Dehydrogenative Homocoupling of Terminal Alkenes on Copper Surfaces: A Route to Dienes

7 AUTHORS, INCLUDING:

Qiang Sun

Tongji University

30 PUBLICATIONS 110 CITATIONS

SEE PROFILE

Lei Xie

Tongji University

6 PUBLICATIONS 5 CITATIONS

SEE PROFILE

Qing Gang Tan

Tongji University

37 PUBLICATIONS 384 CITATIONS

SEE PROFILE

Wei Xu

Tongji University

58 PUBLICATIONS 1,268 CITATIONS

SEE PROFILE

Surface Chemistry Hot Paper

Dehydrogenative Homocoupling of Terminal Alkenes on Copper Surfaces: A Route to Dienes**

Qiang Sun, Liangliang Cai, Yuanqi Ding, Lei Xie, Chi Zhang, Qinggang Tan, and Wei Xu*

Abstract: *Homocouplings of hydrocarbon groups including alkynyl (sp^1), alkyl (sp^3), and aryl (sp^2) have recently been investigated on surfaces with the interest of fabricating novel carbon nanostructures/nanomaterials and getting fundamental understanding. Investigated herein is the on-surface homocoupling of an alkenyl group which is the last elementary unit of hydrocarbons. Through real-space direct visualization (scanning tunneling microscopy imaging) and density functional theory calculations, the two terminal alkenyl groups were found to couple into a diene moiety on copper surfaces, and is contrary to the common dimerization products of alkenes in solution. Furthermore, detailed DFT-based transition-state searches were performed to unravel this new reaction pathway.*

*I*n organic chemistry homocoupling represents an important type of reaction which, for example, includes the Glaser coupling, Ullmann coupling, and Wurtz reaction, and all have been extensively investigated in organic synthesis for both scientific and industrial applications.[1–3] Generally, the reactants of these reactions are hydrocarbons functionalized with C−H or C−X groups (X stands for halogen), and two reactants couple by cleaving either the C−H or C−X bonds and forming a new carbon–carbon bond with the help of carefully selected catalysts. Recently, on-surface chemistry has attracted attention because various well-known chemical reactions have been successfully achieved on surfaces,[4–13] and more interestingly, some reactions that are hard to mediate by conventional chemistry have also been achieved on surfaces.[14–20] Specifically, dehydrogenative coupling of hydrocarbons like alkynes (sp^1),[9,21,22] alkanes (sp^3),[17,18] and arenes (sp^2),[19,20,23] have very recently been introduced onto surfaces with the interest of fabricating novel carbon nanostructures/ nanomaterials or exploring new reaction pathways. To our knowledge, however, on-surface coupling of alkenes (sp^2), another important hydrocarbon, has not been reported so far. It is therefore of utmost interest to complement the database
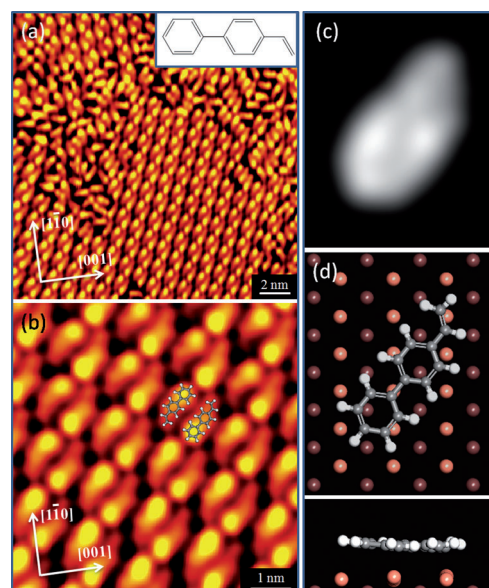
[*] Q. Sun,[+] L. Cai,[+] Y. Ding, L. Xie, C. Zhang, Prof. Dr. Q. Tan, Prof. Dr. W. Xu
Tongji–Aarhus Joint Research Center for Nanostructures and Functional Nanomaterials
College of Materials Science and Engineering
Tongji University, Caoan Road 4800, Shanghai 201804 (P.R. China)
E-mail: xuwei@tongji.edu.cn

[+] These authors contributed equally to this work.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201412307.

Figure 1. a) Large-scale and b) close-up STM images showing the adsorption and arrangement of VBP molecules on Cu(110) at RT. Two scaled molecular models are superimposed on the STM image showing the antiparallel arrangement of the neighboring molecules. The inset shows the chemical structure of the VBP molecule. c) The simulated STM image of a VBP molecule on Cu(110). d) Top and side views of the DFT optimized geometry of a VBP molecule adsorbed on Cu(110).

to extend our fundamental understanding of the on-surface chemistry of hydrocarbons.
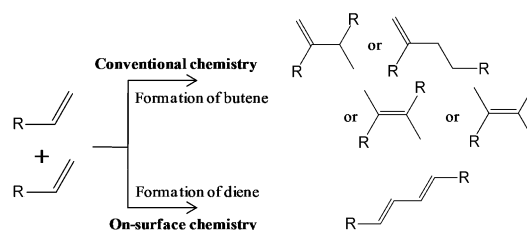
In this study, we chose a molecule which has a terminal alkenyl group connected on a biphenyl backbone (that is, 4-vinyl-1,1′-biphenyl; VBP), as shown in the inset of Figure 1a. As previously reported, the alkenyl groups normally dimerize into different kinds of butene moieties in solution (Scheme 1), and the majority of those studies were focused on increasing

Scheme 1. The dimerization of alkene molecules. Top: formation of four kinds of possible butene structures by conventional wet chemistry reported in the literature. Bottom: formation of a diene structure by on-surface chemistry in this study.

the yield of a particular butene product.[24–26] Herein, we introduce VBP onto surfaces with the aim of studying on-surface coupling behaviors of alkenes. Several metal surfaces with different crystal faces and reactivities [Cu(110), Cu(100), Cu(111), Au(111)] were selected to study the on-surface reaction scenarios of VBP. From the interplay of high-resolution UHV-STM imaging/delicate lateral manipulation and density functional theory (DFT) calculations, we have shown that contrary to the dimerization products of alkenes in solutions, that is, butene moieties, VBP molecules unexpectedly couple to give diene compounds (Scheme 1) on both Cu(110) and Cu(100) surfaces, and with a quite high yield (>80%) on Cu(110). Furthermore, detailed DFT-based CI-NEB calculations have been performed to unravel the reaction pathways for the formation of the diene compound on Cu(110). Our findings thus propose a new homocoupling reaction, that is, the coupling of a terminal alkene, by an on-surface chemistry method. Moreover, this novel strategy presents an efficient route for synthesizing diene compounds on surfaces.

After deposition of VBP at a relatively high coverage (ca. 0.8 monolayer) on Cu(110) held at room temperature, the majority of molecules self-assemble into well-ordered close-packed nanostructures as illustrated in Figure 1a. From the high-resolution submolecularly resolved STM image shown in Figure 1b, we could identify that a single VBP molecule is imaged as a "tadpole" with one round protrusion connected to a dim tail. It is also clear that the STM appearance of a VBP molecule is asymmetrical because of misalignment of the tail along the long axis of the molecule, and could be attributed to the alkene moiety. To gain further insight, we performed DFT calculations on the adsorption geometry and the STM simulation of the VBP molecule on Cu(110). The optimized model of the VBP molecule shows an almost flat-lying geometry on Cu(110) (Figure 1d), and the corresponding simulated STM image calculated at the bias voltage of 2 V is shown in Figure 1c. In comparison with the experimental one where the dim tail and bright protrusion are attributed to the alkene and biphenyl moieties, respectively, a good agreement is achieved. Since the VBP molecule is basically flat on the substrate, it is interesting to note that the alkenyl group has lower density of state than the phenyl group, thus indicating the sp^2 π-system might be different within these two groups.

Interestingly, after annealing the VBP-molecule-covered sample to about 425 K for two hours, we find that the majority of the VBP molecules dimerize and isolately distribute on the surface as shown in Figure 2a. Note that some molecules are desorbed from the substrate in this process. It is seen that the formed dimers have two preferred directions, that is, with their long axis (indicated by the blue arrows in Figure 2a) along ±45° with respect to the $[1\bar{1}0]$ direction of the substrate (as illustrated in Figure 2a). The high-resolution submolecularly resolved STM image presented in Figure 2b clearly shows that the dimer structure consists of two bright protrusions which are assigned to the VBP monomers as compared with their STM appearances and dimensions (see Figure S1 in the Supporting Information). Also, in the middle of the dimer structure a smooth connection (density of states) could be resolved, and should be attributed to the covalent
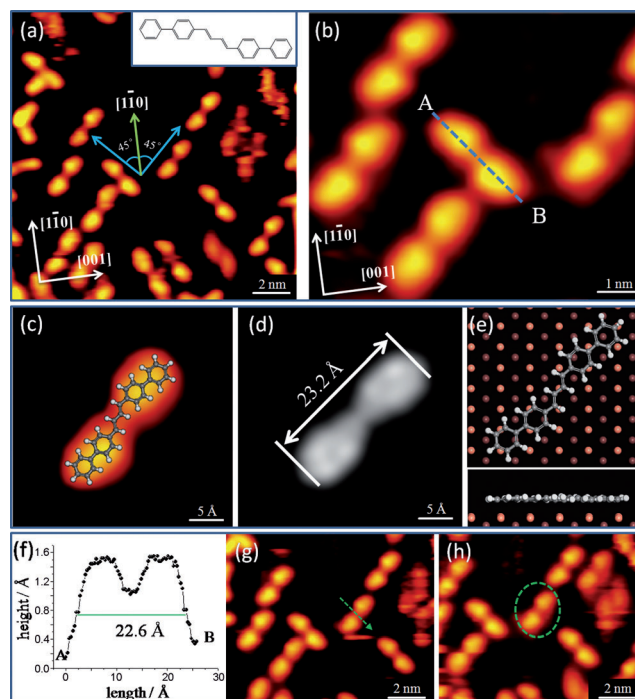

Figure 2. a) Large-scale and b) close-up STM images showing dimerization of VBP molecules on Cu(110) at 425 K. The inset shows the chemical structure of the diene compound. c) High-resolution STM image showing the formed diene compound with the scaled optimized model. d) DFT-based STM simulation and e) the optimized geometry of the diene compound adsorbed on Cu(110). f) Line-scan profile of the diene compound shown in (b). g,h) STM images after a lateral STM manipulation of the diene compound. The green arrow in (g) indicates the direction of the STM manipulation and the green ellipse in (h) shows the diene compound after the STM manipulation. Manipulation parameters: $I_t = -5$ nA, $V_t = -8$ mV.

coupling of the alkenyl groups because of the following reasons: 1) the smooth and seamless STM morphology implies the characteristic feature of covalent linkages between organic molecules;[4–8] 2) since the alkenyl group of the VBP molecule has a lower density of state, as reflected from the STM contrast, it is natural to speculate that the dark connection within the dimer structure should be ascribed to the coupling between alkenyl groups; 3) the covalent coupling between phenyl groups should be ruled out as that reaction would require higher temperatures at about 500 K on Cu(110) as reported previously.[19] Moreover, a closer inspection of the dimer structure allows us to identify that the two bright protrusions (i.e. diphenyl groups) are not coaxial and exhibit a staggered arrangement.

To get further insight into the dimer structure, we have performed thorough DFT calculations based on the above analysis to determine the atomic-scale model of the dimer structure. Firstly, a series of possible butene structures[24–26] are built up and relaxed on Cu(110) (see Figure S2). By comparing the simulated STM images of these butene structures to the STM morphology of the dimer structure shown in Figure 2b, however, none of the butene structures could account for the experimental finding. Secondly, inspired from the recent intensive studies of on-surface dehydrogen-

ation reactions of different hydrocarbons, especially the terminal alkyne molecules,[9,18,21,23] we took the dehydrogenation into account and built up a series of diene structures and relaxed them on Cu(110) (structural models and their relevant energies are shown in Figure S3). Unexpectedly, one of the energetically favorable diene structures shown in Figure 2e is in good agreement with our STM finding, as reflected by the overlap between the scaled optimized model and the experimental STM image (Figure 2c), and the corresponding simulated STM image (Figure 2d) also resembles the experimental one. By comparing the measured dimension of the experimental STM image (Figure 2f) to the theoretical one (Figure 2d), good agreement is achieved as well. Meanwhile, the noncoaxial arrangement of the two biphenyl groups reflected in the STM appearance is well explained from the proposed model of the diene (see Figure S4).

To further verify that two VBP molecules are covalently bonded, we perform the lateral STM manipulations (Figure 2g, h). After manipulation of a diene motif along the green arrow as indicated in Figure 2g, we find that the whole diene motif moves to a new location as indicated by the ellipse in Figure 2h, and the whole structure always remains intact. Note that during the whole process we do not find any indication of possible organometallic intermediates involved in the formation of the diene structure.[27–30] It should also be noted that the yield of the diene structure by the homocoupling of VBP molecules is quite high (more than 80%) on Cu(110), as calculated from a statistical analysis of more than 1000 products (see Figure S5). Similar experiments have also been performed on Cu(100), Cu(111), and Au(111). On the Cu(100) substrate we find that the diene structures can also be formed at the temperature of about 425 K (see Figure S6), and demonstrates the generality of this dehydrogenative homocoupling reaction on copper surfaces. While, the yield of formation of diene structures on Cu(100) is much lower than that on Cu(110). On the Cu(111) and Au(111) substrates, the VBP molecules desorb after gentle annealing and no coupling reaction is observed.

To unravel the mechanism of the dehydrogenative homocoupling of VBP into the diene structure on Cu(110), further calculations, using a DFT-based transition-state search, were performed. Firstly, we considered the reaction pathways involving direct C−H bond dissociation of the terminal alkenyl groups followed by coupling of two dehydrogenated VBP molecules as previously reported for on-surface chemical reactions of hydrocarbons.[17,19,31] Along this path several direct C−H bond dissociation pathways are calculated and plotted as shown in Figure S8, and the energy barriers are calculated to be in the range of 1.7–2.7 eV, while, the energy barriers seem too high when compared to the experimental conditions (i.e., ca. 425 K), and thus rules out the pathway involving direct C−H activation of the alkenyl group.

Then, we considered another reaction pathway which involves coupling of two terminal alkenyl groups of VBP molecules in the first step and subsequent dehydrogenation from the intermediates. This mechanism is accessible because of the unsaturated nature of the alkenyl group just like the dimerization process reported for terminal alkynes on a noble

metal surface.[31] Since the VBP molecules have already formed ordered nanostructures on Cu(110) at room temperature, the surface diffusion is not a problem for the dimerization process. Once two alkenyl groups come in close proximity, a new intermediate dimer structure (Int1 in Figure 3) is formed by forming a new carbon–carbon single
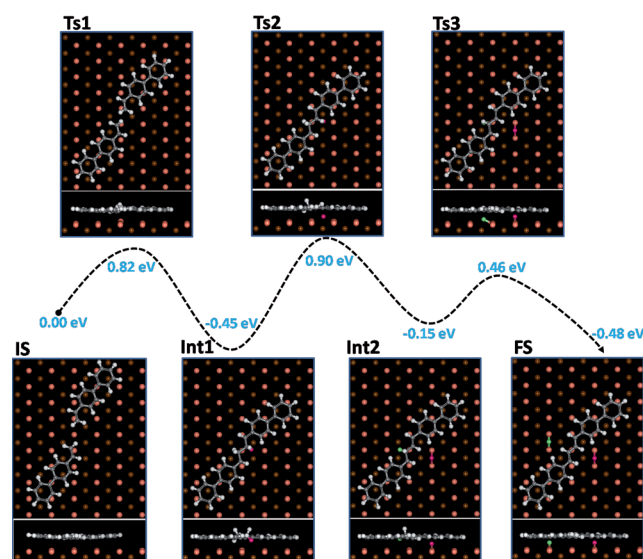

Figure 3. DFT calculated reaction pathway for dimerization of two VBP molecules to give a diene structure. The pathway involves coupling of two terminal alkenyl groups of VBP molecules in the first step and subsequent sequential dehydrogenation processes. The two abstracted hydrogen atoms are rendered in green and red, respectively. Energies of the local minima (IS, Int1, Int2, and FS) and transition states (Ts1, Ts2, and Ts3) along the reaction path are given with respect to the initial state (IS).

bond and turning two terminal sp^2-carbon atoms into sp^3-carbon atoms. The reaction barrier during this process is about 0.82 eV and could be easily achieved under the experimental conditions. The following step-by-step dehydrogenation processes have energy barriers of 1.35 eV and 0.61 eV for abstracting the first and the second hydrogen atoms, respectively. (see the energy curve in Figure 3) Thus, the reaction barrier for the whole pathway is determined to be 1.35 eV, which is appreciably lower than that of direct C−H bond dissociation pathways as mentioned above. The final product of the diene structure is more stable than the two original VBP molecules on Cu(110) by 0.48 eV, and means that the whole reaction process is exothermic and thermodynamically favorable. Moreover, the energy barrier is in reasonable agreement with the experimental condition. We thus think the established reaction pathway for the formation of the diene structure from dehydrogenative homocoupling of the alkenyl groups is plausible and accounts for our experimental findings, although we do not find any evidence of the intermediate states on the surface. According to the above analysis we conclude that the dehydrogenative coupling of terminal alkene is very similar to the one of terminal alkyne,[9,31] and the sp^2 π-system of terminal alkenyl group and phenyl group is indeed different with respect to the dehydrogenative coupling process.

In conclusion, by combining high-resolution UHV-STM imaging and DFT calculations, we have for the first time reported the homocoupling of terminal alkenes on copper surfaces, where a diene compound is formed with an appreciably high yield on the Cu(110) surface. In solution chemistry, the homocoupling of alkene molecules mainly produces butene-type compounds as shown in Scheme 1. However, for on-surface chemistry, the metal substrates effectively facilitate the subsequent dehydrogenation process, thus resulting in new chemical reactions. The whole reaction pathway is further explored by detailed DFT calculations, which involves coupling of terminal alkenyl groups in the first step and subsequent dehydrogenation processes from the intermediates. These novel findings have extended our knowledge in the field of coupling reactions and demonstrated the fascinating potential of on-surface chemistry. Moreover, this new coupling reaction provides a new strategy for synthesizing diene compounds which may have potential applications in organic (opto)electronic devices because of their conjugated nature.

[1] F. D. Mango, *Org. Geochem.* **1997**, *26*, 417.
[2] J. H. Li, Y. Liang, Y. X. Xie, *J. Org. Chem.* **2005**, *70*, 4393–4396.
[3] J. Hassan, M. Sévignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359–1470.
[4] J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. Feng, K. Mullen, R. Fasel, *Nature* **2010**, *466*, 470–473.
[5] Q. Sun, C. Zhang, Z. Li, H. Kong, Q. Tan, A. Hu, W. Xu, *J. Am. Chem. Soc.* **2013**, *135*, 8448–8451.
[6] L. Grill, M. Dyer, L. Lafferentz, M. Persson, M. V. Peters, S. Hecht, *Nat. Nanotechnol.* **2007**, *2*, 687–691.
[7] F. Bebensee, C. Bombis, S. R. Vadapoo, J. R. Cramer, F. Besenbacher, K. V. Gothelf, T. R. Linderoth, *J. Am. Chem. Soc.* **2013**, *135*, 2136–2139.
[8] G. Franc, A. Gourdon, *Phys. Chem. Chem. Phys.* **2011**, *13*, 14283–14292.
[9] Y. Q. Zhang, N. Kepcija, M. Kleinschrodt, K. Diller, S. Fischer, A. C. Papageorgiou, F. Allegretti, J. Bjork, S. Klyatskaya, F. Klappenberger, M. Ruben, J. V. Barth, *Nat. Commun.* **2012**, *3*, 1286.
[10] W. Wang, X. Shi, S. Wang, M. A. Van Hove, N. Lin, *J. Am. Chem. Soc.* **2011**, *133*, 13264–13267.
[11] X. Liu, C. Guan, S. Ding, W. Wang, H. Yan, D. Wang, L. Wan, *J. Am. Chem. Soc.* **2013**, *135*, 10470–10474.
[12] H. Zhou, J. Liu, S. Du, L. Zhang, G. Li, Y. Zhang, B. Z. Tang, H. J. Gao, *J. Am. Chem. Soc.* **2014**, *136*, 5567–5570.
[13] J. Björk, F. Hanke, *Chem. Eur. J.* **2014**, *20*, 928–934.
[14] H. Y. Gao, P. A. Held, M. Knor, C. Mück-Lichtenfeld, J. Neugebauer, A. Studer, H. Fuchs, *J. Am. Chem. Soc.* **2014**, *136*, 9658–9663.
[15] L. E. Dinca, C. Fu, J. M. MacLeod, J. Lipton-Duffin, J. L. Brusso, C. E. Szakacs, D. Ma, D. F. Perepichka, F. Rosei, *ACS Nano* **2013**, *7*, 1652–1657.
[16] C. Urban, Y. Wang, J. Rodríguez-Fernández, R. García, M. Á. Herranz, M. Alcamí, N. Martin, F. Martiin, J. M. Gallego, R. Miranda, R. Otero, *Chem. Commun.* **2014**, *50*, 833–835.
[17] D. Zhong, J. Franke, S. K. Podiyanachari, T. Blömker, H. Zhang, G. Kehr, G. Erker, H. Fuchs, L. Chi, *Science* **2011**, *334*, 213–216.
[18] M. In't Veld, P. Iavicoli, S. Haq, D. B. Amabilino, R. Raval, *Chem. Commun.* **2008**, *13*, 1536–1538.
[19] Q. Sun, C. Zhang, H. Kong, Q. Tan, W. Xu, *Chem. Commun.* **2014**, *50*, 11825–11828.
[20] A. Wiengarten, K. Seufert, W. Auwärter, D. Ecija, K. Diller, F. Allegretti, F. Bischoff, S. Fischer, D. A. Duncan, A. C. Papageorgiou, F. Klappenberger, R. G. Acres, T. H. Ngo, J. V. Barth, *J. Am. Chem. Soc.* **2014**, *136*, 9346–9354.
[21] H. Y. Gao, H. Wagner, D. Zhong, J. H. Franke, A. Studer, H. Fuchs, *Angew. Chem. Int. Ed.* **2013**, *52*, 4024–4028; *Angew. Chem.* **2013**, *125*, 4116–4120.
[22] J. Eichhorn, W. M. Heckl, M. Lackinger, *Chem. Commun.* **2013**, *49*, 2900–2902.
[23] S. Haq, F. Hanke, J. Sharp, M. Persson, D. B. Amabilino, R. Raval, *ACS Nano* **2014**, *8*, 8856–8870.
[24] P. Serna, B. C. Gates, *Angew. Chem. Int. Ed.* **2011**, *50*, 5528–5645; *Angew. Chem.* **2011**, *123*, 5642–5645.
[25] D. C. Leitch, Y. C. Lam, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2013**, *135*, 10302–10305.
[26] E. Rodriguez, M. Leconte, J. M. Basset, K. Tanaka, *J. Catal.* **1989**, *119*, 230–237.
[27] C. Zhang, Q. Sun, H. Kong, L. Wang, Q. Tan, W. Xu, *Chem. Commun.* **2014**, *50*, 15924–15927.
[28] C. Zhang, Q. Sun, H. Chen, Q. Tan, W. Xu, *Chem. Commun.* **2015**, *51*, 495–498.
[29] F. Hanke, S. Haq, R. Raval, M. Persson, *ACS Nano* **2011**, *5*, 9093–9103.
[30] C. J. Villagómez, T. Sasaki, J. M. Tour, L. Grill, *J. Am. Chem. Soc.* **2010**, *132*, 16848–16854.
[31] J. Börk, Y. Q. Zhang, F. Klappenberger, J. V. Barth, S. Stafstrom, *J. Phys. Chem. C* **2014**, *118*, 3181–3187.
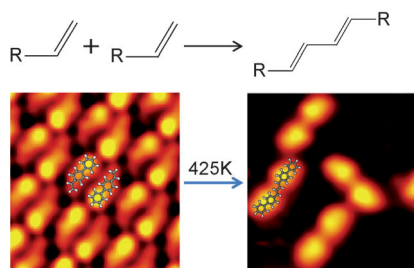
Communications

Surface Chemistry

Q. Sun, L. Cai, Y. Ding, L. Xie, C. Zhang,
Q. Tan, W. Xu* ———————— ▪▪▪▪–▪▪▪▪

Dehydrogenative Homocoupling of
Terminal Alkenes on Copper Surfaces: A
Route to Dienes

On the surface: By combining high-resolution UHV-STM imaging and DFT calculations, the homocoupling of terminal alkenes on copper surfaces is reported. A diene compound is formed with an appreciably high yield on the Cu(110) surface.

These are not the final page numbers! ↗↗