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**Title:** The Stereoselective Formation of trans-Cumulene through Dehalogenative Homocoupling of Alkenyl gem-Dibromides on Cu(110)

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## COMMUNICATION

# The Stereoselective Formation of *trans*-Cumulene through Dehalogenative Homocoupling of Alkenyl *gem*-Dibromides on Cu(110)

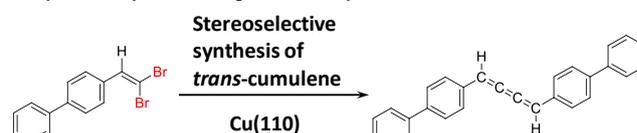
Liangliang Cai, ‡Faming Kang, ‡ Qiang Sun, Wenze Gao, Xin Yu, Honghong Ma, Chunxue Yuan,\* and Wei Xu\*<sup>[a]</sup>

**Abstract:** Stereoselective synthesis of geometrically pure isomers is challenging and important in a variety of chemistry related disciplines and applications. The recently developed on-surface synthesis strategy provides us opportunities in the fabrication of specific nanostructures which remain challenging by conventional solution chemistry. In this work, we choose alkenyl *gem*-dibromides as molecular precursors, and demonstrate the formation of specific *trans*-cumulene products via C-C couplings on Cu(110). This study supplements the database of on-surface synthesis strategies by introducing the alkenyl *gem*-dibromide group on the surface. More importantly, it provides a way to stereoselective synthesis of specific isomers involving C–C double bonds, which may be of substantial utility in stereochemistry.

Stereochemistry spans the entire spectrum of lipidomics, pharmaceuticals, and biochemistry, etc., and different isomers often exhibit distinct differences in physical and chemical properties.<sup>[1–5]</sup> For example, only the (*Z*)-*cis*-clopenthixol has been found to exhibit antipsychotic effects, whereas the neuroleptically inactive (*E*)-*trans*-clopenthixol may have some antimicrobial activity in vitro.<sup>[4,5]</sup> Another prominent example would be the azobenzene molecule that acts as a molecular switch, and the underlying mechanism is based on the *cis*-*trans* isomerization of the N–N double bond.<sup>[6–9]</sup> More recently, surface-assisted *cis*-*trans* isomerization (with respect to the C–C double bond) of an alkene molecule has been studied on a Cu(110) surface.<sup>[10]</sup> It thus turns out that surfaces could potentially influence and even catalyze the molecular isomerization processes.<sup>[10–14]</sup> Due to the intrinsically different properties of isomers, a wealth of studies have therefore been directed toward the synthesis of geometrically pure isomers, and such studies have been mainly performed in solutions to date.<sup>[15,16]</sup>

On the other hand, the recently developed on-surface synthesis strategy has gained increasing attention due to its great potential in the construction of novel nanostructures. Owing to the confinement and catalytic effects of surfaces,<sup>[17–24]</sup> some reactions

that can hardly occur in conventional solution chemistry have also been demonstrated to be feasible on surfaces.<sup>[25–31]</sup> The on-surface synthesis route has thus opened a way to the fabrication of a plethora of nanostructures which remain challenging by solution methods. For example, we have successfully formed *trans*-diene moieties by dehydrogenative homocoupling of terminal alkenes on the Cu(110) surface,<sup>[32]</sup> and more importantly, the corresponding *cis*-diene moieties could be specifically formed by dehalogenative homocoupling of terminal alkenyl bromides on the same surface.<sup>[33]</sup> It is therefore of general interest to extend such an on-surface synthesis strategy to specific formation of *cis*- and *trans*- isomers involving more complicated carbon structures. For on-surface dehalogenative homocoupling reactions, there are some early studies on the generation of carbenes on metal surfaces,<sup>[34]</sup> most of the employed halide precursors have only one halogen attached to a carbon atom. Thus, it is of particular interest to extend such reactions to *geminal* dihalide precursors on surfaces with the aim of generating two unpaired electrons and directly forming carbon scaffolds involving C–C double bonds. Very recently, we designed and synthesized a molecular



**Figure 1.** Schematic illustration shows the stereoselective formation of a *trans*-cumulene product through the dehalogenative C–C homocoupling reactions of an alkenyl *gem*-dibromide molecular precursor on a Cu(110) surface.

precursor functionalized with an alkenyl *gem*-dibromide group (named bBVBP), as shown in Scheme 1, and have successfully formed both *cis*- and *trans*-cumulene products through dehalogenative homocoupling reactions on a Au(111) surface.<sup>[35]</sup> Considering that it was feasible to stereoselectively form *cis*- and *trans*-dienes on a more reactive and anisotropic surface, that is, Cu(110), it would be very interesting to explore the possibility of stereoselective formation of cumulene motifs by employing the Cu(110) surface as the template.

Herein, from the interplay of high-resolution scanning tunneling microscopy (STM) imaging and density functional theory (DFT) calculations, we investigate the debromination and the subsequent C–C homocoupling reactions of alkenyl *gem*-dibromides on Cu(110). It is demonstrated that the debrominations occur below room temperature for both bromine atoms on the Cu(110) surface, which is comparable to that of alkenyl bromides on the same surface.<sup>[33]</sup> Interestingly, the debrominated intermediate is also observed on Cu(110). Moreover, importantly, further anneal induces the C–C couplings

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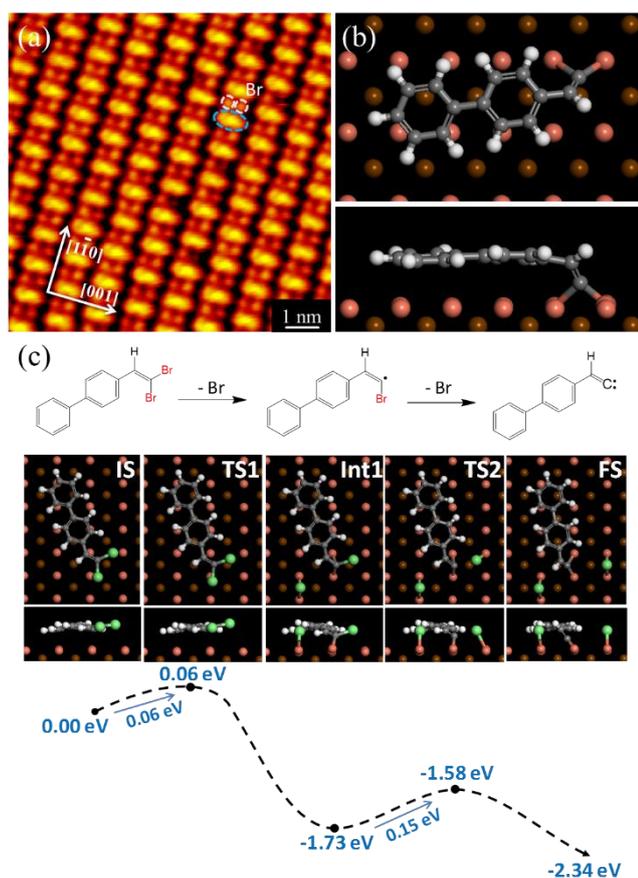
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of intermediates to specific *trans*-cumulenes as schematically shown in Figure 1. This study further supplements the database of on-surface dehalogenative C–C homocoupling reactions by introducing *gem*-dibromides, and demonstrates the feasibility of the specific formation of *trans*-cumulenes on the Cu(110) surface.

After deposition of bBVBP molecules on Cu(110) held at a relatively low temperature ( $\sim 170$  K), we observe the aggregations which consist of two kinds of protrusions that are assigned to the detached bromine atoms (highlighted by a white circle) and the debrominated bBVBP species (highlighted by a blue ellipse) on the surface as shown in Figure 2a. Such low-temperature debrominations suggest relatively low energy barriers for the C–Br bond scissions of the alkenyl *gem*-dibromide group, which is in analogy to that of the alkenyl bromide.<sup>[33]</sup> To reveal the role of the Cu(110) surface in the debromination processes, we have calculated the reaction

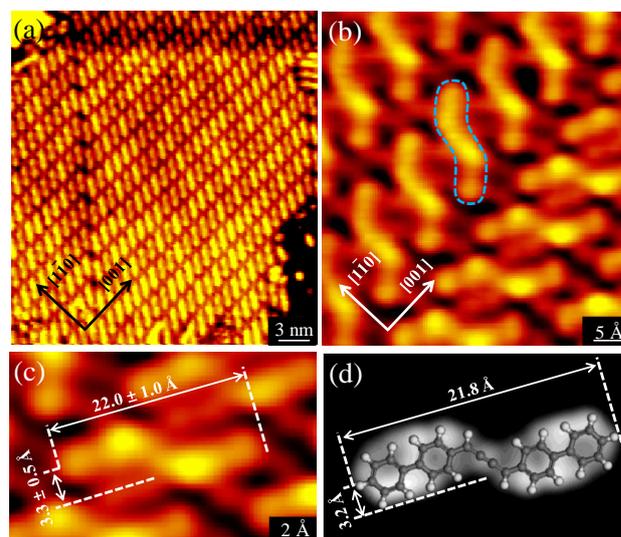


**Figure 2.** (a) The STM image showing after deposition of bBVBP molecules on Cu(110) at  $\sim 170$  K. A debrominated bBVBP molecule and a detached Br atom are indicated by a blue ellipse and a white circle, respectively. (b) Top and side views of the DFT relaxed model of the debrominated species on Cu(110). (c) The DFT-calculated reaction pathway for the successive C–Br bond activations of the bBVBP molecule on Cu(110). The structural models of the initial (IS), transition (TS), intermediate (Int) and final states (FS) along the pathway are also shown. Scanning parameters:  $I_t = 0.72$  nA,  $V_t = -1486.5$  mV.

pathway of successive C–Br bond activations of the bBVBP molecule on the surface. As shown in Figure 2c, the energy barriers are determined to be only 0.06 eV and 0.15 eV for the first and the second C–Br bond activation, respectively, which

indicates that the successive debromination should occur well below room temperature (RT). The whole debromination reaction is exothermic by 2.34 eV. More interestingly, since it is clearly indicated by STM images and DFT calculations that both bromine atoms should be dissociated from the *gem*-dibromide group under the experimental condition ( $\sim 170$  K), then the debromination processes should yield a radical with two unpaired electrons on the terminal carbon atom, which thus yields a surface-stabilized carbene species. As shown in Figure 2b, the DFT calculated adsorption geometry of the debrominated intermediate on Cu(110) shows that it is stabilized by forming two C–Cu bonds with the substrate atoms. The surface-stabilized intermediate is similar to the previously studied N-heterocyclic carbene with unsaturated carbon atoms bonded to the surface, but different in the number of bonding (two C–metal bonds with surface atoms as proposed here in Figure 2c, however in the reference the carbene C is found to be bonded to a single metal atom of the surface).<sup>[36]</sup>

After annealing the sample to  $\sim 430$  K, we observe the formation of ordered islands as shown in Figure 3a. From the close-up STM image (Figure 3b), we identify that the island structure consists of curved structures (as highlighted by blue



**Figure 3.** (a) Large-scale and (b) close-up STM images showing the formation of an ordered island structure after annealing the sample to  $\sim 430$  K. (c) The high-resolution STM image. (d) The corresponding simulated STM image superimposed with the scaled DFT relaxed *trans*-cumulene structure on Cu(110). Scanning parameters:  $I_t = 0.55$  nA,  $V_t = -1486.5$  mV.

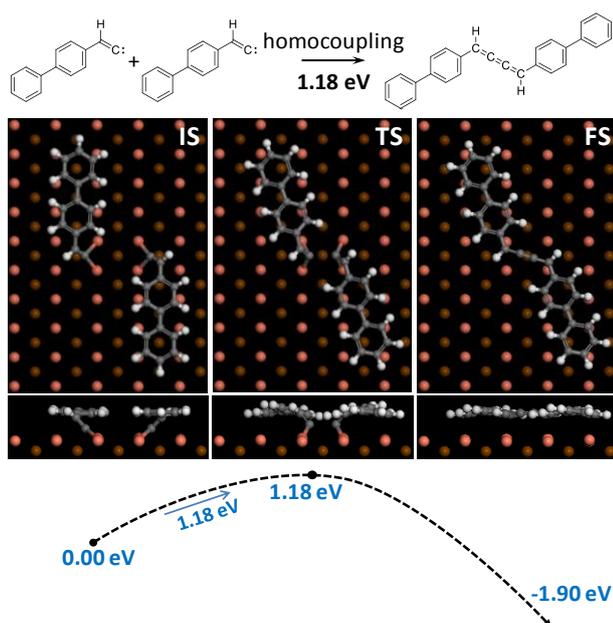
contour) and bromine atoms. With the knowledge of C–C homocouplings of debrominated species on metal surfaces,<sup>[24,33,37]</sup> we assign the curved structure to the C–C coupled product. To further identify the atomic-scale structure of this product, we perform extensive DFT calculations by constructing possible structures. From a detailed comparison of the experimental topography and dimensions (Figure 3c) with the corresponding simulated STM image and the scaled relaxed molecular model (Figure 3d, the simulation was done at the bias value as the experimental one), we conclude that the C–C coupled product should be assigned to a *trans*-cumulene structure with three consecutive C–C double bonds, which is in analogy with the

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*trans*-cumulene structure synthesized on Au(111) very recently.<sup>[35]</sup> It should be noted that both *cis*- and *trans*-cumulenes coexist on the Au(111) surface, while, importantly, in this study we achieve the stereoselective formation of specific *trans*-cumulenes on Cu(110). To rationalize the conclusion, we have performed statistical analysis of the samples at different temperatures (~ 170 K, ~ 300 K, ~ 430 K) as shown in Figure S1 in the Supporting Information. From the statistical analysis out of more than 1000 products, we can identify that the selective formation of *trans*-cumulene on Cu(110) surface is favorable after annealing the surface at ~ 430 K.

To gain fundamental understandings of such a C–C coupling process, we have calculated the possible reaction pathway from debrominated intermediates to *trans*-cumulene products on Cu(110) as shown in Figure 4. From the energy diagram, we determine the energy barrier for the C–C coupling to be 1.18 eV, which is in a reasonable agreement with the experimental condition, *i.e.*, annealing at ~ 430 K. On the basis of the above analysis, we conclude that it is feasible to induce dehalogenative homocoupling reactions of alkenyl *gem*-dibromides on a Cu(110) surface to generate a surface-stabilized carbene intermediate and a *trans*-cumulene product, respectively.

Note that we did not observe the surface stabilized carbene intermediate on Au(111),<sup>[35]</sup> and instead, the formation of both *cis*-



**Figure 4.** The DFT-calculated reaction pathway from the debrominated intermediate to a *trans*-cumulene product on the Cu(110) surface. The structural models of the initial (IS), transition (TS) and final states (FS) along the pathway are also shown.

and *trans*-cumulenes simultaneously occurred right after debrominations at RT. Also note that a comparable example of the stereoselective reaction is the dehalogenative dimerization of 1,1-diiodoethane on Ag(111) surfaces to form 2-Butene.<sup>[38]</sup>

To further analyze the self-assembled nanostructures, we have built the DFT-relaxed models of assembled debrominated bBVP molecules and *trans*-cumulene products on Cu(110) surface, with

their theoretical unit cells depicted in Figure S2 in the Supporting Information, which agree with the experimental results well.

In conclusion, by the interplay of high-resolution UHV-STM imaging and DFT-based transition-state search calculations, we have demonstrated that by introducing the alkenyl *gem*-dibromide group on Cu(110) it is feasible to induce successive dehalogenations to generate surface-stabilized carbene intermediates and to finally form specific *trans*-cumulene products via C–C couplings. More importantly, it provides us the hints that not only the functional groups of molecular precursors<sup>[32,33]</sup> but also the chemical nature of surfaces plays a crucial role in the stereoselective synthesis on surfaces. Such a facile strategy may be of substantial utility in stereochemistry.

## Experimental Section

The STM experiments were carried out in a UHV chamber with a base pressure of  $1 \times 10^{-10}$  mbar. The whole system was equipped with a SPECS variable-temperature “Aarhus-type” STM,<sup>[39,40]</sup> a molecular evaporator and standard facilities for sample preparation. The Cu(110) substrate was prepared by several cycles of 1.5 keV Ar<sup>+</sup> sputtering followed by annealing to 850 K, resulting in clean and flat terraces separated by monatomic steps. After the system was thoroughly degassed, the bBVP molecules were sublimated from the molecular evaporator onto the substrate. The sample was thereafter transferred within the UHV chamber to the microscope, where measurements were performed in a typical temperature range of 100 K ~ 150 K, and the typical scanning parameters were:  $I_t = 0.5 \sim 1.0$  nA,  $V_t = \pm 1000 \sim 2000$  mV. The sample was pre-cooled on the cold STM stage (~ 100 K), during very fast molecular deposition (~ 1 min) the sample will be slightly warmed up to ~ 170 K, after deposition the sample was transferred back to the cold STM stage.

The calculations were performed in the framework of DFT by using Vienna Ab Initio Simulation Package (VASP) code.<sup>[41,42]</sup> The projector augmented wave method was used to describe the interaction between ions and electrons,<sup>[43,44]</sup> and the Perdew-Burke-Ernzerh of generalized gradient approximation exchange–correlation functional was employed.<sup>[45]</sup> Van der Waals corrections to the PBE density functional were also included using the DFT-D3 method of Grimme.<sup>[46]</sup> The atomic structures were relaxed using the conjugate gradient algorithm scheme as implemented in VASP until the forces on all unconstrained atoms were  $\leq 0.03$  eV/Å for geometry optimization. The simulated STM image was obtained using the Tersoff-Hamann method,<sup>[47]</sup> in which the local density of states (LDOS) is used to approximate the tunneling current. The climbing-image nudged elastic band was applied to locate the transition state<sup>[48]</sup> and the reaction pathway was optimized until the forces acting to the path were converged typically to  $\leq 0.03$  eV/Å.

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**Keywords:** *trans*-cumulene • *gem*-dibromide • stereoselective • scanning tunnelling microscope • surface chemistry

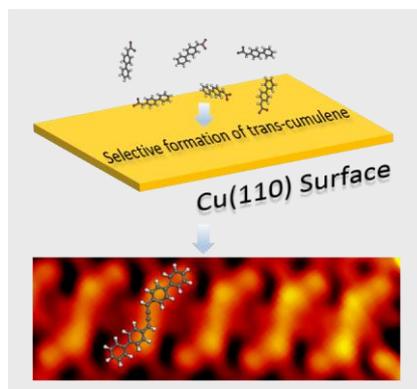
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It is important to selectively prepare the geometrically pure isomers. By the combination of high-resolution UHV-STM imaging and DFT calculations, we demonstrate selective synthesis of trans-cumulene compounds on the special Cu(110) surface and its possible reaction pathway. This is in stark contrast to the previous results on the Au(111) surface, which further proved that surfaces also play a crucial role in the stereoselective synthesis besides the chemical structures of precursors.



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