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On-surface synthesis of organometallic complex *via* metal–alkene interactions†

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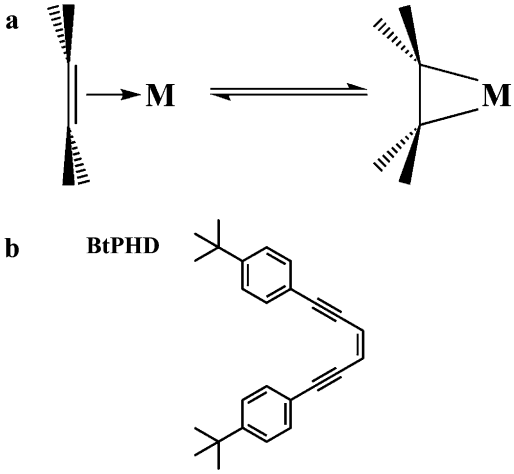
From the interplay of high-resolution scanning tunneling microscopy (STM) imaging/manipulation and density functional theory (DFT) calculations, we have shown that the spontaneous formation of an organometallic complex by copper–alkene interactions can be successfully achieved, where the specific molecular adsorption geometry is revealed to be the key for facilitating such interaction.

The synthesis of organometallic complexes involving direct carbon to metal bonds with characteristics in between ionic and covalent bonds has been an intriguing topic for decades, because of their extensive applications in industrial catalysis.[1] Pioneer research work in Zeise's salt, one of the earliest examples of a metal–alkene complex,[2,3] has been recognized as a solid landmark in the area of organometallic chemistry. Later on, the syntheses of similar complexes (*e.g.*, Grignard reagents[4] and Ziegler–Natta catalysts[5]) in solution have also been well established. Recently, the on-surface formation of organometallic monomers or oligomers has also been achieved, mainly through: (1) low temperature STM manipulation of individual molecules and metal atoms, inducing direct carbon to metal bonding on metal supported ultrathin insulating films[6,7] or metal surfaces;[8–11] or (2) dehalogenation or dehydrogenation processes accompanied with the subsequent formation of carbon to metal bonding on metal surfaces.[12–19] However, the on-surface synthesis of an organometallic complex *via* a spontaneous direct metal–alkene interaction has been rarely reported. Thus, the concept of the synthesis of metal–alkene complexes in solvent-free "dry" ultrahigh vacuum conditions (UHV) on surfaces should be of great interest to be explored and further employed as a possible prototype and novel method to fabricate functional organometallic complexes.



Scheme 1 (a) Illustration of reversible metal to alkene bonding. (b) Chemical structure of the candidate molecule (BtPHD) for exploring the on-surface metal–alkene interaction.

In this communication, we have chosen an organic molecule (henceforth termed "BtPHD") involving an alkene functional group and explored the feasibility of the formation of an organometallic complex *via* metal–alkene interactions (*cf.* Scheme 1) on a Cu(110) surface under UHV conditions. The anisotropic Cu(110) surface was employed as a platform due to its: (1) relatively high chemical activity; (2) well-known 1-D templating effect; (3) free copper adatoms. From the interplay of high-resolution scanning tunneling microscopy (STM) imaging/manipulation and density functional theory (DFT) calculations, we show that the formation of a copper–alkene complex has been successfully achieved in a spontaneous manner without external force (such as STM tip manipulation), and that such a copper–alkene complex is found to be able to dimerize in a relatively high yield. From the DFT-relaxed structural models we could identify that the formation of the copper–alkene complex results in a direct copper to carbon bonding with the characteristic rehybridization of carbon atoms from sp^2 to sp^3, and we also found that the specific molecular adsorption geometry was the key for facilitating this spontaneous metal–alkene interaction. Moreover, the lateral STM manipulations demonstrated that the dimerized organometallic motif could be split into two monomers, and furthermore that the copper atom could be removed from the

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complex, indicating that the copper–alkene interaction is reversible. These findings exhibit the feasibility of the on-surface formation of organometallic complexes with high yields, and may provide a general route to fabricate relevant organometallic catalysts that would be of special significance to organometallic chemistry.

The STM experiments were performed in an UHV chamber (base pressure of 1×10^{-10} mbar) equipped with a variable-temperature "Aarhus-type" STM purchased from SPECS,[20,21] a molecular evaporator, and standard facilities for sample preparation. After the system was thoroughly degassed, the molecules were deposited by thermal sublimation onto a Cu(110) substrate. The sample was thereafter transferred within the UHV chamber to the STM, where the measurements were carried out at ~100 K. All the calculations were carried out in the framework of DFT by using the Vienna ab-initio simulation package (VASP).[22,23] The projector augmented wave method was used to describe the interaction between the ions and electrons.[24,25] We employed the PBE-GGA as the exchange correlation functional,[26] and van der Waals interactions were included using the DFT-D2 method of Grimme.[27] The atomic structures were relaxed using the conjugate gradient algorithm scheme as implemented in the VASP code until the forces on all the unconstrained atoms were $\leq$0.03 eV Å^{-1}. The simulated STM images were based on the Tersoff–Hamann method, in which the local density of states (LDOS) was used to approximate the tunneling current.[28]

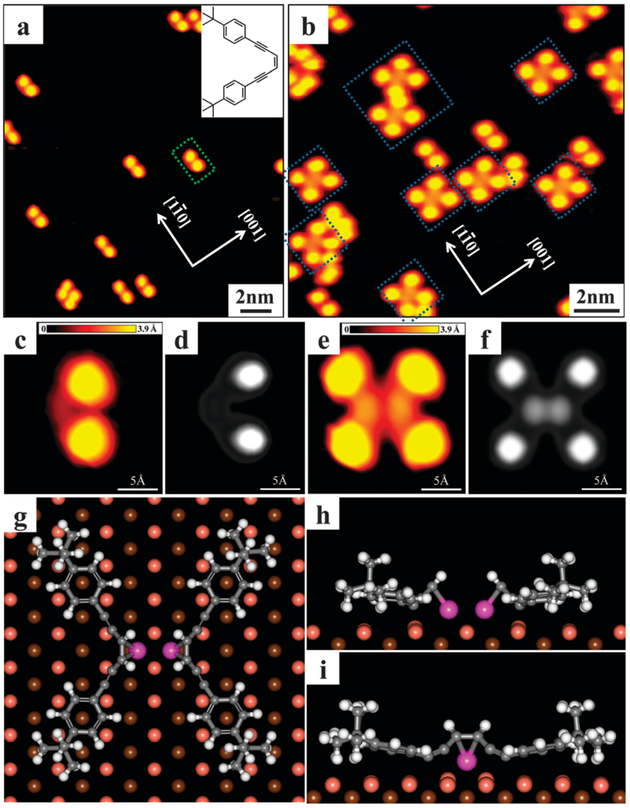

Fig. 1 STM images and relaxed models of the X-shaped organometallic motif. (a) STM image showing the isolated BtPHD molecules adsorbed on a Cu(110) substrate (during deposition the substrate was held at ~170 K). The green dashed rectangle indicates a single BtPHD molecule and the inset shows the chemical structure of the BtPHD molecule. (b) STM image showing the formation of X-shaped motifs after subsequent annealing of the sample to ~250 K. The blue dashed squares indicate the formed X-shaped motifs. Scanning conditions: I_t = 0.65 nA, V_t = −2500 mV. (c) High-resolution STM image of a single BtPHD molecule. (d) Simulated STM image of the BtPHD molecule at a bias voltage of −2500 mV. (e) High-resolution STM image of the X-shaped motif. (f) Simulated STM image of the X-shaped motif at a bias voltage of −2500 mV. (g) Top view, and (h) and (i) two side views of the DFT-optimized structure of the X-shaped motif on Cu(110).

After deposition of the BtPHD molecules on the Cu(110) substrate held at ~170 K, isolated BtPHD molecules are observed with their symmetric axes perpendicular to the direction of the substrate (*cf.* Fig. 1a). Interestingly, after a subsequent annealing of the sample to ~250 K, X-shaped motifs appear as illustrated in Fig. 1b (highlighted by the blue squares). A comparison between the high-resolution STM images of the BtPHD molecule (*cf.* Fig. 1c) and the X-shaped motif (*cf.* Fig. 1e) indicates that: the X-shaped motif may be composed of two BtPHD molecules, as can be seen from the dimension and topography; there is still a subtle difference between the BtPHD molecule and half of the X-shaped motif. In comparison to the initial BtPHD molecule, which is imaged as two bright protrusions connected with one dark bridge (see also the simulated STM image, *cf.* Fig. 1d), each half of the X-shaped motif has a distinguishable density in the center. Previous literature provided inspiration that the conjugated molecules could interact with metal atoms by forming carbon–metal bonds, where the metal atom lies underneath the binding site, and then the specific binding site is revealed as high density area in the STM images.[6–10] Note that at the above-mentioned temperature (~250 K), copper adatoms are available on the substrate.[19,29] We then naturally speculate that in our case the high densities in the center of the X-shaped motif should be attributed to the copper–alkene interaction. On the basis of the above analyses, we then built up structural models of the X-shaped motif and relaxed by DFT methods, with the most favorable one shown in Fig. 1g (more calculation details can be seen in ESI†). In this model, we can identify that the alkene moiety of the BtPHD molecule interacts with a Cu atom with a Cu–C distance of ~2.12 Å forming copper–alkene bonding, where the two C atoms of the alkene moiety form a nearly tetrahedral bonding motif with a sp^2–sp^3 rehybridization characteristic, similar to the previous literature with LT-STM manipulation.[6,7] Due to the copper–alkene interaction, the enediyne moiety is tilted away from the substrate, with a dihedral angle of ~45° (*cf.* Fig. S1, ESI†), resulting in the high density in the center of the BtPHD molecule, as reflected in the STM images. Thus, half of the X-shaped motif is formed by a BtPHD molecule and a Cu atom *via* copper–alkene interactions forming an organometallic complex, and the X-shaped motif is then dimerized by two such organometallic complexes *via* Cu–Cu interactions. The distance between the upright-standing hydrogen atoms on two sides is about 3.9 Å, which is consistent with that between the two densities in the center of the X-shaped motif in the STM image. Based on the proposed model, we also performed STM image simulation, and a good agreement was achieved by comparing the simulated X-shaped motif (*cf.* Fig. 1f) with the experimental one (*cf.* Fig. 1e).

To verify our speculation and the above analysis, we performed delicate lateral STM manipulations on the X-shaped motif. As shown in Fig. 2a–d, after manipulation of the X-shaped motifs in different directions, we can see that the motifs can be split away along the [001] direction of the substrate, and that half of the motif usually diffuses away. The remaining half still shows a high density in the center with the same characteristic as the one in the X-shaped motif, which indicates that the two halves are identical. Also, note that some halves of the X-shaped motif are observed to exist alone (*cf.* Fig. S2, ESI†), implying that one half can stay isolated until meeting with another half to dimerize into the X-shaped motif. To further verify the constitution of the half part, we applied STM manipulation, as shown in Fig. 2e and f. After manipulation of the half motif, we successfully demonstrated that the half motif can be split into a BtPHD molecule (showing the characteristic of two bright protrusions with the dark bridge in the center) and a Cu adatom (a bright protrusion indicated by the arrow in Fig. 2f), indicating that the copper–alkene interaction is reversible. Similar processes have also been illustrated in the previous literature.[7,30] Further theoretical analysis of the electronic structure and the nature of the Cu–alkene bonding and the reaction path of the formation of Cu–alkene interaction are shown in Fig. S3 and S4 (ESI†), respectively. Moreover, the X-shaped motif is calculated to be energetically more favorable than the two isolated BtPHD–Cu organometallic complexes by ∼0.37 eV, which indicates that the dimerization process is thermodynamically favorable. Thus, we propose the following scenario: (1) after deposition of the BtPHD molecules on the Cu(110) surface, the molecules spontaneously interact with copper adatoms at elevated temperatures (still well below RT) and form the BtPHD–Cu organometallic complex *via* copper–alkene interactions; (2) every two formed organometallic complexes then dimerize into one X-shaped motif *via* Cu–Cu interactions.

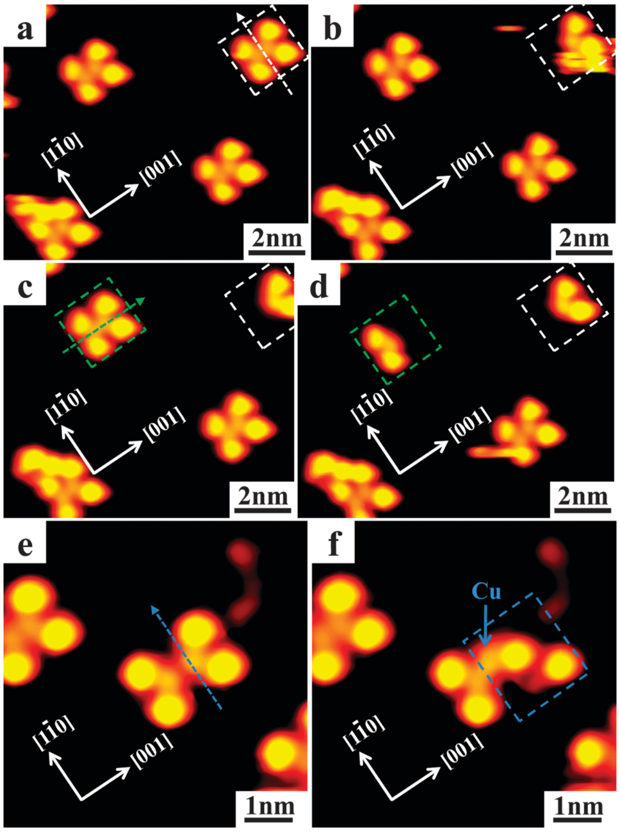

Fig. 2 (a–d) Lateral STM manipulations of the X-shaped motif in the same region. The white arrow in (a) and the green one in (c) indicate the different locations and directions of the manipulations applied, and the white and green squares in (a–d) highlight the evolution of the X-shaped motif from a whole into a half. Scanning conditions: I_t = 0.80 nA, V_t = −2500 mV. (e–f) Lateral STM manipulation of a half of the X-shaped motif. The blue arrow in (e) indicates the location and direction of the manipulation applied, and the blue square in (f) highlights the evolution of half of the X-shaped motif from an intact one into a BtPHD molecule and a Cu adatom. Scanning conditions: I_t = 0.69 nA, V_t = −2500 mV.

Note that in this case, the direct copper–alkene interaction is spontaneous, and the copper–alkene interaction takes place at relatively low temperatures (∼250 K). This raises the interesting question of why such a phenomenon was not generally observed for other conjugated molecules on surfaces. To unravel this mystery, we relaxed the adsorption geometry of the BtPHD molecule on Cu(110) by DFT methods, including vdW interactions. As shown in Fig. 3a, the enediyne moiety of the BtPHD molecule is tilted up in the energetically most favorable adsorption geometry, with a dihedral angle of ∼25°. We then naturally speculated whether this tilted configuration could provide a favorable situation to let the Cu adatom go underneath the alkene moiety and thus facilitate the copper–alkene interaction. To verify our hypothesis, we also conducted control experiments on Ag(110) and Au(111), both computationally and experimentally. As shown in Fig. 3b and c, from the energetically most favorable adsorption geometries on Ag(110) and Au(111), we observe that the alkene moieties of the BtPHD molecule basically adopt flat-lying configurations, and the molecule–substrate orientations are different from that on Cu(110). Interestingly, the codeposition of BtPHD molecules and Cu atoms on Ag(110) and Au(111) surfaces could not result in the formation of BtPHD–Cu organometallic complexes (*cf.* Fig. S5, ESI†), and thus we did not perform calculations on the interactions between the BtPHD molecule and Cu atoms on these two surfaces. Furthermore, we conducted another control experiment by choosing an analogy of the BtPHD molecule (henceforth termed as "DTBT", *cf.* the inset of Fig. 4a) where the enediyne moiety is replaced by a phenyl group, thus resulting in a flat-lying adsorption geometry on Cu(110), as shown in Fig. 4c. After deposition of the DTBT molecules on Cu(110) (held at ∼170 K) at low coverage (*cf.* Fig. 4a), isolated molecules are observed and the profile of the single molecule is imaged and shown to be very similar to that of

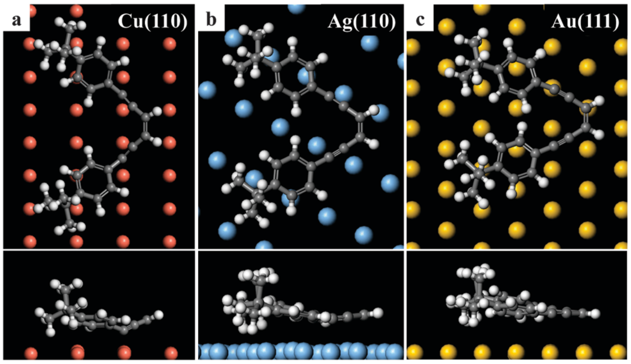

Fig. 3 Top and side views of the DFT-optimized energetically most favorable geometries of the BtPHD molecule adsorbed on (a) Cu(110), (b) Ag(110), (c) Au(111).

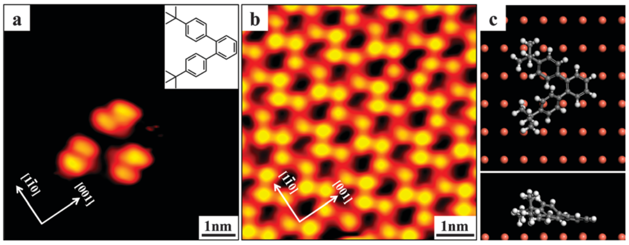

Fig. 4 (a) STM image showing isolated DTBT molecules adsorbed on a Cu(110) surface (during deposition the substrate was held at ∼170 K). The inset shows the chemical structure of the DTBT molecule. (b) STM image showing the self-assembled structure of DTBT molecules after deposition of the molecules at high coverage and a subsequent annealing of the sample to ∼300 K. Scanning conditions: I_t = 0.71 nA, V_t = −2500 mV. (c) Top and side views of the DFT-optimized geometry of the DTBT molecule adsorbed on Cu(110).

the BtPHD molecule. After deposition of the DTBT molecules at high coverage and a subsequent annealing of the sample to ∼300 K, as expected, there is no indication of copper–phenyl interactions and the DTBT molecules form self-assembled ordered structures *via* vdW interactions (*cf.* Fig. 4b). These control experiments unambiguously suggest that the metal–carbon interaction would be hindered by a flat-lying adsorption geometry (as for most conjugated molecules adsorbed on surfaces) unless an external force (such as STM manipulation) is applied to push the metal atoms underneath the molecular planes.[6–10] So in our case, the Cu(110) surface is the prerequisite for the formation of organometallic complex as: (1) it provides sufficient Cu adatoms; (2) the relatively high chemical activity makes the alkynyl group of the BtPHD molecule strongly interact with the substrate, thus inducing the enediyne group to be tilted, which is the key for the spontaneous copper–alkene interaction.

In conclusion, from the interplay of high-resolution STM imaging/manipulation and DFT calculations, we have shown that the formation of an organometallic complex involving copper adatoms by metal–alkene interactions can be successfully achieved in a relatively high yield, where the specific molecular adsorption geometry is the key for facilitating the copper–alkene interaction. Our findings may shed light on the feasibility of synthesizing organometallic complexes with metal–alkene bonding on surfaces, and for utilizing molecular adsorption geometry as a trigger for metal–alkene interactions in more complicated situations (such as the dynamic π system), which is currently being investigated with the hope of providing further insights into surface organometallic chemistry.

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Notes and references

1 R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, Wiley, New Jersey, 2005, ch. 5, p. 125.
2 R. A. Love, T. F. Koetzle, G. J. Williams, L. C. Andrews and R. Bau, *Inorg. Chem.*, 1975, **14**, 2653.
3 L. B. Hunt, *Platinum Met. Rev.*, 1984, **28**, 76.
4 D. P. Curran and M. J. Totleben, *J. Am. Chem. Soc.*, 1992, **114**, 6050.
5 P. Cossee, *J. Catal.*, 1964, **3**, 80.
6 J. Repp, G. Meyer, S. Paavilainen, F. E. Olsson and M. Persson, *Science*, 2006, **312**, 1196.
7 F. Mohn, J. Repp, L. Gross, G. Meyer, M. S. Dyer and M. Persson, *Phys. Rev. Lett.*, 2010, **105**, 266102.
8 W. H. Soe, C. Manzano, N. Renaud, P. de Mendoza, A. De Sarkar, F. Ample, M. Hliwa, A. M. Echavarren, N. Chandrasekhar and C. Joachim, *ACS Nano*, 2011, **5**, 1436.
9 W. H. Soe, C. Manzano, A. De Sarkar, F. Ample, N. Chandrasekhar, N. Renaud, P. de Mendoza, A. M. Echavarren, M. Hliwa and C. Joachim, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **83**, 155443.
10 C. Manzano, W. H. Soe, M. Hliwa, M. Grisolia, H. S. Wong and C. Joachim, *Chem. Phys. Lett.*, 2013, **587**, 35.
11 T. Kumagai, F. Hanke, S. Gawinkowski, J. Sharp, K. Kotsis, J. Waluk, M. Persson and L. Grill, *Nat. Chem.*, 2014, **6**, 41.
12 C. J. Villagómez, T. Sasaki, J. M. Tour and L. Grill, *J. Am. Chem. Soc.*, 2010, **132**, 16848.
13 W. Wang, X. Shi, S. Wang, M. A. Van Hove and N. Lin, *J. Am. Chem. Soc.*, 2011, **133**, 13264.
14 S. Haq, F. Hanke, M. S. Dyer, M. Persson, P. Iavicoli, D. B. Amabilino and R. Raval, *J. Am. Chem. Soc.*, 2011, **133**, 12031.
15 M. Di Giovannantonio, M. El Garah, J. Lipton-Duffin, V. Meunier, L. Cardenas, Y. Fagot Revurat, A. Cossaro, A. Verdini, D. F. Perepichka and F. Rosei, *et al.*, *ACS Nano*, 2013, **7**, 8190.
16 K. H. Chung, B. G. Koo, H. Kim, J. K. Yoon, J. H. Kim, Y. K. Kwon and S. J. Kahng, *Phys. Chem. Chem. Phys.*, 2012, **14**, 7304.
17 H. Walch, R. Gutzler, T. Sirtl, G. Eder and M. Lackinger, *J. Phys. Chem. C*, 2010, **114**, 12604.
18 Q. Fan, C. Wang, Y. Han, J. Zhu, W. Hieringer, J. Kuttner, G. Hilt and J. M. Gottfried, *Angew. Chem., Int. Ed.*, 2013, **52**, 4668.
19 E. A. Lewis, C. J. Murphy, M. L. Liriano and E. C. H. Sykes, *Chem. Commun.*, 2014, **50**, 1006.
20 F. Besenbacher, *Rep. Prog. Phys.*, 1996, **59**, 1737.
21 E. Lægsgaard, L. Osterlund, P. Thostrup, P. B. Rasmussen, I. Stensgaard and F. Besenbacher, *Rev. Sci. Instrum.*, 2001, **72**, 3537.
22 G. Kresse and J. Hafner, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1993, **48**, 13115.
23 G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 11169.
24 P. E. Blöchl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 17953.
25 G. Kresse and D. Joubert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 1758.
26 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
27 S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787.
28 J. Tersoff and D. R. Hamann, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1985, **31**, 805.
29 C. C. Perry, S. Haq, B. G. Frederick and N. V. Richardson, *Surf. Sci.*, 1998, **409**, 512.
30 P. Liljeroth, I. Swart, S. Paavilainen, J. Repp and G. Meyer, *Nano Lett.*, 2010, **10**, 2475.