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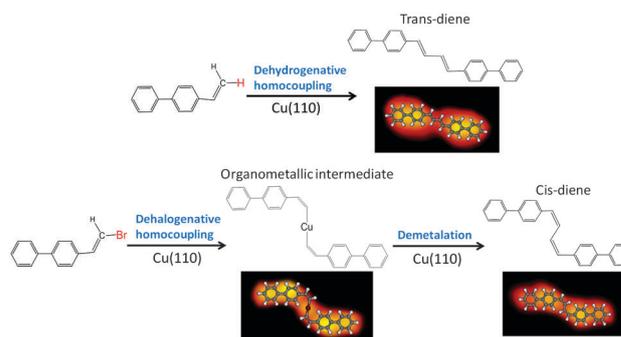
The stereoselective synthesis of dienes through dehalogenative homocoupling of terminal alkenyl bromides on Cu(110)[†]

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We have successfully achieved the stereoselective synthesis of a specific *cis*-diene moiety through a dehalogenative homocoupling of alkenyl bromides on the Cu(110) surface, where the formation of a *cis*-form organometallic intermediate is the key to such a stereoselectivity as determined by DFT calculations.

Recently, the on-surface synthesis of organic molecular precursors, especially hydrocarbons, has aroused significant attention due to its great potential in the construction of novel nanostructures/materials. So far, various well-known chemical reactions have been successfully introduced on surfaces,^{1–8} and furthermore, some reactions that can hardly occur in conventional chemistry have also been demonstrated to be feasible on surfaces.^{9–13} Among the on-surface chemical reactions, the homocoupling reactions of C–X functional groups (X stands for hydrogen or halogens), in particular, represent one of the most efficient ways to fabricate novel surface nanostructures in a controlled way. In this respect, dehydrogenative homocoupling of alkyne (sp¹ hybridized carbon),^{4,5,14,15} alkene¹⁶ and arene^{11,12,17,18} (both sp² hybridized carbon), and alkane (sp³ hybridized carbon)^{10,13} have been introduced on surfaces. Also, the dehalogenative homocoupling of an aryl halide (*i.e.* Ullmann reaction) has been most widely investigated and employed to fabricate various surface nanostructures.^{19–24}

Very recently, we have for the first time investigated the dehydrogenative homocoupling of alkenes on a Cu(110) surface,¹⁶ and we surprisingly found that the on-surface reaction product is a diene moiety, which is different from the typical homocoupling product of alkenes in solution (*i.e.* a butene moiety), and moreover, this on-surface synthesis allows for the formation of specific *trans*-dienes as shown in Scheme 1 (upper panel). Generally, comparison of the on-surface dehydrogenative coupling and the



Scheme 1 Stereoselective synthesis of diene moieties through an on-surface chemistry strategy. Upper: Formation of *trans*-diene by dehydrogenative homocoupling of alkene on Cu(110).¹⁶ Lower: Formation of *cis*-diene by dehalogenative homocoupling of alkenyl bromide on the same surface. The corresponding STM images with the relaxed models are also shown.

dehalogenative coupling indicates that the latter usually yields a higher selectivity and fewer by-products because it is relatively facile for the C–X bond cleavage (X typically stands for Br and I). Therefore, it is of general interest to introduce the dehalogenative homocoupling of alkenyl halides on surfaces as a new type of on-surface reaction, and more importantly, in comparison with the dehydrogenative homocoupling reaction of a similar functional group (*i.e.* terminal alkenyl group) it allows us to dig out the fundamental differences between these two surface reactions and moreover may provide a way to delicately control the product formation on surfaces.

As shown in Scheme 1 (lower panel), here we synthesize an organic molecule which has a terminal alkenyl bromide group functionalized on a biphenyl backbone (shortened as BVBP). Note that the major component of BVBP is in the *trans*-form, *i.e.*, *trans*-BVBP (details of the synthesis are shown in the ESI[†]). From the interplay of high-resolution UHV-STM imaging and density functional theory (DFT) calculations, we unexpectedly found that it is not only feasible to form a diene moiety *via* the dehalogenative homocoupling reaction, but we achieve a stereoselective synthesis of specific *cis*-dienes on Cu(110)

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(Scheme 1 lower panel), where the formation of a *cis*-form organometallic intermediate is the key to such a stereoselectivity because this *cis*-intermediate is determined by extensive DFT calculations to be the most stable one among all of the possible configurations. This study further supplements the database of on-surface C–C coupling reactions by introducing the terminal alkenyl bromides on surfaces. Most importantly, such an on-surface chemistry strategy provides us a relatively facile and efficient method for the stereoselective synthesis of specific diene moieties through dehydrogenative/dehalogenative homocoupling reactions of alkenes/alkenyl bromides on the same surface (*i.e.* Cu(110) here) (Scheme 1), which demonstrates the great potential of on-surface synthesis for exploring new chemistry and constructing novel surface nanostructures.

After the deposition of BVBP molecules on Cu(110) held at low temperatures (~ 170 K), the molecules already debrominate on the surface as shown in Fig. 1a, where the debrominated species and the detached bromine atoms could be observed. Since the evaporation temperature of the BVBP molecule is only ~ 300 K, it is not likely that the debromination occurs in the crucible. To reveal the role of the Cu(110) surface in the debromination process, we have calculated the energy diagram of the C–Br bond cleavage of the BVBP molecule on the surface. As shown in Fig. 1c, the energy barrier is determined to be 0.42 eV, and the debromination reaction is exothermic by 1.11 eV. As also shown in Fig. 1b of the DFT calculated adsorption geometry of the debrominated species on Cu(110), the molecule is stabilized by the formation of C–Cu bonds with the substrate.

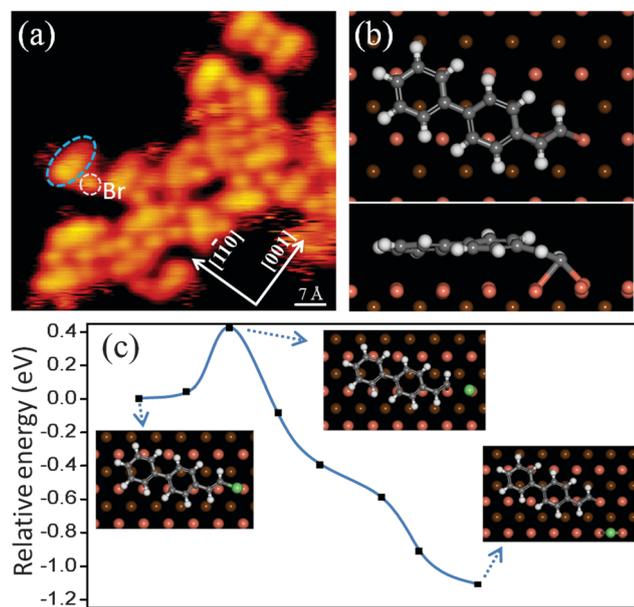


Fig. 1 (a) The STM image showing the debromination of BVBP molecules right after deposition on Cu(110) at ~ 170 K. A debrominated BVBP molecule and a detached Br atom are indicated by blue and white circles, respectively. (b) Top and side views of the DFT optimized model of a debrominated *trans*-BVBP molecule on Cu(110). (c) DFT-calculated energy diagram for the C–Br bond cleavage of the BVBP molecule on Cu(110). The structural models of the initial state, transition state and final state along the pathway are also shown.

Annealing the sample to room temperature (RT) or upon direct deposition of BVBP molecules on Cu(110) at RT, we observe the formation of ordered islands as shown in Fig. 2a and Fig. S1 (ESI †) (a large-scale image), which consist of curved structures and bright protrusions as highlighted by blue and white contours, respectively. The curved structure is composed of two lobes at both ends (which are attributed to the debrominated BVBP molecules) and a single protrusion in the middle (which is attributed to the copper adatom). As it is also known that the aryl bromides usually form the C–Cu–C species after debromination on copper surfaces at RT,^{21,22,25} the curved structure is naturally assigned to the organometallic intermediate. To further identify the atomic-scale structure of this organometallic species,

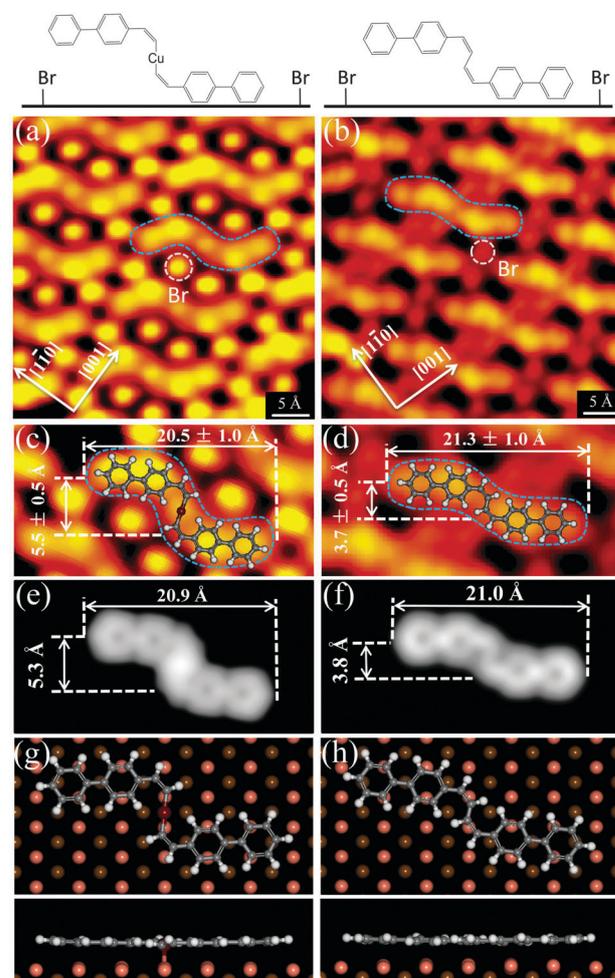


Fig. 2 (a) The STM image showing the formation of organometallic intermediates after deposition of BVBP molecules on Cu(110) at RT. The STM topographies of an organometallic intermediate and a Br atom are indicated by blue and white contours, respectively. (b) The STM image showing the formation of *cis*-diene products after annealing the sample to ~ 400 K. The STM topographies of a *cis*-diene product and a Br atom are indicated by blue and white contours, respectively. (c and d) The close-up STM images of the organometallic intermediate and the *cis*-diene product together with the scaled DFT relaxed models and the measured dimensions, respectively. (e–h) The corresponding simulated STM images and DFT relaxed models of the organometallic intermediate and the *cis*-diene product on Cu(110).

we perform extensive DFT calculations by constructing all of the possible structures (shown in Fig. S2, ESI†). From a detailed comparison of the experimental morphology and dimensions using the scaled molecular model and the simulated STM image (Fig. 2c and e), we distinguish that the formed organometallic species should be assigned to one specific C–Cu–C structure as shown in Fig. 2g (denoted as the *cis*-form organometallic intermediate). The bright protrusions in-between the organometallic species are attributed to the detached bromine atoms which further stabilize the structure by forming hydrogen bonds.^{26,27}

So, the results indicate that the *trans*-BVBP molecular precursors have turned into their *cis*-form during the dimerization process.²⁸ To further clarify this issue, we have performed extensive DFT calculations of the possible reaction pathways of the *cis/trans* isomerization of BVBP on Cu(110). As shown in Fig. S3 (ESI†), one of the pathways shows a relatively low reaction barrier of *cis/trans* isomerization (determined to be 1.04 eV), which is slightly higher than that obtained under the experimental conditions (RT). Such an energy barrier is largely reduced on Cu(110) in comparison with that in the gas phase or in solution (about 2 eV).^{29,30}

After further annealing the sample to ~400 K, ordered island structures are also observed on the surface as shown in Fig. 2b and Fig. S1 (ESI†), where another kind of curved structure is identified as indicated by the blue contour. From the knowledge of the demetalation process involving an organometallic intermediate to a final C–C coupled product for aryl bromides on copper surfaces,^{21,22,25} and also from a detailed comparison of the experimental morphology and dimensions with the scaled model and the simulated STM image (Fig. 2d and f), we distinguish that such a curved structure should be assigned to the specific *cis*-diene product as shown in Fig. 2h. It is noteworthy that no organometallic species was observed for the dehydrogenative homocoupling of alkenes on Cu(110) (*cf.* Scheme 1 upper panel) because the reaction pathway was proposed to be C–C coupling in the first step then followed by a dehydrogenation process, which results in the formation of specific *trans*-diene products.¹⁶

To elucidate the mechanism of the stereoselectivity with respect to the formation of *cis*-dienes we perform further DFT calculations. Since the final *cis*-diene products result from the demetalation of organometallic intermediates, the *cis*-diene configuration should be directly related to that of the intermediate. Experimentally, as shown above we identify that the organometallic intermediates are in a *cis*-configuration (Fig. 2a). From the DFT calculations shown in Fig. 3, we distinguish that the *cis*-form intermediate is indeed the most stable one among all of the possible configurations on Cu(110), which well accounts for the experimental observations. In comparison with the other on-surface reactions like Ullmann coupling and dehydrogenative coupling of terminal alkynes, where organometallic intermediates were also identified,^{15,21} in this study, to the best of our knowledge, this is the first time that the role of the organometallic intermediate in determining the final reaction product with respect to the stereoselectivity has been demonstrated.

In conclusion, by the combination of high-resolution UHV-STM imaging and DFT calculations, we have demonstrated that it is

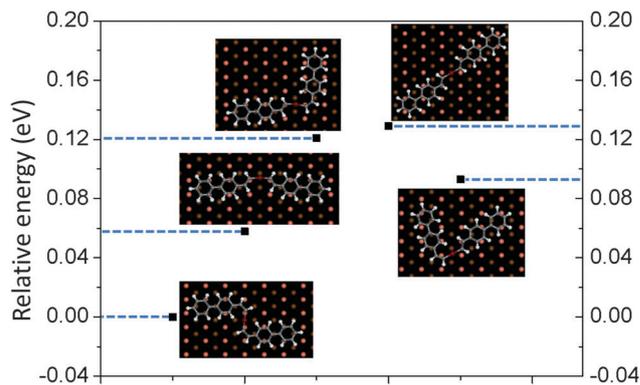


Fig. 3 DFT-calculated the possible configurations of the organometallic intermediate on Cu(110) and their relative energies. All of the energies are compared with the *cis*-form organometallic configuration.

feasible to stereoselectively synthesize specific diene moieties through on-surface dehydrogenative/dehalogenative homocoupling reactions of alkenes/alkenyl bromides on the Cu(110) surface. In synthetic chemistry, stereoselective synthesis is one of the most crucial processes. For instance, in certain biological systems, *cis-trans* isomerization of alkenes (C=C bond) is important because isomers often exhibit tremendous differences in physiological activities and pharmacological effects, *e.g.* *trans*-fatty acid could result in cardiovascular problems while the *cis* state would not.³¹ The findings presented in this study demonstrate the great potential of on-surface chemistry for stereoselective synthesis of dienes, which may also shed light on other stereoselectively related syntheses like enantiomers.

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