

Supporting information for

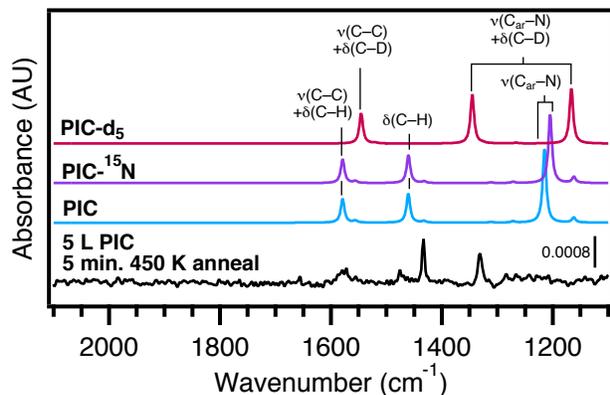
# Formation of Stable Nitrene Surface Species by Reaction of Adsorbed Phenyl Isocyanate at the Ge(100)-2×1 Surface

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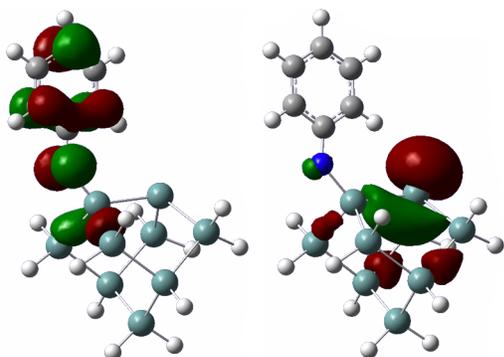
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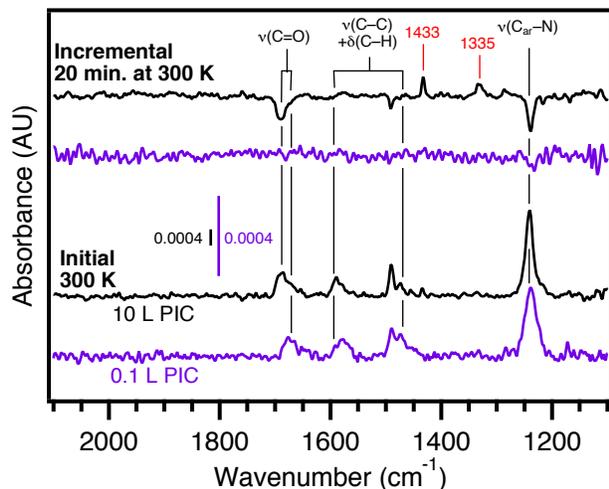
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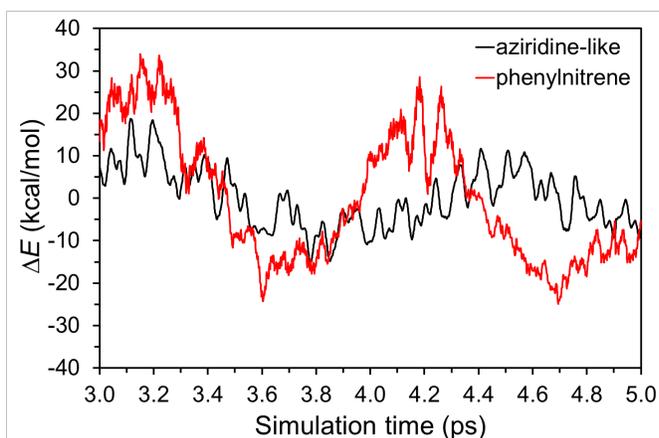
**Figure S1.** DFT calculated spectra of the aziridine-like product in which phenylnitrene bridges between two Ge dimer atoms for: PIC (blue), PIC- $^{15}\text{N}$  (purple), and PIC- $\text{d}_5$  (magenta). For reference, the experimental spectrum of PIC adsorbed at room temperature and annealed to 450 K for 5 minutes is shown in black. The calculated spectra—particularly the frequencies of  $\text{C}_{\text{ar}}\text{-N}$  stretching—do not match well with the experimental spectra of the long-time product. Note that for PIC- $\text{d}_5$ , H=D in vibrational mode labels.



**Figure S2.** Electron density isosurfaces (value = 0.04) for the two molecular orbitals (MOs) containing unpaired electrons of the phenylnitrene product according to natural bond orbital analysis following B3LYP optimization. The MO on the left shows delocalization of the lone pair on nitrogen into the phenyl ring and Ge cluster. The MO on the right shows that the second unpaired electron largely contributes to a dangling bond on the unreacted Ge dimer atom but is also partially delocalized in the Ge cluster.



**Figure S3.** Experimental FTIR spectra of PIC adsorbed on Ge(100)-2 $\times$ 1. Spectra for the surface immediately after adsorption and 20 minutes after the adsorption are shown; the spectra after 20 minutes are shown as incremental spectra (ratioed to the initial spectra). Low coverage (purple; 0.1 L exposure) and saturation coverage (black; 10 L exposure) spectra are shown with 5-fold scaling between the low and saturation coverage spectra to make the peaks in the initial spectra approximately the same size. The fact that growth of peaks associated with the long-time product, such as those at 1335 and 1433 cm<sup>-1</sup> (marked in red) are not seen in the low coverage spectrum suggests that conversion to the long-time product does not occur or occurs much more slowly at low coverages.



**Figure S4.** Total energy fluctuation during DFT-molecular dynamics simulations of phenylnitrene and aziridine-like structures on periodic Ge(100)-2 $\times$ 1 slab at 298 K using a time step of 1.0 fs. The total energies are given relative to the averaged total energies from the respective simulations (non-converged energies from the first 3 ps are not included in the averages).