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Methylaminomethylidyne: A Stable Intermediate Formed on the Pt(111) Surface from the N-Protonation of Methyl Isocyanide

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There are a variety of reasons for interest in the interactions of isocyanides with metals and metal surfaces. The isocyanide functionality is isoelectronic with CO and in analogy with transition metal carbonyls there is an extensive literature on the properties of isocyanides as ligands in transition metal complexes.[1] More recent interest stems from the use of isocyanides to form a new class of self-assembled monolayers.[2] Previous studies of the interactions of isocyanides with metal surfaces have focused on the issue of adsorption site and mode of coordination to the surface. A well-known property of coordinated isocyanides is their electrophilic attack at the nitrogen atom to form iminium-type species.[3] The bonding in these species is thought to involve resonance between MC−NR′R (aminocarbyne) and M=C=$N^+R'R$ (iminium) forms, and in the absence of detailed knowledge about the charge distribution and the MC bond order, the two names are used interchangeably. Formation of these species from isocyanides adsorbed on metal surfaces has not been previously reported, although our recent work on the surface chemistry of related molecules suggests that such reactions should occur. Here we report the unambiguous identification of NH bond formation in the reaction of methyl isocyanide with hydrogen on the Pt(111) surface to form the methylaminomethylidyne species, $CNH(CH_3)$(**1**).

The adsorption of methyl isocyanide (CH_3NC) has been studied on various transition metal surfaces.[4] 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 CH_3NC on Pt(111).[5] They found that at 90 K the molecule adsorbs in a terminally bonded configuration with a linear PtCNC bond characterized by ν(CN) at 2265−2245 cm^{-1}, while at higher coverages a bent bridge-bonded form is also seen with ν(CN) at 1600−1700 cm^{-1}. Decomposition leads to the desorption of H_2 (440−460 K) and HCN (420−610 K). Our work agrees with these observations. Avery and Matheson[5] did not detect any evidence for NH bond formation, yet we have found[6] that a variety of molecules containing CN bonds undergo hydrogenation−dehydrogenation reactions to form aminomethylidyne, CNH_2. This species also forms when surface CN is exposed to hydrogen, with the surface CN being produced from a variety of precursors including cyanogen,[7] HCN,[8] and ethylenediamine.[9] Related to CNH_2 is the $H_2NC\text{-}CNH_2$ species, which forms from the hydrogenation of molecularly adsorbed cyanogen.[7] Both of these species contain an iminium-like functionality, suggesting that other stable surface species of this class might also occur in which one or both of the hydrogen atoms of CNH_2 are replaced with CH_3, or other groups.

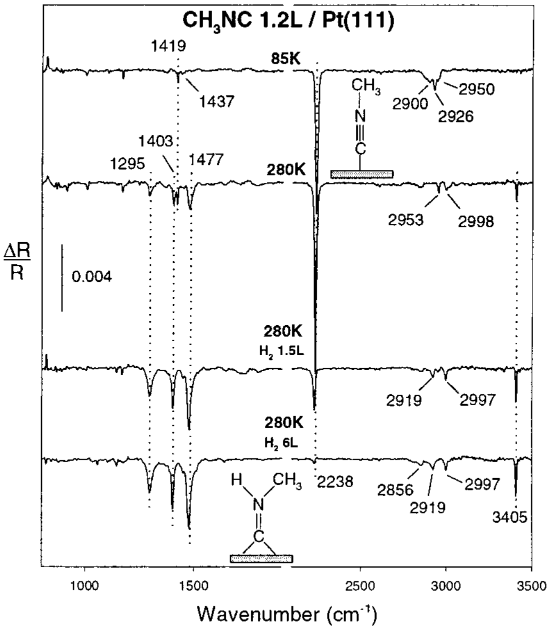

Figure 1. RAIR spectra following exposure of the sample at 85 K to 1.2 L (1 L = 1 × 10^{-6} Torr s) of methyl isocyanide with subsequent heating to 280 K and exposure to H_2 with the sample at 280 K, followed by cooling back to 85 K where the spectra were obtained.

The experiments were performed in a stainless steel ultrahigh vacuum (UHV) chamber with a base pressure of 1 × 10^{-10} Torr that is equipped with instruments for temperature-programmed desorption, low energy electron diffraction, Auger electron spectroscopy, and reflection absorption infrared spectroscopy (RAIRS) using a Fourier transform infrared (FTIR) spectrometer. An MCT (HgCdTe) detector was used to obtain spectra between 800 and 4000 cm^{-1}, using 1024 scans with a resolution of 4 cm^{-1}. Methyl isocyanide was prepared by the method described by Casanova et al.[10] and was stored under vacuum at −78 °C. The Pt(111) surface was cleaned by a procedure described earlier.[8]

Figure 1 shows RAIR spectra obtained after exposing the Pt(111) surface at 85 K to 1.2 L of methyl isocyanide, annealing to 280 K, then exposing to the indicated amounts of hydrogen. Methyl isocyanide exists in various forms in organometallic compounds and some aspects of the structure of the adsorbed species can be inferred from ν(CN) through comparisons with metal−$CNCH_3$ complexes.[1] The intense CN stretch peak at 2238 cm^{-1} in the 85 K spectrum implies a linear PtCNC unit with bonding though the isocyanide carbon to a single Pt atom. The peaks at 1419 and 2926 cm^{-1} are assigned to $\delta(CH_3)$ and ν(CH), respectively. A peak corresponding to the stretch of the C−N single bond occurs at 945 cm^{-1} in the gas phase but is not observed here nor in the earlier HREELS study.[5] As noted elsewhere,[11] the actual intensities of RAIRS peaks, even if symmetry allowed, are often too weak to be observed. The 1419 cm^{-1} peak is just barely above the noise level; its assignment to

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$\delta_s(CH_3)$ depends not only on its observation in this particular spectrum, but also from the fact that it is reproducibly observed in numerous other spectra taken as a function of CH_3NC coverage. In the CH stretch region, the 2926 cm^{-1} peak is part of a broad unresolved multiplet, the appearance of which changes strongly with coverage and annealing temperature. Its shape is attributed to two-dimensional disorder among the adsorbed molecules, possibly combined with Fermi resonances with overtones and/or combinations of the CH_3 deformation modes, a common occurrence for molecules, including adsorbates, containing CH_3 groups.[11]

Upon annealing to 280 K, the spectra change dramatically. Most significantly, a new peak is observed at 3405 cm^{-1}, which is readily assigned to an NH stretch mode. This assignment is unambiguous as 3405 cm^{-1} is well above the range of 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. The spectra indicate that the reaction with hydrogen has converted the terminally bonded isocyanide into an entirely new species, with intense peaks in the lower frequency region at 1477 (ν(CN)), 1403 ($\delta(CH_3)$), and 1295 ($\rho(CH_3)/\delta$(NH)) cm^{-1}. When the adsorbed isocyanide is exposed to D_2, spectra develop corresponding to $CND(CH_3)$, which include an ND stretch peak at 2533 cm^{-1}. Just as for the H_2 exposures, D_2 exposures almost completely eliminate the strong CN stretch at 2238 cm^{-1} and lead to the same set of peaks in the CH stretch region. The 1200−1500 cm^{-1} region shows peaks shifted from those of $CNH(CH_3)$ as would be expected since the CN stretch, CH_3 deformation, and CH_3 rocking modes will contain contributions from the CND bend. In Figure 1, the isocyanide ν(CN) peak appears to increase as it is converted to the new species with the 280 K anneal; the integrated area of the peak actually decreases but its width also decreases by almost a factor of 2, resulting in an increase in peak height, even though the amount of isocyanide decreases. This is likely due to an increase in order in the layer with annealing.

Of particular importance to understanding the nature of the bonding in $CNH(CH_3)$ is the value of ν(CN) at 1477 cm^{-1}, which shifts to 1463 cm^{-1} for $CND(CH_3)$. The value of 1477 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 aminocarbyne. For aminomethylidyne, CNH_2, ν(CN) was found at 1323 cm^{-1} on Pt(111), whereas in an Os complex[12] it was observed at 1482 cm^{-1}. In the H_2NC-CNH_2 species on Pt(111), ν(CN) was observed at 1425 cm^{-1}. These earlier assignments were supported by spectra of the ^{13}C and ^{15}N isotopomers combined with normal mode calculations[13] and, in the case of aminomethylidyne, by independent electronic structure calculations.[14] The value of ν(CN) deduced here is clearly in the range expected for **1**.

Given our previous findings that methylamine undergoes dehydrogenation at the carbon atom to form CNH_2, a reasonable hypothesis is that dimethylamine, $(CH_3)_2NH$, will be similarly dehydrogenated at one of the carbon atoms to form $CNH(CH_3)$. This is confirmed by Figure 2, which compares spectra obtained from methyl isocyanide and from dimethylamine. The spectra are clearly identical, with the exception that ν(CN) of a small amount of unreacted isocyanide is still present in the top spectrum. The fact that the same species is obtained starting from these two distinctly different precursors is further evidence that the species is in fact **1**. This species was also suggested in a RAIRS study of dimethylamine on Ni(111).[15] A reaction scheme summarizing these findings is shown below. The actual binding site of **1** is not established by the spectra, although in a trinuclear Os_3 complex, CNH_2 occupies 2-fold bridge sites.[12]

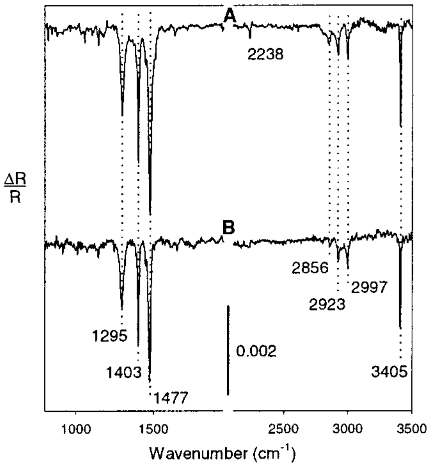
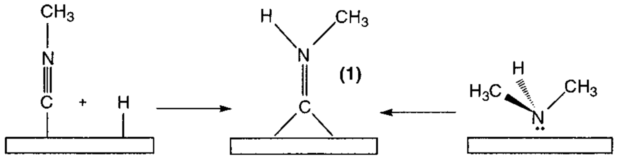


Figure 2. Comparison of RAIR spectra of (A) methylaminomethylidyne prepared as in Figure 1 from a 1.2 L exposure of methyl isocyanide at 85 K followed by a 6.0 L H_2 exposure at 280 K with (B) a spectrum obtained following exposure to 0.4 L of dimethylamine at 85 K followed by an anneal to 350 K. Both spectra were obtained at 85 K.



This work shows that the chemistry associated with the formation of stable species on Pt(111) containing the CNH_2 unit can be extended to $CNH(CH_3)$. This makes it more likely that aminocarbynes of the general formula CNR′R can also form as stable surface intermediates, starting from either an amine or an isocyanide precursor. Given the interest in using isocyanides to form self-assembled monolayers, this work suggests that the desired monolayer might be prepared via a variety of different routes.

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