

Expanding the surface chemistry synthetic toolkit: facile carbon (sp²)-nitrogen(sp²) bond formation on Au[111] and Ag[111]

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Surface assisted synthesis offers a unique pathway towards the creation of atomically precise nanostructures that cannot be achieved in solution. The Ulmann coupling—where surface stabilized radicals form covalent bonds prior to polymerization or cyclization—has emerged as a promising route for accessing novel architectures, in particular graphene nanoribbons where the electronic structure is intimately linked with the atomic structure. This reaction, however, has been limited to the formation of C-C bonds, restricting its overall scope. The ability to create novel linkages on the surface would allow for a deeper understanding of the interplay between atomic and electronic structure. Here we demonstrate facile C-N bond formation on different coinage metal surfaces at substantially lower temperatures than polymerization and subsequent C-C bond formation. Scanning tunneling microscopy and spectroscopy (STM/STS) performed conjointly with first-principles calculations confirm the desired product. The mechanism for C-N formation will be discussed along with strategies for the synthesis of extended 1-dimensional structures.