

## Bottom-up Assembly of Molecular Wagons on a Surface

Carlos J. Villagómez,<sup>†,‡</sup> Takashi Sasaki,<sup>§</sup> James M. Tour,<sup>\*,§</sup> and Leonhard Grill<sup>\*,†,‡</sup>

*Physics Department, Freie Universität Berlin, 14195 Berlin, Germany, Fritz-Haber-Institut of the Max-Planck Society, 14195 Berlin, Germany, Department of Chemistry and Mechanical Engineering and Materials Science, Rice University, Houston, Texas 77005, United States*

Received July 9, 2010; E-mail: tour@rice.edu and; lgr@fhi-berlin.mpg.de

**Abstract:** The bottom-up assembly of molecular building blocks, carrying specific functions, is a promising strategy for the construction of nanomachines. In this study we show how molecules with a mechanical function, i.e., being equipped with wheels, can be connected in a controlled way directly on a surface. By choosing suitable building blocks, assembled dimers and wagon trains can be formed, whereas the length of the chains can be limited by using a heterogeneous mixture of molecules. By using low temperature scanning tunneling microscopy, the chemical nature of the intermolecular connection is determined as a metal–ligand bond, which is stable enough to maintain the wagon train structure at room temperature. The intermolecular bonds can be controllably changed from *trans* to *cis* configurations thereby achieving bond angles of almost 90°.

### Introduction

A central goal in nanotechnology is to create mechanical components,<sup>1</sup> machines,<sup>2</sup> and electronics devices<sup>3</sup> by using individual functional components as building blocks for the assembly of larger machines or circuits with complex functions that can be addressed by external stimuli. These machines need to be constructed with high precision and thus a well-defined chemical structure, containing various individual groups that carry out specific actions of a component or a complete machine equivalent to the macroscopic counterpart. Molecules represent suitable units for such a challenge, in particular because of their recognition ability to selectively form intermolecular bonds at specific locations.<sup>4</sup> Such entities ideally follow the bottom-up approach and are synthesized to operate as motors, switches, shuttles, barrows, or wheels.<sup>1,5</sup> The realization of such molecular machines represents a scientific challenge and is thus the subject of intensive research, for instance in the field of nanovehicles that contain several functional components.<sup>6</sup> This concerns on the one hand organic chemistry—design and synthesis of these machines—and on the other hand experimental physics—the characterization and control of these devices with high spatial resolution at the single molecule level—and thus suggests an interdisciplinary approach. Scanning tunneling microscopy (STM) is probably the most suitable tool for such a task because it permits both visualization and manipulation of single mol-

ecules on a surface, thereby permitting a means to operate individual functional ensembles.

Most of the proposed chemical structures for molecular machines are huge, which renders the deposition under ultrahigh vacuum (UHV) conditions complicated. Using thermal sublimation techniques, such molecules are easily fragmented in the deposition step, as the heating temperature required for an efficient vapor pressure is high.<sup>7</sup> This temperature range can be extended by sublimation from a filament instead of a crucible.<sup>8</sup> Although fragments have been observed to react on a surface to form small assemblies, they do not restore the initial structure.<sup>9</sup> The use of other deposition techniques such as pulse injection<sup>10</sup> or electrospray techniques<sup>11</sup> holds the disadvantage of the simultaneous deposition of solvent and thus complicates the purity of the molecules of interest on the surface. Hence, an attractive route toward the construction of large and sophisticated molecular systems with specific functions is through their bottom-up assembly directly on a surface where diminutive components can be directly volatilized and thereby deposited, followed by their assembly into large structures.

In the recent past, it was shown that supramolecular networks can be formed in a reliable way by using various intermolecular interactions.<sup>12</sup> However, the necessary stability of molecular machines requires rather strong and thus covalent bonds between the molecular building blocks. This could be metal–ligand

<sup>†</sup> Freie Universität Berlin.

<sup>‡</sup> Fritz-Haber-Institut of the Max-Planck Society.

<sup>§</sup> Rice University.

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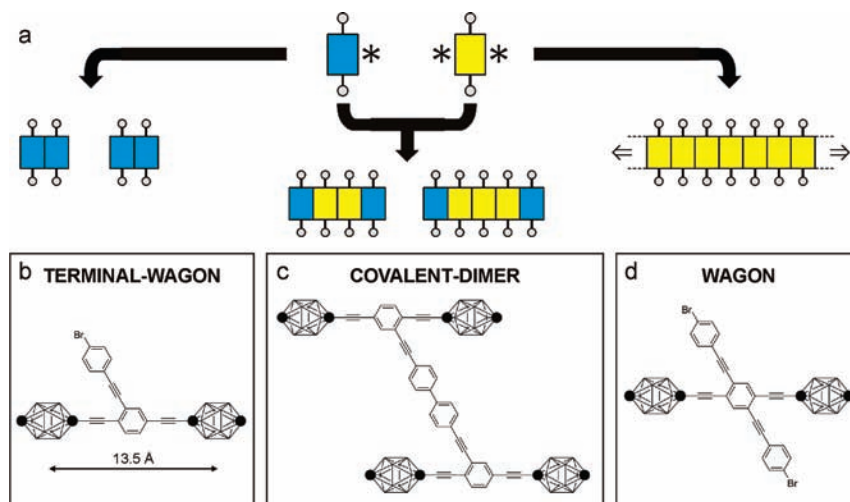
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**Figure 1.** (a) Concept of the construction of dimers (left), short trains (by mixing terminal-wagons and wagons; center), and long wagon trains (right) on a Cu(111) surface by bottom-up assembly of individual molecules. The building blocks are equipped with either one or two available binding sites (indicated by an asterisk) and are therefore named “terminal-wagons” (blue rectangles) and “wagons” (yellow rectangles), respectively. The use of only one building block leads to homogeneous structures (dimers of two (blue) molecules or long chains of (yellow) wagons, respectively), while the mixture of two building blocks allows for the formation of heterogeneous structures and chains with restricted length. (b–d) Chemical structures of the three molecules used: terminal-wagons, covalent-dimers, and wagons. The molecules are supplied with “wheels” of *p*-carborane, which have BH at every intersection except at the points denoted by •, representing C and CH at positions ipso and para, respectively.

bonds<sup>13</sup> or, with higher stability, carbon–carbon bonds, which have even permitted the lifting of the assemblies far off the surface.<sup>14</sup> In this work, we show how molecules with a potential mechanical function, molecular wheels attached to a central platform, can be chemically assembled on a surface to build dimers and trains of wagons. Homo- and heterogeneous mixtures of different molecular building blocks lead to predetermined ensembles and thus underscore the control of the process.

Typically, hopping of molecules occurs when they are directed by STM manipulation on a surface. However, in analogy to the macroscopic case, a rolling motion is advantageous for two reasons: (1) It is directional even on a flat surface, where hopping motion can occur in any direction toward the next adsorption site. (2) Rolling might be more suitable to overcome atomic-scale obstacles than hopping. Thus, the development of nanoscale “vehicles” is of great interest.<sup>6</sup> The characteristic current signal of a rolling motion during STM manipulation has been reported for simple molecular triptycene wheels connected in dimers.<sup>15</sup> The slight corrugation of the copper surface represents an important prerequisite for the rolling, as only hopping motion is observed on flat surfaces under the same manipulation conditions. However, the use of spherical molecules is intuitively more promising in order to induce a rolling motion. It was shown by lateral manipulation that fullerenes can rotate during their hopping from one adsorption site to the next on a Si(100) surface.<sup>16</sup> In a next step, such spherical molecular cages were combined in a single molecule, realizing the first nanocar,<sup>17</sup> where the wheels are represented by fullerenes.

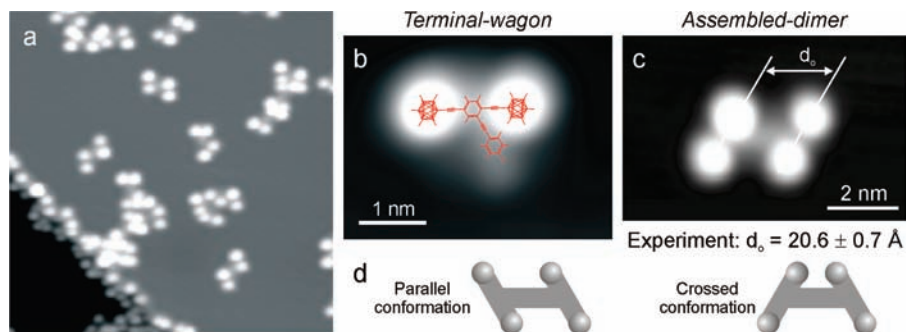
In this work, a transition is presented, starting from individual two-wheeled molecules to their controlled contiguously linked assembly. Depending on the selection of the basic building block, different assemblies should be created (Figure 1a). On the basis of our recent work concerning the on-surface-synthesis of molecules by the controlled dissociation of halogen atoms,<sup>14,18,19</sup> we used Br atoms at specific side groups of the molecules in order to enable activation and connection of the molecules at these points. The basic idea of our study is to find a way to connect such functional molecules in a stable manner, taking advantage of covalent bonds. We avoided the influence of side chains, previously attached to the molecules for enhanced solubility in the formerly studied nanocars.<sup>17</sup> In contrast to previous studies with fullerene wheels, we have used spherical *p*-carborane molecules at the periphery of the axles, which should act as rotatable wheels in a manner similar to that shown in our recent studies of carborane-wheeled nanocar movement on glass.<sup>20,21</sup>

## Experimental Details

Experiments have been performed in an ultrahigh vacuum chamber with a base pressure of  $10^{-10}$  mbar. The molecules are deposited onto clean Cu(111) and Au(111) samples that were cleaned by conventional sputtering and annealing cycles.<sup>22</sup> Images were taken with a low temperature STM (LT-STM),<sup>23</sup> running at 7 K or higher temperatures, in constant-current mode while applying a bias voltage to the sample. The molecules were prepared using standard transition-metal coupling procedures to afford the carbo-

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**Figure 2.** (a) STM image ( $28.5 \times 28.5 \text{ nm}^2$ ) of the Cu(111) surface with terminal-wagons (500 mV, 100 pA). (b) STM image of a single terminal-wagon molecule (200 mV, 100 pA), dominated by two lobes that are related to the *p*-carborane wheels. (c) STM image (500 mV, 100 pA) on Cu(111) of one assembled-dimer formed by two terminal-wagons in the parallel conformation. The characteristic parameter is the indicated axle–axle distance  $d_0$ . (d) Schemes of the parallel and crossed axle conformation.

rene-wheeled and bromide-tipped moieties essential for the later requisite surface linking. According to the design of our molecular building blocks with either one or two potentially reactive sites (Figure 1a), we are calling the monomers “terminal-wagons” and “wagons”, respectively, and the polymers “trains of wagons” or “wagon trains” for the convenience of the description. Moreover, model dimers (called covalent-dimers) were synthesized *ex situ* for comparison. All monomeric compounds were characterized by  $^{13}\text{C}$  and  $^1\text{H}$  NMR, mass spectrometry, and further by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to ensure molecular integrity at the deposition temperatures (see Supporting Information).<sup>6</sup> Sublimation temperatures of the studied molecules (see Figure 1b–d) were around 100 °C (terminal-wagons), 255 °C (covalent-dimers), and 220 °C (wagons). Molecular dimensions in the gas phase are determined by molecular mechanics calculations (HyperChem software).

## Results and Discussion

We first synthesized the so-called “terminal-wagon” molecules, which consist of a central bromide-tipped half-chassis and an axle with a carborane “wheel” at each end (Figure 1b). We had envisioned connecting these entities pairwise into molecular dimers (Figure 1a) directly on the surface. After their deposition onto a Cu(111) surface, kept at room temperature, the appearance is dominated by two intense lobes, reflecting the *p*-carborane wheels, and a weaker structure due to the central organic backbone (Figure 2a,b). The wheels appear at an average height of  $2.6 \pm 0.2 \text{ \AA}$ , which is constant for bias voltages from  $-1.5 \text{ V}$  to  $+1.5 \text{ V}$ , in contrast to  $\text{C}_{60}$  molecules with different STM contrasts for different adsorption geometries.<sup>24</sup> Although individual terminal-wagons are found on the surface, most of the molecules arrange in islands and about 16% of the molecules are found in isolated dimers, formed by two terminal-wagons (see Figure 2c), enabled by the molecular mobility at room temperature. Such a dimer of terminal-wagons, called an assembled-dimer in the following, consists of four lobes (apparent height of  $2.6 \text{ \AA}$ ) and a connection between them ( $1 \text{ \AA}$  height). The most common conformation consists of two parallel axles (as in Figure 2c). This conformation appears about four times more often than a crossed conformation (see Figure 2d), revealing the expected higher steric hindrance in the latter case. The high selectivity of this bond formation between terminal-wagons (i.e., only dimers and no trimers, tetramers, etc., are present) clearly shows that the newly formed intermolecular bond is based on the presence of the Br atoms at the

phenyl group of the terminal-wagons. This is confirmed below when more than one Br atom is used in each building block. If only weak attractive van der Waals interactions, which tend to cause close-packed structures, were the reason for the molecular assembly, this selectivity would hardly be present.

By precisely measuring the molecular dimensions, the chemical composition of the intermolecular bridge can be determined. Figure 2c shows a single assembled-dimer, where the distance  $d_0$  between the two carborane–carborane axles is found to be  $20.6 \pm 0.7 \text{ \AA}$ . Different bond types could in principle explain the assembly of the terminal-wagons. On the one hand, the dissociation of the Br atoms could lead to the formation of a covalent carbon–carbon bond (Figure 3a), according to the on-surface-synthesis process.<sup>18</sup> Moreover, it is well-known that at room temperature, copper adatoms are diffusing on the Cu(111) surface, which can be used for the formation of metal–ligand bonds.<sup>25</sup>

In the present case, this would enable the formation of either Br–Cu–Br bonds (Figure 3b), mixed C–Cu–Br bonds (Figure 3c), or C–Cu–C bonds (Figure 3d). Attractive interaction between two Br substituents seems unlikely because their electrostatic interaction would rather be repulsive (such a bond would lead to  $d_0 = 22.75 \text{ \AA}$ ). Other bonds, such as hydrogen bonds and  $\pi$ – $\pi$  stacking, can be excluded due to the chemical structure of the molecules and the adsorption geometry. These bonds lead to different characteristic distances  $d_0$  between the wheel axles of two neighboring molecules as indicated in Figure 3a–d. It turns out that only one possibility, the connection of two arenes via a copper atom (Figure 3d), is in agreement with the experimentally determined distance and hence shows that the assembled-dimers are stabilized by metal–ligand bonds. Note that spontaneous Br dissociation from the molecular building blocks upon adsorption had been expected, due to the catalytic activity of the surface, and was already observed to enable the connection of other aromatic systems.<sup>26–28</sup> This means that the formation of a carbon–carbon bond, which was expected according to the on-surface-synthesis process, is probably suppressed because copper is known to undergo

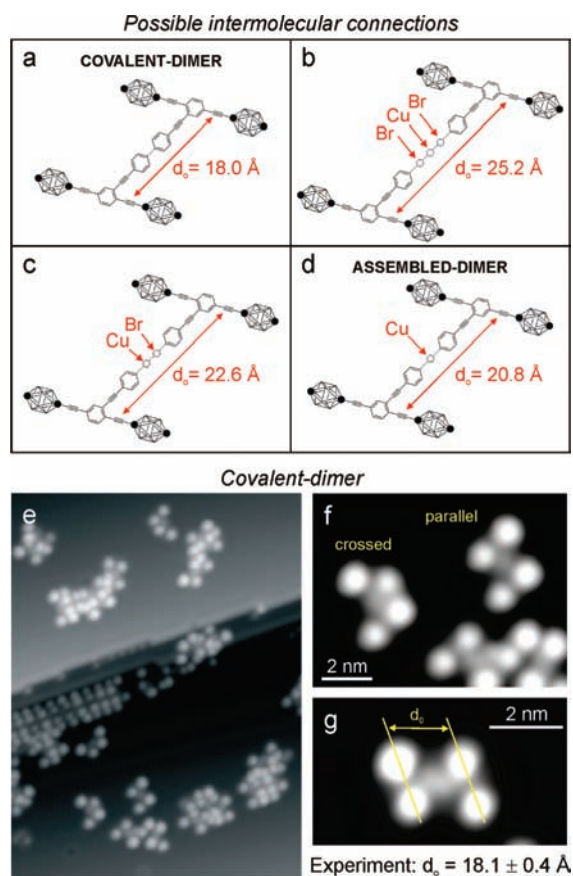
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**Figure 3.** (a–d) Axle–axle distances  $d_0$  obtained from gas phase calculations (HyperChem) for several possible intermolecular connections between the two terminal-wagons. (e) STM image ( $29 \times 38 \text{ nm}^2$ ) of the Cu(111) surface after sublimation of covalent-dimers (500 mV, 100 pA). (f) STM image (500 mV, 100 pA) of two covalent-dimers, in the crossed (left) and parallel conformation (right). These were assembled *ex situ* and deposited on the surface. (g) STM image (400 mV, 74 pA) of a single covalent-dimer, again synthesized *ex situ*, with the experimental  $d_0$  distance.

reductive elimination only when in the *cis* configuration;<sup>29</sup> in the present case these arenes about the copper atom are likely held in a *trans* configuration, due to the surface adsorption interactions and steric constraints between the two halves. Note that heating of the sample to 250 °C, which is a typical temperature to induce on-surface-synthesis on Au(111),<sup>14</sup> causes decomposition of the terminal-wagon molecules.

In order to get further insight into the chemistry of the assembled-dimers, we have synthesized *ex situ* the so-called covalent-dimers (Figure 1c), with a smaller distance between the two axles (18.0 Å from calculations) than for the assembled-dimers above. After deposition onto Cu(111) at room temperature, single molecules and clusters of molecules (preferentially indented dimers) are found (Figure 3e). Single covalent-dimers (Figure 3f) appear very similarly to the assembled-dimers above with two opposite wheels along the diagonal appearing higher (3.2 Å) than the other two (2.3 Å). The chassis is found at  $1.3 \pm 0.1 \text{ \AA}$  height. The different chemistry is reflected in the lateral dimensions, as the axle–axle distance of  $18.1 \pm 0.4 \text{ \AA}$  (Figure 3g) is shorter in the present case and fits very well to the gas-phase value of the covalent-dimer.

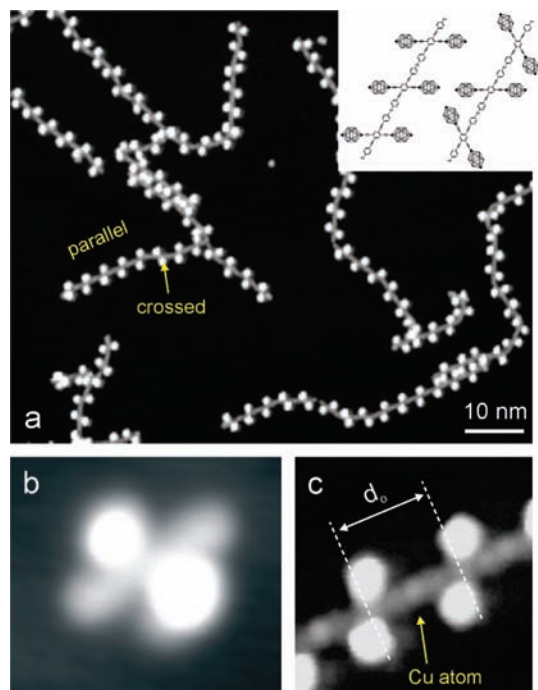
Both dimers, assembled and covalent ones, are found in parallel and crossed conformations (see Figure 2d), whereas the parallel conformation is more common, due to steric hindrance between the wheels (see Supporting Information). Interestingly, the parallel/crossed ratio is not the same for assembled-dimers and covalent-dimers. While it is around 4 for assembled-dimers, it is smaller around 2 for covalent-dimers (determined from 63 and 155 molecules, respectively). This is an interesting result because, due to the smaller wheel axle distance (18 Å), more steric hindrance and thus a larger ratio could be expected in the case of covalent-dimers. However, the covalent-dimers are synthesized *ex situ*, and the wheels probably remain just as they landed upon the surface during the deposition. On the contrary, the axle conformations of the assembled-dimers are influenced by activation energies during the surface-assembly, and hence the higher steric energy crossed-axle conformation is avoided during the assembly process. This explains the larger parallel/crossed axle conformation ratio of 4 in the assembled-dimer case. Both types of molecules, assembled and covalent-dimers, turn out to exhibit rather variable bond angles in their structure upon STM manipulation (see Supporting Information). The important difference between the two cases is that during manipulation of the covalent-dimers, no fragmentation or bond dissociation was ever observed, revealing the high stability of their chemical structure, while the assembled-dimers could be separated at the position of the metal–arene bond. Note furthermore that STM manipulation only leads to conformational changes and not to a lateral dislocation of the entire molecule. This is an indication of a rather strong molecule–substrate interaction, which hinders the motion of the entire molecule and does not enable the study of wheel rolling.

After the successful assembly of dimers from terminal-wagons, we proceed to other building blocks, wagons, which should allow the formation of extended structures. Note that a similar compound, synthesized with hydrogen bonding sites at opposite positions,<sup>30</sup> recently showed linear growth of chains, but the method did not allow resolution down to the single molecule level. In analogy to the dimer formation, our wagon molecules (Figure 1d) are designed to form long chains of molecules functionalized with wheels, namely wagon trains. According to their design, the wagon molecules spontaneously form chains after deposition of the molecules onto clean Cu(111), kept at room temperature (Figure 4a). These wagon trains are very long with a maximum length that depends on the coverage, because it changes the number of available building blocks. At 0.13 monolayers (ML), chains up to 115 nm in length (55 contiguous wagons) with an average of around 24 nm (12 contiguous wagons) were observed. At 0.07 ML, shorter chains with a maximum length of 46 nm were imaged with an average length of about 20 nm.

The assembly process is very efficient, connecting almost all available molecules, except those adsorbed at the step edges. As can be seen in the STM image (see also Supporting Information), adjacent wagons have the axles preferentially oriented in the same, parallel, direction. Alternating orientations (i.e., crossed conformations, see Figures 2d and 4a) typically lead to a curvature of the entire wagon train in contrast to the straight sections with parallel conformations. The high efficiency of this process does not allow the observation of isolated wagon molecules. This can be performed more easily on Au(111) (see

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**Figure 4.** (a) STM image (57 nm  $\times$  47 nm, 500 mV, 25 pA) of a chain assembled from wagon molecules on Cu(111). Inset: The structure on the left shows two parallel axle arrangements while that on the right shows two crossed interactions. (b) STM image (4 nm  $\times$  3.5 nm, 400 mV, 64 pA) of a single wagon adsorbed on a terrace of Au(111). (c) STM image (5 nm  $\times$  5 nm, 200 mV, 20 pA) on Cu(111) of the connection between two wagons, the characteristic distance  $d_0$  is determined as  $20.8 \pm 0.7$  Å.

below), and the corresponding STM image (Figure 4b) shows the characteristic appearance. The protrusion at the end of the chassis in Figure 4b with a height of about 1.4 Å most likely corresponds to Br substituent atoms at the ends because these are not expected to undergo oxidative addition to the Au adatoms on Au(111). Note that the sublimation of the wagons from the evaporator was performed at 220 °C and thermal analysis studies showed the bromides stable at that temperature. On Cu(111), a similar protrusion is visible at the end of the train with the same height (and the same distance from the wheel axle), where it probably reflects a Cu atom that has attached after oxidative addition of Cu into the arene–Br bond. A clearly shorter distance and lower height would be expected for a pure phenyl termination. Note that the same interpretation is valid for individual terminal-wagons (Figure 2b).

The axle distance  $d_0$  between two neighboring, connected wagons (Figure 4c) in a wagon train is found to be  $20.8 \pm 0.7$  Å, which fits perfectly to the calculated value of 20.8 Å (Figure 3d) for the assembled-dimer and confirms that here also the molecular assembly is based on the formation of metal–arene bonds, using Cu adatoms of the substrate. Note that the copper atom that bridges the two wagon building blocks can even be resolved in the STM images, due to its slightly larger apparent height (Figure 4c), while the arene–arene bond of the covalent-dimer (Figure 3g) does not exhibit such a protrusion.<sup>14</sup> It is important to note that the Cu–arene bond is rather strong (218 kJ/mol<sup>31</sup>), which is an important prerequisite for the construction of nanomachines. This causes a remarkable stability of these

structures and even allows imaging at room temperature, where wagon trains maintain their connection during thermal diffusion (see Supporting Information).

The observed formation of metal–arene bonds relies on the presence of metallic adatoms on the surface. Copper adatoms are available on Cu(111) surfaces for the formation of metal–ligand bonds at elevated temperatures above 150 K<sup>32</sup> because they continuously detach from step edges at room temperature.<sup>33</sup> When going from Cu(111) to other, less reactive, noble metal surfaces such as silver or gold, the conditions for the formation of metal–ligand bonds drastically change. Ag(110) for instance does not offer adatoms at room temperature<sup>13,34</sup> and neither does Au(111), the latter of which we therefore chose as a substrate to confirm our interpretation. The reduced reactivity also affects the interaction with organic molecules, which is typically weaker for Au(111) than for Cu(111).<sup>35</sup> Our experiments reveal that after deposition onto Au(111), the molecules form close-packed structures and do not show any signature of interconnecting in the same way as on Cu(111) (see Supporting Information). This is further evidence of the metal–arene bond on Cu(111) because adatoms are absent on Au(111). While molecular activation, i.e., dissociation of the Br atoms from the core, is not required in the case of Cu(111), because this occurs spontaneously upon adsorption as discussed above, it is necessary on Au(111) where heating to 250 °C is typically used.<sup>19</sup> However, in the present case we found that all molecules decompose when the Au(111) surface is heated to 200 °C and only fragments are found. Thus, the absence of metal adatoms on the Au(111) substrate prevents the polymerization of the molecules because the activation temperature is likely higher than the organic decomposition temperature.

Although the bond between the wagons is rather strong, it can intentionally be cleaved by STM manipulation (Figure 5a,b). Remarkably, after such a dissociation of wagon–wagon bonds, single copper atoms are observed in the vicinity of the detached wagon, that were not present formerly. Two of them are present in Figure 5b (marked by arrows) because two bonds have been broken over several manipulation steps. Their nature is determined by comparison with Cu adatoms that are artificially created by controlled indentation of the tip into the surface.<sup>36</sup> The corresponding two height profiles in Figure 5c are in perfect agreement, indicating that a Cu adatom is detached upon breaking the bond, which confirms the assignment of the wagon–wagon connections to metal–ligand bonds. Note that such Cu adatoms always appear after bond breaking but never after further lateral manipulation of the single wagon.

Deposition onto a cooled substrate (kept at about 60 K) leads to the adsorption of single molecules in a random hit-and-stick mode on the surface without any formation of assembled-dimers or wagon trains for the different terminal-wagon and wagon molecules, respectively. This shows the importance of diffusion and the need for sufficient thermal energy for the assembly process. The necessity to have Cu adatoms available could therefore not be investigated, because the cooling not only suppresses the adatom formation but also the required thermal diffusion that is required for bond formation.

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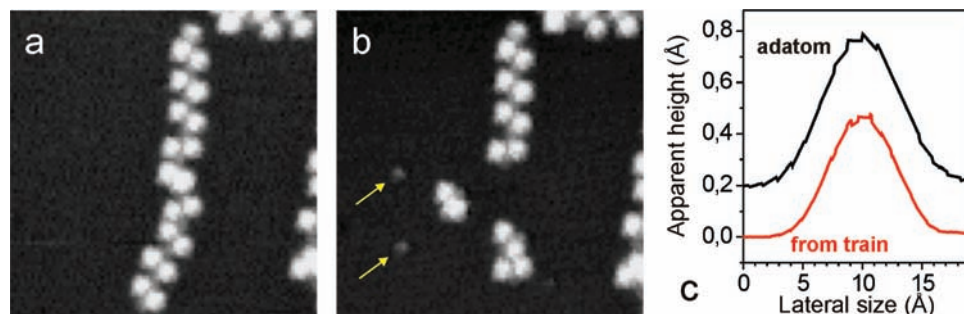
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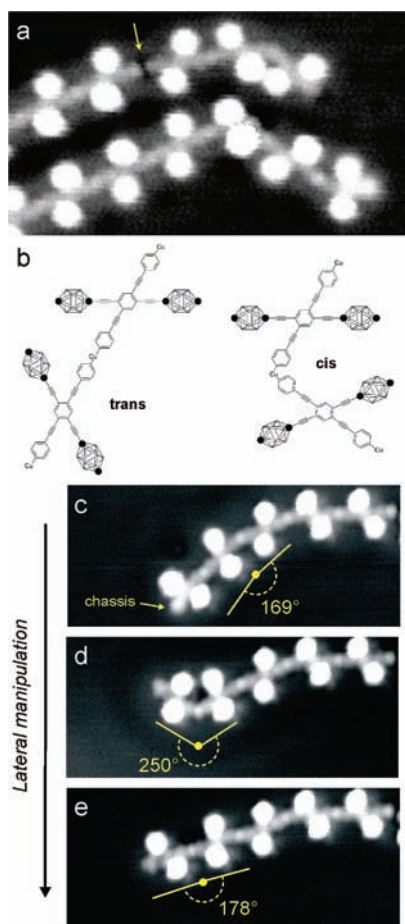
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**Figure 5.** (a, b) Lateral STM manipulation on Cu(111) between the two STM images ( $21 \text{ nm} \times 21 \text{ nm}$ ,  $500 \text{ mV}$ ,  $25 \text{ pA}$ ), causing the dissociation of a wagon train. Small protrusions, marked by arrows in b, remain from the train. (c) Height profile across one of these protrusions (lower curve) in comparison with that of Cu adatoms on the surface (upper curve), which are created by soft indentation of the STM tip into the surface. The latter curve has been shifted upward by  $0.2 \text{ \AA}$ .



**Figure 6.** Changing bond angles of the connected wagon trains on Cu(111). Some chains in the STM image (a) ( $14 \text{ nm} \times 8 \text{ nm}$ ,  $744 \text{ mV}$ ,  $27 \text{ pA}$ ) have a kink in the last wagons, reflecting a *cis* conformation. These kinks can be found anywhere within the wagon trains but preferentially close to the ends. The arrow marks a gap between two wagons (see text). (b) *Trans* and *cis* conformations of the wagon trains. (c–e) STM images ( $14 \text{ nm} \times 6 \text{ nm}$ ,  $200 \text{ mV}$ ,  $20 \text{ pA}$ ) during a lateral manipulation series of the chain revealing that it is possible to change the conformation from *trans* (linear conformation with  $\theta_1 = 169^\circ$ ) to *cis* (kinked conformation with  $\theta_1 = 250^\circ$ ) and back to *trans* ( $\theta_1 = 178^\circ$ ).

The most common arrangement of wagon trains is the parallel axle arrangement with the arenes appearing to be situated transoid about the copper atom. However, sometimes crossed axles in the wagon trains are found and even *cis* conformations about the copper junction atoms (Figure 6a). However, reductive elimination to form the arene–arene bond is likely retarded by

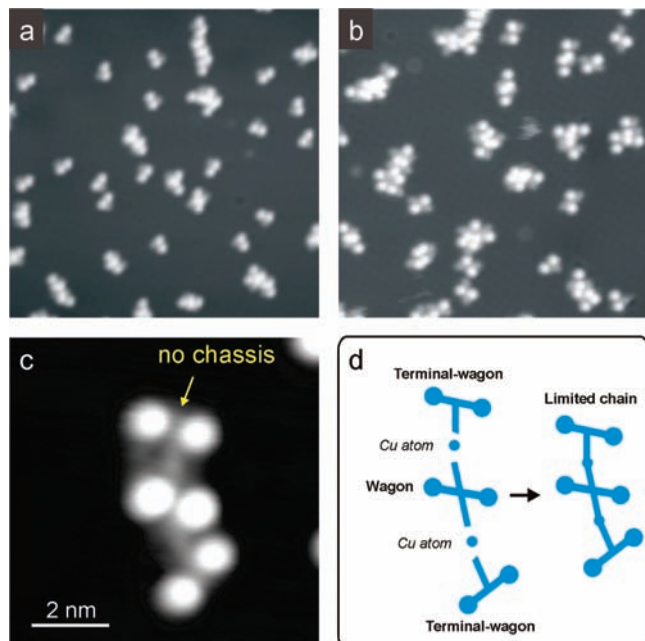
the strong surface adsorption of the ligands and the severe wheel-to-wheel steric interactions that would ensue since the units are surface-adsorbed and unable to rapidly free themselves of the steric overlap.

Note that in a few cases, a gap (i.e., depression) is found between two neighboring wagon molecules (marked by an arrow in Figure 6a). Its origin is unclear, but even though of probably different chemical composition than the arene–copper–arene and arene–arene bonds, there is obviously some attractive interaction.

Note that the *cis* conformation, due to the steric interaction between the wheels, is of considerably higher energy than the *trans* configuration (sketched in Figure 6b). In the assembled-wagons, the *cis* conformation is not observed, probably because the number of adsorbed units that need to migrate in order to ensure a transoid configuration is only two (i.e., the two halves of the assembled-dimer).

When single wagon trains are manipulated by laterally moving the STM tip across the wheels, no collective motion of the entire train, which might suggest a rolling motion of the wheels, is observed. Only very few wagons are displaced instead, due to the rather strong molecule–substrate interaction (similar to what we observed in the dimers). Through these STM-induced perturbations, the modification of the metal–arene bond angle can be studied by comparing images before and after such a manipulation. Figure 6c–e presents a series where the orientation of two neighboring wagons with respect to each other is controllably and severely modified by almost  $90^\circ$  of bond-angle change, while the other wagons in the chain remain unchanged. The achieved change from the *trans* to *cis* (and back to *trans*) configuration is sketched in Figure 6b. Note that the copper atom at the intermolecular bridge is clearly visible, representing the pivoting point of the bending, in agreement with its chemical function of linking to wagons in a wagon train. Nevertheless, the metal–arene bond is maintained. During such a manipulation series, the neighboring wagon axle conformations can even be changed between parallel and crossed without disconnecting the train, meaning that the carborane axle must have been lifted off the surface. Note that some axle orientations are not possible in a *cis* configuration, because of steric hindrance between the carborane wheels, as becomes clear from the scheme in Figure 6b.

After demonstration of the successful assembly of wheel-equipped molecules either to dimers with limited length or to long wagon trains of extended length, the consequent challenge is to control the chain length by mixing molecular building blocks (see central sketch in Figure 1a). Heterogeneous struc-



**Figure 7.** Heterogeneous assembly of wagon trains with limited length. (a) STM image ( $45.2 \times 45.2 \text{ nm}^2$ , 500 mV, 110 pA) of terminal-wagons adsorbed on a cooled Cu(111) sample, kept at about 60 K, to avoid thermal diffusion and the undesired formation of assembled-dimers. Subsequently, wagon molecules were further deposited onto this surface, kept at about 60 K. The corresponding STM image ( $32 \times 32 \text{ nm}^2$ , 500 mV, 30 pA) is shown in b. (c) STM image (500 mV, 100 pA) of the short wagon train after heating the sample to room temperature in c, the chain is composed of two terminal-wagons and one wagon in between as sketched in d. The assignment of the terminal-wagons is made by the absence of the chassis at the end (marked by an arrow in c), in accord with their chemical structure.

tures based on coordination bonds were recently grown with the intent of forming supramolecular rings.<sup>37</sup> In our study, the structures consist of functional molecules that are equipped with wheels: wagons and terminal-wagons, whereas the latter ones should “cap” the wagon trains as terminal groups.

The two species are deposited one after the other, because simultaneous deposition would not independently permit control of the two molecular fluxes from the crucible. In order to avoid assembly of the first deposited species (terminal-wagons to assembled-dimers or wagons to long chains, respectively) before the second one arrives, deposition of terminal-wagons and wagons, respectively (Figure 7a and 7b), is done onto the cooled surface, suppressing diffusion and therefore assembly.

According to the building block design, STM images after heating the sample at room temperature with both molecular species adsorbed (Figure 7c) show much shorter trains than for the deposition of only wagon molecules. Moreover, while long wagon trains, due to the chemical structure of the wagons, exhibit a protrusion at their end (Figure 6), this is not the case for terminal-wagons (Figure 2b). This difference is visible in Figure 7c, where the successful capping of a short wagon train by terminal-wagon molecules is apparent in the image as lacking

terminal protrusions, i.e., no terminal chassis is visible in contrast to the ends of the chain in Figure 6c.

The deposited ratio of wagon to terminal-wagon building blocks on the surface was about 3/5. Based on this value, a composition of two terminal-wagons interconnected by, theoretically, 1.2 wagon molecules can be assumed in a first approximation, corresponding to a train length of 4.6 nm (or about one wagon unit between two half-cars). In the experiments, an average chain length of  $5.5 \pm 1.6 \text{ nm}$  is found, which is in good agreement with the model. On the other hand, this is much shorter than the average length of 20–30 nm that was found for a train which consisted exclusively of wagon building blocks and thus confirms the successful length restriction by using a heterogeneous mixture. Although the average length is also influenced by the total coverage on the surface (as shown above), this result shows that it is possible to control the wagon train length by adding terminal-wagon molecules, which terminate the chains and limit their length. Furthermore, it demonstrates the possibility of assembling heterogeneous structures of more than one functional molecular species.

## Conclusions

In summary, we demonstrate the successful bottom-up assembly of functional molecules, equipped with carborane wheels, into stable structures on a Cu(111) surface. The relatively strong interaction between the individual units is determined as a metal–arene bond by the characteristic distance between the assembled units, their appearance in STM images, the presence of a Cu adatom after disruption, and their stability. Accordingly, deposition onto a Au(111) surface does not lead to molecular assembly, because of the lack of metallic adatoms. The assembly process could be shown for two molecular species, terminal-wagons and wagons, leading to dimers of limited length (i.e., two building blocks) or long wagon trains, respectively, as desired. Wagon trains are found in *trans* and *cis* configurations, which can also be created artificially by manipulation. Although the molecular function, i.e., rolling of the wheels, could not be demonstrated because of the high diffusion barrier on the surface, it is most likely preserved as carborane rotation around the wheel axle is presumably possible because of the very low alkyne rotational barrier. Finally, mixing of components, so that one fraction contains terminal moieties rather than bifunctional species, affords the expected short trains due to the restricted growth.

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**Supporting Information Available:** Detailed experimental procedures and characterizations of the molecular compounds and further STM images are included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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