Experimental Methods

Experiments were performed in two different UHV chambers, both of which have been previously described elsewhere.\(^1\) The first UHV chamber is custom built, has a base pressure of \(<1 \times 10^{-10}\) mbar and incorporates a mass spectrometer (Hiden) to perform TPD experiments. The Cu(111) crystal was cleaned via cycles of Ar\(^+\) sputtering followed by annealing to 750 K. TPDs were run with a heating rate of 1 K/s and the sample was held at 80 K during exposures of both BB and EBB. BB was detected by monitoring m/z 77 and m/z 156. m/z 156 is displayed in all traces. Small amounts of benzene from impurities in the BB sample and decomposition of phenyl groups on the surface are observed and we monitor for this by tracking m/z 78.\(^2, 3\) B-B was tracked using m/z 154. EBB was tracked via m/z 105, 169 and 185. m/z 169 is displayed in the figures. EB-EB was tracked using m/z 210 and m/z 195. m/z 210 is displayed in Figure 1 as it is the parent ion. However, for figure 3 where the amounts of each cross coupling product desorbing from the surface is very small, m/z 195 is displayed as this mass to charge ratio gives
the largest signal. Ethylbenzene was tracked using m/z 91 and small amounts are observed, as was the case for benzene in BB. The cross coupling product B-EB was tracked via m/z 167 and m/z 182. m/z 167 is displayed as this maximizes the signal. m/z 2, 18 and 28 are all monitored to track H₂, H₂O and CO as these gases are always present in the chamber background. We do observe small amounts of H₂ desorbing at high temperature due to the decomposition of a small amount of phenyl groups on the Cu surface. This H₂ desorption accompanies the desorption of benzene and toluene.

The second UHV chamber is a Omicron LT-STM with a base pressure of <10⁻¹¹ mbar. The Cu(111) crystal was cleaned via cycles of Ar⁺ sputtering followed by annealing to 1000 K in a separate preparation chamber with a base pressure of 1 × 10⁻¹⁰ mbar. BB and EBB were exposed to the crystal at 5 K. Anneals below 300 K were performed by removing the sample from the cryogenically cooled stage and placing it in a room-temperature sample holder until it warmed to the desired temperature. Anneals above 300 K were performed using a resistively heated manipulator. All STM images were obtained at 5 K. BB and EBB were obtained from Sigma Aldrich with 99.9% purity and degassed via repeated freeze, pump, thaw cycles.

References

