Supporting Information

Reaction pathways for HCN on transition metal surfaces

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Figure S1: Mass spectra of $5.0 \times 10^{-8}$ Torr of $^{12}\text{C}^{14}\text{N}$ (a), $^{13}\text{C}^{14}\text{N}$ (b), and $^{12}\text{C}^{15}\text{N}$ (c). The synthesized products were determined to be pure by comparing the relative intensity of mass number 26 for $^{12}\text{C}^{14}\text{N}$ (27 for the heavier isotopes) with that of the electron impact mass spectrum of HCN in the NIST database. An intensity of 20% relative to the parent mass number (27 for $^{12}\text{C}^{14}\text{N}$ and 28 for the heavier isotopes) agrees with the national standard indicating successful synthesis and purification of HCN.
Figure S2: RAIR spectra of H\textsuperscript{12}C\textsuperscript{14}N on Pd(111) taken at 90 K on clean Pd(111). The band at 821 cm\textsuperscript{-1} seen in the 1.5 L spectrum that shifts to 844 cm\textsuperscript{-1} for 5.0 L is due to the HCN bending mode, which only appears in the multilayer spectra. Solid HCN begins forming at exposures of 2.5 L as indicated by the broad C-H stretching mode at 3184 cm\textsuperscript{-1}.
Figure S3: RAIR spectra of a) 1.0 L H$^{13}\text{C}^{14}\text{N}$ and b) 1.0 L H$^{12}\text{C}^{15}\text{N}$ on Pd(111) taken at 90 K after annealing for 1 minute at the indicated temperatures.
Figure S4: RAIR spectra taken at 90 K after annealing to 300 K for 1 min of H$^{12}$C$^{14}$N on Pd(111) pre-exposed to H$_2$ (a) and exposed to H$_2$ after HCN exposure (b). Pre-exposure to H$_2$ reduced the amount of aminocarbyne formed more than for post-HCN exposure to H$_2$. 
Figure S5: TPR spectra of 5.0 L HCN on Pd(111) taken from 90-1000 K at a heating rate of 1.5 K/s. Desorption of H₂ and HCN were observed at ~400 K. Although observed in other studies, C₂N₂ was not observed as a desorption product in this work.
Calculated adsorption energies of various fragments using different methods

Based on the adaptive summing method of Hensley et al.,\textsuperscript{3} when the GGA-RPBE $\Delta E_{\text{ads}}$ value for a gas molecule falls roughly below 70\% of the corresponding value in optB86b-vdW, one may expect the contribution of vdW to the adsorption energy on a transition metal surface like Pd(111) to become significant. Table S1 lists the $\Delta E_{\text{ads}}$ of several surface species that may be referenced directly to stable gas-phase species. See Ref. 3 for definition of the parameters $x$ and $f$. An adaptively weighted sum of GGA-RPBE and optB86b-vdW $\Delta E_{\text{ads}}$ is found to be on average more accurate than that calculated using either functional alone. When $f = 1$ (as is the case for all the organic species listed in Table S1), this sum consists entirely of the optB86b-vdW $\Delta E_{\text{ads}}$. When $f = 0$, the sum consists entirely of the GGA-RPBE $\Delta E_{\text{ads}}$. Thus Table S1 indicates that GGA-RPBE under-binds the organic species but is adequate for describing H adsorption, on Pd(111). Comparison with available literature data suggests this conclusion to be correct.

Table S1: DFT-calculated adsorption energies ($\Delta E_{\text{ads}}$, in eV) of several molecular and atomic intermediates in HCN decomposition on Pd(111), and their associated adaptive summing parameters ($x$ and $f$).

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta E_{\text{ads}}$</th>
<th>$\Delta E_{\text{ads}}$</th>
<th>$x$</th>
<th>$f$</th>
<th>Exp. Lit.</th>
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<tbody>
<tr>
<td></td>
<td>GGA-RPBE</td>
<td>optB86b-vdW</td>
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<tr>
<td>HCN upright</td>
<td>0.00\textsuperscript{2}</td>
<td>-0.56\textsuperscript{2}</td>
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<td>1.00</td>
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<td>1.00</td>
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<td>$(\text{HCN})_2$\textsuperscript{a}</td>
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<td>-1.02\textsuperscript{2,3}</td>
<td>0.86</td>
<td>1.00</td>
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<tr>
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<tr>
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<td>-0.57\textsuperscript{4}</td>
<td>0.31</td>
<td>0.01</td>
<td>-0.44\textsuperscript{5}</td>
</tr>
</tbody>
</table>

Each adsorbate is located on a (2×2) surface unit cell at 1/4 ML coverage. $\Delta E_{\text{ads}}$ is with respect to each adsorbate in gas phase and is non-ZPE corrected.

\textsuperscript{1} From Ref. 2
\textsuperscript{2} With respect to gas-phase HCN.
\textsuperscript{3} Per unit of HCN.
\textsuperscript{4} With respect to gas-phase H$_2$, per H atom.
\textsuperscript{5} From Ref. 4.
References