

# Formation of Iminium (C=NH<sub>2</sub>) Species from Cyanogen (C<sub>2</sub>N<sub>2</sub>) and Hydrogen on Pt(111)

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**Abstract:** Fourier transform reflection–absorption infrared spectroscopy (FT-RAIRS) was used to study the chemistry of cyanogen (C<sub>2</sub>N<sub>2</sub>) and hydrogen on Pt(111). The partial dissociative adsorption of cyanogen at 300 K results in the formation of the well-known molecularly adsorbed  $\alpha$  state and dissociatively adsorbed  $\beta_1$  and  $\beta_2$  states. The  $\alpha$  and  $\beta_2$  states were found to undergo hydrogenation at this temperature, forming the respective iminium (C=NH<sub>2</sub>) containing species diaminoethylene ((CNH<sub>2</sub>)<sub>2</sub>) and aminomethylidyne (CNH<sub>2</sub>), while the  $\beta_1$  state is shown to be inert toward hydrogenation. Isotopic substitution experiments utilizing <sup>13</sup>C and <sup>15</sup>N show diaminoethylene to be the hydrogenation product of C<sub>2</sub>N<sub>2</sub> that forms on Pt(111), while incremental <sup>2</sup>H exchange reactions confirm that (CNH<sub>2</sub>)<sub>2</sub> possesses a high degree of symmetry and a likely  $\mu_2\eta^2$ -bridge bound configuration. Diaminoethylene undergoes partial decomposition at  $\sim$ 377 K, forming a mixture of CNH<sub>2</sub> dimers, CNH<sub>2</sub> monomers, and possibly HNC. These secondary decomposition products undergo subsequent decomposition between 425 and 450 K, forming HCN<sub>(g)</sub> and CN<sub>ads</sub>.

## 1. Introduction

The hydrogenation of nitriles to amines is an important catalytic process that occurs on Group VIII transition metal surfaces.<sup>1</sup> The unambiguous identification of novel intermediates formed during the hydrogenation/dehydrogenation of such CN containing species on platinum or other transition metal surfaces is therefore of interest. Recent reflection absorption infrared spectroscopy (RAIRS) studies conducted in this laboratory<sup>2–7</sup> have shown that a new class of surface intermediates, containing iminium (C=NH<sub>2</sub>)-like functionalities, can be derived from a wide range of precursor molecules containing the CN moiety. The simplest iminium species, aminomethylidyne (CNH<sub>2</sub>), has been observed during the thermal decomposition of hydrogen cyanide (HCN), azomethane (CH<sub>3</sub>N<sub>2</sub>CH<sub>3</sub>), and methylamine (CH<sub>3</sub>NH<sub>2</sub>).<sup>2–4,7</sup> It has also recently been demonstrated that a diiminium species, diaminoethylene (H<sub>2</sub>NCCNH<sub>2</sub>), is formed via the hydrogenation of cyanogen (C<sub>2</sub>N<sub>2</sub>) on Pt(111).<sup>5–7</sup> In this paper the results of further detailed RAIRS investigations focusing on the chemistry of cyanogen and hydrogen on Pt(111) are presented. We argue that not only can adsorbates possessing iminium (C=NH<sub>2</sub>)-like functionalities offer new insights into previous work on platinum surfaces,<sup>8–18</sup> but there is also evidence that they form on Rh(111)<sup>19</sup> and are

consistent with data obtained in studies on Ni(111)<sup>20</sup> and on Pd surfaces.<sup>21–27</sup>

The chemistry of cyanogen on platinum and other transition metal surfaces has been thoroughly investigated by using a number of experimental techniques including Auger electron spectroscopy (AES), high resolution electron energy loss spectroscopy (HREELS), low energy electron diffraction (LEED), near-edge X-ray absorption fine structure (NEXAFS) and thermal desorption spectroscopy (TDS).<sup>8–18,22–28</sup> Hoffmann *et al.*<sup>13</sup> used <sup>12</sup>C<sub>2</sub><sup>14</sup>N<sub>2</sub> and <sup>13</sup>C<sub>2</sub><sup>15</sup>N<sub>2</sub> to characterize three cyanogen desorption peaks from Pt(111) seen at 370, 670, and 740–780 K, which were labeled  $\alpha$ ,  $\beta_1$ , and  $\beta_2$ , respectively. It was shown that the  $\alpha$  peak originates from molecularly adsorbed C<sub>2</sub>N<sub>2</sub>, as no scrambling among the C<sub>2</sub>N<sub>2</sub> isotopomers was observed. On the basis of the extent of isotopic scrambling at higher temperatures, the  $\beta_1$  and  $\beta_2$  cyanogen desorption peaks were

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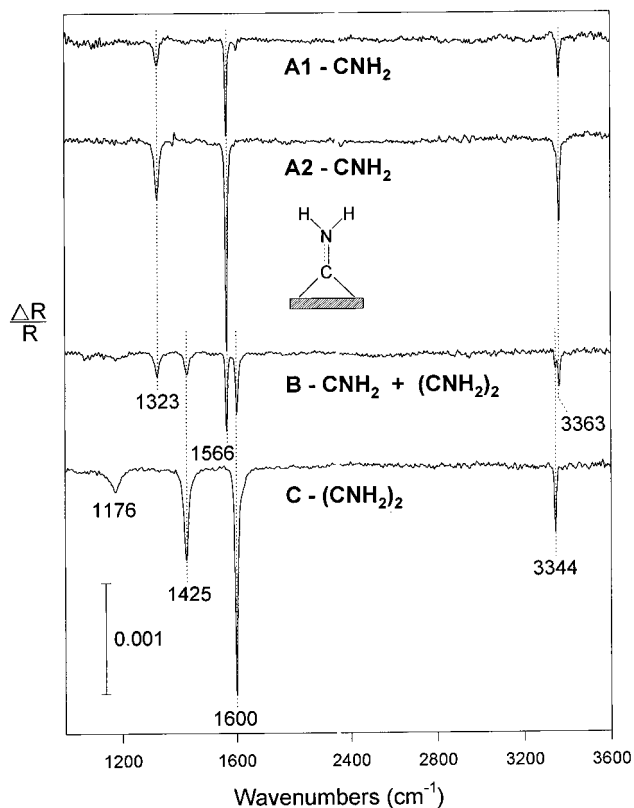
found to be due to recombinative desorption of island and isolated CN<sub>ads</sub>, respectively. The hypothesis that the  $\alpha$  and  $\beta$  states consist of molecularly and dissociatively adsorbed C<sub>2</sub>N<sub>2</sub> is indirectly confirmed by the observation that only  $\beta$  peaks (due to CN recombinative desorption) were observed in TDS studies of HCN on platinum and palladium surfaces.<sup>10,21,22,31</sup> An XPS investigation of cyanogen on Pt(111)<sup>14</sup> showed that the  $\alpha$ ,  $\beta_1$ , and  $\beta_2$  states have respective N 1s binding energies of 397.7, 398.0, and 397.0 eV. Here and elsewhere<sup>5</sup> we show that the IR spectra of the cyanogen-derived hydrogenation products provide new insights into the nature of C<sub>2</sub>N<sub>2</sub> adsorption and dissociation on Pt(111). For example, our data show that both molecular and dissociative adsorption of cyanogen occurs at 300 K, a conclusion that was suggested but not proven by previous work. Furthermore, we associate adsorbed CN that cannot be hydrogenated with island ( $\beta_1$ ) CN, while the isolated ( $\beta_2$ ) CN is found to be hydrogenated to aminomethyldiynide (CNH<sub>2</sub>).

The hydrogenation of cyanogen has been studied with a variety of techniques, including HREELS and XPS, on both Pt and Pd surfaces.<sup>14,16,22,23</sup> Lloyd and Hemminger<sup>16</sup> found that cyanogen undergoes hydrogenation at ~273 K on Pt(111) and that the resulting species undergoes dissociation above 430 K. The hydrogenated cyanogen adsorbate has HREELS bands at 3350, 1560, and 1450 cm<sup>-1</sup>, which were assigned to the respective  $\nu(\text{NH})$ ,  $\nu(\text{CN})$ , and  $\delta(\text{HNC})$  modes of a diimine species, HN=CH-CH=NH. A complementary XPS study<sup>14</sup> of C<sub>2</sub>N<sub>2</sub> + H<sub>2</sub>, ethylenediamine, and HCN on the same surface showed that a common intermediate, possessing a N 1s binding energy of 399.3 eV, is formed via either the hydrogenation of C<sub>2</sub>N<sub>2</sub> or the decomposition of ethylenediamine. Kordesch<sup>22,23</sup> *et al.* reported that C<sub>2</sub>N<sub>2</sub> does not undergo direct hydrogenation on Pd(111) or Pd(100), but instead dissociates to yield CN followed by partial hydrogenation to form a rehybridized HCN species (HC=N). Bands attributable to the  $\delta(\text{HCN})$  and  $\nu(\text{CH})$  modes of this species were observed at 1540 and 3307 cm<sup>-1</sup>, respectively. On the basis of similar HREEL spectra, this species was also proposed as a common intermediate in the decomposition of HCN, ethylenediamine, and *s*-triazine on the same surfaces.<sup>27</sup> However, a variety of surface intermediates containing CN and H have been proposed,<sup>14-17,20-28</sup> many of which would yield similar surface vibrational spectra. As the results reported here demonstrate, the small frequency shifts associated with <sup>15</sup>N, <sup>13</sup>C, and incremental <sup>2</sup>H substitution, which are readily measurable with RAIRS but not with HREELS, are often consistent with only one of several possible intermediates.

## 2. Experimental Section

All the experiments discussed below were carried out in a stainless steel ultra high vacuum (UHV) chamber with a base pressure of  $\sim 1 \times 10^{-10}$  Torr. A detailed description of this system can be found elsewhere.<sup>29</sup> Briefly, the UHV chamber is equipped with a quadrupole mass spectrometer (QMS), LEED, and AES. It is coupled to a commercial Fourier transform infrared (FTIR) spectrometer. The IR beam enters and exits the chamber through differentially pumped O-ring sealed KBr windows before reaching the detector. Two types of IR detector were used; an MCT (HgCdTe) detector was used to obtain spectra between 4000 and 800 cm<sup>-1</sup>, while a more sensitive InSb detector with a low wavenumber cutoff of 1900 cm<sup>-1</sup> was used to acquire complementary spectra from 4000 to 1900 cm<sup>-1</sup>. The RAIR spectra were recorded at 85 or 300 K, using either 1024 or 2048 coadded scans with a resolution of 4 cm<sup>-1</sup>.

The Pt(111) surface was exposed to cyanogen (C<sub>2</sub>N<sub>2</sub>) by back filling the chamber with C<sub>2</sub>N<sub>2(g)</sub>. The exposures of all gasses used were derived from uncorrected ion gauge readings. The cyanogen isoto-



**Figure 1.** RAIR spectra (A1 and A2) obtained after the sample is exposed to C<sub>2</sub>N<sub>2</sub> at 300 K, annealed to 550 K, and finally exposed to 10 L of H<sub>2</sub> at 300 K. For A1 the initial C<sub>2</sub>N<sub>2</sub> exposure was 2.0 L, while for A2 it was 0.5 L. Spectra B and C were both obtained following exposures of 0.25 L of C<sub>2</sub>N<sub>2</sub> and 10 L of H<sub>2</sub>, but in different orders. In B C<sub>2</sub>N<sub>2</sub> was exposed first, while in C H<sub>2</sub> was exposed first. All spectra were acquired with an MCT detector.

omers used were in each case prepared via the thermal decomposition of the appropriate AgCN salt. Ag<sup>12</sup>C<sup>14</sup>N (99%) was obtained from Aldrich Chemical Co., while Ag<sup>13</sup>C<sup>14</sup>N and Ag<sup>12</sup>C<sup>15</sup>N were synthesized by reacting AgNO<sub>3(aq)</sub> with solutions of K<sup>13</sup>C<sup>14</sup>N (99%) and K<sup>12</sup>C<sup>15</sup>N (98+%). Both potassium cyanide salts were obtained from Cambridge Isotope Laboratories. Each cyanogen isotopomer, once prepared, was further purified by performing several freeze-pump-thaw cycles. Each C<sub>2</sub>N<sub>2</sub> isotopomer was checked with the QMS, and no impurities, including H<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub>, were detected.

The Pt(111) surface was cleaned by the same procedure detailed previously.<sup>3</sup> Briefly, the crystal was heated in  $5 \times 10^{-8}$  Torr of O<sub>2</sub> at ~825 K for 1 h. This was then followed by dosing 1–2 L (1 langmuir (L) =  $1 \times 10^{-6}$  Torr s) of O<sub>2</sub> at 85 K and subsequently performing a TDS experiment from 85 to 1000 K. The crystal surface was judged free of carbon when a *m/e* 32 peak at 720 K, due to recombinative desorption of atomic oxygen, was observed in the absence of any CO<sub>2</sub> (*m/e* 44) peak above 300 K.

## 3. Results

Figure 1 shows the RAIR spectra obtained after coadsorbing 0.25–2.0 L of C<sub>2</sub>N<sub>2</sub> with 10 L of H<sub>2</sub> on Pt(111) at 300 K under various conditions. Annealing 2.0 and 0.5 L of C<sub>2</sub>N<sub>2</sub> to 550 K followed by the adsorption of 10 L of H<sub>2</sub> at 300 K results in spectra A1 and A2, each of which have bands at 1323, 1566, and 3363 cm<sup>-1</sup>. These bands are assigned to the respective  $\nu(\text{CN})$ ,  $\delta(\text{NH}_2)$ , and  $\nu(\text{NH})_{\text{sym}}$  modes of aminomethyldiynide (CNH<sub>2</sub>), which is formed via the hydrogenation of CN.<sup>3,7</sup> The formation of CNH<sub>2</sub> is consistent with the generation of CN from C<sub>2</sub>N<sub>2</sub> (via C–C bond cleavage) during the initial 550 K anneal. Although the cyanogen exposure for A1 was four times that of A2, the IR bands of A2 are uniformly more intense by a factor of  $2.37 \pm 0.03$ . This indicates that a 2.0 L cyanogen exposure

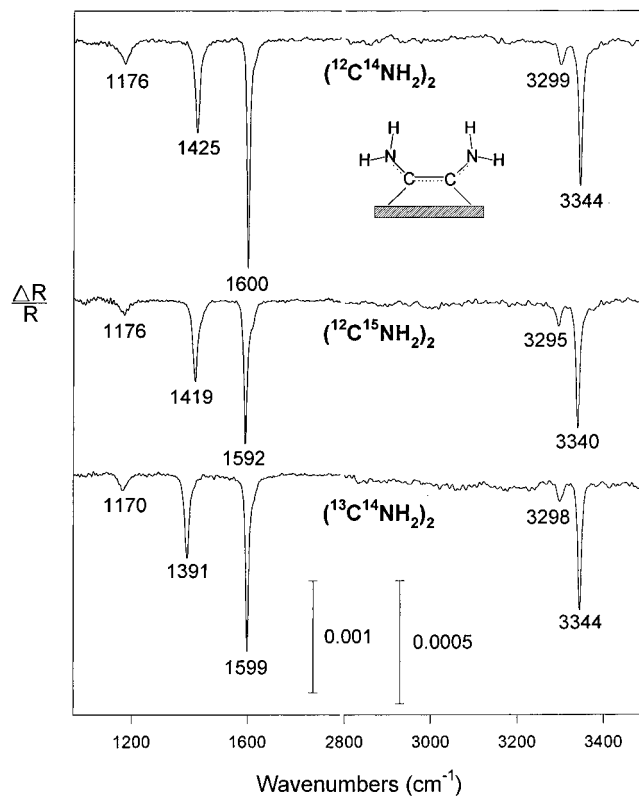
**Table 1.** Observed Frequencies ( $\text{cm}^{-1}$ ) for the Hydrogenation Products of Surface (CN)<sub>x</sub> Species ( $x = 1$  or 2)

precursor species	hydrogenated species	obsd freq ( $\text{cm}^{-1}$ )
$\alpha$ C <sub>2</sub> N <sub>2</sub>	(CNH <sub>2</sub> ) <sub>2</sub>	3344, 1600, 1425, 1176
$\beta_1$ CN		
$\beta_2$ CN	CNH <sub>2</sub>	3363, 1566, 1323

gives ~58% less CNH<sub>2</sub> than a 0.5 L exposure. The fact that less CNH<sub>2</sub> is formed from a higher initial C<sub>2</sub>N<sub>2</sub> dose can be readily explained in terms of the  $\beta_1$  and  $\beta_2$  states of adsorbed CN that were identified by thermal desorption.<sup>13</sup> As we discuss in more detail in section 4, we thus assume that only the  $\beta_2$  state, or isolated form of CN, is hydrogenated to aminomethylidyne while the  $\beta_1$  (island) state appears to be inert toward hydrogenation.

A 0.25 L exposure of C<sub>2</sub>N<sub>2</sub> followed by 10 L of H<sub>2</sub> at 300 K yields spectrum B, which contains six bands at 1323, 1425, 1566, 1600, 3344, and 3363  $\text{cm}^{-1}$ . The bands at 1323, 1566, and 3363  $\text{cm}^{-1}$  are clearly due to the presence of aminomethylidyne (CNH<sub>2</sub>). As summarized in Table 1, the three additional bands are assigned to the respective  $\nu(\text{CN})$ ,  $\delta(\text{NH}_2)$ , and  $\nu(\text{NH})_{\text{sym}}$  modes of diaminoethylene (CNH<sub>2</sub>)<sub>2</sub>, the hydrogenation product of C<sub>2</sub>N<sub>2</sub>. The characterization of this new species was accomplished by the use of <sup>15</sup>N and <sup>13</sup>C isotopic substitution experiments, as described below. The formation of both aminomethylidyne and diaminoethylene, the respective hydrogenation products of CN and C<sub>2</sub>N<sub>2</sub>, indicates that cyanogen must initially undergo partial dissociative adsorption on Pt(111) at 300 K. The preadsorption of 10 L of H<sub>2</sub> followed by 0.25 L of C<sub>2</sub>N<sub>2</sub> at 300 K gives rise to spectrum C, which contains only four bands at 1176, 1425, 1600, and 3344  $\text{cm}^{-1}$  due to the formation of (CNH<sub>2</sub>)<sub>2</sub>. The band that appears at 1176  $\text{cm}^{-1}$ , which is too weak to be observed in B, is assigned to the  $\nu(\text{CC})$  mode of diaminoethylene. The preadsorption of H<sub>2</sub> apparently inhibits the dissociative adsorption of cyanogen, as only bands due to the hydrogenation product of C<sub>2</sub>N<sub>2</sub> (diaminoethylene, (CNH<sub>2</sub>)<sub>2</sub>) are observed in spectrum C. A comparison of the individual peak heights of the 1425, 1600, and 3344  $\text{cm}^{-1}$  bands of diaminoethylene in spectra B and C yields an average B/C peak height ratio of  $0.24 \pm 0.03$  for the three pairs of bands. This result suggests that the bands assigned to diaminoethylene are in fact due to a single species, since the relative intensities of these bands only varies by  $\pm 3\%$  for different coverages. If we assume that all of the C<sub>2</sub>N<sub>2</sub> becomes hydrogenated to form (CNH<sub>2</sub>)<sub>2</sub> in both B and C, then the relative IR peak heights imply that ~24% of the original 0.25 L C<sub>2</sub>N<sub>2</sub> dosed at 300 K adsorbs molecularly as  $\alpha$  C<sub>2</sub>N<sub>2</sub>, while the remainder is adsorbed dissociatively as  $\beta$  CN.

The two different diaminoethylene coverages of spectra B and C in Figure 1 yield IR bands that differ by a factor of 4.2 in intensity, but that occur at essentially identical frequencies. From this we can assume that spectra obtained by initially exposing the surface to 10 L of H<sub>2</sub> followed by even lower C<sub>2</sub>N<sub>2</sub> exposures would yield diaminoethylene spectra with intensities proportional to cyanogen exposures, at least up to 0.25 L. Although this low diaminoethylene coverage regime was not explored in detail, numerous spectra were obtained by exposure to hydrogen followed by cyanogen exposures >0.25 L. It was found that the maximum intensity for the diaminoethylene IR bands occurred for the conditions of spectrum C of Figure 1. Higher C<sub>2</sub>N<sub>2</sub> exposures gave weaker and more complex spectra, which may be due to either diaminoethylene perturbed by adsorbate-adsorbate interactions (similar to high coverages of CNH<sub>2</sub><sup>4</sup>) or possibly to the formation of a distinctly different chemical species. Consequently the focus of this paper

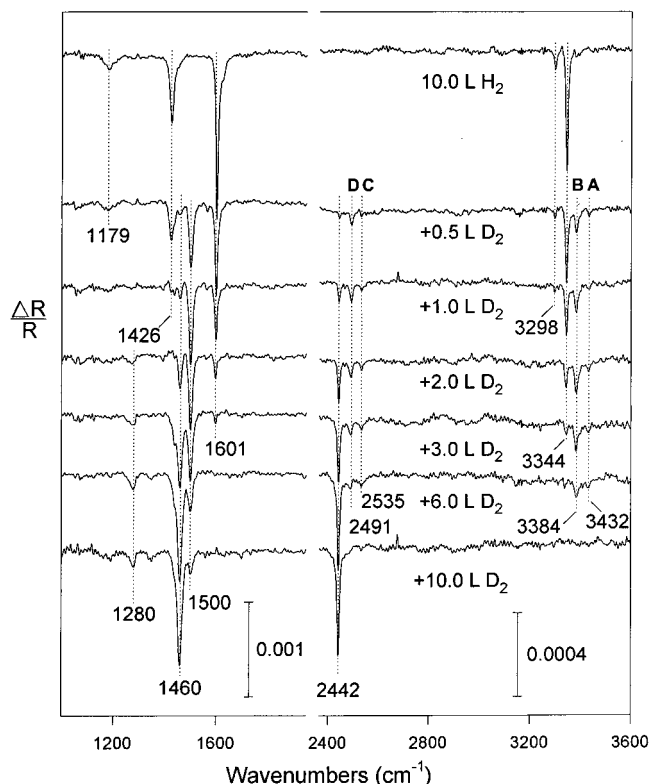
**Figure 2.** Comparison of (CNH<sub>2</sub>)<sub>2</sub> isotopomer spectra obtained after dosing the sample with 10 L of H<sub>2</sub>, followed by 0.25 L each of <sup>12</sup>C<sub>2</sub><sup>14</sup>N<sub>2</sub>, <sup>12</sup>C<sub>2</sub><sup>15</sup>N<sub>2</sub>, and <sup>13</sup>C<sub>2</sub><sup>14</sup>N<sub>2</sub>, respectively, at 300 K. Spectra above 1950  $\text{cm}^{-1}$  were acquired with an InSb detector.**Table 2.** Experimental Frequencies ( $\text{cm}^{-1}$ ) of Various Diaminoethylene, (CNH<sub>2</sub>)<sub>2</sub>, Isotopomers and Relative Isotopic Shifts ( $\text{cm}^{-1}$ ) Observed with <sup>15</sup>N, <sup>13</sup>C, and D Substitution for Diaminoethylene, (CNH<sub>2</sub>)<sub>2</sub>

a. Experimental Frequencies					
isotopomer	$\nu(\text{NX})_s$	$\nu(\text{NX})_s$	$\delta(\text{NX}_2)$	$\nu(\text{CN})$	$\nu(\text{CC})$
( <sup>12</sup> C <sup>14</sup> NH <sub>2</sub> ) <sub>2</sub>	3344	3299	1600	1425	1176
( <sup>12</sup> C <sup>15</sup> NH <sub>2</sub> ) <sub>2</sub>	3340	3295	1592	1419	1176
( <sup>13</sup> C <sup>14</sup> NH <sub>2</sub> ) <sub>2</sub>	3344	3298	1599	1391	1170
( <sup>12</sup> C <sup>14</sup> ND <sub>2</sub> ) <sub>2</sub>	2442	2409	1460	1280	
( <sup>12</sup> C <sup>15</sup> ND <sub>2</sub> ) <sub>2</sub>	2436	2405	1446	1274	
( <sup>13</sup> C <sup>14</sup> ND <sub>2</sub> ) <sub>2</sub>	2440		1430	1254	
b. Relative Isotopic Shifts					
mode	( <sup>12</sup> C <sup>15</sup> NH <sub>2</sub> ) <sub>2</sub> ( <sup>12</sup> C <sup>14</sup> NH <sub>2</sub> ) <sub>2</sub>	( <sup>13</sup> C <sup>14</sup> NH <sub>2</sub> ) <sub>2</sub> ( <sup>12</sup> C <sup>14</sup> NH <sub>2</sub> ) <sub>2</sub>	( <sup>12</sup> C <sup>15</sup> ND <sub>2</sub> ) <sub>2</sub> ( <sup>12</sup> C <sup>14</sup> ND <sub>2</sub> ) <sub>2</sub>	( <sup>12</sup> C <sup>14</sup> NH <sub>2</sub> ) <sub>2</sub> ( <sup>12</sup> C <sup>14</sup> ND <sub>2</sub> ) <sub>2</sub>	
$\nu(\text{NX})_s$	-4 (-4) <sup>a</sup>	0 (0)	-6 (-10)	-902 (-926)	
$\nu(\text{NX})_s$	-4 (-)	-1 (-)	-4 (-)	-890 (-)	
$\delta(\text{NX}_2)$	-8 (-8)	1 (-1)	-14 (-16)	-140 (-210)	
$\nu(\text{CN})$	-6 (-11)	-34 (-33)	-6 (-)	-145 (-)	

<sup>a</sup> Values in parentheses are for aminomethylidyne (CNH<sub>2</sub>). <sup>b</sup> X = H or D.

is on the conditions that yielded the simplest and most intense IR bands of the isolated (CNH<sub>2</sub>)<sub>2</sub> species.

Figure 2 shows the RAIR spectra obtained after dosing 10 L of H<sub>2</sub> followed by 0.25 L each of <sup>12</sup>C<sub>2</sub><sup>14</sup>N<sub>2</sub>, <sup>12</sup>C<sub>2</sub><sup>15</sup>N<sub>2</sub> and <sup>13</sup>C<sub>2</sub><sup>14</sup>N<sub>2</sub>, at 300 K. The fact that the InSb detector used for the 1950–4000  $\text{cm}^{-1}$  region in Figure 2 is more sensitive than the MCT detector, used for Figure 1, allows the additional band at ~3299  $\text{cm}^{-1}$  to be detected. The results of all isotopic substitution experiments are summarized in Table 2a. The data suggest an adsorbate of general formula (CNH<sub>2</sub>)<sub>2</sub>. Thus, the two high-frequency bands at 3344 and 3299  $\text{cm}^{-1}$  are both red shifted by 4  $\text{cm}^{-1}$  with <sup>15</sup>N substitution, but remain virtually



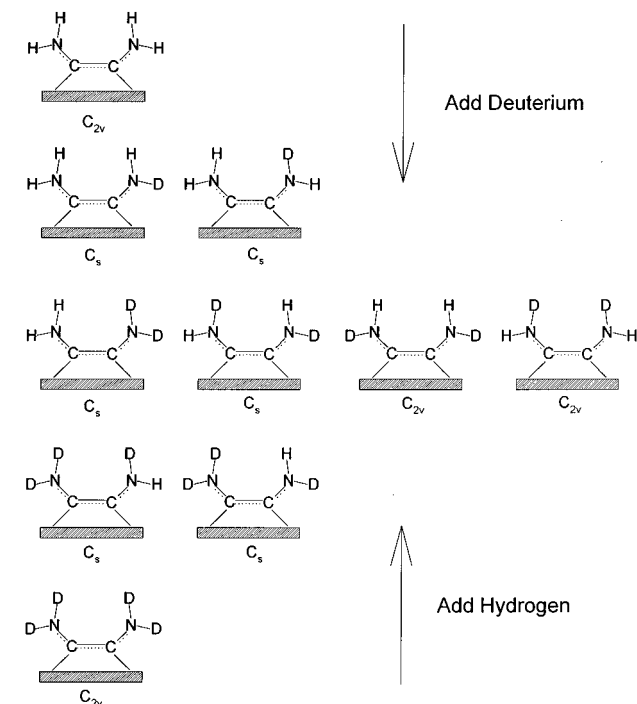
**Figure 3.** The top spectrum was obtained after first dosing the sample with 10 L of H<sub>2</sub>, followed by 0.25 L of <sup>12</sup>C<sub>2</sub><sup>14</sup>N<sub>2</sub> at 300 K. Subsequent spectra were recorded following exposures equal to the indicated cumulative doses of D<sub>2</sub>.

unaffected by <sup>13</sup>C substitution. This clearly shows that these bands are due to  $\nu(\text{NH})$  modes. The band at 1600 cm<sup>-1</sup> is downshifted by 8 cm<sup>-1</sup> with <sup>15</sup>N but negligibly affected by <sup>13</sup>C substitution, indicating that the band is due to a  $\delta(\text{NH}_2)$  mode. The 1425-cm<sup>-1</sup> band is downshifted by 34 and 6 cm<sup>-1</sup> respectively with <sup>13</sup>C and <sup>15</sup>N substitution, indicating that it is due to a  $\nu(\text{CN})$  mode. The band at 1176 cm<sup>-1</sup> is clearly due to a  $\nu(\text{CC})$  mode since it is downshifted by 6 cm<sup>-1</sup> with <sup>13</sup>C, yet is unaffected by <sup>15</sup>N substitution. The almost identical relative intensities and isotopic shifts of the analogous bands of aminomethylidyne (CNH<sub>2</sub>),<sup>3,5</sup> summarized in Table 2b, confirm that both species possess similar internal coordinates and iminium (C=NH<sub>2</sub>)-like functionalities. The low number of observed bands in the spectra is consistent with the vibrational modes of a planar (CNH<sub>2</sub>)<sub>2</sub> adsorbate, possessing a high degree of symmetry, most likely bonded to the substrate through both carbon atoms as shown in the inset of Figure 2. These findings indicate that the adsorbate that gives rise to the observed spectra is diaminoethylene (H<sub>2</sub>NC=CNH<sub>2</sub>), an interpretation supported by both recent normal mode calculations and experimental studies.<sup>5-6,30</sup>

The effects of deuterium exchange on the spectrum of diaminoethylene are shown in Figure 3. The top RAIR spectrum was obtained after exposure to 10 L of H<sub>2</sub> followed by 0.25 L of <sup>12</sup>C<sub>2</sub><sup>14</sup>N<sub>2</sub> at 300 K. Additional spectra were recorded following subsequent doses of D<sub>2</sub> equal to total cumulative exposures of 0.5, 1.0, 2.0, 3.0, 6.0, and 10.0 L. Bands due to the  $\nu(\text{CC})$ ,  $\nu(\text{CN})$ ,  $\delta(\text{NH}_2)$ ,  $\nu_1(\text{NH})_{\text{sym}}$ , and  $\nu_2(\text{NH})_{\text{sym}}$  modes of (<sup>12</sup>C<sup>14</sup>NH<sub>2</sub>)<sub>2</sub>, seen in Figure 3 at 1179, 1426, 1601, 3298, and 3344 cm<sup>-1</sup>, gradually disappear with increasing D<sub>2</sub> exposure to be replaced by four new bands at 1500, 2491, 2535, 3384, and 3432 cm<sup>-1</sup>. These new bands are interpreted as the respective  $\delta(\text{HND})$ ,  $\nu_1(\text{ND})$ ,  $\nu_2(\text{ND})$ ,  $\nu_1(\text{NH})$ , and  $\nu_2(\text{NH})$  modes of a series of "mixed" <sup>12</sup>C<sub>2</sub><sup>14</sup>N<sub>2</sub>H<sub>(4-x)</sub>D<sub>x</sub> (x = 1-3) isomers.

**Table 3.** Observed Frequencies (cm<sup>-1</sup>) for the "Mixed" C<sub>2</sub>N<sub>2</sub>H<sub>(4-x)</sub>D<sub>x</sub> Isotopomers (x = 1-3)

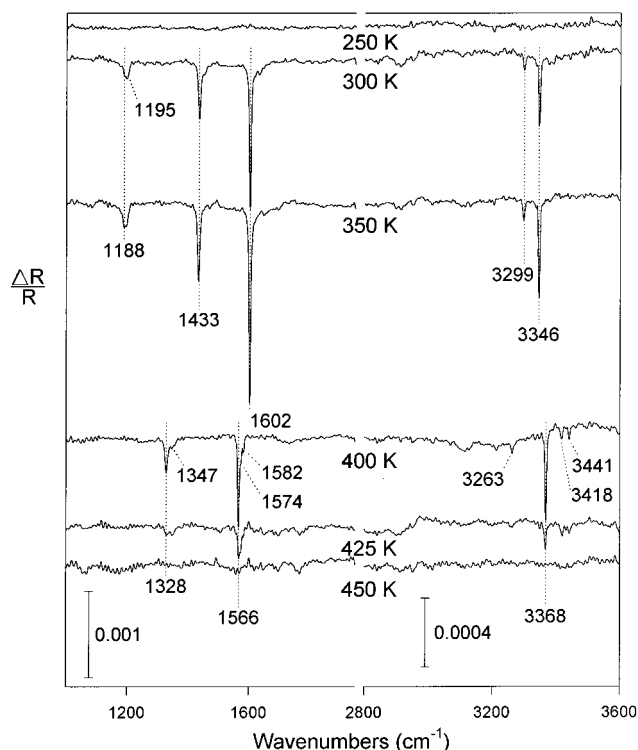
isotopomer	$\nu(\text{ND})$				$\delta(\text{HND})$
	A	B	C	D	
<sup>12</sup> C <sub>2</sub> <sup>14</sup> N <sub>2</sub> H <sub>(4-x)</sub> D <sub>x</sub>	3432	3384	2535	2491	1500
<sup>12</sup> C <sub>2</sub> <sup>15</sup> N <sub>2</sub> H <sub>(4-x)</sub> D <sub>x</sub>	3416	3376	2522	2481	1485
<sup>13</sup> C <sub>2</sub> <sup>14</sup> N <sub>2</sub> H <sub>(4-x)</sub> D <sub>x</sub>	3431	3383	2532	2488	1487



**Figure 4.** The possible structures and symmetries of the geometric isomers that can be formed from (CNH<sub>2</sub>)<sub>2</sub> with incremental deuterium substitution.

The position of these and analogous bands, derived from experiments performed with <sup>12</sup>C<sub>2</sub><sup>15</sup>N<sub>2</sub> and <sup>13</sup>C<sub>2</sub><sup>14</sup>N<sub>2</sub>, are given in Table 3. If it is assumed that (CNH<sub>2</sub>)<sub>2</sub> possesses C<sub>2v</sub> symmetry, then six of the possible eight mixed isomers formed will have C<sub>s</sub> symmetry, while the remaining two will retain C<sub>2v</sub> symmetry. The symmetries of the various C<sub>2</sub>N<sub>2</sub>H<sub>(4-x)</sub>D<sub>x</sub> isotopomers are summarized in Figure 4. Both the C<sub>2</sub>N<sub>2</sub>H<sub>3</sub>D and C<sub>2</sub>N<sub>2</sub>HD<sub>3</sub> species are comprised of pairs of C<sub>s</sub> symmetry geometric isomers, while the disubstituted C<sub>2</sub>N<sub>2</sub>H<sub>2</sub>D<sub>2</sub> species is made up of two pairs of C<sub>s</sub> and C<sub>2v</sub> symmetry isomers. As many as 64 bands (9 and 5 observable modes for each C<sub>s</sub> and C<sub>2v</sub> geometric isomer, respectively) could, in principle, arise from such a large number of mixed isotopomers. However, only five new peaks are observed upon partial deuteration in Figure 3. A detailed consideration of the nature of the vibrational modes and their statistical distribution among the mixed isotopomers indicates that many of the symmetry allowed bands are expected to be very weak.<sup>30</sup> Two pairs of NH and ND stretch bands, at 3432 (A), 3384 (B), 2535 (C), and 2491 cm<sup>-1</sup> (D), all appear at higher frequencies than the corresponding  $\nu(\text{NH})_{\text{sym}}$  and  $\nu(\text{ND})_{\text{sym}}$  modes of the fully hydrogenated or deuterated species. This key finding indicates that the symmetry of the adsorbate is lowered upon partial deuteration, which in turn confirms that the bands of (<sup>12</sup>C<sup>14</sup>NH<sub>2</sub>)<sub>2</sub>, originally observed at 3298 and 3344 cm<sup>-1</sup>, must be due to symmetry allowed  $\nu(\text{NH})_{\text{sym}}$  modes. Bands at 1280, 1460, and 2442 cm<sup>-1</sup>, due to the respective  $\nu(\text{CN})$ ,  $\delta(\text{ND}_2)$ , and  $\nu(\text{ND})_{\text{sym}}$  modes of (<sup>12</sup>C<sup>14</sup>ND<sub>2</sub>)<sub>2</sub>, become increasingly dominant with higher D<sub>2</sub>

(30) Mills, P. Ph.D. Thesis, University of Illinois at Chicago, 1997.



**Figure 5.** RAIR spectra obtained at 85 K as a function of annealing temperature, after first dosing the sample with 10 L of H<sub>2</sub> followed by 0.25 L of <sup>12</sup>C<sub>2</sub><sup>14</sup>N<sub>2</sub> at 85 K. Spectra recorded after annealing to 100, 150, and 200 K are similar to the 250 K anneal spectra shown, in that no IR peaks are observed.

**Table 4.** Observed Frequencies (cm<sup>-1</sup>) and Stable Temperature Ranges (K) of Surface Species Originally Formed from Cyanogen (C<sub>2</sub>N<sub>2</sub>) and Hydrogen Dosed at 85 K

temp range (K)	species present	obsd freq (cm <sup>-1</sup> )
85–250	C <sub>2</sub> N <sub>2</sub> + H <sub>ads</sub>	
300–350	(CNH <sub>2</sub> ) <sub>2</sub>	3346, 3299, 1602, 1433, 1188
400–425	CNH <sub>2</sub> dimers	3441, 3263, 1574, 1347
	CNH <sub>2</sub> monomers	3368, 1566, 1328
450–630	HNC	3418, 1582
	CN	

exposures and are essentially the only bands observed for a 10 L D<sub>2</sub> exposure, showing that complete deuteration occurs for a sufficiently large cumulative dose of D<sub>2</sub>.

Figure 5 shows the RAIR spectra obtained after first adsorbing 10 L of H<sub>2</sub> followed by 0.18 L of <sup>12</sup>C<sub>2</sub><sup>14</sup>N<sub>2</sub> on Pt(111) at 85 K. Each of the spectra were subsequently recorded at 85 K, following annealing to the indicated temperatures. The frequencies observed for the various surface species formed during each anneal are given in Table 4. Spectra recorded following 100, 150, and 200 K anneals (not shown) were similar to the 250 K spectra of Figure 5, with no detectable RAIR bands. Bands due to (CNH<sub>2</sub>)<sub>2</sub>, at 1188, 1433, 1602, 3299, and 3346 cm<sup>-1</sup>, observed for the 300 and 350 K anneals, show that diaminoethylene forms between 250 and 300 K and undergoes subsequent thermal decomposition between 350 and 400 K. The slight frequency shifts observed for several of the (CNH<sub>2</sub>)<sub>2</sub> bands between Figures 1–3 and Figure 5 are likely due to the fact that the spectra were recorded at 300 and 85 K, respectively. A total of nine new bands, attributable to decomposition products of (CNH<sub>2</sub>)<sub>2</sub>, are observed at 1328, 1347, 1566, 1574 (shoulder), 1582, 3263, 3368, 3418, and 3441 cm<sup>-1</sup> after annealing to 400 K. On the basis of previous studies,<sup>3,4</sup> these bands are assigned to three distinct (CNH<sub>2</sub>)<sub>2</sub> decomposition products: CNH<sub>2</sub> monomers, with familiar intense bands at 1328, 1566, and 3368

cm<sup>-1</sup>; CNH<sub>2</sub> dimers, with bands at 1347, 1574, 3263 and 3441 cm<sup>-1</sup>, and possibly HNC, with bands at 1582 and 3418 cm<sup>-1</sup>. The fact that the largest bands seen at 400 and 425 K are due to CNH<sub>2</sub> monomers suggests that C–C bond cleavage is an initial step in diaminoethylene decomposition. The bands at 1347, 1574, 3263, and 3441 cm<sup>-1</sup> can be assigned to CNH<sub>2</sub> dimers on the basis of observation of the same set of bands in a recent study<sup>4</sup> of CNH<sub>2</sub> aggregation. These results clearly show that diaminoethylene undergoes thermal decomposition between 350 and 400 K, forming a variety of products, which in turn undergo further decomposition between 425 and 450 K. No adsorbates were detected with RAIRS after annealing to temperatures ≥ 450 K.

Complementary temperature programmed desorption (TPD) spectra<sup>30</sup> were recorded from 85 to 1000 K. Desorption products having *m/e* values consistent with the generation of H<sub>2</sub>, HCN, C<sub>2</sub>N<sub>2</sub>, and C<sub>6</sub>H<sub>12</sub>N<sub>6</sub> were monitored. Hydrogen (*m/e* = 2) TPD peaks were observed at 241–319 and 377 K. These peaks are assigned to the formation of H<sub>2</sub> via recombinative H<sub>ads</sub> desorption and (CNH<sub>2</sub>)<sub>2</sub> decomposition, respectively. The observation of the H<sub>2</sub> peak at 377 K is consistent with the RAIRS results of Figure 5, indicating that (CNH<sub>2</sub>)<sub>2</sub> decomposes between 350 and 400 K. Although no adsorbates were detected with RAIRS at or above 450 K, TPD peaks due to HCN (*m/e* 27) and C<sub>2</sub>N<sub>2</sub> (*m/e* 52) desorption were observed at 460 and 630 K, respectively. These peaks, assigned to CNH<sub>2</sub> decomposition (HCN) and recombinative desorption of CN (C<sub>2</sub>N<sub>2</sub>), have also been observed during previous studies of CN containing species on Pt(111).<sup>2,14–16,18,25,28,31</sup> No desorption of benzene 1,2,3,4,5,6-hexamine, (C<sub>6</sub>N<sub>6</sub>H<sub>12</sub>, *m/e* 168), the expected cyclotrimerization product of (CNH<sub>2</sub>)<sub>2</sub>, was detected.

## 4. Discussion

**1. The Hydrogenation of Surface (CN)<sub>x</sub> Species.** A more detailed understanding of CN hydrogenation chemistry on Pt(111) can be gained by considering the results presented here in terms of the properties of CN produced from cyanogen dissociation and the nature of the reaction of CN and H produced from the dissociation of HCN, as determined by earlier studies. A variety of molecules containing CN, including HCN and C<sub>2</sub>N<sub>2</sub>, dissociate on Pt(111) to give adsorbed CN. The CN itself does not undergo further dissociation, but recombines to desorb as cyanogen at temperatures above 600 K. In several cases, the recombinative desorption of C<sub>2</sub>N<sub>2</sub> occurs as two distinct peaks, β<sub>1</sub> and β<sub>2</sub>. Presumably, the association of the β<sub>1</sub> TPD peak with relatively unreactive island CN and the β<sub>2</sub> peak to reactive isolated CN holds regardless of the initial source of CN. Thus, much of the difference between the reaction of CN with H from HCN dissociation and the hydrogenation of CN produced from C<sub>2</sub>N<sub>2</sub> can be related to differences in the relative amounts of β<sub>1</sub> and β<sub>2</sub> CN.

Previous RAIRS studies<sup>3,4</sup> show that HCN exposures of 0.1–0.2 L result in the formation of isolated CNH<sub>2</sub> with bands practically identical in frequency and relative intensity to those observed in spectra A1 and A2 of Figure 1. However, unlike CN derived from C<sub>2</sub>N<sub>2</sub>, small partially hydrogen-bonded aminomethylidyne aggregates are formed following HCN exposures greater than ~0.2 L, with larger fully hydrogen-bonded CNH<sub>2</sub> aggregates appearing for HCN exposures greater than ~0.4 L. A complementary XPS analysis<sup>4</sup> showed that both CNH<sub>2</sub> and CN, with respective N<sub>1s</sub> binding energies of 399.7 and 397.8 eV, are formed via the decomposition and subsequent rehydrogenation of HCN. The CNH<sub>2</sub> (399.7 eV)/CN (397.8 eV) peak

(31) Hagans, P. L.; Guo, X.; Chorkendorff, I.; Winkler, A.; Siddiqui, H.; Yates, J. T., Jr. *Surf. Sci.* **1988**, *203*, 1–16.

area ratio was found to decrease from 3.2 to  $2.0 \pm 0.2$  for increasing HCN exposures of 1.0 to 20.0 L. The conversion of some CN to CNH<sub>2</sub> by background H<sub>2</sub> is presumably why the initial CNH<sub>2</sub>/CN ratio is consistently greater than the expected value of unity. While we have unpublished XPS data showing that the CNH<sub>2</sub>/CN ratio after an initial 20.0 L HCN exposure rises from 2.0 to  $2.6 \pm 0.2$  following a 50.0 L dose of H<sub>2</sub> at 300 K, no additional amount of hydrogen would convert all of the CN to CNH<sub>2</sub>. Like the CN produced from C<sub>2</sub>N<sub>2</sub> dissociation, HCN dissociation also leads to a form of CN that cannot be hydrogenated. Our observations that only some forms of adsorbed CN can be hydrogenated and of the forms that can be some produce aminomethylidyne aggregates while others do not are similar to the observation of Hoffmann *et al.*,<sup>13</sup> that some forms of adsorbed CN lead to the desorption of isotopically scrambled cyanogen following consecutive adsorption of <sup>12</sup>C<sub>2</sub><sup>14</sup>N<sub>2</sub> and <sup>13</sup>C<sub>2</sub><sup>15</sup>N<sub>2</sub>, while other forms do not. A complete understanding of these observations will thus require future study with techniques that can directly determine the nature of the various forms that adsorbed CN can assume on Pt(111).

## 2. The Structure of Diaminoethylene, (CNH<sub>2</sub>)<sub>2</sub>, on Pt(111).

On the basis of the similarities between the observed frequencies of each of the CN containing adsorbates seen with both HREELS<sup>16,22–23</sup> and RAIRS,<sup>2–7</sup> it seems likely that a common type of intermediate forms from a variety of CN containing precursors on both platinum and palladium surfaces. A comparison of the relative isotopic shifts seen with deuterium substitution for the proposed diimine (HN=CH-CH=NH) species and rehybridized HCN species (observed with HREELS) with the RAIRS data for diaminoethylene and aminomethylidyne supports the hypothesis that the common intermediate(s) observed in each case most likely possess iminium (C=NH<sub>2</sub>)-like functionalities. Specifically, the  $\nu(\text{NH})$  (3344 cm<sup>-1</sup>) and  $\delta(\text{NH}_2)$  (1600 cm<sup>-1</sup>) modes of (CNH<sub>2</sub>)<sub>2</sub> are shifted by complete deuterium substitution by -902 and -140 cm<sup>-1</sup> respectively to 2442 and 1460 cm<sup>-1</sup>. Almost identical shifts of -890 and -110 cm<sup>-1</sup> were seen in the earlier HREEL spectra<sup>16</sup> that were assigned to the diimine species, which is proposed to form on Pt(111), as the 3350 and 1560 cm<sup>-1</sup> bands shift to 2460 and 1450 cm<sup>-1</sup>. On the (100) and (111) surfaces of palladium,<sup>23</sup> bands at 3306 and 1540 cm<sup>-1</sup> that are assigned to a rehybridized form of HCN also shift by similar amounts of -887 and -112 cm<sup>-1</sup>. While this suggests that the HREEL spectra previously assigned to rehybridized HCN are in fact due to CNH<sub>2</sub>, additional experiments that could distinguish between these two species are needed to confirm this. Aminomethylidyne has also been shown by HREELS<sup>19</sup> to form on Rh(111) while electronic structure calculations<sup>32</sup> indicate that it is a stable species on Ni(111). However, CNH<sub>2</sub> was not found to form in a recent study of HCN on a polycrystalline Pt surface.<sup>33</sup> Further work is clearly needed to establish the full extent of the role of iminium-like intermediates in CN chemistry on transition metal surfaces.

While our results cannot directly establish how diaminoethylene bonds to the platinum atoms of the surface, a few general conclusions can be made based on symmetry selection rules and by analogy to related systems. One possibility suggested by organometallic clusters containing CNH<sub>2</sub><sup>34</sup> and C<sub>2</sub>(NR)<sub>2</sub>-AlEt<sub>2</sub><sup>35</sup> fragments is that the (CNH<sub>2</sub>)<sub>2</sub> adsorbate adopts a  $\mu_2\eta^2$  (bridge bound) configuration with its molecular plane normal

to the Pt(111) surface. A species such as this would necessarily possess C<sub>2v</sub> symmetry, with seven allowed A<sub>1</sub> modes. The five bands observed at 3344, 3299, 1600, 1425, and 1176 cm<sup>-1</sup> can be assigned to the adsorbate's  $\nu(\text{NH})_{\text{sym}}$ ,  $\nu(\text{NH})_{\text{asym}}$ ,  $\delta(\text{NH}_2)$ ,  $\nu(\text{CN})$ , and  $\nu(\text{CC})$  modes, while the skeletal A<sub>1</sub>  $\delta(\text{NCC})$  and  $\delta(\text{NCpt})$  modes that were not observed are presumably below 800 cm<sup>-1</sup>. The two allowed  $\nu(\text{NH})_{\text{sym}}$  modes are consistent with the "sym-sym" and "asym-asym" NH stretch combinations of the adsorbate's two individual CNH<sub>2</sub> moieties, as both of these motions are also totally symmetric with respect to the symmetry operations of the adsorbate. The differences in intensity observed for these two modes can be explained in terms of the proposed geometry. Consider the components of the NH bonds along the surface normal, the z axis, as indicated by the structural drawing in the inset of Figure 2. One pair of NH bonds has a large +z component while the other has a small -z component. The weaker band at 3299 cm<sup>-1</sup> is therefore assigned to the "sym-sym"  $\nu(\text{NH})_{\text{sym}}$  mode, since the net dynamic dipole moment normal to the surface associated with the in-phase stretching of the NH bonds will be less than that associated with the "asym-asym" mode, which is therefore associated with the more intense band at 3344 cm<sup>-1</sup>.

To gain further insight into the nature of the bonding of diaminoethylene from the IR spectra, normal mode calculations were conducted.<sup>6,30</sup> While the details of these calculations are described elsewhere,<sup>6,30</sup> two conclusions are particularly noteworthy. First, the calculations were performed for two different structures, both based on  $\mu_2\eta^2$ -Pt<sub>2</sub>(CNH<sub>2</sub>)<sub>2</sub> models with C<sub>2v</sub> symmetry. In one model, the Pt-Pt and C-C bonds are parallel and each C atom makes one C-Pt bond. In the other model, the Pt-Pt bonds are perpendicular to the C-C bond, and hence to the C<sub>2</sub>N<sub>2</sub>H<sub>4</sub> plane, and each C atom makes two C-Pt bonds. It was found that the parallel model gave better agreement with the results. Second, the calculations showed that the  $\nu(\text{CC})$  mode of  $\mu_2\eta^2$ -diaminoethylene (H<sub>2</sub>NC=CNH<sub>2</sub>), with a fundamental at 1176 cm<sup>-1</sup>, has substantial contributions from CC, CN, and CPt stretch internal coordinates. Knowledge of the composition of this mode aided the interpretation of the spectra in several ways. For example, it readily explains how the observed intensity of the "CC" stretch does not violate the surface dipole selection rule, which forbids the observation of modes that are strictly parallel to the surface. It also explains how the derived force constant for the CC bond, associated with an olefinic bond order of  $\approx 1.8$ , can at the same time be consistent with a CC stretch frequency of 1176 cm<sup>-1</sup>.

**3. The Thermal Chemistry of C<sub>2</sub>N<sub>2</sub> and H<sub>2</sub>.** The annealing data of Figure 5 show that diaminoethylene forms between 250 and 300 K. This agrees with previous TDS, HREELS, and XPS<sup>14–16</sup> results, which found that the hydrogenation product of cyanogen on Pt(111) is formed between 250 and 273 K and is stable up to 430 K. While the annealing spectra show that diaminoethylene undergoes complete thermal decomposition before 450 K, observation of additional IR bands following a 400 K anneal shows that (CNH<sub>2</sub>)<sub>2</sub> undergoes partial decomposition between 350 and 400 K. The TDS results<sup>30</sup> support these findings as the hydrogen peak observed at 377 K verifies that (CNH<sub>2</sub>)<sub>2</sub> does decompose between 350 and 400 K.

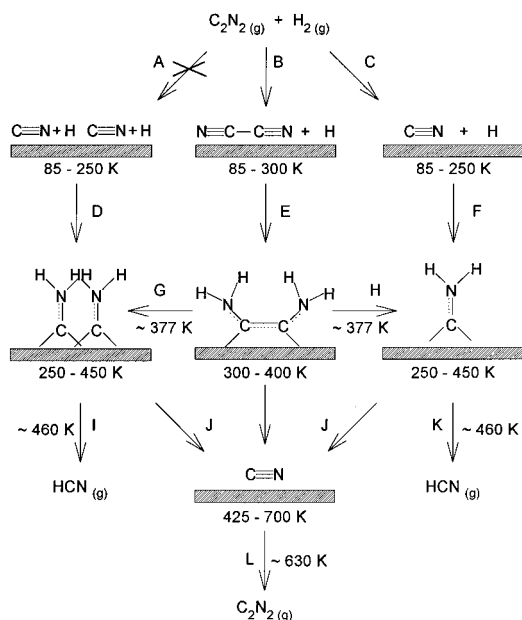
The bands of the secondary decomposition products of (CNH<sub>2</sub>)<sub>2</sub> are assigned to three distinct species: CNH<sub>2</sub> monomers, with familiar intense bands at 1328, 1566, and 3368 cm<sup>-1</sup>; small CNH<sub>2</sub> aggregates/dimers with bands at 1347, 1574, 3263, and 3441 cm<sup>-1</sup>; and a previously uncharacterized species with bands at 1582 and 3418 cm<sup>-1</sup>. The identification of the various aminomethylidyne species observed within this narrow temperature range was aided by the results of a number of

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**Figure 6.** A reaction scheme that summarizes the surface chemistry of cyanogen and hydrogen on Pt(111), as established by this study.

complementary studies.<sup>2-4</sup> Likely candidates for the species that gives rise to bands at 1582 and 3418  $\text{cm}^{-1}$  include iminoethanenitrile ( $\mu\text{-NH}=\text{CCN}$ ) and bridge bound hydrogen isocyanide ( $\mu\text{-HNC}$ ). Iminoethanenitrile, a possible  $-3\text{H}$  dehydrogenation product of  $(\text{CNH}_2)_2$ , has been identified as a ligand within a  $\text{Os}_3\text{H}(\mu\text{-NH}=\text{CCN})(\text{CO})_{10}$  cluster,<sup>34</sup> effectively being derived from the reaction between hydrogen ( $\text{Os}_3\text{H}_2(\text{CO})_{10}$ ) and cyanogen ( $\text{C}_2\text{N}_2$ ). Since iminoethanenitrile contains both  $\text{C}=\text{N}$  and  $\text{NH}$  internal coordinates, analogous imine stretch bands should be observed between 1471–1689 and 3400–3500  $\text{cm}^{-1}$ , respectively. While the experimental values of 1582 and 3418  $\text{cm}^{-1}$  do indeed fall within these ranges, the presence of iminoethanenitrile is deemed unlikely since this species would also give rise to a characteristic  $\nu(\text{CN})$  mode in the 2240–2222  $\text{cm}^{-1}$  region. An inspection of the spectra shows no additional bands in this region. Peaks due to common  $\text{CO}$  (background) and  $\text{CO}_2$  (purge) contaminants would be expected to straddle, but not mask, the region of interest. An additional inconsistency with the assignment of the 1582- $\text{cm}^{-1}$  band to the  $\nu(\text{CN})$  mode of  $\mu\text{-NH}=\text{CCN}$  is that the  $\text{C}=\text{N}$  bond is assumed to lie parallel to the surface, likely making it undetectable. In contrast to iminoethanenitrile, hydrogen isocyanide does not possess a nitrile functionality, but does contain both  $\text{C}=\text{N}$  and  $\text{NH}$  bonds. An “upright” bridge bound  $\mu\text{-HNC}$  species would therefore be expected to give rise to both  $\nu(\text{NH})$  and  $\nu(\text{CN})$  bands close to the observed experimental frequencies. Such bridge bound isocyanide species are well-known in the organometallic literature, existing as ligands in a number of clusters<sup>34–37</sup> such as  $\text{Os}_3\text{H}_2(\mu\text{-CNH})(\text{CO})_{10}$ .<sup>34</sup> In conjunction with these findings, the bands of the  $(\text{CNH}_2)_2$  decomposition product observed at 3418 and 1582  $\text{cm}^{-1}$  are tentatively assigned to the  $\nu(\text{NH})$  and  $\nu(\text{CN})$  modes of  $\mu\text{-HNC}$ .

Several features of the  $(\text{CNH}_2)_2$  decomposition mechanisms are revealed by these studies, and are summarized in Figure 6. The  $\text{H}_2$  TPD peak at 377 K and the observation of  $\text{CNH}_2$  monomers and dimers as decomposition products suggest that both  $\text{NH}$  and  $\text{CC}$  bond scission occur. The desorption of  $\text{HCN}$  (460 K) and  $\text{C}_2\text{N}_2$  (630 K) due to  $\text{CNH}_2$  decomposition ( $\text{HCN}$ ) and recombinative desorption of  $\text{CN}$  ( $\text{C}_2\text{N}_2$ ) indicates that  $\text{CN}$

cleavage does not occur and confirms that  $\text{CN}_{\text{ads}}$  is stable on the surface to elevated temperatures. Similar  $\text{HCN}$  and  $\text{C}_2\text{N}_2$  desorption peaks have also been observed for a wide assortment of  $\text{CN}$  containing species on  $\text{Pt}(111)$ .<sup>2,14–16,18</sup> The assignment of all bands observed during the annealing experiments is summarized in Table 4. While  $\text{CC}$  cleavage provides a direct route to the formation of  $\text{CNH}_2$  dimers and/or a pair of non-hydrogen bonded monomers, the order in which the  $\text{CC}$  and  $\text{NH}$  bonds break in diaminoethylene may explain how an  $\text{HNC}$  species (with the  $\text{CN}$  axis oriented along the surface normal),  $\text{CNH}_2$  monomers, and ultimately  $\text{CN}$  are produced. In previous studies of  $\text{CNH}_2$ , derived from  $\text{HCN}$ , azomethane ( $\text{CH}_3\text{N}_2\text{CH}_3$ ), and methylamine ( $\text{CH}_3\text{NH}_2$ ),<sup>2–4,7</sup> the bands observed here that are attributed to an upright form of  $\text{HNC}$  were not detected. However, a single band observed at 3347  $\text{cm}^{-1}$  during the conversion of  $\text{HCN}$  to  $\text{CNH}_2$  was tentatively assigned<sup>3</sup> to an  $\mu_2\eta^2\text{-HNC}$  species with both the  $\text{C}$  and  $\text{N}$  atoms bonding to the surface. It seems likely that during the thermal decomposition of diaminoethylene,  $\text{CC}$  followed by  $\text{NH}$  bond scission results in the formation of  $\text{CNH}_2$  and  $\text{CN}$ . The apparent small amount of  $\text{HNC}$  formed may be explained in terms of the opposite decomposition mechanism, i.e.  $\text{NH}$  followed by  $\text{CC}$  bond scission, since  $\text{NH}_2\text{CC}=\text{NH}$  would give rise to both  $\text{CNH}_2$  and  $\text{HNC}$  upon  $\text{CC}$  cleavage. Although this mechanism is somewhat speculative, there is ample precedent for it. The interconversion of iminium and imine species is well-known, and has been shown to proceed through both protonation/deprotonation<sup>34,36</sup> and disproportionation<sup>37</sup> pathways for a number of organometallic species. Interestingly, the  $\mu$ -isocyanide ligands of the binuclear iridium complex  $\text{Ir}_2(\text{CNR})_4(\text{dmpm})_2$ <sup>35</sup> have been shown to undergo a number of analogous Lewis acid induced reactions. The addition of  $\text{BH}_3$  to this cluster results in the formation of  $\text{Ir}_2(\mu\text{-CN}(\text{BH}_3)\text{R})_2(\text{CNR})_2(\text{dmpm})_2$ , which contains a pair of  $\mu\text{-CN}(\text{BH}_3)\text{R}$  aminocarbyne (iminium) species. When the more powerful  $(\text{AlEt}_2)_2$  reagent is used in place of  $\text{BH}_3$ ,  $\text{Ir}_2(\text{C}_2(\text{NR})_2\text{AlEt}_2)(\text{CNR})_2(\text{dmpm})_2$  is generated. The carbon atoms of the cluster's two adjacent  $\mu$ -isocyanide ligands couple to form a  $\text{C}-\text{C}$  bond within a planar five-membered  $\text{C}_2\text{N}(\text{R})_2\text{-Al}$  ring fragment. The structural similarities between  $(\text{CNH}_2)_2$ , as well as the  $\text{CNH}_2$  dimers formed upon its subsequent decomposition, and the analogous  $\text{C}_2\text{N}(\text{R})_2\text{Al}$  and pair of  $\mu\text{-CN}(\text{BH}_3)\text{R}$  fragments generated through the reactions of various Lewis acids with  $\text{Ir}_2(\text{CNR})_4(\text{dmpm})_2$  show that similar chemical processes likely occur for both Group VIII transition metal adsorbates and ligands.

No RAIR spectra showing features directly attributable to either  $\text{C}_2\text{N}_2$  or  $\text{CN}$  were observed under conditions where one or both species are known to be present on the surface. This strongly suggests that these adsorbates bond with their molecular axes parallel to the metal surface, a conclusion consistent with the HREELS and NEXAFS results of Kordesch *et al.*<sup>22,25</sup> In the relevant HREELS<sup>22</sup> study of cyanogen on  $\text{Pd}(111)$ , ‘perpendicular’  $\delta(\text{NCCN})$  and weak  $\nu(\text{CC})$  modes were detected in the absence of any  $\nu(\text{CN})$  modes, while in a related NEXAFS<sup>25</sup> study,  $\text{C}_2\text{N}_2$  and  $\text{CN}$  were found to bond with their molecular axes parallel to the metal surface.

## 5. Conclusions

1. Cyanogen ( $\text{C}_2\text{N}_2$ ) undergoes partial dissociative adsorption on  $\text{Pt}(111)$  at 300 K forming chemisorbed  $\text{C}_2\text{N}_2$  (B) and  $\text{CN}$  (C) molecules, corresponding to the  $\alpha$  and  $\beta$  cyanogen thermal desorption peaks.

2. Spectra obtained following  $^{15}\text{N}$ ,  $^{13}\text{C}$ , and incremental  $^2\text{H}$  isotopic substitution show that hydrogenation at 300 K of molecularly adsorbed cyanogen (B) yields diaminoethylene,

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(CNH<sub>2</sub>)<sub>2</sub> (E). The spectra are most consistent with a planar C<sub>2v</sub> structure for diaminoethylene with the molecular plane perpendicular to the surface.

3. The β<sub>2</sub> (isolated) CN species undergo hydrogenation at 300 K, forming aminomethylidyne (CNH<sub>2</sub>) (F).

4. The fact that relatively less CNH<sub>2</sub> is ultimately formed from a higher initial dose of C<sub>2</sub>N<sub>2</sub> shows that the β<sub>1</sub> (island) form of CN<sub>ads</sub> is inert toward hydrogenation. This in turn suggests that only a dense β<sub>2</sub> (isolated) CN/H overlayer, derived from the *in situ* decomposition of species containing H, N, and C,<sup>2,4</sup> can give rise to aminomethylidyne aggregates (D), as similar CNH<sub>2</sub> aggregates cannot be formed by the post-adsorption of H<sub>2</sub> to high coverages of CN<sub>ads</sub> derived from C<sub>2</sub>N<sub>2</sub> (A).

5. Diaminoethylene undergoes partial decomposition at ~377 K, forming a mixture of CNH<sub>2</sub> dimers (G), CNH<sub>2</sub> monomers

(H), and possibly HNC. These secondary decomposition products undergo subsequent decomposition between 425 and 450 K, forming HCN<sub>(g)</sub> or HNC<sub>(g)</sub> (I, K) and CN<sub>ads</sub> (J). The remaining surface CN groups are removed via recombinative desorption at elevated temperatures as C<sub>2</sub>N<sub>2(g)</sub> (L).

6. The absence of RAIRS bands due to C<sub>2</sub>N<sub>2</sub> (B) and β CN (C, J) under conditions where these adsorbates are known to be present suggests that these linear molecules lie with their molecular axes parallel to the surface.

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