Supporting Information

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**SI Text**

At the crossing segment, the secondary beam contains small amounts of ~1% diacetylene dimers [(C4H2)2; \( m/z = 100 \)]. This dimer does not contribute any signal to \( m/z = 75 \); however, it can contribute to inelastic scattering signal to \( m/z = 74 \) via its C6H2 fragment formed in the detector on electron impact ionization followed by reaction within the \((\text{C}_4\text{H}_2)_2\) species. This finding is evident from the TOF spectra recorded at \( m/z = 75 \) and 74 at the CM angle of 29.0°. (Fig. S1). At \( m/z = 75 \), signal could be fit only from reactive scattering of the D1-ethynyl radical (C2D) with diacetylene forming D1-triacetylene (C6HD) plus atomic hydrogen. At \( m/z = 74 \), two components are necessary to fit the TOF spectrum: a reactive scattering component, which signal originates from dissociative electron impact ionization of the C6HD neutral (blue line), and a second component of inelastically scattered diacetylene dimers. The reactive scattering signal at \( m/z = 75 \) and 74 could be fit both with identical CM functions as depicted in Fig. 3. The CM functions to fit the nonreactively scattered signal at \( m/z = 74 \) are distinctively different from those used for the reactive scattering signal. They are depicted in Fig. S2; this wide angle scattering likely results from the decay of long lived \( \pi \)-complexes back to the reactants; a similar pattern was observed in the reaction of transition metals with unsaturated hydrocarbons (1). Note that considering carbon, dicarbon, tricarbon, and D1-ethyl in the primary beam, tricarbon molecules are about a factor of 10 more abundant than carbon, dicarbon, and D1-ethyl. They present the dominating species capable of forming \( \pi \)-complexes. Due to the deuterium-deuterium \( \sigma \)-bond, molecular deuterium cannot form \( \pi \)-complexes.

Fig. S1. TOF spectra recorded at the center-of-mass (CM) angle of $m/z = 75$ and 74. Contributions from the reactive and nonreactive signals are depicted in blue and red, respectively.
Fig. S2. CM functions used to fit the nonreactive signal at m/z = 74 via a decay of long lived π-complexes formed in the reaction of tricarbon molecules back to the reactants.