Supporting Information

for

Scanning Tunneling Microscopy Study of the Structure and Interaction between Carbon Monoxide and Hydrogen on the Ru(0001) Surface

Barbara A. J. Lechner,[1,i] Xiaofeng Feng,[1,ii] Peter J. Feibelman,[2] Jorge I. Cerdá,[3] and Miquel Salmeron[,1]*

[1] Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

[2] 1401 Sigma Chi Road NE, Albuquerque, NM 87106, USA

[3] Instituto de Ciencia de Materiales de Madrid, ICMM-CSIC, Cantoblanco, 28049 Madrid, Spain

* mbsalmeron@lbl.gov

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[i] Present address: Chair of Physical Chemistry, Department of Chemistry, Technical University of Munich, Lichtenbergstr. 4, 85748 Garching, Germany

[ii] Present address: Department of Physics, University of Central Florida, Orlando, FL 32816, USA

1) Evidence for the presence of hydrogen in the triangular island phase

When keeping a sample inside a cryostat held at 77 K, such as in our low temperature STM experiments presented here, contaminations by background gas – in particular CO and H_2 – and molecules released from the cryostat walls need to be taken into account. At 77 K, the cryostat walls act as a reservoir of previously dosed gas which can be released with time or when a new dosing cycle induces replacement reactions on the Au-coated Cu walls. A mass scan during dosing of CO into the cryostat held at 77 K showed a rise in both the m/q = 28 and the m/q = 2 signal, thus indicating exposure of the sample to CO and H_2 simultaneously. Only when cooled below 17 K (with liquid helium), the pumping effect of the cryostat is sufficient to prevent hydrogen contamination of a reactive surface.[1] Reference experiments comparing exposure of Ru(0001) to CO inside the cryostat cooled with liquid helium and with liquid nitrogen, respectively, confirmed that pure CO structures (see Fig. S1) can be obtained inside a 4 K cryostat while the initial surface always contains H adatoms when prepared inside a 77 K cryostat. The H adatoms can be removed by subsequent annealing to 300 K.

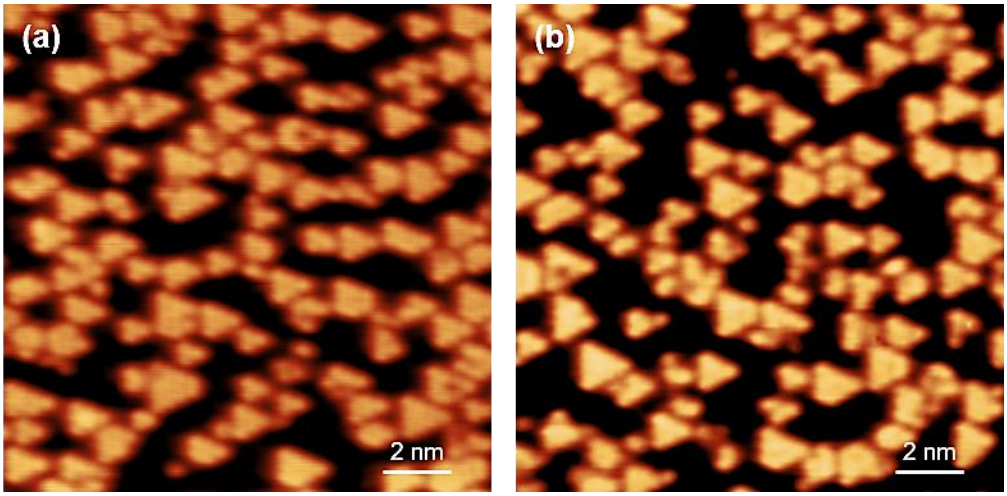

Figure S1: To confirm the (1×1) background between the CO islands is covered with hydrogen, we prepared the triangular island phase by co-depositing CO and H_2 at 77 K and subsequent annealing to 150 K to obtain the triangular island phase (a). We then dosed the same amount of H_2 that we used to obtain the (1×1)-H structure shown in Fig. 1f onto this sample at 77 K (b). No significant difference of the surface before and after depositing additional H_2 is observed. Notably, the distinct lack of hydrogen vacancies on the surface after exposure to H_2 at 77 K confirms that the area between the CO islands had already been covered in hydrogen and thus no further dissociative adsorption took place. *Imaging parameters:* (a) I_t = 15 pA, V_b = 303 mV; (b) I_t = 16 pA, V_b = 307 mV.

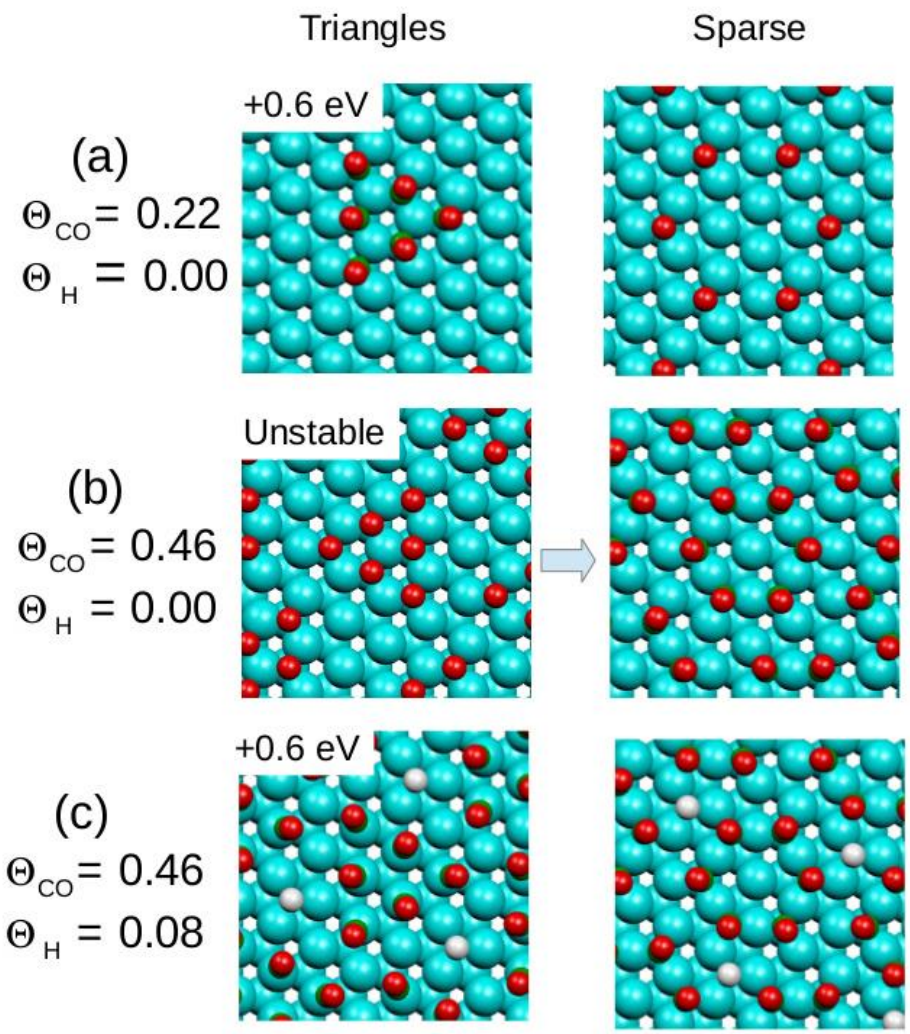

Figure S2: Comparison between triangular packed (left column) and sparse (right column) CO arrangements. (a) Low CO coverage $(3\sqrt{3}\times3\sqrt{3})$R30°-6CO structures. The most favorable triangular phase (all COs at *hcp* sites with the center of the triangle at an *fcc* site) is 0.6 eV less favorable than if the COs are shifted away from each other. In the latter case, the nearest neighbor (NN) CO–CO distance is $\sqrt{3}a_{Ru}$. (b) Same as (a) but for a larger CO coverage, $(\sqrt{13}\times\sqrt{13})$R13.9°-6CO. Here, the 6CO triangle centered at a *top* site and with all molecules at *fcc* sites relaxes towards the sparse structure on the right, with a NN distance of $2/3\sqrt{3}a_{Ru}$. Again, the sparse arrangement becomes much more favorable than any of the metastable triangular geometries. (c) The same sparse geometry as in (b) still remains much more favorable after adding a H atom in the unit cell (in particular, it is 0.6 eV more stable than the *hcp* centered triangle with all COs at *top* sites). These results clearly indicate that compact triangular CO motifs should hardly appear at low (or zero) H coverages.

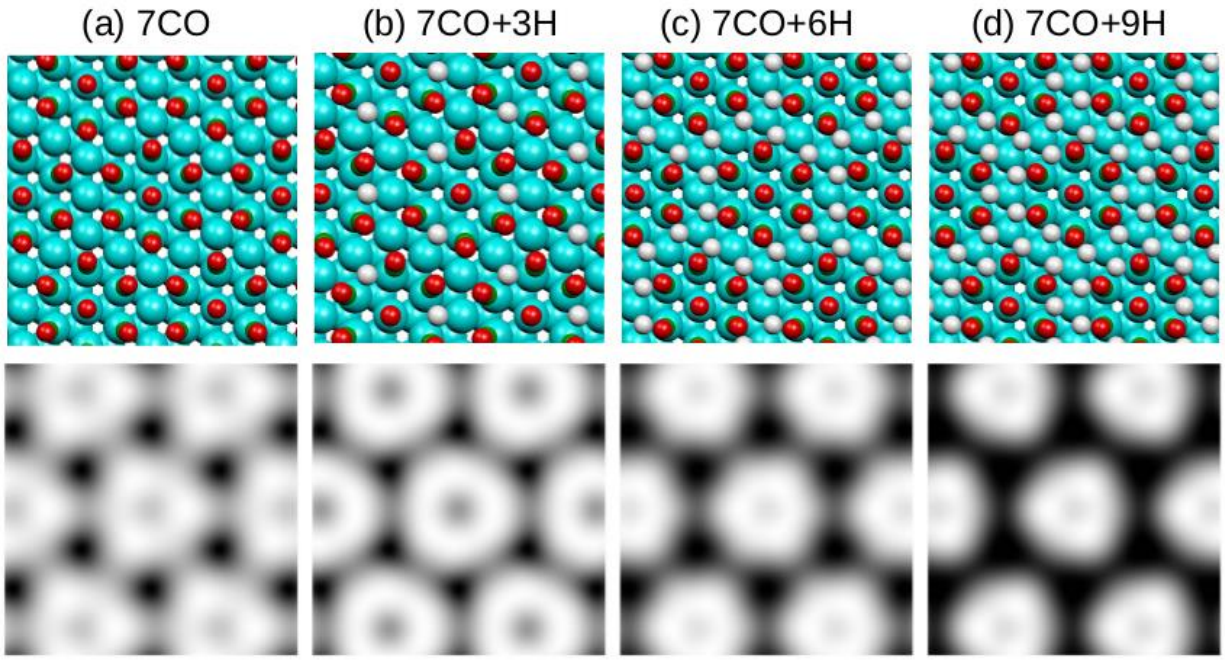

Figure S3: Top view (top row) of the relaxed geometry and STM simulation (bottom row) for the Ru(0001)-$(2\sqrt{3}\times2\sqrt{3})$R30°-7CO structure. (a) Assuming a pure CO phase with all C atoms close to *top* sites. Due to symmetry arguments the central CO lies vertical while the intermolecular repulsion shifts the surrounding 6 COs radially away from the central CO so that they end up tilted by around 10°. Notice that from the STM image alone (obtained with a metallic tip) one cannot infer the actual coverage and structure of this phase since the overlap between the molecular orbitals hinders the resolution. The remainder of the columns correspond to the same phase but after adding (b) 3 H, (c) 6 H and (d) 9 H atoms. In comparison with the top inset in Fig. 1(e), the agreement is excellent for case (a), but progressively worsens as the H coverage is increased.

2) Periodic arrays of islands

Some of the STM experiments showed periodically arranged CO islands on parts of the surface, such as in Fig. S4, where the surface was annealed to 300 K and cooled back down before all hydrogen was desorbed. Measuring the inter-island distances and angles with respect to the substrate lattice, we find an array of 6CO triangular islands with a $(\sqrt{13}\times\sqrt{13})$R13.9° unit cell ($\Theta_{CO}$ = 0.46 ML) and a 9CO truncated triangular structure (one apex molecule missing) with a $(3\sqrt{3}\times\sqrt{13})$R13.9° unit cell ($\Theta_{CO}$ = 0.48 ML). We based the unit cells for the DFT calculations on these experimental results to ensure that the interaction with neighboring islands is similar to that found in the experiments.

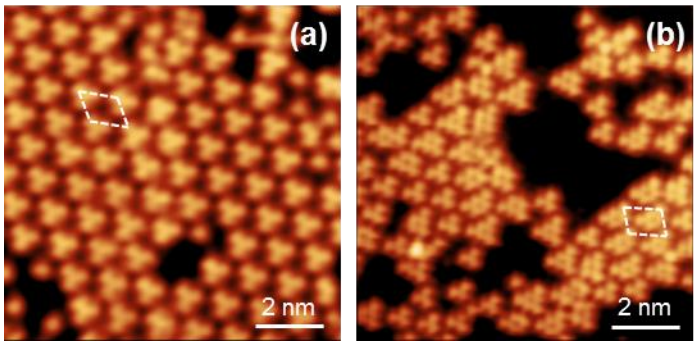

Figure S4: After partial hydrogen desorption, the CO molecules can form a periodic array of islands. By measuring the average distance between the islands and the angle compared to the Ru(0001) lattice measured before dosing adsorbates, we determined (a) the $(\sqrt{13}\times\sqrt{13})$R13.9°-6CO and (b) the $(3\sqrt{3}\times\sqrt{13})$R13.9°-9CO unit cell (see dashed white lines). *Imaging parameters:* (a) I_t = 63 pA, V_b = 50 mV; (b) I_t = 75 pA, V_b = 103 mV.

3) Structure of the islands

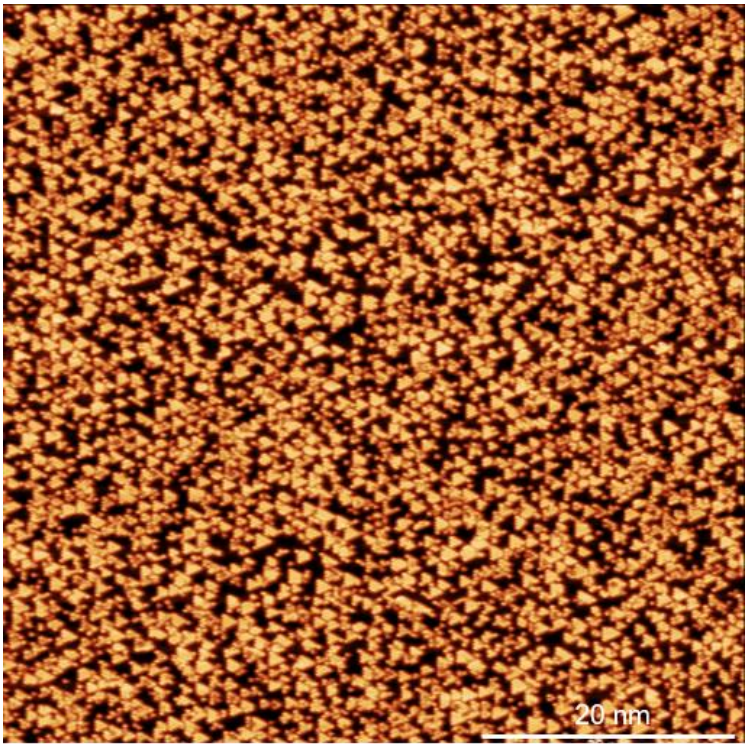

Figure S5: Large-scale image of a Ru(0001) terrace covered in the mixed CO+H triangular island structure, confirming that the adsorbates are evenly distributed on the surface and the island orientation remains the same across a 100×100 nm^2 area. *Imaging parameters*: I_t = 50 pA, V_b = 52 mV.

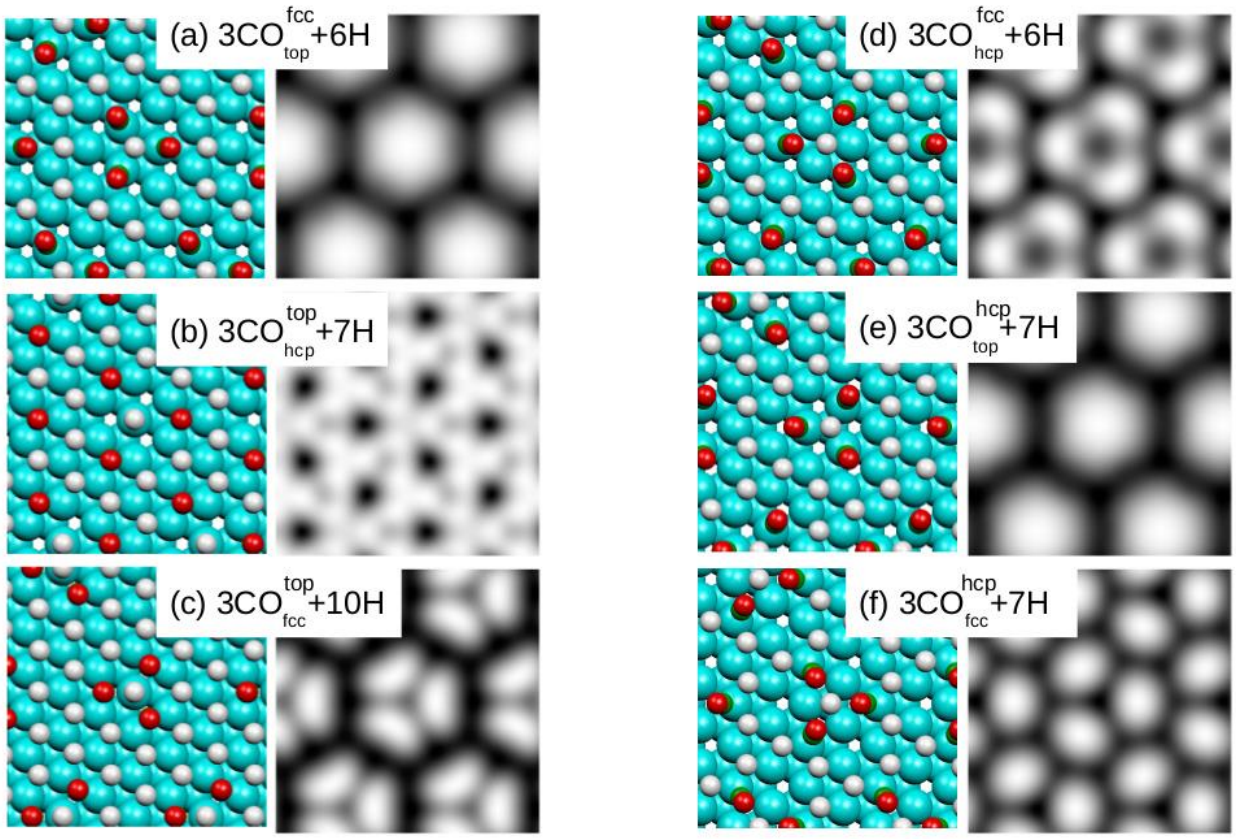

Figure S6: Top view (left panels) of the relaxed geometries and STM simulations (right panels) for the same Ru(0001)-(2√3×2√3)R30°-3CO+nH model structures of Fig. 4, but after adding an H atom at the triangle's epicenter, giving (a) $3CO^{fcc}_{top}$+6H, (b) $3CO^{top}_{hcp}$+7H, (c) $3CO^{top}_{fcc}$+10H, (d) $3CO^{fcc}_{hcp}$+6H, (e) $3CO^{hcp}_{top}$+7H, and (f) $3CO^{hcp}_{fcc}$+7H (see main text for the nomenclature employed to denote the structures). Note that in (b) the CO molecules shift from the *hcp* sites (where they were originally placed) towards adjacent *fcc* sites in order to reduce the repulsion with the added H. In (f) 3 Hs have been removed with respect to the equivalent model in Fig. 4. Clearly, none of the simulated images resembles the aspect of the triangular islands observed experimentally, ruling out the presence of any hydrogen inside the triangular islands.

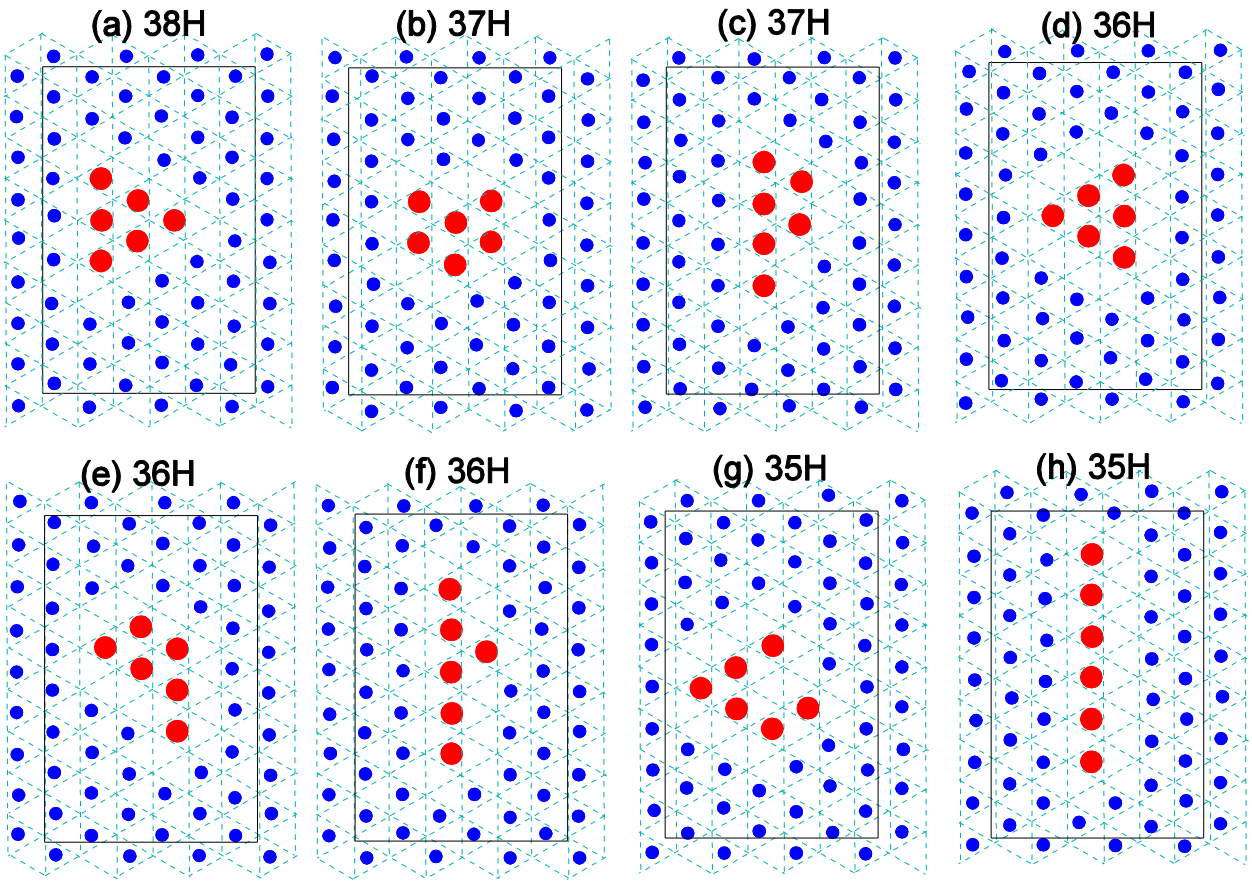

Figure S7: Sketches of different $6CO_{hcp}$ islands surrounded by a H-(1×1) background. In all of them, the same rectangular supercell containing 48 Ru atoms has been considered with all *fcc* sites assumed to be occupied by Hs except those residing closer than $4/3a_{Ru}$ to any CO molecule, which are left empty. The number of hydrogen atoms surrounding the different island shapes varies: (a) 38H, (b-c) 37H, (d-f) 36H, and (g-h) 35H. Clearly, our deduced $6CO_{hcp}^{fcc}$ triangular configuration (panel (a)) maximizes the number of H atoms in the unit cell and, hence, corresponds to the largest packing density possible. The same reasoning applies to the $3CO_{hcp}^{top}$ triangular islands (not shown).

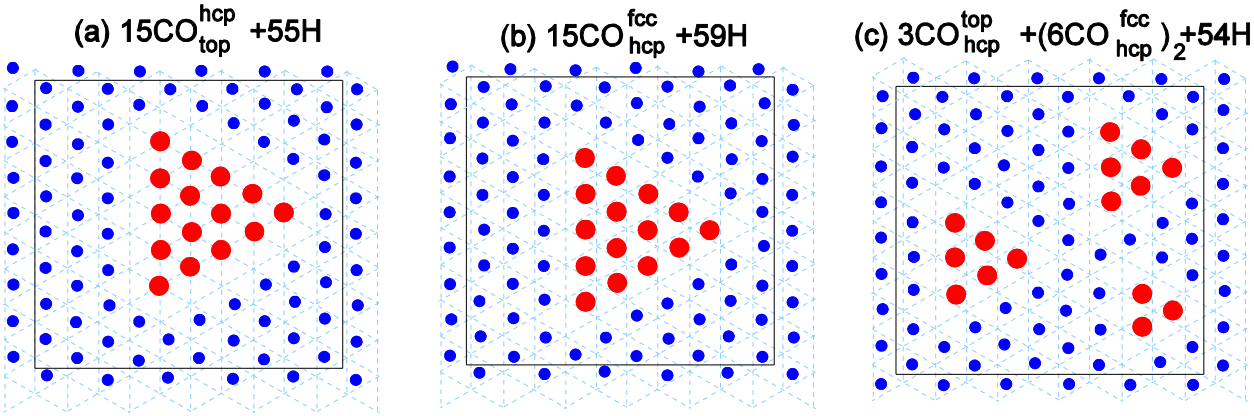

Figure S8: Sketches of an 80 Ru atom supercell containing 15 CO molecules surrounded by a H-(1×1) background under different geometries. (a) Our deduced $15CO^{hcp}_{top}$ model, which can accommodate up to 55 H adatoms. (b) A hypothetical $15CO^{fcc}_{hcp}$ triangular model based on the $6CO^{fcc}_{hcp}$ structure deduced earlier. Here, the H coverage is significantly larger than in (a), suggesting that the experimental absence of such islands is due to the large CO–CO repulsion accumulated in these large CO clusters. Recall that in the $15CO^{hcp}_{top}$case (panel (a)), and because of the large shifts and bending of the molecules moving away from each other (see main text), this repulsion is reduced and the structure can be stabilized albeit with a smaller H coverage. (c) An alternative model based on one $3CO^{top}_{hcp}$and two $6CO^{fcc}_{hcp}$ triangles shows that the number of H adatoms (H coverage) is almost the same as in (a), explaining why the three types of islands coexist on the surface, as observed experimentally.

4) Thermal stability of the islands

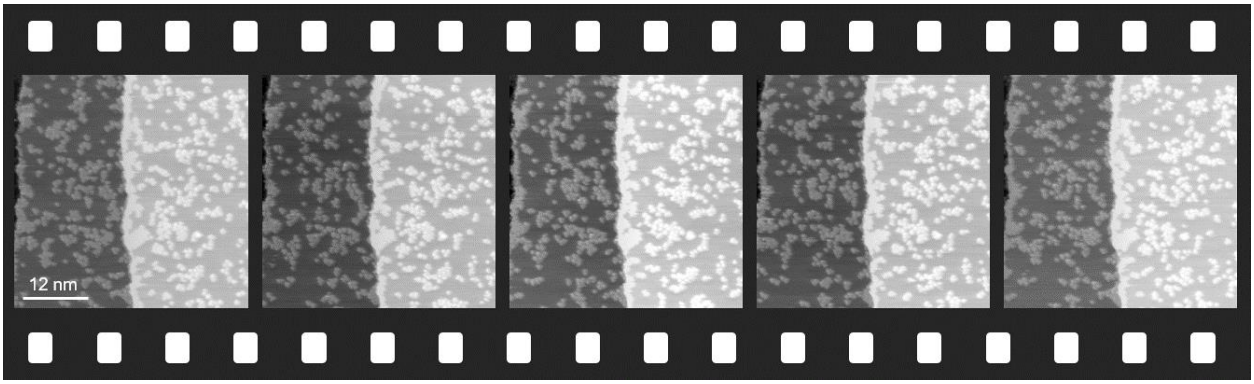

Figure S9: Consecutively recorded images of the same sample area show that even at 170 K, the CO islands retain their triangular shape and the alternating orientation, here pointing down on the left terrace and up on the right terrace. However, the islands are no longer static but instead reorder and diffuse on the terrace. The time between two images is 65 sec. Imaging parameters: I_t = 50 pA, V_b = 300 mV.

Movie S1: STM movie created from 25 consecutive images at 180 K, recorded with a rate of 15 sec/frame. The movie thus spans a total time of 6 min 30 sec. The mobility of the islands is significantly increased compared to the 170 K measurements shown in Fig. S7 and the islands are less distinctly triangular in shape. Imaging parameters: I_t = 54 pA, V_b = 250 mV.

References

(1) Natterer, F. D.; Patthey, F.; Brune, H. Quantifying Residual Hydrogen Adsorption in Low-Temperature STMs. *Surf. Sci.* **2013**, *615*, 80–87.