Elucidating the binding modes of N-heterocyclic carbenes on a gold surface

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Contents

- 1. Supporting Information
 - 1.1 Chemical structures and deposition procedure
 - 1.2. Mobility of IBu inside the layer
 - 1.3. Configuration of the dimers
 - 1.4. Overview images of low and high coverages of IMe
 - 1.5. Au 4f XPS data
 - 1.6. C 1s XPS data for IBu and IMe
 - 1.7. STM, XPS and DFT results for I/Pr
- 2. Chemical synthesis
- 3. Experimental details
- 4. Computational details

1.1. Chemical structures and deposition procedure



Figure S.1. Schematic representation of the deposition procedures leading to IBu and IMe and the expected side products.

1.2. Mobility of IBu inside the layer

Figure S2 shows two consecutive images of an island of IBu on Au(111) where the dynamics of the molecules inside the layer is analyzed by marking the positions of the holes in the layer. In Figure S2.B the holes that stayed in the same position as in Figure S2.A are marked with white circles. The holes that newly appeared are marked with green circles and the holes that disappeared are marked in black. Between these two images (recording time: 8 min. per image), 8 holes disappeared and 11 holes newly appeared.



Figure S.2. A) + B) Show two consecutive STM-images of an island of IBu on Au(111) where in the holes in the layer are marked by white circles. In B) the holes that newly appeared are marked green and the position of holes that disappeared are marked black. (1.0V, 15pA)

1.3. Configuration of the dimers

To determine the exact position of the two IBu molecules inside one dimer, the different angles and distances in Figure S.3.A are analyzed. The experimentally measured angles represented by \bullet_E and \blacktriangle_E . in Figure S3.A and B are 100° and 80° respectively, the length of the dotted line is $A_E = 0.99 \pm 0.05$ nm. Figure S3.C shows the gas-phase optimized structure of a single IBu molecule and its dimensions. The angle \blacktriangle_T between the two butyl groups in the optimized structure is 140° leaving the long side of this triangle to be $A_T = 1.18$ nm.

From the two experimentally obtained angles, \blacktriangle_E (100°) is closest to the relaxed gas-phase value and therefore is most likely to represent the angle between the two butyl groups belonging to one molecule. Taking this experimental angle of 100° and combining it with the theoretical chain length B_T,

the expected experimental length of $A_{CALC} = 0.98$ nm which is in good agreement with the measured $A_E = 0.99 \pm 0.05$ nm. This confirms that the angle \blacktriangle_E is between two butyl chains belonging to the same molecule.



Figure S.3. A) High-resolution STM-image of the ordered self-assembling structure of IBu on Au(111) after annealing (2.0V, 120pA). One dimer is schematically indicated with a cross, including the angles and distances used for the analysis. B) Amplification of the schematic in A. The two angles which are measured to determine the orientation of the dimers are marked \bullet_E and \blacktriangle_E . C) The DFT optimized structure of IBu in the gas phase and the dimensions A_T , B_T and angle \blacktriangle_T measured from it. D) Shows a triangle representing the expected dimensions of IBu calculated using the experimental angle \blacktriangle_E and the theoretical arm length B_T . This results in an expected A_{CALC} = 0.98 nm, which is an excellent match with the experimentally obtained value of $A_E = 0.99 \pm 0.05$ nm.



1.4. Overview images of low and high coverage of IMe on Au(111)

Figure S.4. A) Overview STM-image of IMe on Au(111) which shows how the molecules first self-assemble at the step-edges. Due to the mobility of the molecules, individual molecules or small islands on the metal terraces are not observed (-1.0V, 10pA). B) Overview STM-image of the high-coverage self-assembly of IMe on Au(111), as observed previous by Wang et al. ¹ (-1.0V, 40pA)

1.5. Au 4f XPS data

To investigate the possibility of charge accumulation during the formation of bis(IBu)Au and IMe-Au on the Au(111) surface, bis(IMe)Au⁺ and IMe-Au-Cl⁺ were synthesized ex-situ (i.e. in solution). Thermal evaporation of these complexes turned out to be impossible as they degraded upon heating. Therefore, XPS measurements on these compounds deposited under UHV conditions were not possible.

Alternatively, XPS measurements were performed on the bis(IMe)Au⁺ and IMe-Au-CI (with Au in oxidation state +1) complexes in powdered form. As a reference for energy calibration, powdered gold was mixed with the powdered NHC-complexes. To approximate the binding motif of IMe on Au(111) as closely as possible, IMe-coated nanoparticles were also prepared by reducing the IMe-Au-CI complex with NaBH₄ in presence of the gold powder as a support and internal Au reference. The XPS results are shown in Figure S.5. For comparison the Au 4f data of IMe and IBu on the Au(111) surface are included. In the spectra of IMe-coated nanoparticles, IMe on Au(111), IBu on Au(111) and powdered gold only the characteristic Au 4f_{7/2} and 4f_{5/2} doublet is found. In contrast to this, for bis(IMe)Au⁺ and IMe-Au-Cl additional spectral signatures at higher binding energies, which are indicative for charged Au species, can be observed². These can be associated with the Au-atoms in the respective complexes. Both bis(IMe)Au⁺ and IMe-Au-Cl show a shift to higher binding energy, indicating a positive charge as expected. The fact that this extra peak at a higher binding energy is not visible in the spectra of IMe and IBu on Au(111), indicates that the NHC-Au/NHC-Au-NHC species at the surface are neutral. However, it should be noted that the majority of the Au 4f signal arises from the bulk Au atoms of the Au(111) substrate and only a small amount of the Au 4f signal originates from those Au atoms directly bound to the NHCs. Furthermore, depending on the exact charging state for species adsorbed on the Au(111) surface, the associated core level shifts could be less pronounced. In this case the related signal could be masked by the background signal of the bulk Au atoms. Nevertheless, our data show no experimental indication for a significant charging of the Au atoms for IMe-Au and bis(IBu)Au species adsorbed on the Au(111) surface.



Figure S.5. Experimental XPS results for the Au 4f core levels of IMe on Au(111), IBu on Au(111), a gold powder reference, bis(IMe)⁺ mixed with gold powder, IMe-Au-CI mixed with gold powder and IMe coated nanoparticles. The upper two spectra (IMe and IBu on Au(111) surface respectively) are measured in a different UHV system than the lower four spectra (powder measurements), which has led to small differences in the energy resolution. The Au 4f_{7/2} peak was used as a reference in all cases and placed at 84 eV.

This is further supported by a Bader charge analysis for the NHC-Au and bis(NHC)Au species, which did not show a significant charge accumulation at the Au-atom for IMe-Au and IMe-Au-IMe. This is in line with the measured XPS data for the Au 4f signal. Thus, our experimental and theoretical data consistently indicate that the NHC complexes formed at the surface are charge neutral.

1.6. C 1s XPS data for IMe and IBu

We also investigated the carbon peak of both compounds (Figure S6). Since IBu has 6 more chemically different carbon atoms in the aliphatic chain as compared to IMe, the comparison of these data is less straightforward. The obtained C 1s peak maximum for IMe is 286.3 eV, which is again in agreement with earlier experiments.³ The obvious broadening of the C 1s peak in case of IBu is conclusively explained by the extra carbon atoms in the alkyl chain of IBu (blue).⁴ The remaining carbon atoms with identical chemical environments in both molecules are the backbone carbons (red) and the carbon that binds to the metal atom (orange). Especially for the backbone atoms, a flat or an up-standing confirmation should make a big difference for the interaction with the surface. When comparing the exact binding energies for this carbon species (red peaks) in the data obtained for IBu and IMe we find 286.1 eV and 286.5 eV, respectively. Therefore, a shift of 0.4 eV to lower binding energies for IBu is found as compared to IMe, which is almost identical to the shift in the N 1s peak. This indicates that both shifts are caused by the same type of chemical interaction. Furthermore, we also find a good match with our theoretical XPS data where we obtained a C 1s shift of -0.7 eV for IBu.

Comparing the specific experimental binding energies of the metal-binding carbon atom (orange peak), we find 285.4 eV (IBu) and 286.1 eV (IMe) which gives even an experimental shift of -0.7 eV for IBu. Again, this shift is also reflected well by our theoretical shift of -0.6 eV.



Figure S.6. Experimental XPS results for the C 1s core levels of IBu (top) and IMe (bottom) on Au(111). The different carbon species in the molecules are marked by different colors, which correspond to the colors of the different peaks fitted to the experimental data.⁴

1.7. STM, XPS and DFT results for IPr

In addition to IMe and IBu we also investigated 1,3-di-isopropylimidazol-2-ylidene (I/Pr) by DFT, STM and XPS. This special substituent represents a good intermediate substituent to investigate the effect of elongation on the binding mode, besides the methyl and butyl substituents. Isopropyl is much bigger than the methyl group of IMe, but has a smaller van der Waals interaction with the surface than the butyl chains of IBu due to its bulky shape. Furthermore, I/Pr is very interesting from a chemical point of view because branched substituents might influence the catalytic activity of the surface more than linear substituents and will therefore give additional insights

The STM images in Figure S.6.A and B show that for I[/]Pr no long-range order is observed. The molecules are ordered in small patches which are shifted or rotated with respect to each other. An explanation for this could be the possible interaction between the isopropyl groups of neighbouring molecules, which can also be in different orientations with respect to the ring of the molecule. The dimension of the molecule (Figure S.6.C) and the absence of a bright protrusion representing a Auatom indicate that I[/]Pr stands in an upright fashion. Furthermore, the high mobility of the molecules at lower coverage points at the Up_{ad}-configuration rather than the Up_{surf}-configuration. The DFT optimized geometry (Figure S.6.D and E) shows an Up_{ad}-configuration and a distance of 4.80 Å of the N-atoms to the surface. This is similar to the distance measured for IMe (See Figure 5). Finally, the N 1s core levels of I[/]Pr on Au(111) (Figure S.6.F) confirm this hypothesis with a single peak at a binding energy of 401.0 eV in agreement with the XPS data for IMe.

The Up_{ad}-configuration of both I/Pr and IMe indicates that the formation of IBu-Au-IBu complexes is mostly a result of the elongation of the side-groups which increase the van der Waals interaction with the surface considerably.



Figure S.7 A) STM-overview and B) close-up images of I^PPr on Au(111) which show that although the molecules are ordered on a small scale, long-range order is missing. (A: 1.1V, 5 pA; B: 2.0 V, 3 pA) C) The height profile measured along the arrow in S.6.B) with the resulting experimental (green) and calculated (red) distances. D) Topand E) side-view of the DFT optimized configuration of I^PPr on Au(111). F) Experimental results for the N 1s core levels of I^PPr on Au(111).

2. Chemical synthesis

General information

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. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F₂₅₄ aluminium plates (Merck). TLC plates were visualized by exposure to short wave ultraviolet light (254 nm, 366 nm). Flash column chromatography was performed on Merck silica gel (4063 mesh). 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 (MeOD: δ_H = 4.87 ppm, δ_C = 49.00 ppm). Coupling constants (*J*) are quoted in Hz. High resolution mass spectra were either recorded on a Bruker MicroTOF or on a Thermo Scientific Orbitrap LTQ XL. IMe, I/Pr, (IMe)AuCl, and bis(IMe)Au+Cl were prepared as described elsewhere. ^{1,5-7}

Synthesis of 1,3-dibutylimidazolium hydrogencarbonate



1.3-dibutylimidazolium hydrogencarbonate

Following an adjusted literature procedure ⁸, 1,3dibutylimidazolium iodide (554.8 mg, 1.8 mmol) were dissolved in ddH₂O (18 mL). The solution was sparged with CO₂ for one minute, after which hydrogen peroxide (115 μ L (30% w/v), 1.15 mmol in 0.3 mL water) was

added. Strong CO₂ sparging was continued for 1 h while stirring. During that time, the solution turned yellow to brown and a purple precipitate formed. The mixture was filtered and washed with 3 mL of water resulting in a clear colorless filtrate solution, leaving the insoluble iodine as a violet solid residue. Water was removed by lyophilization to give a white solid. The resulting solid was triturated and sonicated in acetone (3 x 3 mL), which was then decanted off. Subsequent drying under vacuum afforded the desired product as a white powder (321 mg, 1.32 mmol, 74% yield). By addition of an aqueous silver nitrate solution (1 M) to an aliquot of the product, no formation of a yellow silver iodide precipitate could be observed, monitoring the complete removal of the iodide counter ion.

¹**H NMR** (300 MHz, CD₃OD): δ (ppm): 7.63 (s, 1H), 4.19 (t, *J* = 7.4 Hz, 2H), 1.84 (p, *J* = 7.3 Hz, 2H), 1.33 (h, *J* = 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). The N₂CH and HCO₃ protons could not be observed due to rapid exchange with the deuterated solvent on the NMR time scale. ¹³C NMR (101 MHz, CD₃OD): δ (ppm): 161.3, 123.8, 50.6, 33.1, 20.5, 13.7. **HRMS** (ESI): m/z calculated for [M-HCO₃⁻]⁺: 181.1699, measured 181.1706.



50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 f1 (ppm)

3. Experimental details

<u>STM</u>

The STM experiments are performed in a low-temperature STM (Createc LT-STM) with a base pressure of 1x10⁻¹⁰ mbar. The Au(111) surface was cleaned by several cycles of Argon ion sputtering and subsequent annealing. All molecules were deposited from a quartz crucible at 60 °C (IMe), 70 °C (I/Pr) and 45 °C (IBu) for 4-10 minutes, onto the metal surface held at room temperature. All measurements were acquired at liquid nitrogen temperatures (78K), in constant-current topography mode. The bias voltage is always given with respect to the sample.

XPS (UHV)

Prior to XPS measurements, the coverage of the samples is checked by a low-temperature scanning probe microscopy (SPM) system (Scienta Omicron, LT-STM/AFM) under ultrahigh-vacuum conditions and at liquid-nitrogen temperatures (~77 K).

XPS experiments were carried out under UHV conditions at a base pressure of $2\times10-10$ mbar. The UHV system is directly connected to the LT-STM/AFM chamber, allowing *in situ* sample transfer. The experiments were performed with a monochromated AI K α X-ray source. Photoelectron detection was conducted in normal emission with a SPECS PHOIBOS 100 hemispherical analyzer and a 2D delay-line detector. The binding energies were calibrated with the Au 4f peak of the substrate.⁹

Powder XPS measurements were carried out on a Thermo Scientific K-Alpha XPS system. Experiments were performed with a monochromated Al K α X-ray radiation. Charge compensation is achieved with a combination of ion gun utilizing low energy electrons and argon ions. The powder species were applied to an area covered with non-conducting tape (3M). Pure gold powder (99.99% Sigma Aldrich) was applied to the same stripe as a further charge reference and all measurements were carried out under identical charge compensation settings. For the measurements on the bis(IMe)Au⁺ and IMe-Au-Cl⁺ complexes the Au powder was directly mixed for an internal charge referencing. For IMe-Au nanoparticles on gold, IMeAuCl (1 equiv., 20 wt.-% towards Au powder) was reduced with NaBH₄ (5 equiv.) in presence of Au powder in ethanol (the solution turns black by adding NaBH₄) The solution was stirred for 3h and was then precipitated with water and the solid was isolated by centrifugation. After drying, the solid was analyzed by XPS. The binding energies were calibrated with the Au 4f 7/2 peak.

4. Computational details

Using the Vienna Ab Initio Simulation Package (VASP)^{10,11} geometry optimizations were performed at the Density Functional Theory (DFT) level using the optPBE-vdw functional¹² together with projected augmented wave (PAW) pseudo-potentials. The cut-off energy of the plane wave basis set is 400 eV. The electronic states are approximated by gaussian distributions with a standard deviation of 0.1 eV. For the geometry optimization, the convergence criteria for the forces on the nuclei was 0.015 eV/ Å and 10^{-8} eV for the electronic relaxation. For the brillouin zone integration we used a 2x2x1 k-point grid. The slab model for the Au(111) surface consists of four layers of a periodic 5x6 unit cell with a gold lattice constant of 4.18 Å, which was determined by optimizing the bulk structure. The four layers are separated by 40 Å. The molecule adsorbed one side of the slab model and the upper two layers were fully relaxed during the geometry optimization.

Based on the optimized geometries and according to reported studies^{13,14}, core level calculations were performed using the Slater-Janak transition state model (SJ model).The eigenenergies, which are considered in this model, correspond to a half occupied core level.

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