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Communication

Cyclopropenylidenes as Strong Carbene Anchoring Groups on Au Surfaces

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ABSTRACT: The creation of stable molecular monolayers on metallic surfaces is a fundamental challenge of surface chemistry. N-Heterocyclic carbenes (NHCs) were recently shown to form self-assembled monolayers that are significantly more stable than the traditional thiols on Au system. Here we theoretically and experimentally demonstrate that the smallest cyclic carbene, cyclopropenylidene, binds even more strongly than NHCs to Au surfaces without altering the surface structure. We deposit bis(diisopropylamino)cyclopropenylidene (BAC) on Au(111) using the molecular adduct BAC−CO_2 as a precursor and determine the structure, geometry, and behavior of the surface-bound molecules through high-resolution X-ray photoelectron spectroscopy, atomic force microscopy, and scanning tunneling microscopy. Our experiments are supported by density functional theory calculations of the molecular binding energy of BAC on Au(111) and its electronic structure. Our work is the first demonstration of surface modification with a stable carbene other than NHC; more broadly, it drives further exploration of various carbenes on metal surfaces.

Cyclopropenylidene, the smallest aromatic molecule displaying a carbene center, has received widespread theoretical and experimental interest due to its unique electronic structure, chemical reactivity, and existence in interstellar space.[1−5] Cyclopropenylidene, however, is too unstable to be isolated as a free carbene. First reported as a stable crystalline solid by Bertrand and co-workers, bis(dialkylamino)cyclopropenylidenes (Figure 1a) consist of the cyclopropenylidene ring functionalized with two dialkylamino groups.[2,3,6] The presence of these dialkylamino groups stabilizes the free carbene and, combined with the highly strained nature of the ring and the resulting small angle at the carbenic carbon, produce a molecule capable of remarkably strong σ-donation. Most experimental and theoretical investigations indicate that bis(dialkylamino)cyclopropenylidenes are in fact better σ-donors than N-heterocyclic carbenes (NHCs) while having a smaller footprint.[7] Carbenes have recently received intense attention due to their rich coordination chemistry[8−10] and ability to form ultrastable self-assembled monolayers on metal surfaces.[11−16] While diazomethane derivatives have been used to assemble carbene molecules on Ru surfaces,[16] most recent studies have focused on NHCs, prompting the question whether carbenes such as bis(dialkylamino)cyclopropenylidenes could strongly bind to metal surfaces.

In this work, we investigate for the first time the functionalization of metal surfaces with bis(diisopropylamino)-cyclopropenylidene (BAC). Using density functional theory (DFT), we first present a detailed theoretical picture of the bonding energetics and geometry of BAC to a Au(111) surface. We then develop a simple synthetic approach to

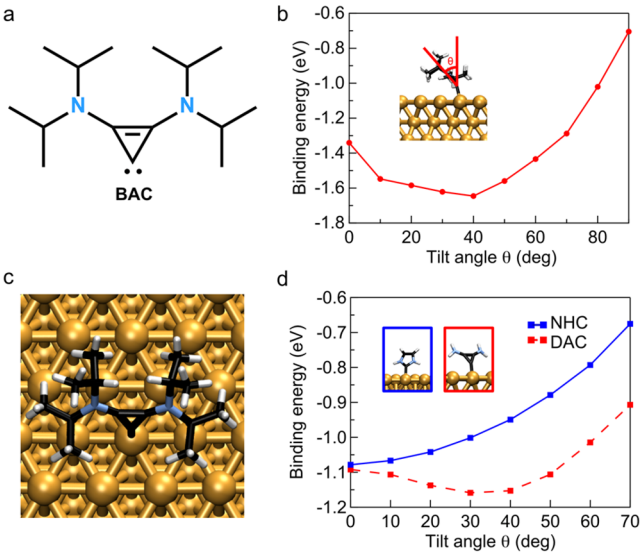

Figure 1. (a) Chemical structure of BAC. (b) Calculated binding energy of BAC as a function of tilt angle θ. (c) Structure of BAC absorbed on the Au(111) surface for $\theta = 40°$. (d) Calculated binding energy of DAC and NHC cores on the Au(111) surface as a function of tilt angle θ.

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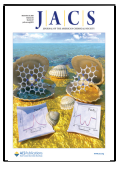

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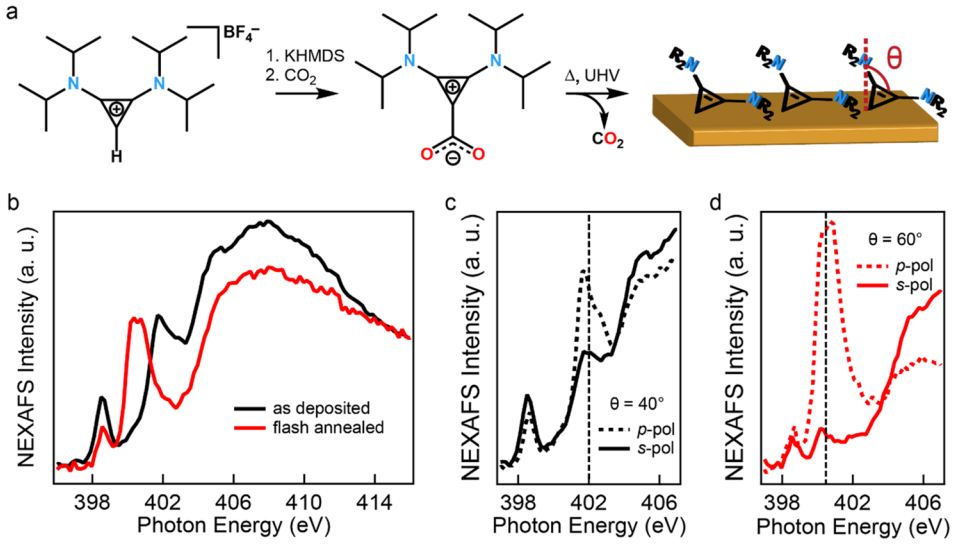

Figure 2. (a) Synthesis of BAC−CO_2 and subsequent vapor deposition onto Au(111). (b) Magic angle NEXAFS spectra collected at the N K-edge of the BAC deposited on the Au(111) substrate at 100 °C (black) and then annealed at 200 °C (red). (c, d) NEXAFS N K-edge spectra of the BAC deposited at 100 °C (c) and annealed at 200 °C (d) collected with the electric field of the incident photons perpendicular (*p*-pol) and parallel (*s*-pol) to the surface. The dashed vertical black line indicates the N 1s → π^* LUMO absorption peak in both (c) and (d).

deposit BAC on Au(111) surfaces in ultrahigh vacuum (UHV) and use synchrotron radiation to probe the geometry of the carbenes on the surface through high-resolution X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS). To support these measurements, we image the surface-bound BACs using high-resolution scanning tunneling microscopy and atomic force microscopy (STM and AFM). Overall, our results indicate that cyclopropenylidenes are attractive anchoring groups to modify metal surfaces.

We first model the bonding of BAC to a Au(111) surface using atomistic DFT-based simulations with van der Waals interactions. We start by determining the orientation of the cyclopropenylidene ring relative to the Au(111) surface, which is modeled as three Au layers, each containing 36 atoms (section 2 of the Supporting Information (SI)). For these simulations, the tilt angle (θ) of the ring relative to the surface normal is fixed and all other atoms, including the surface Au atoms, are fully relaxed. This is done by allowing the C atoms in the cyclopropenylidene ring to shift rigidly in any direction. The resulting energy profile is shown in Figure 1b. In the vertical orientation (θ = 0°), the binding energy is −1.34 eV, close to that of NHC on a Au(111) surface (−1.49 eV).[15] The favored adsorption site for BAC is an atop site with a Au−C distance of 2.2 Å. As the molecule is tilted and θ increases, the binding energy increases due to the contributions from the Au−C dative bond and the van der Waals interactions with the surface. The binding energy reaches a maximum at θ = 40° (Figure 1b, c) and decreases for larger θ due to a reduction of the BAC−Au orbital overlap and steric repulsion between the isopropyl N-substituents and the surface. The calculated binding energy at θ = 40° is −1.65 eV, larger than the reported value of −1.49 eV for ^{Me}NHC on Au(111).[15]

To quantify the steric role of the isopropyl N-substituents, we calculate the adsorption properties of a BAC molecule in which the isopropyl groups are replaced with H atoms (diaminocyclopropenylidenes, DAC). The binding energy is shown in Figure 1d as a function of tilt angle up to θ = 70° (for θ > 70°, the Au contact atom is extracted from the surface and these geometries are thus excluded). Comparison with Figure 1b reveals that both BAC and DAC adopt roughly similar tilt angles on the Au(111) surface but the binding energy of BAC is significantly larger (by 0.2−0.4 eV) than that of DAC. When the tilt angle is large, however, the binding energy decreases more rapidly for BAC due to the increased steric repulsion with the surface. Similar to observations of NHCs bound to Au,[17] we find that dispersive interactions between the surface and the cyclopropenylidene core and pendent isopropyl groups contribute significantly to the binding energy. These results suggest that the binding energy of cyclopropenylidenes to a Au substrate could be further increased by functionalizing the ring with amino groups bearing substituents that can strongly interact with the surface.

We also compare the binding energies of DAC and dihydroimidazol-2-ylidene (NHC) to understand the effect of the ring structure. Figure 1d presents the calculated binding energy of both model carbenes as a function of tilt angle. When θ = 0°, the binding energies of both molecules are similar and close to −1.10 eV. However, the DAC ring can sustain a stable geometry for larger θ whereas the NHC core cannot. This is seen even when calculated DAC or NHC rings are bound to a single Au atom (Figure S2). These results suggest that cyclopropenylidene rings can form stronger and less constrained bonds to a Au(111) surface.

To validate these predictions and experimentally probe the binding of BAC to a Au surface, the BAC−CO_2 adduct was synthesized and used as a precursor that thermally decomposes in UHV to generate free BAC, which can be deposited from the gas phase onto the Au(111) surface (Figure 2a). We deposited BAC by thermal decomposition/sublimation of the BAC−CO_2 precursor on Au(111) surfaces and performed X-ray calculations of the C 1s core-electron binding energies for BAC on a Au surface (Figure S8). We performed XPS measurements on as-deposited and annealed monolayers.[15] The XPS reveals the presence of C and N on the Au(111) surface and the absence of O, consistent with the BAC anchored to the surface without the CO_2 moiety (Figure S4). Moreover, the C 1s photoemission spectrum is well

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reproduced by DFT calculations of the C 1s core-electron binding energies for BAC on a Au surface (Figure S8). We performed X-ray polarization dependent NEXAFS measurements to determine the average orientation of the BAC ring relative to the Au(111) surface normal (Figure 2a). For this measurement, we focus on the N K-edge NEXAFS spectra because the C K-edge NEXAFS spectrum contains a complex fine structure with significant contribution from the isopropyl groups (Figure S9).

We then examine the electronic structure of the unoccupied molecular orbitals in both the as-deposited and annealed films by comparing NEXAFS spectra in the magic angle configuration (Figure 2b). Under these specific conditions, the orientations of the molecules do not influence the NEXAFS signal.[18] We notice a substantial change of the measured NEXAFS spectra between the two films, with a shift of the main absorption peak from ∼402 to ∼400.5 eV after annealing at 200 °C. Note that the peak at ∼398.5 eV, which grows with X-ray exposure, is likely due to molecular fragmentation caused by the beam and not an intrinsic property of the BAC. DFT-based half-core-hole calculations of the X-ray absorption spectra of the BAC molecule coupled to a Au dimer (Figure S10a) allow us to assign the absorption peaks at ∼402 eV in the as deposited film and at ∼400.5 eV in the annealed film to the same N 1s → π^* LUMO transition (Figure S10b). Of particular note, our DFT calculations reveal that the excitation energy of this transition strongly depends on the Au−C distance (Figure S10a). Although the observed energy difference is not fully reproduced by DFT, our calculations show a clear trend toward lower excitation energies with decreasing Au−C distances, indicating a stronger binding of the BAC to Au surface upon annealing. Annealing may enable molecular migration to undercoordinated Au sites, e.g., adatoms, enhancing electronic coupling.

We next measure NK-edge NEXAFS spectra of a BAC monolayer deposited on Au(111) at 100 °C with the incident photon electric field directed either perpendicular (*s*-polarization) or parallel (*p*-polarization) to the surface normal to determine the average molecular surface orientation.[18] From the intensity difference of the N 1s → π^* LUMO transition absorption peaks (at ∼402 eV) measured using *s*- and *p*-polarizations (Figure 2c), we calculate an average $\theta \sim 40°$, consistent with our DFT calculations (Figure 1b). After annealing the sample to 200 °C, the linear dichroism of the N 1s → π^* LUMO transition (at ∼400.5 eV) is enhanced (Figure 2d), resulting in $\theta \sim 60°$. This average tilt angle is larger than DFT-based predictions, suggesting that annealing encourages BAC migration to undercoordinated Au sites, thus energetically favoring larger angles.

The orientation of NHCs on the surface is primarily determined by the N-substituents.[15] For BAC, the increased distance between the N-substituted and the carbenic carbon allows for relaxation of the molecule onto the surface and thus a greater tilt angle θ. NHCs can pull adatoms from the Au(111) substrate, forming flat-lying bis(NHC) complexes with the adatom on the surface.[15,19,20] These adatoms can be spectroscopically identified as satellite peaks in the XPS Au 4f spectrum.[15,21] By contrast, we see no evidence for such adatom formation when BAC is deposited on Au(111). The XPS Au 4f spectrum has no satellite peaks indicative of adatom formation (Figure S4).[22]

To support our spectroscopic and theoretical data, we imaged individual BAC molecules anchored to the Au surface with STM and AFM. Using the BAC−CO_2 precursor, we deposited a sub-monolayer of BAC on a Au(111) surface at ∼5 K in ultrahigh vacuum. Figure 3a shows an STM image of the

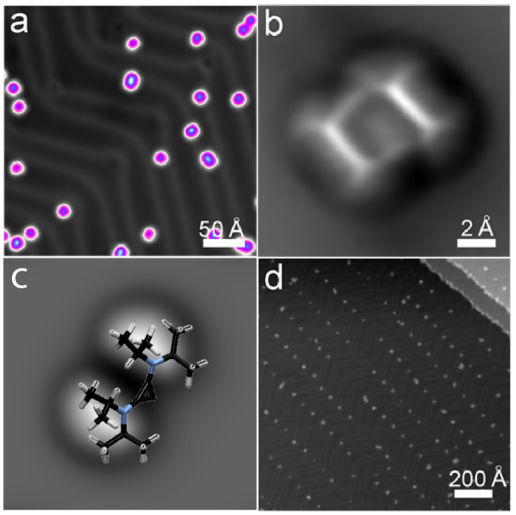

Figure 3. (a) STM image of BACs on the Au(111) surface (where the herringbone reconstruction is visible) (0.2 V, 50 pA). (b) High-resolution AFM image of a single BAC molecule. (c) Simulated AFM image for a single BAC. (d) STM image of the BAC molecules on the Au(111) surface after annealing to 110 °C for a few seconds (0.2 V, 50 pA).

BACs affixed to the surface. Although a few dimers or clusters are visible, the molecules are generally well dispersed and separated with no preferred anchoring sites. We performed high resolution AFM imaging at 5 K of a single BAC using a CO-functionalized tip (Figure 3b). The BAC features two bright lobes attributed to the isopropyl groups. We simulated AFM images of the adsorbed molecule taken with a CO-functionalized tip using a probe particle model.[23] The simulation of the most stable geometry ($\theta = 40°$) reproduces the main experimental observations (Figure 3c). The two bright features, separated by ∼5 Å, result from the repulsion of the hydrogen atoms in the terminal methyl groups of the diisopropyl substituents furthest from the surface. The molecule measures ∼10 Å across, the confirmed diameter of BAC bound to reported metal-BAC complexes.[24] The three-membered ring is hidden underneath the bulky alkyl groups, expected for $\theta = 40°$.

The BAC-functionalized surface was heated at 110 °C for a few seconds and imaged again using STM to examine changes to the bound BACs. Figure 3d details the rearrangement of the molecules on the surface. At this temperature, the molecules are clearly mobile on the surface and relocate to the herringbone edges. The undercoordinated elbow sites of the herringbone structure are more favorable binding sites for BACs, corroborating the NEXAFS results.

In summary, we have studied for the first time the functionalization of a Au surface with cyclopropenylidene carbenes. Our results indicate that BACs bind more strongly to the surface than NHCs, making them highly suitable as surface binding ligands. Compared to NHCs, BACs have a unique structure with the bulky substituents away from the carbenic carbon. High resolution X-ray absorption spectroscopy supported by DFT-based calculations and single molecule imaging reveal how this structure allows BACs to adopt tilted

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orientations that maximize their binding energy without Au-adatom formation. This work opens an exciting new area of investigation in the rapidly developing field of self-assembled carbene monolayers on surfaces.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c10743.

Synthetic details, DFT calculations, XPS and NEXAFS details, STM and AFM details (PDF)

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Notes

The authors declare no competing financial interest.

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