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An Electron-rich Cyclic (Alkyl)(Amino) Carbene on Au(111), Ag(111) and Cu(111) Surfaces

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Dedicated to Prof. Albert Eschenmoser on the occasion of his 95th birthday

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Abstract: The structural properties and binding motif of a strongly sigma-electron donating N-heterocyclic carbene are investigated on different transition metal surfaces. The examined cyclic (alkyl)(amino) carbene (CAAC) is found to be mobile on surfaces and molecular islands with short-range order could be found at high coverage. By combining scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculations our study highlights how CAACs bind to the surface, which is of tremendous importance to gain understanding for heterogeneous catalysts bearing CAACs as ligands.

In recent years, N-heterocyclic carbenes (NHCs) have gained great attention in a broad range of applications as catalysts and as ligands for p-block elements and transition metals.^[1] Due to their strong σ -donating properties and their tunable side-groups, NHCs are privileged ligands for NHC-metal complexes and the stabilization and functionalization of nanoparticles^[2] and surfaces^[3]. Cyclic (alkyl)(amino) carbenes (CAAC) are a prominent class of NHCs which exhibit even stronger σ-donating properties than imidazole-based NHCs.[4] Therefore, CAACs are especially valuable ligands for Rh-based hydrogenation catalysts, which can be used to hydrogenate highly functionalized (hetero)aromatic rings with excellent functional group tolerance and conformational control.^[4c,5] Moreover, they are also used as ligands for metathesis catalysts and are even able to activate small molecules like H₂, CO, NH₃, silanes, phosphenes and organoboron species due to their high nucleophilicity.^[6] On heterogeneous surfaces, Johnson and coworkers showed that CAACs can insert into Si-H bonds, which does not result in a binding mode comparable to a single carbene bond in CAACmetal complexes.^[7] Bullock and coworkers further studied their behavior in Rh-catalyzed hydrogenation reactions and exclusively found the protonated CAAC coordinating to the surface.^[7,8] Over the last years, several studies of NHCs on surfaces have been reported including STM and XPS investigations.[3b,9] The formation of ultra-stable self-assembled monolayers was shown, as well as the mobility of some NHCs due to the formation of ballbot-like species and the influence of the N-substituents on the binding mode to the surface.^[3b,9a,9b,9d] However, the fundamental behavior of CAACs is only rarely explored and there is no report of CAACs on transition metal surfaces. Furthermore, investigations of CAACs with molecular resolution, which would be necessary to design more efficient and selective catalysts, are not reported. Thus, we investigated the on-surface behavior of

DiMeCAAC^[10] (Fig.1.A) which is a rather small and structurally simple CAAC. To avoid contamination of the surface by salts and solvent the CO₂-adduct was used.^{[[9a,9d]} DiMeCAAC • CO₂ was synthesized *via* the formation of the free carbene and subsequent treatment with dry CO₂, which led in precipitation of the pure material. GC-MS measurements revealed that the free CAAC can be generated without destruction.

After vacuum depositing DiMeCAAC for 10 minutes at 60 $^\circ$ C on a Au(111) crystal which was kept at room temperature, an almost



Figure 1. A) The deposition procedure for DiMeCAAC. B) Overview STM image of a full layer of DIMeCAAC on Au(111) (-2.0V; 25pA). C) Small scale STM image where the individual molecular features appear as a bright ellips (methyl groups pointing upwards) and a dimmer shadow (Dipp group) (-2.0V; 25pA). D, E) Side- and top-view of the DFT-optimized geometry of the upstanding binding mode of DiMeCAAC on Au(111).

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completely covered sample was obtained (Fig.1.B). In the molecular monolayer three preferential directions of short-range order can be recognized as is indicated in Figure 1.B. However, the long-range packing is not well-ordered, which is caused by the multiple different orientations the molecular features adopt on the surface.

The same repeating shape can be recognized in the STM contrast, represented by a bright ellipse with a dimmer shadow (solid circle in Fig.1.C). The distance between the different bright spots is measured to be 1.02±0.09 nm. This value is the average of distances measured along all three directions as indicated in Fig.1.B where obvious defects are ignored. Since DiMeCAAC forms no well-ordered self-assembly, a unit cell cannot be defined. However, this consistent value for the intermolecular distance indicates that the packing is not completely disordered.

DFT simulations predicted an upright binding mode for DiMeCAAC on Au(111) (Figure 1.D) with the di-*is*opropylphenyl (Dipp) group perpendicular to the CAAC ring and parallel to the surface, which minimizes steric hindrance. Considering this optimized structure, the two methyl groups in the backbone point upwards and should thus give the brightest STM contrast. The bright dots in Fig.1.C are therefore assigned to these groups. Based on these considerations, the Dipp group is attributed to the dimmer shadow. The distance between these two features (arrow in Fig.1.C) is measured to be 0.44 ± 0.2 nm, which is in good agreement with the DFT-calculated distance of 0.46 nm between the upstanding methyl groups and the edge of the Dipp group. Not all molecular features appear equally bright (dotted circle in Fig.1.C), which is attributed to a possible tilting in the adopted binding configuration (see below).

When a lower coverage (~80%) of DiMeCAAC is deposited on Au(111), two observations can be made. Firstly, an adsorption preference at the elbow positions and the fcc phases of the herringbone reconstruction is observed (Fig.2.A and S.1), which is in agreement with the behavior of other NHCs.^[9a] Secondly, in between the islands the STM contrast is blurred and the visibility of the Au(111) herringbone reconstruction reduced. This is an indication of mobility of the molecules on the surface. To illustrate this, series of STM images are recorded on a low coverage (~20%) sample (Fig.2.B-D). Small molecular islands have nucleated from the elbow positions of the herringbone reconstruction (Fig.2.B). The shape of the islands in this image is transferred to the subsequent STM images in Fig.2.C and D. Here it can be observed clearly how molecules appear and disappear, thereby changing the shape of the island in between subsequent images. The adsorption energy of DiMeCAAC on Au(111) is calculated to be E_{ads}=2.49 eV, which indicates a strong binding. This energy is comparable to the adsorption energy calculated for a mobile NHC (IPr, 2.78 eV) observed earlier.^[9a] Here it was shown that NHCs, after binding to a gold atom, can extract this atom from the surface and thereby forming a so-called ballbot species. The observed mobility of DiMeCAAC at low coverage indicates that CAACs are also capable of forming such species (Fig.2.E). The adsorption energy of such a DiMeCAAC-Au ballbot-like species was calculated to be 4.11 eV, which is significantly higher than the adsorption energy of the surfacebound species. Furthermore, the mobility of such a DiMeCAAC-Au species was investigated by DFT calculations. The differences in binding energy along the lateral diffusion pathway were found to be smaller than 0.04 eV (See SI) which indicates low diffusion barriers.

The preferred adsorption position of a DiMeCAAC-Au species is calculated to be at the hollow site of the Au(111) surface (See SI). Based on this, a possible, theoretical close-packed self-assembled structure was calculated (Fig.2.F). The distance between the adatoms in this image is 0.89 nm, which is smaller than the experimentally determined average value of 1.02 ± 0.09 nm. This shows that DiMeCAAC can not easily assemble in a well-ordered, close-packed self-assembly as the STM images

clearly indicate (Fig.1.B). In principle, the atomic lattice of the surface is driving the organization of DiMeCAAC-Au species on the surface due to the prefered adsorption at the hollow sites. Since the main interaction of these species with the surface is via the gold atom, molecules can arrive in any orientation at an island of molecules. However, due to the bulky Dipp group and the asymmetric structure of the molecule, intermolecular interactions are possible and rotation of individual ballbots in a molecular island is limited. Combined with the mobility of the molecules and the required high coverage for STM imaging this makes it more difficult to reach the optimized self-assembled structure. Still, by positioning the atomic lattice over the STM images, preferred adsorption at or very close to the hollow site can be observed for the majority of the molecules (See SI). Attempts to deposit slower (70 min at 45 °C) did not result in an improved order in the molecular layer. Also annealing of the sample after deposition could not induce a better odered structure, but rather leads to desorption of the molecules. Additionally the calculated DiMeCAAC-Au configuration (Fig.2.E) allows for slight tilting to the sides when the distance to neighbouring molecules is larger. This explains the differences in brightness observed in Fig.1.C. DiMeCAAC was also investigated on Ag(111) and Cu(111), which gave similar results as on Au(111), as can be seen from the STM images in the SI.



Figure 2. A) Overview STM image of a ~80% coverage of DiMeCAAC on Au(111) showing a preferred adsorption at the fcc phase of the herringbone reconstruction (-2.0V; 16pA). B-D) Subsequent STM images of the same area of a low coverage (~20%) sample showing a changing size of the molecular islands due to appearing and disappearing molecules (-2.0V; 17pA). E) DFT-optimized geometry of a DiMeCAAC-Au ballbot species on the surface. F) A theoretical close-packed self-assembly of DiMeCAAC-Au ballbot-like species on Au(111).

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To confirm the intact deposition of DiMeCAAC and to obtain more chemical information about the species on the surface, GC-MS measurements of DiMeCAAC • CO₂ and XPS measurements of DiMeCAAC on Au(111) were performed. A requirement for GC-MS analysis is the intact evaporation of the molecule. At inlet temperatures of more then 200 °C the molecule will decarboxylate as expected and releases the free CAAC, which resulted in a single peak with the mother ion peak at m/z = 285.30 (See SI). This is in agreement with the mass of the free CAAC within the error of the quadrupole mass analyzer used. Since DiMeCAAC only has one nitrogen atom we used N 1s XPS analysis as a marker to investigate the intact nature of DiMeCAAC on the surface. The resulting XPS spectrum is plotted in Figure 3.A. At 400.7 eV a clear single peak is observed as is expected for the deposition of intact molecules. XPS literature for CAACs bound to transition metals is not available. However, for NHCs bound to Au(111) surfaces or nanoparticles typically N 1s binding energies around 400 to 401 eV are reported.[3b,9d,9e,11] We therefore conclude that the peak at 400.7 eV corresponds to surface-bound CAAC molecules. Additionally the O 1s XPS spectrum shows negligible traces of oxygen on the surface, confirming the removal of CO₂ during sample preparation.



Figure 3. *A*) *N* 1s XPS spectrum of a monolayer of DiMeCAAC on Au(111) with a peak at 400.7 eV. The corresponding STM image can be found in Fig.1.B. B) O 1s XPS spectrum of the same sample showing a negligible trace of oxygen on the surface confirming the removal of CO₂ during sample preparation.

In summary we showed the successful deposition of DiMeCAAC on different transition metal surfaces via evaporation of the CO2 adduct in UHV. Molecular islands with short-range order were found, however due to the unsymmetric nature and bulky side group of the molecule a well-ordered, close-packed selfassembled structure cannot be obtained. At lower coverage prefered adsorption at the fcc phase of the herringbone reconstruction was observed. Furthermore series of STM images showed that DiMeCAAC is mobile on the surface, which can be explained by the formation of ballbot-like species as observed previously for other NHCs. Furthermore, the intact deposition of DiMeCAAC was confirmed by a single peak in the N 1s XPS spectrum and the removal of the CO2 groups has been confirmed by the O 1s XPS spectrum. This investigation of a CAAC on different surfaces opens the way for further studies on more complex (chiral, functional) CAAC ligands.

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Keywords: Au(111) surface • CAAC • Scanning Probe Microscopy • Ligand • X-ray photoelectron spectroscopy

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3

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Entry for the Table of Contents



Served on a (golden) tray! A highly reactive and electron-rich CAAC derivative is deposited on a surface after which its binding mode and ordering are investigated for the first time. Mobile CAAC-Au species are found which form islands on the surface. These results open the door for more on-surface studies of the highly relevant class of CAACs.