60}\text{NiCpH}_2^+$  and suggest that it is covalently bound. Results similar to those obtained for 1,4-cyclohexadiene were observed for 1,3-cyclohexadiene and 1,4-dihydronaphthalene, each experiment showing formation of complexes and intermediates of the dehydrogenation reaction. In addition, a cluster of ions is seen which corresponds to the direct addition of CHD,  $\text{CHD} + \text{H}_2$ , and  $\text{CHD} + 2\text{H}_2$  to nickelocene, suggesting that the nickelocene molecular ion itself can undergo complexation and participate in the dehydrogenation reaction. When  $\text{NiCp}^+$  or  $\text{Ni}(\text{Cp})_2^{2+}$  ions are collided with hydrogen gas, the formation of  $\text{NiCpH}_2^+$  is observed, but no reaction is detected for bare  $\text{Ni}^+$ , further supporting the importance of the Cp group in energy transfer during this reaction. The observation of the stable  $\text{H}_2$  adduct when Cp is bound to Ni suggests that the Cp group provides a means of converting internal energy into vibrational energy in the reaction complex, and this may be a primary reason for generation of dihydride complexes from  $\text{NiCp}^+$  and not from  $\text{Ni}^{2+}$  itself. This also explains the formation of  $\text{NiH}_2^{2+}$  from  $\text{Ni}(\text{Cp})_2^{2+}$  in the surface and gaseous collisions. The relatively low stability of  $\text{NiH}_2^+$  (dissociation energy of 22 kcal/mol) should make this ion very sensitive to excess internal energy.

There are two possible mechanistic channels for the formation of  $\text{NiH}_2^{2+}$  in the nickelocene ion/surface and ion/molecule collisions. The first one is the direct insertion of  $\text{Ni}^+$  into  $\text{H}_2$ , formed during the dissociation of the nickelocene ion to generate  $\text{C}_{10}\text{H}_8^+$ . According to theory,<sup>6</sup> the insertion occurs in the  $^2\text{D}$  ground electronic state of  $\text{Ni}^+$ , rather than in the  $^4\text{F}$  first excited state. The first excited ionic state is 1.04 eV higher in energy;<sup>23</sup> thus, the possibility of any excited state formation in low-energy fragmentation of nickelocene molecular ion is not likely. However, the absence of  $\text{NiH}_2^{2+}$  in the gas-phase ion/molecule reaction between  $\text{Ni}^+$  and  $\text{H}_2$ , but the presence of  $\text{NiCpH}_2^+$  in collisions of  $\text{NiCp}^+$  with  $\text{H}_2$ , suggests that insertion, while possible under appropriate conditions, is not a likely pathway. This is consistent with the low dissociation energy of  $\text{NiH}_2^+$  (22 kcal/mol). The second mechanistic channel involves hydrogen abstraction concerted with Cp ring fusion to produce  $\text{C}_{10}\text{H}_8^+$ . Nickelocenium ion is bent in the condensed phase,<sup>24</sup> and one of the lowest energy vibrations is the bending mode of  $[\text{C}_5\text{H}_5-\text{Ni}-\text{C}_5\text{H}_5]^+$ . The internal energy transfer through collisional activation could excite one of these modes, leading to the formation of  $\text{C}_{10}\text{H}_8$  and  $\text{NiH}_2^{2+}$  or the complementary products,  $\text{C}_{10}\text{H}_8^+$  and  $\text{NiH}_2$ . In fact, the intensities of  $\text{C}_{10}\text{H}_8^+$  and  $\text{NiH}_2^{2+}$  parallel one another as changes are made in electron impact energy and collision energy in the gas phase ion/molecule reaction experiment, even though  $\text{C}_{10}\text{H}_8^+$  can be formed through other channels as well,<sup>25</sup> e.g., via fragmentation of  $\text{C}_{10}\text{H}_{10}^+$ . This mechanism can also explain the presence of  $\text{C}_{10}\text{H}_8^+$  in ferrocenium and cobaltocenium spectra, although  $\text{MH}_2^{2+}$  ions are not observed. The proposed mechanism is in agreement with higher energy collision experiments as well, where an increase in collision energy favors dissociation of the projectile to yield bare metal ions.

In conclusion, we have found a new intramolecular double hydrogen transfer reaction in the nickelocenium ion leading to the formation of  $\text{NiH}_2^{2+}$ . Intramolecular hydrogen transfer reactions are well-known from studies of gas-phase unimolecular reactions of organic ions, such as molecular ions of ethers, esters, and steroids.<sup>26</sup> The abstraction of hydrogen from alkanes is also a well-established metal ion reaction.<sup>5</sup> Although the

experiments do not give direct evidence on the mechanism of hydride formation, evidence and precedence suggest that the reaction proceeds through a concerted pathway. The experimental observations reported in this study suggest that metal dihydrides could be possible intermediates in catalytic dehydrogenation reactions. The gas-phase ion/molecule reactions observed for mass-selected ions are similar to previously reported ion/molecule reactions in the ion source<sup>22</sup> and suggest that dehydrogenation occurs through an ion/molecule complex, whose formation is stabilized by the presence of Cp groups on the bare  $\text{Ni}^+$  projectile.

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## References and Notes

- (1) See for example: Izumi, Y. *Adv. Catal.* **1983**, *32*, 215. Pines, H. *Adv. Catal.* **1987**, *35*, 323.
- (2) Che, M.; Bennett, C. O. *Adv. Catal.* **1989**, *36*, 55. Suss-fink, G.; Meister, G. *Adv. Organomet. Chem.* **1993**, *35*, 41.
- (3) Muller, J.; Passon, B.; Schmitt, S. J. *Organomet. Chem.* **1980**, *195*, C21.
- (4) Blomberg, M. R. A.; Schule, J.; Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1989**, *111*, 6156.
- (5) For review of recent literature, see: Eller, K.; Schwarz, H. *Chem. Rev.* **1991**, *91*, 1121.
- (6) Zhang, H.; Balasubramanian, K. *J. Phys. Chem.* **1992**, *96*, 6981.
- (7) Bomberg, M.; Brandemork, V.; Patersson, L.; Siegbahn, P. *Int. J. Quantum Chem.* **1983**, *23*, 855.
- (8) Low, J. J.; Goddard III, W. A. *J. Am. Chem. Soc.* **1984**, *106*, 8321; *Organometallics* **1986**, *5*, 609.
- (9) Balasubramanian, K. *J. Chem. Phys.* **1987**, *87*, 2801.
- (10) Balasubramanian, K.; Feng, P. Y. *J. Chem. Phys.* **1990**, *92*, 541.
- (11) Kight, L. B., Jr.; Cobranchi, S. T.; Herlong, J.; Kirk, T.; Balasubramanian, K.; Das, K. K. *J. Chem. Phys.* **1990**, *92*, 2721.
- (12) The experimental setup has been described in: Winger, B. E.; Laue, H.-J.; Horning, S. R.; Julian, Jr., R. K.; Lammert, S. A.; Riederer, Jr., D. E.; Cooks, R. G. *Rev. Sci. Instrum.* **1992**, *63*, 5613. In a typical experiment, the ions are generated by 70 eV electron impact. The mass- and energy-selected ion beam emerging from the BE (B = magnetic sector, E = electrostatic sector) stage is decelerated and collided at a desired impact energy and at a 35° angle (relative to the normal) with a surface held in a high vacuum chamber maintained at  $1 \times 10^{-8}$  Torr. The scattered ions are energy-selected and mass-analyzed by the EQ stage. All chemicals were from Aldrich Chemical (Milwaukee, WI) and used without further purification.
- (13) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3359.
- (14) Riederer, Jr., D. E.; Cooks, R. G.; Linford, M. R. *Org. Mass Spectrom.*, submitted.
- (15) In an ion/surface reaction, a projectile ion (or its fragment) upon low-energy collision with a chemically active surface undergoes chemical reaction(s) with the active groups or atoms at the surface. Hydrogen, fluorine, and alkyl group abstractions have been observed. Under certain conditions, the ions can also deliver species to the surface which become covalently bonded.
- (16) For a review of this form of ion fragmentation, see: Cooks, R. G.; Ast, T.; Mabud, Md. A. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 209.
- (17) Pradeep, T.; Riederer, Jr., D. E.; Hoke, S. H.; Ast, T.; Cooks, R. G.; Linford, M. *J. Am. Chem. Soc.*, in press. Pradeep, T.; Ast, T.; Cooks, R. G.; Feng, B. *J. Chem. Phys.*, in press.
- (18) Chemical sputtering involves charge exchange between the projectile and the surface with subsequent ejection of the ionized products into the gas phase. See: Vincenti, M.; Cooks, R. G. *Org. Mass Spectrom.* **1988**, *23*, 317.
- (19) Williams, D. H.; Cooks, R. G. *Chem. Commun.* **1968**, 663.
- (20) Ion/molecule collision experiments were performed using a Finnigan TSQ 700 triple quadrupole mass spectrometer. Ions were generated by electron impact. Nickelocene was introduced into the ion source (100 °C) using a solids probe without additional heating. Laboratory collision energies in the range 2–50 eV were used in the experiments. Xenon and reagent gases were introduced into the second quadrupole using a needle valve at the reported nominal pressures.
- (21) Hettich, R. L.; Freiser, B. S. *Organometallics* **1989**, *8*, 2447.
- (22) Müller, J.; Goll, W. *Chem. Ber.* **1973**, *106*, 1129.

(23) Moore, C. E. Atomic Energy Levels, NSRDS-NBS, 1971.

(24) Rajasekharan, M. V.; Bucher, R.; Diess, E.; Zoller, L.; Salzer, A. K.; Moser, E.; Weber, J.; Ammeter, J. H. *J. Am. Chem. Soc.* **1983**, *105*, 516. Armstrong, D. R.; Fortune, R.; Perkins, P. G. *J. Organomet. Chem.* **1986**, *111*, 19. Ammeter, J. H. *J. Magn. Reson.* **1984**, *30*, 2990.

(25) See for example: Miller, S. A.; Riederer, Jr., D. E.; Cooks, R. G.; Cho, W. R.; Lee, H. W.; Kang, H. *J. Phys. Chem.* **1994**, *98*, 245.

(26) See for example: Budzikiewicz, H.; Dejarassi, C.; Williams, D. H. *Interpretation of Mass Spectra of Organic Compounds*; Holden-Day: San Francisco, CA, 1964. McLafferty, F. W. *Interpretation of Mass Spectra*, 5th ed.; University Science Books: Mill Valley, CA, 1993. Tokes, L.; Jones, G.; Dejarassi, C. *J. Am. Chem. Soc.* **1968**, *90*, 5465.

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