Supporting Information

Imaging Successive Intermediate States of the On-Surface Ullmann Reaction on Cu(111): Role of the Metal Coordination

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Figure S1 – Four different radicals imaged by AFM

We evaluated the appearance of four different TP-radicals (Figure S1), which were measured with three different CO tips. For all radicals we find that one phenyl ring appears darker than the other two rings implying a bending of one ring towards the surface. The darkest phenyl ring of each radical can be clearly identified in the contrast enhanced versions of the AFM images (red arrows in e-h). In addition to this overall bending one corner of the corresponding ring is bent stronger towards the surface than the other corner. We carefully checked the surface tilt in slow and fast scanning direction for up- and downward scans, in order to rule out possible influences of tilted scanning planes (or z-drift). A possible influence of a tilted CO molecule, however, cannot be ruled out completely since asymmetric dark halos are observed around the molecules.
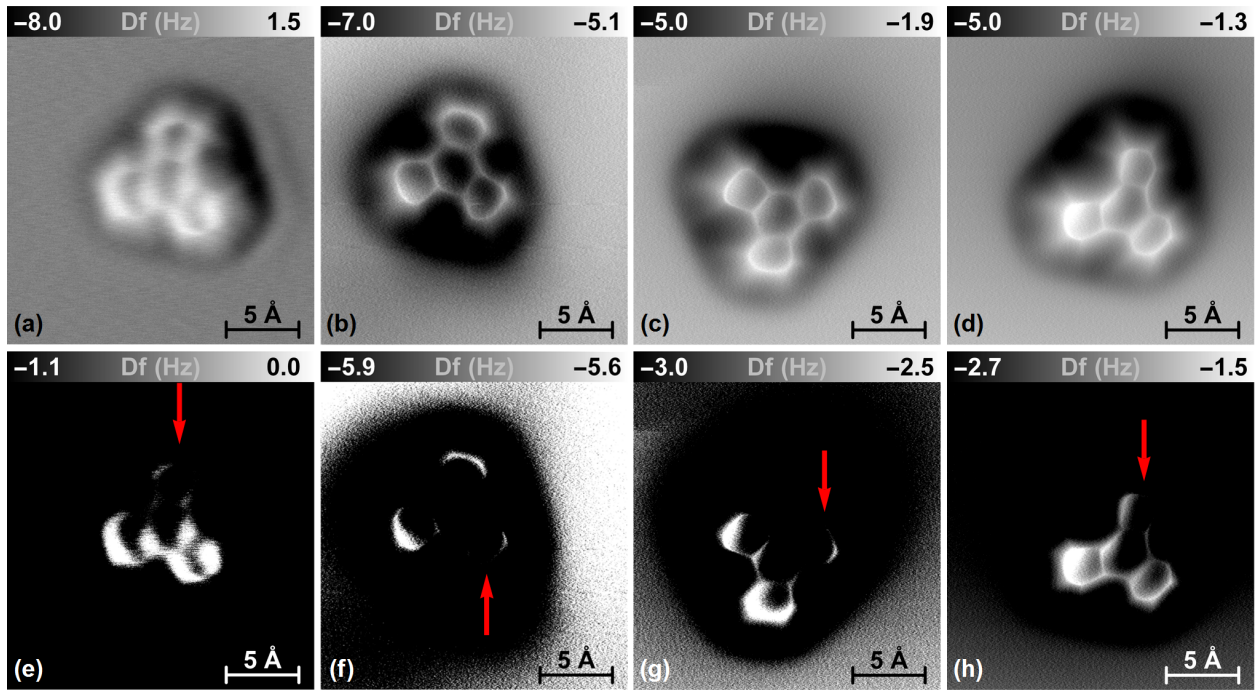

Figure S1: AFM frequency shift images of four different TP-radicals shown with full (a-d) and enhanced contrast (e-h) (please compare different color bars). Three different CO tips were used (radicals in (c) and (d) measured with same tip). Red arrows indicate the darkest phenyl ring of each radical. (Oscillation amplitude of 40 pm in (a) and 130 pm in (b-d))

Figure S2 − Formation of organometallic intermediates

We observe the formation of organometallic intermediates after heating the sample to 295 K. We find no BTP molecules on the surface but only radicals and *cis*- and *trans*-intermediates (Figure S2). The overall intermediate to radical ratio at 295 K is approximately 0.65.
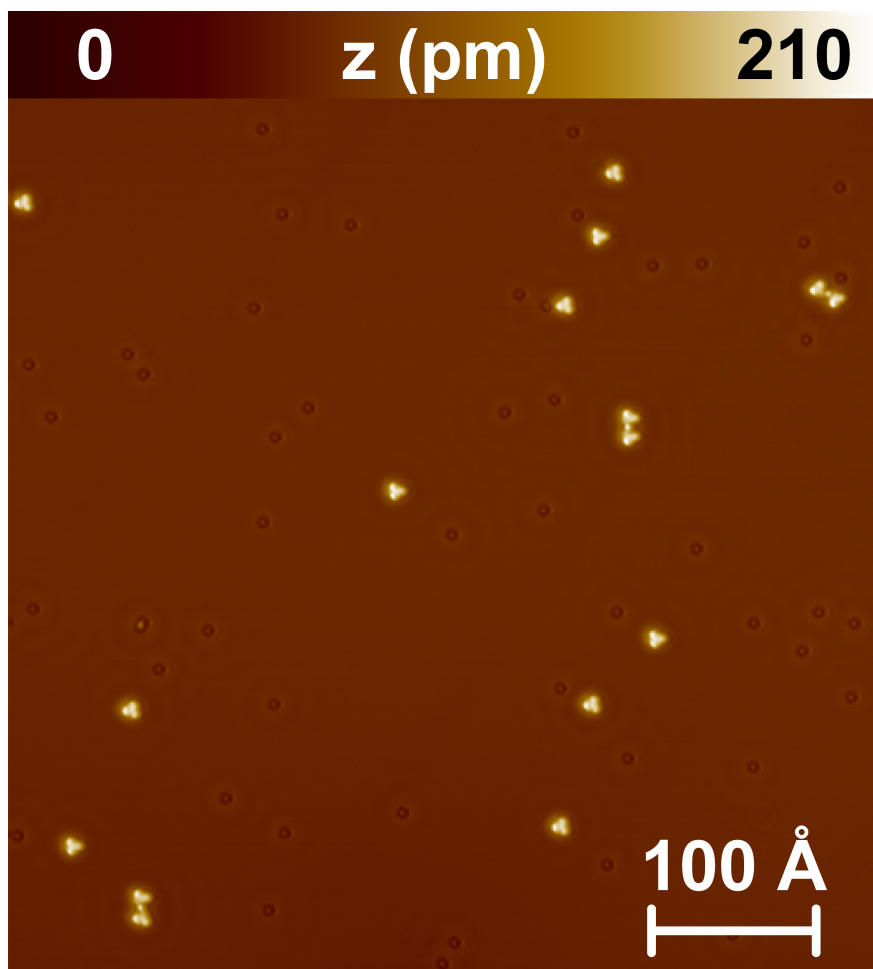

Figure S2: STM overview image showing 10 radicals, 3 intermediates (1 *cis* and 2 *trans*) and approximately 1 CO molecule per 50 nm^2. Image measured at 5 K subsequent to 295 K sample heating. CO molecules are imaged as sombrero like structures due to CO functionalized STM tip. ($I = 100$ pA and $U = 200$ mV).

Figure S3 – *cis*-Intermediate and adsorption angle

Figure S3 (a)-(e) shows an AFM image and DFT calculations for the *cis*-intermediate (cf. Figure 4 in manuscript). For the characterization of the adsorption angle between the intermediate state and copper lattice we imaged surface atoms and chemical structure of the *cis*-intermediate in a single AFM scan (Figure S3 f). For this purpose, the tip-sample distance was decreased by 280 pm above the copper surface (top part of the image). In order to determine the adsorption angle, we aligned a Cu(111) lattice to the atomically resolved surface and a structural model to the chemical structure of the molecule. The experimental data reveals an adsorption angle of $35 \pm 5°$. The adsorption angles of the two calculated configurations [surface atom (b,c) vs. adadtom (d,e)] states are 40 and 32°, respectively, which is in good accordance to our experimental results.
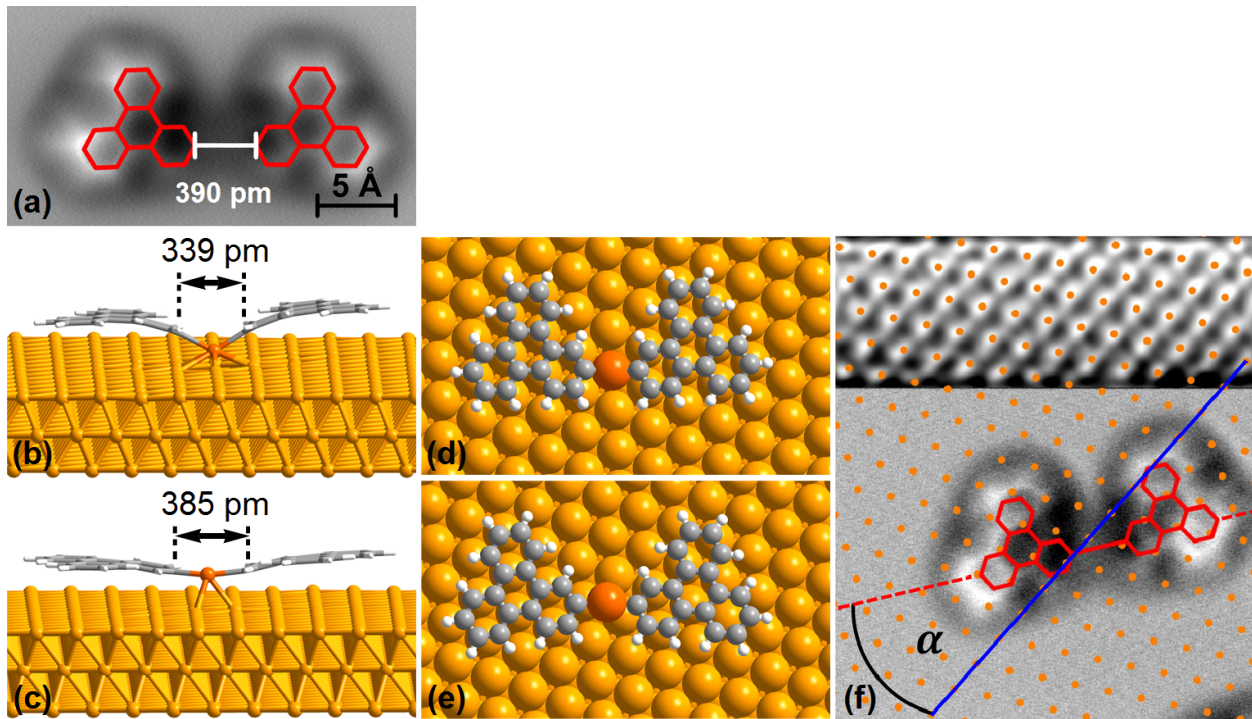

Figure S3: (a) AFM frequency shift image of *cis*-intermediate with fit of structural model. (b-e) DFT-D3 calculations [PBE-D3/pw (PAW P)] for two different organometallic *cis*-intermediate states [surface atom (b,c) vs. adatom (d,e)]. (f) AFM frequency shift image resolving copper surface (top) and chemical intermediate-structure (bottom) superimposed with Cu(111) lattice (orange) and structural model (red). Copper surface is low pass filtered for clearness.

Figure S4 – Clustering of bistriphenylene molecules

We observe the formation of bistriphenylene after heating the sample to 660 K, with a balanced ratio of *cis*- to *trans*-bistriphenylene (Figure S4). Thereby, we find *cis*-bistriphenylenes almost exclusively as part of small clusters with bromine atoms and other molecules (Figure S4 a). In contrast, *trans*-bistriphenylene only partially forms clusters and also can be found as individual molecules (Figure S4 b).
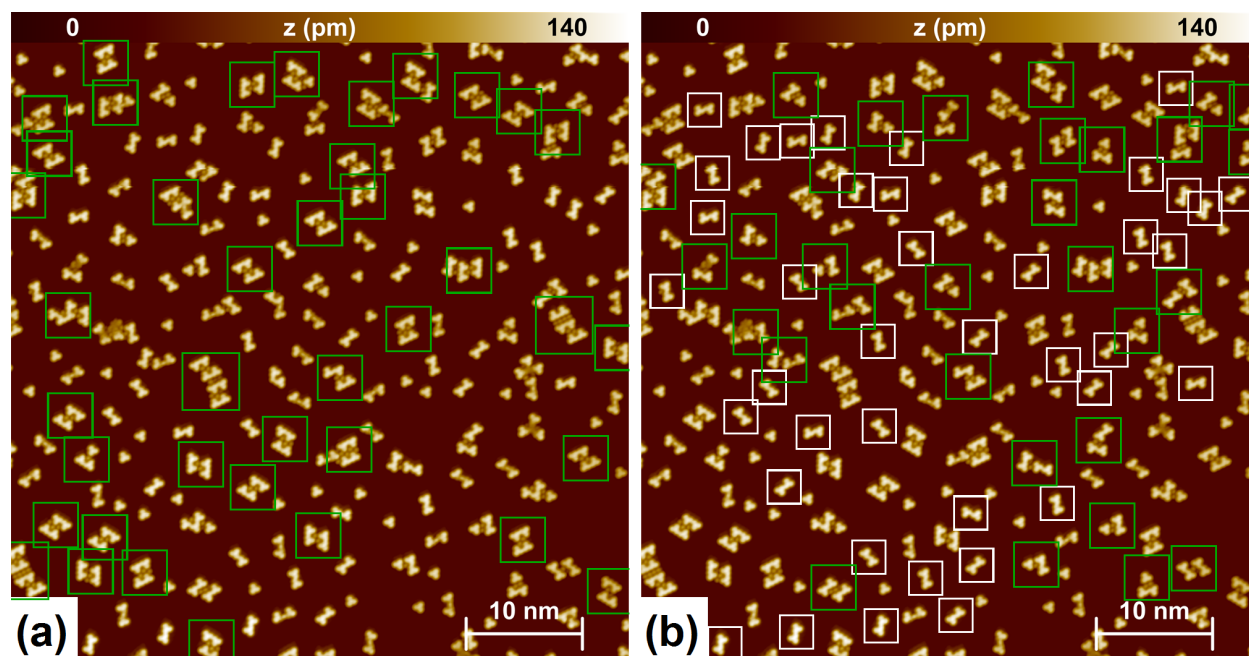

Figure S4: *Cis*- and *trans*-bistriphenylene highlighted in STM overview scan, showing radicals, intermediates and bistriphenylenes. *Cis*-bistriphenylenes highlighted in (a), *trans*-bistriphenylenes highlighted in (b). Bistriphenylene is either adsorbed individually (white) or as part of small molecular clusters (green). (a) All *cis*-bistriphenylenes (80 in total) are part of clusters. (b) Approximately half of the *trans*-bistriphenylenes have formed clusters (38 of 79), the rest is adsorbed individually.

Calculated reaction energies

In order to further analyze the two possible intermediate states, their energies of formation starting from two isolated adsorbed TP radicals were calculated based on our DFT results. The obtained values are given in table S1 together with those for five elementary reactions necessary to describe the intermediate formation. In the case of the type (1) intermediate containing a lifted copper surface atom [(TP)2 (ads)], a reaction energy of −0.25 eV was calculated (reaction f). By contrast, 1.97 eV are released upon formation of the second type of intermediate including an additional copper atom [Cu(TP)2 (ads), reaction g]. In previous DFT investigations, the formation of a copper adatom was calculated to be 0.83 or 0.97 eV,[1,2] with the adatoms located at energetically preferred fcc-sites of the Cu(111) surface. Taking this formation energy of the adatom into account, the type (2) intermediate is favored by about 0.91 and 0.77 eV, respectively, compared to type (1). These findings further corroborates the conclusion based on the observed structural parameters which are in better agreement with a type (2) intermediate as well. It can however not be excluded that transient type (1) intermediates are formed prior to a quick replacement of the lifted copper atom by a second one diffusing from the bulk to the surface. This might be one possibility how the intermediate (2), which is thermodynamically preferred is formed. This questions will be addressed among others in a follow-up investigation in order to understand the full reaction mechanism of the Ullmann-type coupling of BTP.

Table S1: Calculated reaction energies (eV) for the formation of the two possible *trans*-intermediates of the Ullmann-type coupling of BTP (in parentheses: values for the *cis*-form).

| Elementary reactions	ΔE	
a TP(g) + Cu(111) → TP(ads)	–4.11	
b 2 TP(g) + Cu(111) → (TP)2 (ads)	–8.44	(–8.46)
c Cu(g) + Cu(111) → Cu(ads)	–3.34	
d Cu(TP)2 (g) + Cu(111) → Cu(TP)2 (ads)	–7.29	(–7.30)
e 2 TPgas + Cu(g) → Cu(TP)2 (g)	–6.24	(–6.23)
Intermediate formation[a]	ΔE	
f 2 TP(ads) → (TP)2 (ads)	–0.23	(–0.25)
g 2 TP(ads) + Cu(ads) → Cu(TP)2 (ads)	–1.97	(–1.98)

[a] $f = -2a + b$, $g = -(2a + c) + d + e$

Synthesis of 2-bromotriphenylene (BTP) and NMR spectra

BTP was synthesised according to literature.[3] It was purified by consecutive sublimation (120 °C, 0.02 mbar). Chemicals were purchased from Sigma-Aldrich, Acros, TCI Europe, and Alfa Aesar. They were used without further purification.

NMR spectra

Spectra were measured on Avance II 200 MHz "Microbay" (AV 200). All spectra were referenced to the residual solvent peak of $CDCl_3$ ([1]H: 7.26 ppm).

1H NMR (200 MHz, $CDCl_3$ + 0.03 % TMS): 8.76 (d, J = 2.1 Hz, 1H), $8.70 - 8.53$ (m, 4H), 8.50 (d, J = 8.8 Hz, 1H), $7.78 - 7.60$ (m, 5H).
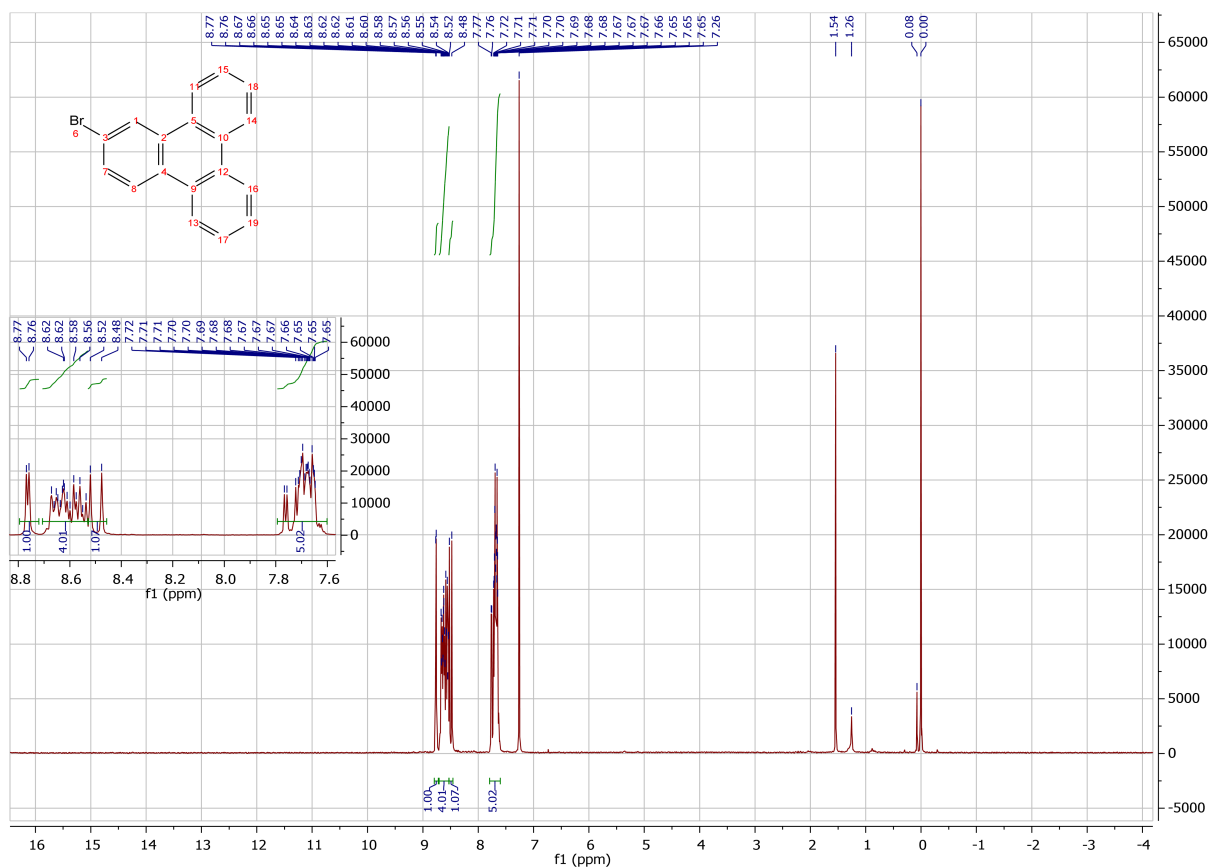
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