

# Formation of Methylaminocarbyne from Methyl Isocyanide on the Pt(111) Surface

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Reflection absorption infrared spectroscopy and temperature-programmed desorption were used to investigate the adsorption of methyl isocyanide ( $\text{CNCH}_3$ ) on the Pt(111) surface and its reaction to form methylaminocarbyne ( $\text{CNHCH}_3$ ). In agreement with previous studies, methyl isocyanide is found to adsorb at on-top sites at low coverages and at both on-top and 2-fold bridge sites at higher coverages. Hydrogen reacts with the N-atom of methyl isocyanide adsorbed at on-top sites to form methylaminocarbyne, whereas at higher coverages where bridge-site occupation occurs the reaction is suppressed. The formation of an NH bond is indicated by the appearance of a sharp peak at  $3405\text{ cm}^{-1}$  upon annealing a low coverage of methyl isocyanide to temperatures of 200 to 280 K. The formation of the NH bond is accompanied by loss of the intense isocyanide stretch at  $2235\text{ cm}^{-1}$  and its replacement by a new set of peaks in the  $1200\text{--}1500\text{ cm}^{-1}$  region that are readily assigned to the modes of methylaminocarbyne. Spectral assignments and interpretation are aided by results for the  $\text{CNDCH}_3$  and  $^{13}\text{CNHCH}_3$  isotopomers.

## Introduction

The interaction of isocyanides with transition metals has been extensively studied in the context of organometallic chemistry.<sup>1</sup> Studies of the chemistry of isocyanides on transition metal surfaces have been more limited and have mainly focused on the structure of the adsorbed molecule and the adsorption site, which is inferred from the vibrational frequency of the isocyanide CN stretch on the basis of correlations with the structures of isocyanide coordination complexes. The reactive chemistry of isocyanides on surfaces has received almost no attention despite the fact that a rich variety of reactions of isocyanides as ligands in coordination complexes are well-known. Among these reactions are protonation and alkylation at the nitrogen atom, which has a high basicity leading to high reactivity toward electrophilic species. Here we provide a detailed description of the N-protonation of methyl isocyanide ( $\text{CNCH}_3$  or  $\text{CNMe}$ ) on the Pt(111) surface to form methylaminocarbyne ( $\text{CNHCH}_3$ ). This reaction is well-known in the organometallic literature but has not been previously reported in studies of isocyanides on surfaces.

The adsorption of  $\text{CNMe}$  has been studied on various transition metal surfaces.<sup>2</sup> The previous study most relevant to the present one is that of Avery and Matheson who used high-resolution electron energy loss spectroscopy (HREELS) to study  $\text{CNMe}$  on Pt(111).<sup>3</sup> They found that at 90 K the molecule adsorbs in a terminally bonded configuration with a linear  $\text{PtCNC}$  bond characterized by  $\nu_{\text{CN}}$  at  $2265\text{--}2240\text{ cm}^{-1}$ , while at higher coverages a bent-bridge-bonded form is also seen with  $\nu_{\text{CN}}$  at  $1600\text{--}1770\text{ cm}^{-1}$ . Decomposition leads to the desorption of  $\text{H}_2$  (440–460 K) and  $\text{HCN}$  (420–610 K). Our work agrees with these observations. Avery and Matheson<sup>3</sup> did not detect any evidence for NH bond formation nor did they give any reason to suspect that it might occur. Yet we have found<sup>4</sup> that a variety of molecules containing CN bonds undergo hydrogenation–dehydrogenation reactions to form the aminomethyldyne,  $\text{CNH}_2$ , species. This species forms directly when surface

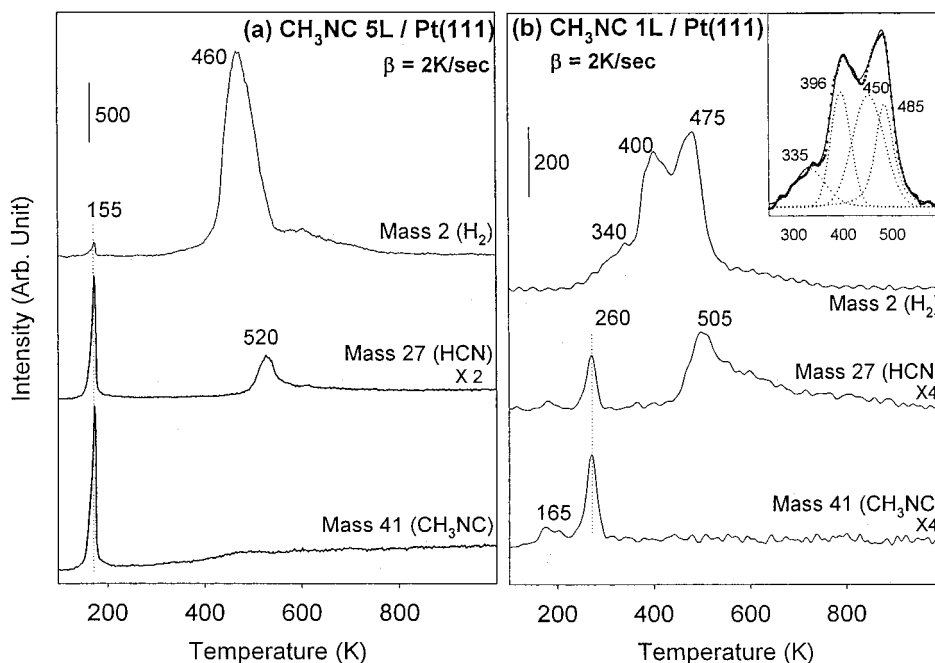
CN is exposed to hydrogen, with the surface CN being produced from a variety of precursors including cyanogen,<sup>5</sup>  $\text{HCN}$ ,<sup>6</sup> and ethylenediamine.<sup>7</sup> Related to  $\text{CNH}_2$  is the  $\text{H}_2\text{NC}\text{--}\text{CNH}_2$  species, which forms from the hydrogenation of molecularly adsorbed cyanogen.<sup>5</sup> Both of these species contain what is alternatively known as an iminium or aminocarbyne functionality. In our previous work we have generally labeled  $\text{CNH}_2$  as aminomethyldyne, following the example used in a report of its formation in an osmium complex.<sup>8</sup> The term aminocarbyne appears to be in more widespread use and is the name we adopt here. In particular, aminocarbynes are widely discussed as the products of electrophilic attack at the highly basic nitrogen atom of adsorbed isocyanides ( $\text{CNR}'$ ) to form aminocarbynes of the form  $\text{CNR}'$ , where R and R' can be a variety of groups including H and alkyls.<sup>9</sup> Our previous work showing the proclivity toward forming  $\text{CNH}_2$  on Pt(111) suggests that higher aminocarbynes might also form and the organometallic literature suggests that adsorbed isocyanides are the most likely route to these species.

In a brief earlier report,<sup>10</sup> we showed that methylaminocarbyne is readily formed from both the hydrogenation of chemisorbed methyl isocyanide as well as from the partial dehydrogenation of dimethylamine. The present work goes well beyond the previous paper by showing the correlation between TPD and RAIRS data, by showing how the N-protonation reaction is suppressed at higher  $\text{CNMe}$  coverages, by showing how  $\text{CNHCH}_3$  readily undergoes deuterium exchange at the NH bond but not at the CH bonds to form  $\text{CNDCH}_3$ , and by presenting data for the  $^{13}\text{CNHCH}_3$  isotopomer. The thermal decomposition of  $\text{CNHCH}_3$  at temperatures of 400 K and above leads to other stable surface intermediates, which are common to the surface chemistry of dimethyl and trimethylamine. A description of these other surface intermediates will be presented elsewhere.<sup>11</sup>

## Experimental Section

The experiments were performed in a stainless steel ultrahigh 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>12</sup> A turbo molecular pump is used to pump the

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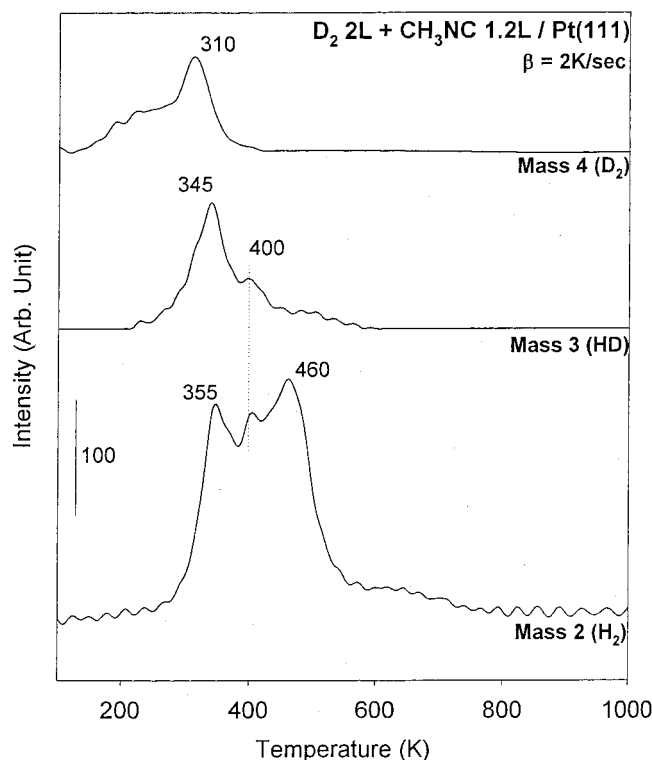
**Figure 1.** TPD spectra of methyl isocyanide on Pt(111) following exposures of (a) 5 L, and (b) 1 L. The sample was cooled to 85 K, exposed to methyl isocyanide, and heated at a rate of 2 K/s. Mass 16 ( $\text{CH}_4$ ) and mass 52 ( $\text{C}_2\text{N}_2$ ) were also monitored but not detected.

chamber and the bearings for the pump were replaced during the course of these experiments. This resulted in a slight decrease in pumping speed, which in turn gave higher coverages for the same exposure. The data presented in Figures 5 and 7 for  $^{13}\text{CNCH}_3$  were obtained at the lower pumping speed, while all other data were obtained at the higher pumping speed. The UHV chamber is equipped for Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and temperature-programmed desorption (TPD) experiments with a quadrupole mass spectrometer (QMS). It is coupled to a commercial Fourier transform infrared (FTIR) spectrometer. The IR beam enters and exits the UHV chamber through differentially pumped O-ring sealed KBr windows and passes through a polarizer before reaching an MCT (HgCdTe) detector, which was used for all of the spectra reported here. All RAIR spectra were taken with a resolution of  $4\text{ cm}^{-1}$ . In cases where the sample was annealed to a temperature above 85 K, the sample was then cooled back to 85 K before the spectrum was acquired. The background reference spectrum was also taken at 85 K. Methyl isocyanide was prepared by the method described by Casanova et al.<sup>13</sup> and was stored under vacuum at  $-78\text{ }^\circ\text{C}$ . The  $^{13}\text{CNCH}_3$  isotopomer was prepared by a different method<sup>14</sup> based on the reaction of methyl iodide and  $\text{Ag}^{13}\text{CN}$ . The  $\text{Ag}^{13}\text{CN}$  was prepared as an insoluble precipitate from the reaction of  $\text{K}^{13}\text{CN}$  (99%  $^{13}\text{C}$ ) and  $\text{AgNO}_3$  in aqueous solution. The Pt(111) surface was cleaned by a procedure described earlier.<sup>6</sup> Briefly, the crystal was heated in  $1 \times 10^{-7}$  Torr of  $\text{O}_2$  at  $\sim 825\text{ K}$  for 1 h after  $\text{Ar}^+$  bombardment followed by dosing 2 L (1 L =  $1 \times 10^{-6}$  Torr s) of  $\text{O}_2$  at 85 K and subsequently performing a TPD experiment from 85 to 1000 K. The surface was judged free of carbon when a  $m/e = 32$  peak at 720 K, due to recombinative desorption of oxygen, was observed in the absence of any  $\text{CO}_2$  ( $m/e = 44$ ) desorption above 300 K. The absence of impurities other than carbon was verified with Auger electron spectroscopy.

## Results

**1. Temperature-Programmed Desorption.** Figure 1 shows TPD results obtained after (a) 5 L and (b) 1 L exposures of

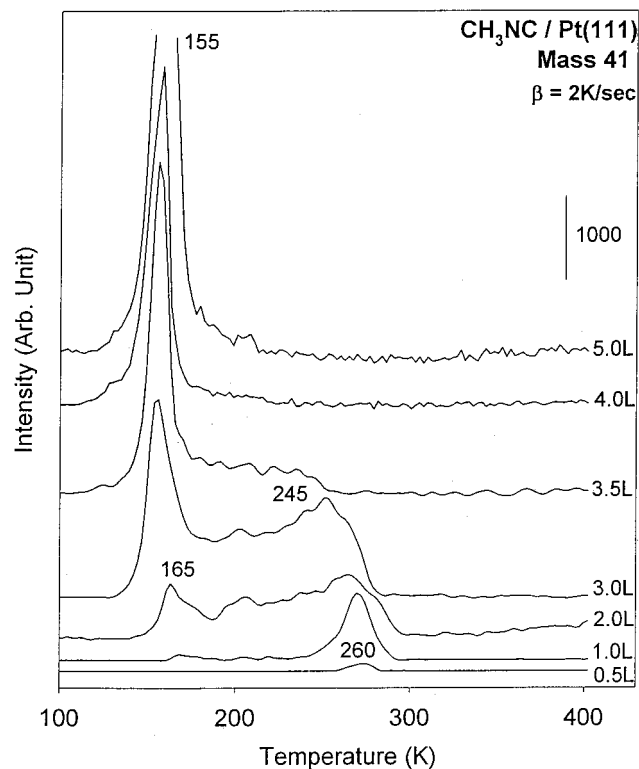
methyl isocyanide to the Pt(111) surface at 85 K. The TPD data at the higher coverage (5 L) is in good agreement with the results of Avery and Matheson.<sup>3</sup> They observed the desorption of hydrogen ( $m/e = 2$ ) and HCN ( $m/e = 27$ ) at 460 and 520 K, respectively. They also observed mass 41 peaks at 135 K due to desorption of CNMe multilayers and at 430 K, which they attributed to acetonitrile, NCMe, produced by isomerization of CNMe. We did not observe the 430 K peak nor did we obtain any other evidence for isomerization. As shown in Figure 1a, CNMe ( $m/e = 41$ ) multilayers desorb at 155 K and hydrogen and HCN fragments are observed at the same temperature. Since recombinative desorption of hydrogen occurs below 390 K,<sup>15,16</sup> the hydrogen peak at 460 K is attributed to surface reaction limited desorption, indicating the decomposition of adsorbed CNMe or other surface species. For a Pt(111) surface directly exposed to HCN, HCN desorption is observed at  $\sim 460\text{ K}$  due to the decomposition of the surface intermediate, aminocarbyne ( $\text{CNH}_2$ ). Thus, the desorption of HCN at 520 K is also attributed to surface reaction limited desorption. One indication of the presence of CN on a Pt(111) surface is the desorption of cyanogen ( $\text{C}_2\text{N}_2$ ) ( $m/e = 52$ ),<sup>7,17,18</sup> which was monitored but not detected. However, it generally desorbs over a broad temperature range from 600 to 800 K making it difficult to observe for low CN coverages. As shown elsewhere,<sup>11</sup> following annealing to 400 K and above some surface CN is detected by a more sensitive way through its hydrogenation to surface  $\text{CNH}_2$ , which gives readily detectable RAIRS peaks. For the lower coverage case in Figure 1b, hydrogen is observed to desorb at 400 K as well as at 475 K with some tailing on the high temperature side similar to what is seen for the higher coverage in Figure 1a. As shown in the inset, the hydrogen peak can be fit to four peaks at 335, 396, 450, and 485 K. The peak at 335 K is readily assigned to recombinative desorption of background hydrogen whereas the peak at 396 K is assigned to dehydrogenation of  $\text{CNHCH}_3$ , as indicated by the RAIRS results described below. This assignment is also supported by the TPD results shown in Figure 2 obtained following a 2 L  $\text{D}_2$ -plus-1.2 L CNMe exposure at 85 K. The  $\text{H}_2$  desorption is similar to what is seen in Figure 1b, whereas  $\text{D}_2$  ( $m/e = 4$ ) desorbs with



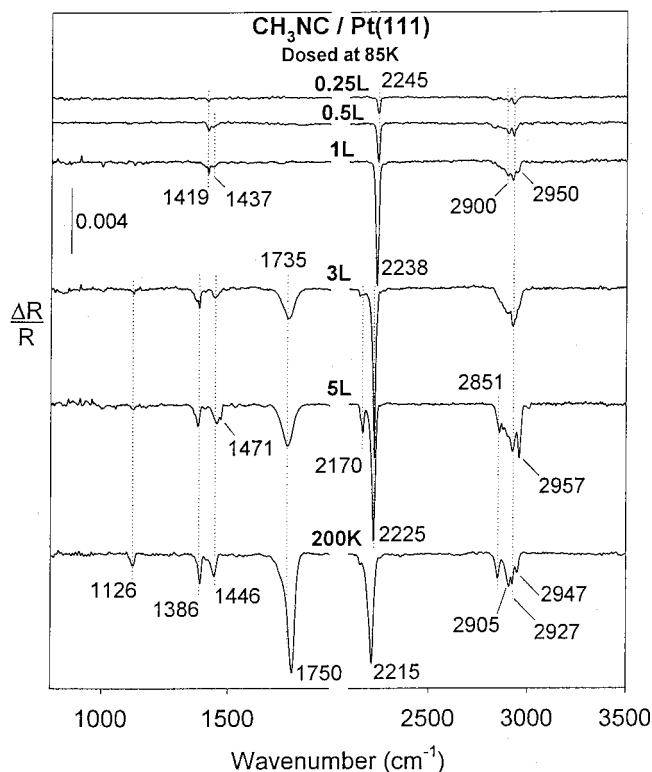
**Figure 2.** TPD spectra of  $H_2$ , HD, and  $D_2$  obtained after exposing 2 L of deuterium to the sample at 85 K followed by 1.2 L of methyl isocyanide also at 85 K.

a peak at 310 K with tailing to lower temperatures due to recombinative desorption. Mass 3 (HD) desorbs as two peaks at 345 and 400 K, with the one at 345 K attributed to the recombinative desorption of deuterium and background hydrogen and the other peak at 400 K associated with dehydrogenation of deuterium-substituted methylaminocarbyne,  $CNDCH_3$ . As will be described later, the formation of  $CNHCH_3$  is suppressed at higher methyl isocyanide coverages, which accounts for the absence of an  $H_2$  TPD peak at  $\sim 400$  K for the high coverage case in Figure 1a. The  $m/e = 41$  peak at 255 K in Figure 1b was not seen in the previous study on Pt(111).<sup>3</sup> However, as shown in Figure 3, this peak depends on coverage and is absent at the highest coverages, which corresponds to the conditions used by Avery and Matheson.<sup>3</sup> At 0.5 L, a peak is observed at 260 K that shifts to 245 K at 3 L. Another peak at 165 K is seen after 1 L. This peak increases in intensity and is shifted to 155 K with increasing exposure. The peak at 155 K is not saturated with increasing coverage and is attributed to multilayer desorption.

**2. RAIRS.** Figure 4 shows RAIR spectra obtained as a function of CNMe exposure to the surface at 85 K. The last spectrum is taken after annealing the 5 L dosed surface to 200 K. The assignments of adsorbed CNMe are inferred through comparisons with IR spectra of metal– $CNCH_3$  complexes.<sup>1</sup> No significant changes in the RAIR spectra are observed between 0.25 and 1 L. The intense peak that shifts from 2245 to 2225  $cm^{-1}$  is assigned to the CN stretch of CNMe bound to a single Pt atom with a linear PtCNC unit. This linear bonding form has a local symmetry of  $C_{3v}$  and only totally symmetric  $A_1$  modes—the symmetric CH stretch, symmetric  $CH_3$  deformation, the C–N single bond stretch, and the isocyanide CN stretch—are allowed according to the surface dipole selection rule. The peaks at 1419 and 2927  $cm^{-1}$  are assigned to  $CH_3$  deformation and C–H stretch modes, respectively. A peak corresponding to the C–N stretch near 945  $cm^{-1}$  is not observed here nor in



**Figure 3.** TPD spectra for mass 41 ( $CNCH_3$ ) obtained as a function of methyl isocyanide exposure. The desorption peak at 155 K is not saturated with increasing exposures.



**Figure 4.** RAIR spectra obtained as a function of methyl isocyanide exposure at 85 K. The last spectrum is taken after a 5 L exposure at 85 K with subsequent heating to 200 K, followed by cooling back to 85 K.

the earlier HREELS study.<sup>3</sup> As noted elsewhere,<sup>19</sup> the actual intensities of RAIRS peaks, even if symmetry allowed, are often too weak to be observed. The CH stretch shows a broad band consisting of several poorly resolved components, attributable

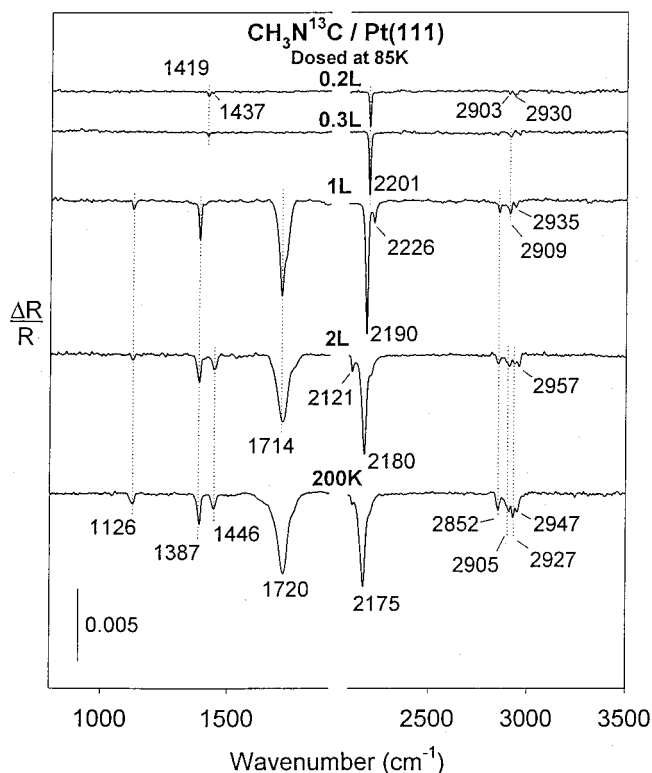
**TABLE 1: Vibrational Frequencies (cm<sup>-1</sup>) for Adsorbed CH<sub>3</sub>NC on Pt(111)**

	gas phase <sup>20</sup> (C <sub>3v</sub> )	linear (C <sub>3v</sub> )	bent bridge (C <sub>s</sub> )	multilayer
C–N stretch (a <sub>1</sub> )	945			
CH <sub>3</sub> rocking (e)	1129		1126	
CH <sub>3</sub> deformation (a <sub>1</sub> )	1429	1419	1386	
CH <sub>3</sub> deformation (e)	1467		1446 <sup>a</sup>	1471
CN stretch (a <sub>1</sub> )	2166	2238	1740	2170
CH sym stretch (a <sub>1</sub> )	2966	2927	2851	2957
CH asym stretch (e)	3014			

<sup>a</sup> There is some ambiguity as to the assignment of this peak, which is discussed in the text.

in part to two-dimensional disorder among the adsorbed molecules, as indicated by the fact that the peaks become sharper with annealing. Additional components in the CH stretch region are also likely due to Fermi resonances between the CH stretch fundamental and overtones and combinations of the CH<sub>3</sub> deformation modes, a common occurrence for molecules, including adsorbates, containing CH<sub>3</sub> groups.<sup>19</sup> The terminally bonded molecule has a CN stretch frequency that is blue-shifted from the value of the gas-phase molecule at 2166 cm<sup>-1</sup>. For exposures of 3 L and above, a second strongly red-shifted CN stretch peak is observed at 1735 cm<sup>-1</sup>. This corresponds to a reduction in the CN bond order from 3 to 2, indicative of the rehybridization associated with bridge bonding between two Pt atoms. The development of the 1735 cm<sup>-1</sup> peak is accompanied by peaks at 1386 and 1446 cm<sup>-1</sup> that are readily assigned to CH<sub>3</sub> deformation modes. With a 5 L exposure new peaks corresponding to the multilayer appear at 1471, 2170, and 2957 cm<sup>-1</sup> that are quite close to the gas-phase values of 1467, 2166, and 2966 cm<sup>-1</sup> and are assigned to the asymmetric CH<sub>3</sub> deformation, CN stretch, and CH stretch, respectively.<sup>20</sup> As expected, the multilayer peaks disappear after annealing the sample to 200 K, in agreement with the TPD results showing multilayer desorption at 155 K. The 200 K anneal also results in an increase in the bridge-bonded-to-terminal ratio, a slight shift of the 1735 cm<sup>-1</sup> peak to 1750 cm<sup>-1</sup>, and a sharpening of all peaks. An additional peak assigned to the CH<sub>3</sub> rocking mode of the bridge-bonded form is now clearly visible at 1126 cm<sup>-1</sup>. The presence of the CH<sub>3</sub> rock, which would be forbidden by the surface dipole selection rule for an upright molecule, indicates that the single N–C bond is tilted with respect to the surface normal. The fairly intense double C=N bond stretch at 1750 cm<sup>-1</sup> strongly suggests, but does not prove, that the C=N bond is not parallel to the surface. The results of Figure 4 thus fully support the structure of the bridge-bonded form (Figure 10b) suggested by Avery and Matheson.<sup>3</sup> The vibrational frequencies for methyl isocyanide are listed in Table 1.

Figure 5 shows the dependence of the spectra on exposure to <sup>13</sup>CNCH<sub>3</sub> with the surface at 85 K and the results of a 200 K anneal following the 2.0 L exposure. Because of the different relationship between exposure and coverage that was described in the Experimental Section, the 1 L exposure in Figure 5 corresponds to an exposure between 1 and 3 L in Figure 4. Nevertheless, the same trend of on-top occupancy followed by adsorption at bridge sites pertains. Additional experiments with <sup>12</sup>CNMe taken at the time of the <sup>13</sup>CNCH<sub>3</sub> data show a similar exposure–coverage relationship as seen in Figure 5. Furthermore, the extensive set of data we have obtained for both isotopomers reveals which features are fully reproducible and which are dependent on the exact dosing conditions used. Annealing to 200 K or higher leads to more consistent results. Some contamination of the <sup>13</sup>CNCH<sub>3</sub> with <sup>12</sup>CNMe is indicated in Figure 5 by the CN stretch peak at 2226 cm<sup>-1</sup>. The main

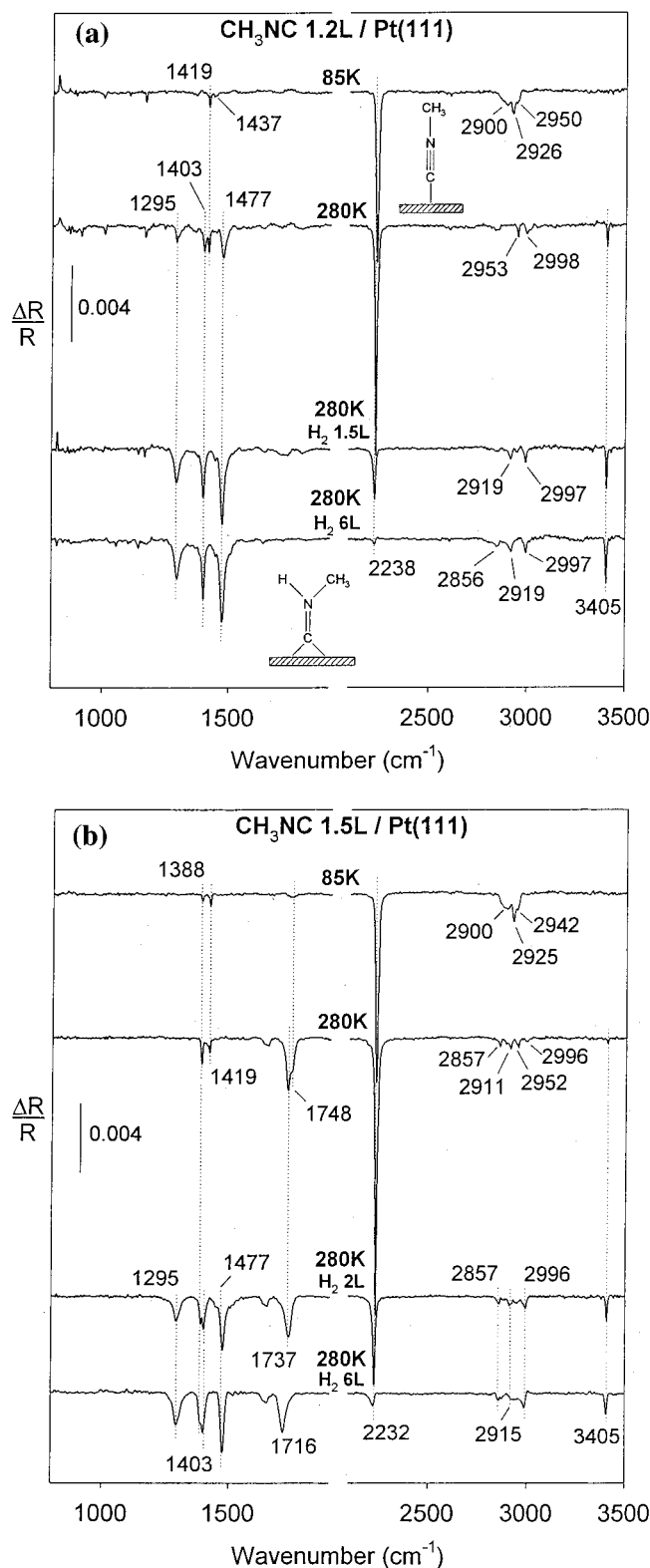


**Figure 5.** RAIR spectra obtained as a function of <sup>13</sup>CNCH<sub>3</sub> exposure at 85 K. The last spectrum is taken after a 2 L exposure at 85 K with subsequent heating to 200 K, followed by cooling back to 85 K where the spectra were obtained.

features of the spectra change in expected ways upon <sup>13</sup>C substitution. The CN stretch shows the largest shift, changing for the 200 K annealed spectra from 2215 to 2175 cm<sup>-1</sup> for the on-top form and from 1750 to 1720 cm<sup>-1</sup> for the bridge-bonded form. The CH<sub>3</sub> deformation modes at 1419 cm<sup>-1</sup> for on-top CNMe and at 1387 cm<sup>-1</sup> for the bridge-bonded form are at essentially the same values for <sup>13</sup>CNCH<sub>3</sub> and <sup>12</sup>CNCH<sub>3</sub>. Other differences between Figures 4 and 5 reflect subtle differences in the way the overlayers were prepared. For example, in Figure 4, the CN stretch of the bridge-bonded CNMe appears as a single broad peak (fwhm = 32 cm<sup>-1</sup>) with a low frequency tail, whereas in Figure 5 the peak consists of at least two distinct components, indicating subtly different forms of the bent-bridge species. There are two possible assignments for the CH<sub>3</sub> deformation peak, which occurs at 1446 cm<sup>-1</sup> in both figures. It may be the symmetric deformation corresponding to two different forms of the bent-bridge species. This is suggested by the fact that it does not appear at coverages where the 1387 cm<sup>-1</sup> peak is already prominent, such as in the 1 L spectrum in Figure 5. Or it may be due to the asymmetric deformation, which, like the CH<sub>3</sub> rock at 1126 cm<sup>-1</sup>, would be allowed for the bent-bridge structure. The CH stretch region also appears quite different in the two cases, in ways that cannot be due simply to the effects of isotopic substitution. Again, this most likely reflects subtly different forms of the adsorbed isocyanide produced by the different dosing conditions used in the two experiments.

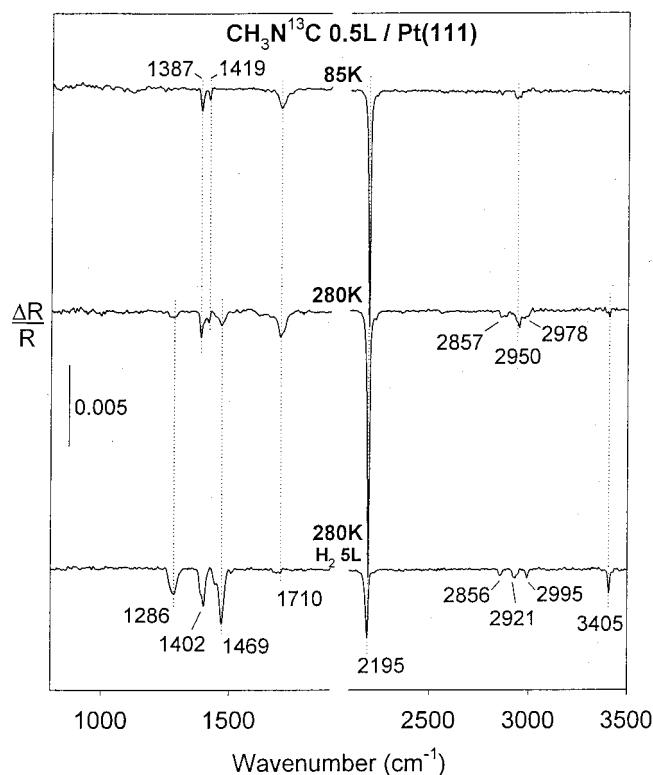
Figure 6 shows RAIR spectra obtained after exposing (a) 1.2 L and (b) 1.5 L of methyl isocyanide to the Pt(111) surface at 85 K, annealing to 280 K, then exposing to the indicated amounts of hydrogen. In Figure 6a, the 85 K spectrum shows almost the same peaks as the 1.0 L spectrum in Figure 4. The 280 K anneal results in pronounced changes in the spectra. Most significantly, a new peak is observed at 3405 cm<sup>-1</sup>, which





**Figure 6.** RAIR spectra obtained after exposing (a) 1.2 L and (b) 1.5 L of methyl isocyanide to the sample at 85 K with subsequent heating to 280 K and exposure to the indicated amount of H<sub>2</sub> at 280 K, followed by cooling back to 85 K where the spectra were obtained.

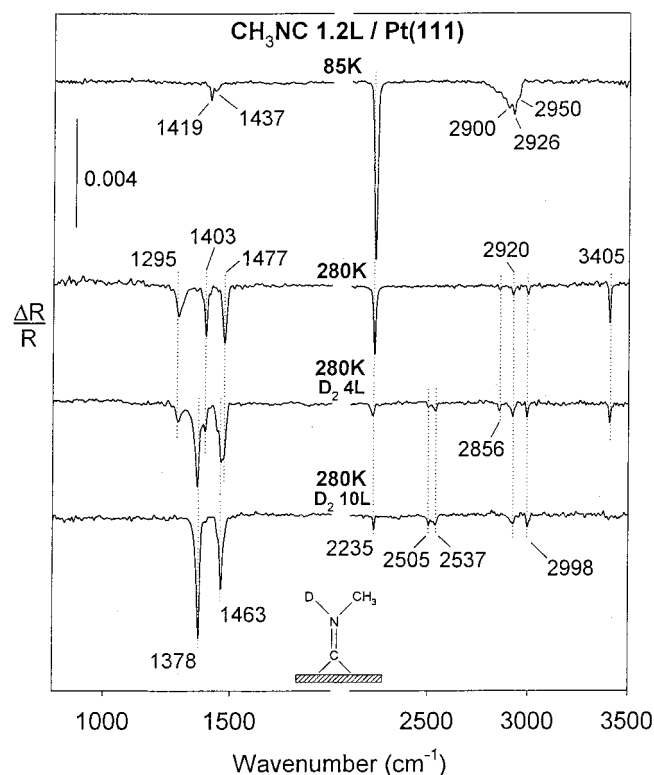
is readily assigned to an NH stretch mode. This assignment is unambiguous as it is well above the range of possible CH stretching vibrations. The NH bond is evidently formed from the reaction with background hydrogen, which is invariably present in even the best UHV environments. The lower two spectra show the effect of deliberately exposing the surface to hydrogen, which causes the NH stretch peak to increase in



**Figure 7.** RAIR spectra obtained after exposing 0.5 L of <sup>13</sup>CNCH<sub>3</sub> to the sample at 85 K with subsequent heating to 280 K and exposure to 5 L of H<sub>2</sub> at 280 K, followed by cooling back to 85 K where the spectra were obtained.

intensity. The NH bond formation reaction is strongly dependent on coverage and for the slightly higher CNMe exposure of 1.5 L (Figure 6b), the NH stretch peak is much weaker. In fact, NH bond formation is not detected at all for CNCH<sub>3</sub> exposures over 2 L, regardless of the hydrogen exposure. This is likely due to the absence of hydrogen adsorption sites as suggested by the TPD results showing little or no recombinative desorption of hydrogen for the higher CNCH<sub>3</sub> exposures. The temperature at which the reaction occurs also depends on coverage and occurs as low as 200 K for a 0.5 L CNCH<sub>3</sub> exposure. The increase of the NH stretch peak intensity with increasing hydrogen exposure is accompanied by a decrease in intensity of the CN stretch peak at 2232 cm<sup>-1</sup>, whereas  $\nu(\text{CN})$  of the bent-bridge species undergoes only a modest decrease in intensity accompanied by a change in shape and a shift downward to 1716 cm<sup>-1</sup>. The spectra indicate that the reaction of the adsorbed isocyanide with hydrogen produces an entirely new species, CNHCH<sub>3</sub>, with intense peaks in the lower frequency region at 1477 ( $\nu_{\text{CN}}$ ), 1403 ( $\delta(\text{CH}_3)$ ), and 1295 cm<sup>-1</sup> ( $\rho(\text{CH}_3)/\delta(\text{NH})$ ). The CNHCH<sub>3</sub> species exists as a ligand in organometallic complexes, with  $\nu(\text{NH})$  at 3300 cm<sup>-1</sup> and  $\nu(\text{CN})$  at 1582 cm<sup>-1</sup> in an Os complex<sup>21</sup> and  $\nu(\text{NH})$  at 3338 cm<sup>-1</sup> and  $\nu(\text{CN})$  at 1525 cm<sup>-1</sup> in a Ni complex.<sup>22</sup>

Figure 7 shows RAIR spectra obtained after exposing <sup>13</sup>CNMe to the surface at 85 K, annealing the sample to 280 K, followed by a 5 L hydrogen exposure. The spectra show the characteristic peaks for <sup>13</sup>CNHCH<sub>3</sub>. As expected, the NH and CH stretch peaks for <sup>13</sup>CNHCH<sub>3</sub> and <sup>12</sup>CNHCH<sub>3</sub> are at the same values, as is the peak at 1403 cm<sup>-1</sup>. This supports assignment of the 1403 cm<sup>-1</sup> peak to a CH<sub>3</sub> deformation mode. The peak at 1477 cm<sup>-1</sup> is shifted to 1469 cm<sup>-1</sup>, while the one at 1295 cm<sup>-1</sup> is shifted to 1286 cm<sup>-1</sup>. The methylaminocarbene species can also be produced on Pt(111) from the partial dehydrogenation of dimethylamine and data for C<sup>15</sup>NHCH<sub>3</sub> following



**Figure 8.** RAIR spectra obtained after a 1.2 L exposure of methyl isocyanide to the sample at 85 K, subsequent heating to 280 K and exposure of the sample to the indicated amounts of  $\text{D}_2$  at 280 K, followed by cooling back to 85 K where the spectra were obtained.

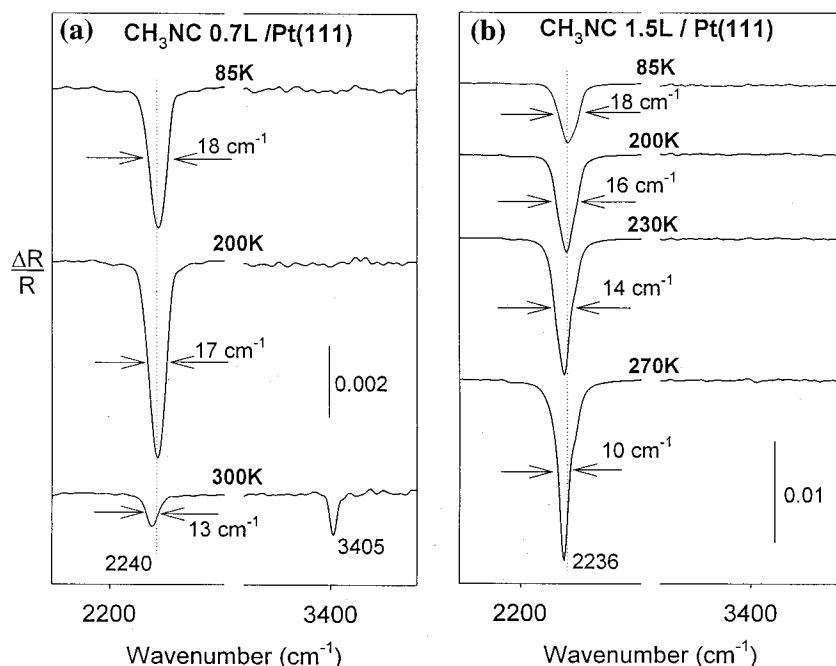
adsorption of  $^{15}\text{NH}(\text{CH}_3)_2$  shows that the  $1295 \text{ cm}^{-1}$  peak is shifted to  $1291 \text{ cm}^{-1}$  and the  $1477$  peak to  $1466 \text{ cm}^{-1}$  by  $^{15}\text{N}$  substitution.

The results of deuterium exposure after dosing methyl isocyanide are shown in Figure 8. The upper spectra are obtained after exposing 1.2 L of methyl isocyanide to the sample, annealing to 280 K, then exposing to 4 and 10 L of  $\text{D}_2$ . When the adsorbed isocyanide is exposed to  $\text{D}_2$ , spectra develop

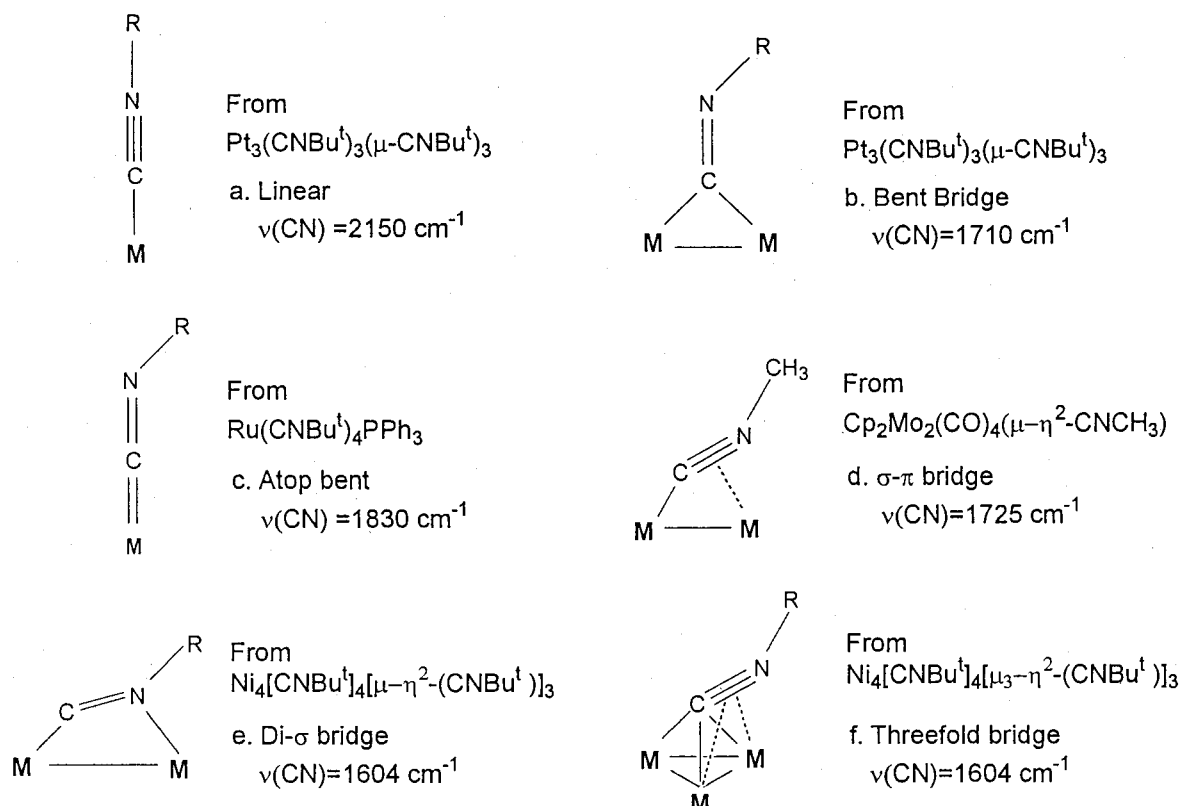
corresponding to  $\text{CNDCH}_3$ . The peaks at  $1477$  ( $\nu_{\text{CN}}$ ) and  $1403$  ( $\delta(\text{CH}_3)$ )  $\text{cm}^{-1}$  are shifted to  $1463$  and  $1378 \text{ cm}^{-1}$ , respectively. The strong shift with deuterium substitution is due to the fact that although these modes do not nominally involve deuterium atom motion, they have significant contributions from the CND bend. A fundamental due to the CND bend is not observed, indicating that it has an undetectably low intensity as it is unlikely that it has shifted to below the cutoff of our detector at  $\sim 800 \text{ cm}^{-1}$ . Strong variations in intensities upon deuterium substitution are commonly observed in RAIR spectra.<sup>19</sup>

Two peaks are observed in the ND stretch range at  $2505$  and  $2537 \text{ cm}^{-1}$ . There is only one NH stretch fundamental, and it is allowed for the  $C_s$  point group. In a Ni complex,  $\nu(\text{NH})$  and  $\nu(\text{ND})$  peaks are observed at  $3338$  and  $2480 \text{ cm}^{-1}$ , respectively.<sup>22</sup> The same frequency ratio for the surface species would imply that  $\nu(\text{ND})$  should be at  $2530 \text{ cm}^{-1}$ ; thus the peak observed at  $2537 \text{ cm}^{-1}$  is assigned to the ND stretch fundamental. Although a definitive assignment of the  $2505 \text{ cm}^{-1}$  peak is not possible, it is likely due to a combination band that gains intensity through a Fermi resonance with  $\nu(\text{ND})$ . Jentz et al. also observed two ND stretches in deuterium-substituted aminocarbyne ( $\text{CND}_2$ ), even though only one ND stretch fundamental is allowed, and they assumed one of the peaks is due to the  $\delta(\text{ND}_2) + \nu(\text{CN})$  combination band.<sup>6</sup> Just as for  $\text{H}_2$  exposure,  $\text{D}_2$  exposure almost completely eliminates the strong CN stretch peak at  $2235 \text{ cm}^{-1}$  and leads to the same set of peaks in the CH stretch region. The results clearly show that deuterium readily exchanges with hydrogen at the NH bond but not at the  $\text{CH}_3$  group. Similar deuterium exchange effects were also observed for aminocarbyne.<sup>6</sup>

The isocyanide  $\nu(\text{CN})$  peak in Figure 6a appears to increase as it is converted to the new species with the 280 K anneal. Actually, because the peak width decreases with annealing temperature, the height increases even though the integrated area actually decreases. The behavior of the line shape with annealing at different coverages is shown in Figure 9. At 0.7 L, the isocyanide  $\nu(\text{CN})$  peak shows a slight decrease in both width and height and hence a decrease in area that accompanies the development of the  $3405 \text{ cm}^{-1}$  peak, reflecting the conversion



**Figure 9.** The behavior of the CN stretch line shape with annealing following exposures of (a) 0.1 L, and (b) 1.5 L of methyl isocyanide.



**Figure 10.** The structure and CN stretch values of various isocyanide ligands in organometallic complexes, refs 23a–f.

of the terminal methyl isocyanide to methylaminocarbene. In contrast, at the higher isocyanide coverage associated with a 1.5 L exposure there is no NH bond formation and the CN stretch becomes both narrower and more intense with a fwhm of only  $10 \text{ cm}^{-1}$ . The integrated area has increased by a factor of 2 following the 270 K anneal. The sharpening of the peak is presumably due to a decrease in disorder of the overlayer but this would not explain the overall increase in peak area. In Figure 6b, the increase in intensity of the CN stretch peak at  $2232 \text{ cm}^{-1}$  is also accompanied by an increase in intensity of the CN stretch peak of the bridge-bonded species. At the same time, there is considerable change in the CH stretch region with the anneal in Figure 6b, showing a net decrease in the overall CH stretch peak area and the development of four distinct peaks in this region for the post-annealed sample. These results strongly suggest the presence of a form of adsorbed isocyanide with a CN stretch of negligible intensity that transforms upon annealing into a form with a strong CN stretch peak.

## Discussion

**1. Molecular Adsorption of Methyl Isocyanide below 200 K.** Our results are in agreement with the conclusion of Avery and Matheson<sup>3</sup> that methyl isocyanide adsorbs on the Pt(111) surface molecularly at 85 K. For temperatures below 200 K, we do not detect any reactive chemistry and the spectra can therefore be interpreted in terms of various forms of the coordinated molecule. One way to assign the RAIR spectra to specific forms of adsorbed methyl isocyanide is through comparisons with the spectra of isocyanide organometallic complexes. A large variety of such complexes are known<sup>11</sup> but, unfortunately, characterization of the complexes with vibrational spectroscopy is often limited to the value of the CN stretch. As shown in Figure 10,  $\nu(\text{CN})$  varies over an extremely wide range corresponding to the wide variety of coordination modes found

in the organometallic literature.<sup>23</sup> The observation of RAIR spectra with an intense peak at  $2245 \text{ cm}^{-1}$  at low coverage at 85 K, indicates that  $\text{CNCH}_3$  adsorbs on a Pt atom (on-top site) with a linear CNC unit. Due to adsorbate–adsorbate interactions  $\nu(\text{CN})$  varies from 2214 to  $2257 \text{ cm}^{-1}$ , depending on coverage. From the fact that  $\nu(\text{CN})$  for the on-top molecule is close to the value for the gas-phase molecule ( $2166 \text{ cm}^{-1}$ ), Avery and Matheson<sup>3</sup> concluded that it bonds only via  $\sigma$  donation from the HOMO with no  $\pi$  back-donation into the LUMO, which has CN antibonding character. The fact that it is slightly higher than the gas-phase value was attributed simply to mechanical coupling to the surface, a conclusion they<sup>3</sup> supported with unpublished normal mode calculations. These conclusions regarding the on-top species are quite straightforward and we have nothing to add to them.

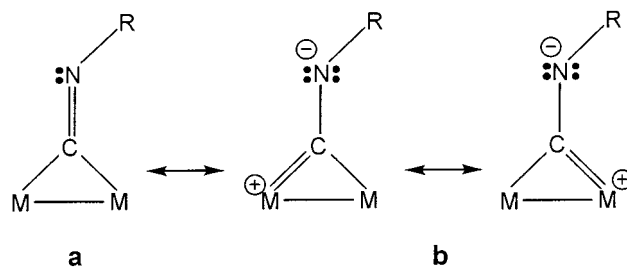
An additional CN stretch peak at  $1735 \text{ cm}^{-1}$  is observed at higher coverages and is assigned to a bent-bridge species with the CN bond aligned along the surface normal as in Figure 10b. A bent CNC unit is strongly supported by observation of a methyl rock at  $1126 \text{ cm}^{-1}$ , which would be forbidden if the N–C single bond were oriented along the surface normal. Avery and Matheson noted that although the spectra are consistent with the bent-bridge form, the evidence does not definitively exclude coordination modes c–e in Figure 10 that are known in the organometallic literature. Vibrational spectra were also assigned to the bent bridge form on Rh(111) and Pd(111).<sup>2d,e</sup> For CO on Pt(111), on-top sites are occupied first followed by bridge site adsorption at higher coverages. The order is different for CNMe on both Pd(111) and Rh(111) but, like for Pt(111), the order follows the same trend as for CO on these metals.

One aspect of the low-temperature adsorption behavior where our findings differ from those of Avery and Matheson<sup>3</sup> is in the TPD results. They did not present TPD data over a full range of coverages and therefore did not observe the desorption of

the parent molecule ( $m/e = 41$ ) for submonolayer coverages. At our lowest coverage (0.25 L), only one  $m/e = 41$  peak is observed at 260 K. This peak shifts to 245 K and a second peak appears at 165 K with increasing exposure. The peak at 165 K increases in intensity and shifts to 155 K whereas the peak at 245 K disappears over 3 L. The 165 and 155 K peaks are presumably due to second layer and higher multilayers, respectively. In contrast to the TPD results, no decrease in  $\nu(\text{CN})$  intensity is observed with RAIRS for annealing temperatures up to 280 K for the 1.2 and 1.5 L exposures, Figures 6a and 6b, respectively. This strongly implies that a form of  $\text{CNCH}_3$  is present on the surface that does not contribute to the  $\nu(\text{CN})$  peak. Ceyer and Yates observed similar TPD spectra for the  $\text{CNCH}_3/\text{Ag}(311)$  system,<sup>24</sup> where a peak at 185 K is observed at the lowest coverage and was assigned to a form of  $\text{CNCH}_3$  with the NC bond parallel to the surface. It was assumed to be weakly coordinated through the CN  $\pi$  bond. Although  $\pi$ -bonded species are observed for alkenes on various metal surfaces,<sup>25</sup> no corresponding organometallic compounds for CN are known. However,  $\eta^2\text{-RNC}$  species exist as ligands in a Ni complex<sup>23c</sup> and the isomer, acetonitrile ( $\text{NCCH}_3$ ), adsorbs on  $\text{Pt}(111)$  with the CN stretch unobservable with RAIRS, presumably because the CN bond is parallel to the surface.<sup>4</sup> A weak  $\pi$ -bonding interaction between acetonitrile and  $\text{Pt}(111)$  is also suggested by the low desorption temperature of  $\sim 240$  K for the monolayer and  $\sim 150$  K for multilayers.<sup>26,27</sup> A similarly coordinated form of  $\text{CNMe}$  might also have an unobservably weak CN stretch peak, but other modes should be observable. The RAIR spectra for 0.25, 0.5, and 1 L of  $\text{CNMe}$  (Figure 4) show peaks at 1437, 2900, and 2950  $\text{cm}^{-1}$ , which might be assigned to the  $\text{CH}_3$  deformation, and symmetric and asymmetric CH stretch modes of a  $\pi$ -bonded  $\text{CNMe}$  species. As revealed by the  $^{13}\text{CNMe}$  data of Figure 5, the appearance of the CH stretch region depends on the exact dosing conditions. If in addition to desorbing at low temperature, some of the  $\pi$ -bonded form also converted into the linear or bent-bridge forms with annealing, this would account for the increase upon annealing of  $\nu(\text{CN})$  for both the linear and bent-bridge forms of  $\text{CNMe}$  seen in Figures 6a and 6b. In the case of ethylene on  $\text{Pt}(111)$  and other metal surfaces, some of the low-temperature form desorbs while the rest converts to ethynyl ( $\text{CCH}_3$ )<sup>25</sup> when the sample is annealed. Although a weakly adsorbed form of  $\text{CNMe}$  with the CN bond parallel to the surface would reconcile the TPD and RAIRS data, its existence would have to be confirmed with a technique, such as photoelectron diffraction, that can more directly determine bond orientations on surfaces.

**2. Formation of Methylaminocarbyne (200–350 K).** At sufficiently low coverages, the thermal chemistry of methyl isocyanide is relatively simple. If there is sufficient hydrogen on the surface, either from background adsorption or through deliberate  $\text{H}_2$  exposure, it undergoes N-protonation at a temperature of 280 K to form  $\text{CNHCH}_3$ , which is stable up to 370 K. Although  $\text{CNHCH}_3$  has not been identified in previous surface science studies, in organometallic chemistry bent-bridge as well as terminal isocyanides are known to readily undergo N-alkylation and N-protonation reactions to form aminocarbynes.<sup>22,28</sup> Whereas our results clearly show that the on-top (terminal) isocyanide readily forms  $\text{CNHCH}_3$ , the results are less definitive for the bent-bridge form, which is present only at high  $\text{CNMe}$  coverages. If the bent-bridge  $\text{CNMe}$  could be produced at low coverage, it might also react to form the aminocarbyne. In fact, the formation of aminocarbynes from bent-bridge isocyanides has been rationalized in some detail in the organometallic literature. In the case of  $\text{Ir}_2$  and  $\text{Ni}_2$

complexes, bridging isocyanide ligands have been described as resonance structures between (a)  $\mu$ -isocyanide and (b)  $\mu$ -ami-

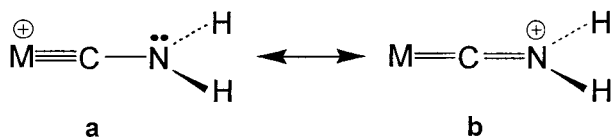


docarbyne canonical forms, with the latter contributing to facile N-protonation and N-alkylation reactions.<sup>22,28</sup> The greater the contribution from the  $\mu$ -aminocarbyne form, the greater the tendency of bent-bridge isocyanides to undergo N-protonation. Since the  $\mu$ -aminocarbyne form would have a lower CN stretch frequency, a simple correlation between  $\nu(\text{CN})$  and tendency to form the aminocarbyne might be expected for various bent-bridge isocyanides. However, this would not explain our observation of the preferential conversion of the on-top isocyanide to the aminocarbyne. One possibility is that at the relatively high coverages where the bent-bridge form is seen, hydrogen may be displaced from the surface. This is consistent with the fact that at coverages where the bent-bridge form is seen, N-protonation of the terminal isocyanide is also suppressed. It is also consistent with the idea that empty sites around the isocyanide may be needed for the reaction to occur, and that such sites would be less available at high coverages.

Of particular importance to understanding the nature of the bonding in  $\text{CNHCH}_3$  is the value of  $\nu(\text{CN})$  at 1477  $\text{cm}^{-1}$  (1463  $\text{cm}^{-1}$  for  $\text{CND}(\text{CH}_3)$ ). The value of 1477  $\text{cm}^{-1}$  is much lower than the CN stretch of coordinated isocyanides and is indicative of a CN bond order between 1 and 2, as is characteristic of an iminium species. For aminocarbyne,  $\text{CNH}_2$ ,  $\nu(\text{CN})$  was found at 1323  $\text{cm}^{-1}$  on  $\text{Pt}(111)$ , whereas in an Os complex<sup>8</sup> it was observed at 1482  $\text{cm}^{-1}$ . In the  $\text{H}_2\text{NC}-\text{CNH}_2$  species on  $\text{Pt}(111)$ ,  $\nu(\text{CN})$  was observed at 1425  $\text{cm}^{-1}$ . These earlier assignments were supported by spectra of the  $^{13}\text{C}$  and  $^{15}\text{N}$  isotopomers combined with normal mode calculations<sup>29</sup> and, in the case of aminocarbyne, by independent electronic structure calculations.<sup>30</sup> The value of  $\nu(\text{CN})$  deduced here is clearly in the range of values expected for  $\text{CNHCH}_3$ . Rather than try to deduce a bond order from a frequency alone, particularly from highly mixed skeletal modes, it is better to examine the value of the associated force constants obtained in conjunction with a first principles electronic structure calculation based on a model system. Such calculations are currently underway and preliminary results fully support assignment of the spectra to the methylaminocarbyne species.<sup>31</sup>

The present work demonstrates that our earlier observations on the ready formation of the simplest aminocarbyne,  $\text{CNH}_2$ , from a variety of precursors can be extended to at least one higher aminocarbyne,  $\text{CNHCH}_3$ . This suggests that aminocarbynes may have a prominent yet hitherto unrecognized role in surface chemistry. In the organometallic literature, aminocarbynes are well-known and are often discussed in the context of other carbyne ligands. A simple comparison of the molecular orbital diagrams of the carbynes  $\text{CH}^+$ ,  $\text{CCH}_3^+$ , and  $\text{CNH}_2^+$  reveals that the latter has the largest HOMO–LUMO gap and that the LUMO is basically the carbon 2p orbital oriented parallel to the  $\text{CNH}_2$  plane.<sup>32</sup> A monometallic aminocarbyne complex is necessarily represented as a resonance between (a) aminocarbyne and (b) azavinylidene structures.





An important question that our work does not answer is the nature of the aminocarbene adsorption site on the Pt(111) surface. A large number of monometallic aminocarbene complexes are known suggesting that on-top site adsorption may be possible. However, the same thing is true for alkylidyne, yet ethylidyne ( $\text{CCH}_3$ ) is definitely known to occupy the 3-fold hollow site on Pt(111).<sup>33</sup> By analogy, aminocarbynes might be expected to also occupy the 3-fold hollow site. However, in several trinuclear clusters where 3-fold coordination is possible, only 2-fold bridging coordination is found. There is not sufficient information available to determine if there is a definitive correlation between CN stretch frequency and coordination number, but we note that our CN stretch frequencies are somewhat lower than found in aminocarbynes coordinated to only one or two metal atoms. The more general question is that now that it has been demonstrated that a surface aminocarbene can be readily formed from the electrophilic attack at the nitrogen atom of an adsorbed isocyanide, to what extent can other properties of aminocarbynes coordinated to metals be extended to metal surfaces. For example, they are known to be intermediates in carbon-carbon coupling reactions in isocyanide complexes.<sup>9</sup> Clearly, there is a great deal of work yet to be done on the role of aminocarbynes in surface chemistry.

## Conclusions

In accord with previous studies we find that methyl isocyanide (CNMe) adsorbs at low temperatures at on-top sites at low coverages followed by both on-top and bent-bridge forms at higher coverages. At coverages low enough that only on-top CNMe is seen, protonation at the N atom to form the methyl aminocarbene ( $\text{CNHCH}_3$ ) species occurs. This reaction is well-known in the organometallic literature of coordinated isocyanides but had not been previously reported in surface studies of isocyanides. The NH bond of the aminocarbene readily undergoes isotopic exchange when the surface is exposed to deuterium, indicating the labile nature of the bond. Spectra of the  $^{13}\text{CNHCH}_3$  and  $\text{CNDCH}_3$  isotopomers allow for more definitive spectral assignments, and in particular indicate that the CN stretch occurs at  $1477\text{ cm}^{-1}$ , a value intermediate between CN single and double bonds as is characteristic of aminocarbynes.

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