

Electronic Supplementary Information (ESI)

N-Heterocyclic carbenes on the close packed coinage metal surfaces: Bis-carbene metal adatom bonding scheme of monolayer films on Au, Ag and Cu

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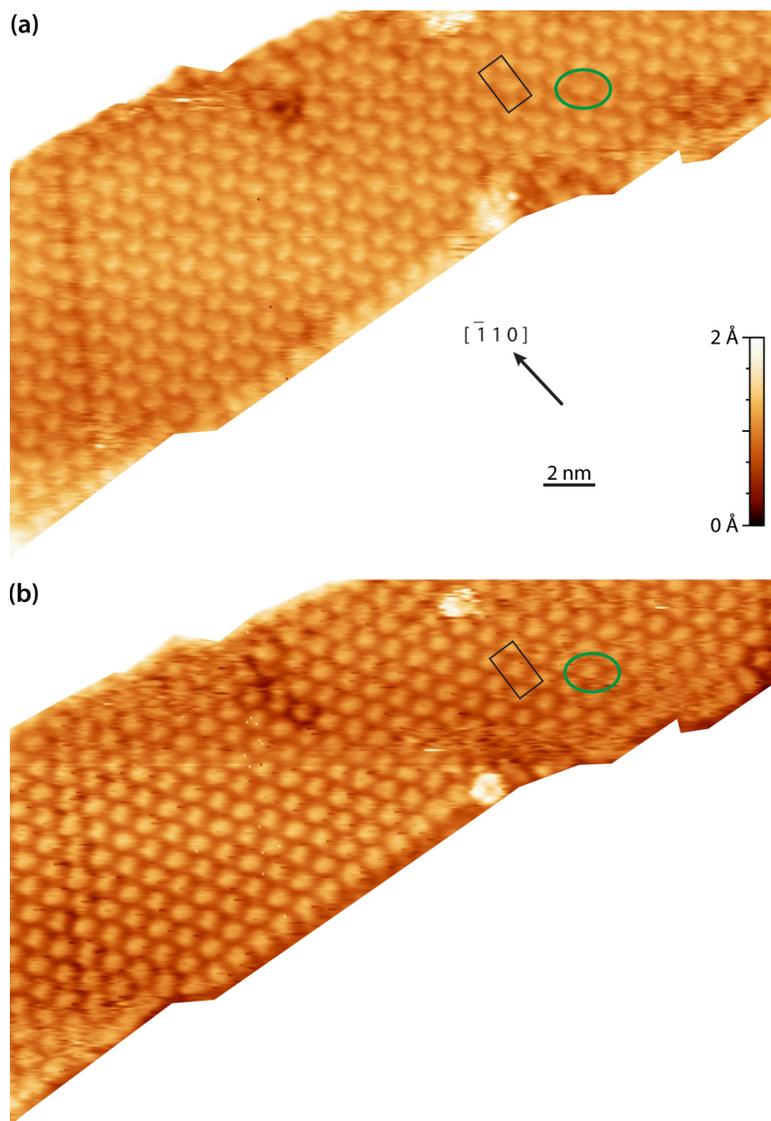


Figure S1: Consecutive STM images of Cu(IMe)_2 on Cu(111) revealing different imaging of the Cu(IMe)_2 units. (a) In Cu(IMe)_2 (example circled in green), the IMe moieties are imaged. Note that the lateral resolution does not allow a clear distinction of the two IMe in the same complex at this scale. The high symmetry axis of the substrate and the unit cell are indicated. ($T_{\text{STM}} = 98 \text{ K}$, $I_t = 0.08 \text{ nA}$, $U_s = -1.58 \text{ V}$) (b) Here each complex (example circled in green) is imaged as a more bright and round protrusion centered at the Cu atom of the complex. ($T_{\text{STM}} = 98 \text{ K}$, $I_t = 0.09 \text{ nA}$, $U_s = -1.58 \text{ V}$)

Atom density on the reconstructed Au(111)

The nearest neighbour separation on the face centred cubic Au single crystal crystal is 2.88 \AA . The herringbone reconstruction is created by a compression of the 23 atoms of the surface layer to 22 atoms of the underlying atomic layer along a surface high symmetry axis. This gives rise to the herringbone

reconstruction periodicity of $22 \times 2.88 = 63.34 \text{ \AA}$ and the surface layer has 2 extra atoms every $63.34 \times 2.88 \times \sqrt{3} \text{ \AA}^2$. When we observe a reduction in the periodicity of the herringbone reconstruction to $\sim 71 \text{ \AA}$, the surface layer has 2 extra atoms per $71 \times 2.88 \times \sqrt{3} \text{ \AA}^2$. The difference of the extra atoms (1 atom per 1464 \AA^2) is ejected as adatoms. For an area of $300 \times 300 \text{ \AA}^2$ (which is the area of the STM image in Fig. 4a) this difference corresponds to ~ 61 ejected Au atoms. Assuming these are forming a circular close packed island with a density of 1 atom per $2.88 \times 2.88 \sin 60^\circ$, the diameter of this island would be $2\sqrt{61 \times 2.88 \times 2.88 \sin 60^\circ / \pi} = 2.4 \text{ \AA}$.

Further results from the DFT calculations

We obtained the following values for the work function of the surfaces:

Clean Au(111) surface: 5.47 eV

Au(111) with two ad-atoms in the cell: 5.29 eV

Two Au(IMe)₂ in the cell: 3.26 eV

Two Au(IMe) in the cell: 3.76 eV

One Au(IMe)₂ and one ad-atom in the cell: 4.00 eV

The adsorption and formation of Au(IMe)₂ and Au(IMe) thus decrease the work function, hinting at a transfer of electrons from the adsorbates to the substrate.

The Au 4f core-level binding energies was calculated using the VASP code.¹ An Au atom in the middle of the slab, representing the bulk, was used as the reference. The Au 4f of the surface atoms are shifted to lower binding energies by 0.3 eV. Without the adsorbate the Au 4f of the ad-atoms is less bound by 0.9 eV. In the Au(IMe)₂ complexes the 4f of the Au atoms shift by 1.0 eV to stronger binding.

References

1. G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15–50.