Table of Contents

1. Supporting Figures S2-S6
2. Experimental details S7
3. Computational details S7
4. Chemical synthesis S7
5. Reference S8
Supporting Figures

Figure S1. Van der Waals representation of the two slab models.

Figure S2. Large-scale STM image of the clean Au(110)(2x1) surface before adsorption of the carbene molecules (2.0 V; 21 pA).
Figure S3. Binding motifs and binding energies of IMe adsorbed on the Au(110)(2x1) surface. Ball-and-stick model of the optimized geometries (top and side view): (A) \(A_{\text{topA}}\) (\(E_{\text{bind}}\): 1.76 eV), (B) \(A_{\text{topB}}\) (\(E_{\text{bind}}\): 1.78 eV), (C) \(A_{\text{facet}}\) (\(E_{\text{bind}}\): 1.98 eV), (D) \(A_{\text{facet}^*}\) (\(E_{\text{bind}}\): 1.92 eV), (E) \(A_{\text{trenchA}}\) (\(E_{\text{bind}}\): 1.58 eV) and (F) \(A_{\text{trenchB}}\) (\(E_{\text{bind}}\): 1.48 eV). Note that at the optimized configurations \(A_{\text{facet}^*}\) and \(A_{\text{trenchB}}\), the IMe-bound surface atom is slightly pulled out, however, no molecular ballbot is formed. (carbon: black, nitrogen: blue, hydrogen: white; for clarity cyan: gold atom bonded to the IMe in the adsorbed state (A))

Figure S4. The suppressed mobility of the NHC molecules on the Au(110) surface is confirmed by sequentially recorded STM images of the same surface area. During these four STM measurements the molecules stay in position and only some drift is observed. (-1.1 V; 23 pA).
Figure S5. Formation of the molecular ballbot. Ball-and-stick model of the optimized geometries before and after formation of the IMe–Au species together with the calculated transition energy and optimized structure (The same colour coding as in the previous figure is used. In addition, for clarity green: gold atom of the ballbot species, moving surface atom indicated by asterisks).

Figure S6. Dynamics of a molecular ballbot. Diffusion of the molecular ballbot parallel to the reconstruction of the surface (A) at the facets and (B) in the trenches. (C) Dynamics perpendicular to the reconstruction of the surface, which includes the pushing of an adjacent gold atom from the top-row position. Both the calculated transition energy and the optimized structures are depicted (The same color coding as in the previous figure is used. In addition, for clarity violet: gold atom moved into the trench, red arrow: calculated path of the on-surface dynamics).
Figure S7. STM images showing three further examples of IMe-induced defects in the Au(110) (2x1) surface. (A) Low coverage, 0 hours at RT, -1.0 V, 30 pA; B) Low coverage, 95 hours at RT, -1.2 V, 30 pA; C) Middle coverage, 0 hours at RT, -1.0 V, 21 pA.

Figure S8. Energy profile calculated for the induced zipper-type restructuring of the extended slab model. The same labelling as in the main text is used.

Figure S9. Formation of Au nanorods by the zipper-type restructuring. A) STM image showing the long range over which the newly formed (3x1)-AR trenches run. They can even extend over step edges by forming nanorods protruding from the step edge. (Low coverage, 95 hours at RT, -1.2 V, 30 pA) B) STM image showing a further example of the typical zipper structure at places where the original (2x1) reconstruction transforms in the (3x1)-AR trenches. (Middle coverage, 125 hours at RT, -2.0 V, 21 pA).
Figure S10. Additional STM-images confirming that the restructuring of the surface occurs on surface terraces. (-2.0 V; 28 and 26 pA respectively).

Figure S11: Schematic representation of the adsorption sites employed to analyze the STM images in Figure 4 of the main text (blue square: Atop, green circle: Abridge and yellow triangle: IMe-Au species in the trench of Au(110)(3x1)(AR)).

Figure S12: Analysis (including the statistical error) of the distribution over the three adsorption positions as a function of time at RT for the middle coverage sample (a) and as a function of coverage (b).
2. STM experiments

The STM experiments are performed in a low-temperature STM (Createc LT-STM) with a base pressure of 1x10⁻¹⁰ mbar. The Au(110) surface was cleaned by several cycles of Argon ion sputtering and subsequent annealing. This resulted in a clear (2x1) reconstructed surface with a measured distance of 0.79±0.02 nm between the trenches. IMe was deposited from a quartz crucible at 50 °C onto the metal surface held at room temperature for 1 minute (low coverage, 0.09 mol/nm²), 3 minutes (middle coverage, 0.26 mol/nm²) and 6 minutes (high coverage, 0.42 mol/nm²). Within 5-10 minutes after deposition the samples are transferred to the cold (77 K) STM for inspection. Afterwards, the samples are kept inside the vacuum at room temperature and measured again after certain times. All measurements are recorded in constant-current topography mode. The bias voltage is always given with respect to the sample. For every data point in the statistical analysis at least three STM images from different areas of the surface are used. Depending on the coverage of the sample and the available image size the total amount of counted molecules per data point is 700-9000.

3. Computational Details:

The software package VASP code [1] was used in combination with projector-augmented-wave-based pseudopotentials [2] to performed in the framework of periodic density functional theory (DFT) the atomistic calculations. Local correlation was described with the Local-density approximation (LDA), whereas all nonlocal correlation effects were treated with the van der Waals density functional known as vdW-DF. [3] The optPBE GGA-type functional [4] was used for the exchange energy. The energy cut-off was set to 400 eV. The Au(110) surface was modelled by two periodic slab model as shown in Figure S1. The bottom two layers were kept fix at the optimized bulk position. A 4x4x1 K-mesh was used for the small (Figure S1a) and a 1x1x1 K-mesh for the extended slab model (Figure S1a) calculations, respectively. Molecules are adsorbed on one side of the slab and dipole corrections to the energy are carried out accordingly. Ionic relaxation for all stable structures was carried out until all forces were smaller than 20 meV/Å. The transition states for the indicated dynamics of the carbene species at the Au surface were determined by the nudged elastic band climbing image method. [5]

4. Molecules Synthesis:

All reactions were carried out in oven-dried glassware under an atmosphere of argon. Dry solvents (<50 ppm H₂O) were purchased from Acros Organics, Sigma-Aldrich or Carl Roth and stored over molecular sieves under argon atmosphere. Commercially available chemicals were obtained from Acros Organics, Sigma-Aldrich, Alfa Aesar, ABCR, TCI Europe, Combi-Blocks, Johnson-Matthey and Heraeus and used as received unless otherwise stated. ¹H and ¹³C NMR spectra were recorded at room temperature on a Bruker AV 300 or AV 400 and Agilent 600 (DD2). Chemical shifts (δ) were given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale.

**Synthesis of 1,3-bis(dimethyl)imidazolium-2-carboxylate – Ime:** According to a procedure by Andrieu et al. [6] N-Methylimidazole (400 µL, 5.00 mmol, 1.0 equiv) and dimethylcarbonate (840 µL, 10.0 mmol, 2.0 equiv) were heated in dry methanol (5 mL) at 140 °C overnight using a microwave. The solution was cooled down to room temperature, evaporated and the residue was washed with dry Et₂O (3 x 10 mL) and dried in high vacuum to yield a white solid (426 mg, 3.03 mmol, 61 %). NOTE: This reaction builds up a high pressure during the reaction. We measured a peak pressure of around 15 bar. Take PRECAUTION and perform this reaction ONLY in a suitable pressure vial. ¹H NMR (300 MHz, D₂O): δ = 7.36 (s, 2H), 3.97 (s, 6H). ¹³C NMR (75 MHz, D₂O): δ = 158.7, 140.9, 122.4, 36.7.
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