In Situ Formation of N-Heterocyclic Carbone-Bound Single-Molecule Junctions

Evan A. Doud,‡§ Michael S. Inkpen,‡⊥ Giacomo Lovat,‡ Enrique Montes,§ Daniel W. Paley,‖ Michael L. Steigerwald,§ Héctor Vázquez,§⊥⊥ Latha Venkataraman,§⊥⊥⊥ and Xavier Roy⊥⊥⊥⊥

‡Department of Chemistry, ‡Department of Applied Physics and Applied Mathematics, and †Columbia Nano Initiative, Columbia University, New York, New York 10027, United States
§Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, Prague 16200, Czech Republic

ABSTRACT: Self-assembled monolayers (SAMs) formed using N-heterocyclic carbenes (NHCs) have recently emerged as thermally and chemically ultrastable alternatives to those formed from thiols. The rich chemistry and strong σ-donating ability of NHCs offer unique prospects for applications in nanoelectronics, sensing, and electrochemistry. Although stable in SAMs, free carbenes are notoriously reactive, making their electronic characterization challenging. Here we report the first investigation of electronic transport across single NHC-bound molecules using the scanning tunneling microscope-based break junction (STM-BJ) technique. We develop a series of air-stable metal NHC complexes that can be electrochemically reduced in situ to form NHC−electrode contacts, enabling reliable single-molecule conductance measurements of NHCs under ambient conditions. Using this approach, we show that the conductance of an NHC depends on the identity of the single metal atom to which it is coordinated in the junction. Our observations are supported by density functional theory (DFT) calculations, which also firmly establish the contributions of the NHC linker to the junction transport characteristics. Our work demonstrates a powerful method to probe electron transfer across NHC−electrode interfaces; more generally, it opens the door to the exploitation of surface-bound NHCs in constructing novel, functionalized electrodes and/or nanoelectronic devices.

INTRODUCTION

A key design feature of nanoscale electronic devices is the chemical group that establishes the physical and electronic contact at the molecule−electrode interface. The nature of this interaction, i.e., covalent,1−4 dative,5 or supramolecular,6 can be exploited to tune the stability and function of the connected component. One family of linkers with emerging potential are the carbenes, neutral molecules comprising a divalent carbon component. One family of linkers with emerging potential are capable of rapidly displacing preformed thiol−Au SAMs.12 Given their strong donor binding to metals and unique electronic structure,9 this family of molecules offers exciting new prospects for surface functionalization, with potential applications in selective heterogeneous catalysis,4−7 nano-technology,10,18,19 and sensing.10,11,13,20 Essential to such developments is an improved understanding of both the electronic coupling between the carbene and the metal surface and the electron transport across the carbene−electrode interface. Despite theoretical interest,21,22 these features have never been experimentally investigated.

In this work, we describe a novel strategy to probe the electronic properties of NHCs on Au electrodes. Using the scanning tunneling microscope-based break junction (STM-BJ) technique,2,23 we form NHC−electrode contacts via in situ electrochemical conversion of a metal NHC complex in the junction (Figure 1a). By measuring the electrical transport properties of a series of NHC-bound single-molecule junctions, we find that the conductance (G) of the junction depends on the metal atom in the precursor. Our hypothesis, supported by transport calculations based on density functional theory (DFT), is that as the complex is reduced at the STM tip the NHC remains coordinated to the metal atom. This atom subsequently binds to the electrode surface and establishes a conductive contact. By extending the backbone of the NHC-bound single-molecule junction, we observe a clear exponential...
decay of conductance, indicating a coherent nonresonant transport mechanism. These results establish our approach as a robust yet flexible strategy to form NHC-linked molecular junctions.

**EXPERIMENTAL SECTION**

**STM-BJ Details.** Conductance measurements were carried out using the STM-BJ technique, which has been described in detail elsewhere. Conductance measurements for all complexes were performed using 10 μM solutions in PC. The Au tip was coated with an insulating layer to suppress background ionic current. The insulated tips were created by driving a mechanically cut gold tip through Apiezon wax. 1D conductance histograms were constructed using logarithmic bins (100 per decade) without any data selection.

**Synthesis of NHC1–AuCl.** The NHC1–AuCl complex was synthesized using a modified literature procedure. NHCl1–II (45 mg, 100 μmol; synthesis detail in Supporting Information) was suspended in 8 mL of THF. KO'Bu (12 mg, 110 μmol) was added to the suspension, and the reaction was stirred for 1 h. The mixture was then filtered through Celite, and (SMe)2AuCl (31 mg, 105 μmol) was added to the filtrate. The reaction was stirred for 3 h, protected from light. Activated carbon (100 mg) was added to the reaction, which was stirred for 1 h and then filtered through Celite. The solvent was then removed in vacuo. The solid residue was redissolved in DCM and filtered, and the solvent was removed in vacuo to yield the pure complex NHCl1–AuCl as a light-yellow powder (yield = 48 mg, 86%). Analogueous procedures were used to prepare the other NHC–MCl complexes.

**Computational Details.** The electronic and transport properties of molecular junctions were calculated using first-principles methods based on DFT-NEGF. We modeled the junction by attaching the molecular backbone on the carbene side to an Au adatom for NHCl1–AuCl, an Ag adatom for NHCl1–AgCl, and a Cu adatom for NHCl1–CuCl (without including the Cl atom). To simplify geometry optimization, the isopropyl groups were replaced with methyl groups, resulting in negligible changes in conductance. The SMe side was attached to an Au adatom for all junctions. The supramolecular structure was placed between two electrodes that consisted of a 4×4 face-centered cubic (fcc) Au(111) surface. We optimized the junction structure by relaxing the coordinates of the molecular backbone and the Au atoms to a force threshold smaller than 0.02 eV/Å, also optimizing the interelectrode vertical separation. In the calculations, the exchange correlation was described using the GGA approximation in the PBE implementation. We used a double-ζ polarized local-orbital basis for molecular atoms and a single-ζ basis for Au atoms. We performed subsequent transport calculations at optimized geometries by adding additional Au(111) layers. We used Monkhorst–Pack grids of 5×5×1 and 15×15×1 for calculating the electronic structure and transmission spectra, respectively. Transmission eigenchannels were computed at the center of the Brillouin zone.

**RESULTS AND DISCUSSION**

Our first objective was to measure the transport properties of a linear aromatic molecule utilizing an NHC as the contacting group. To achieve this goal, we exploited a new in situ electrochemical-reduction approach to form the single-molecule junction using the STM-BJ technique (Figure 1a). For this method, the molecule is terminated by an aurophilic thiomethyl group (SMe) on one end and a benzannulated NHC on the other end. The NHC is capped with one of a series of metal chloride complexes; the resulting air-stable metal NHC precursors are labeled NHCl1–MCl (M = Au, Ag, Cu). Synthetic details are included in the Experimental Section. A single-molecule junction is established when the SMe binds to the electrode surface via an Au–S bond, and the metal NHC complex is reduced at the STM tip. We have developed this innovative strategy because we were unable to characterize the single-molecule transport characteristics of NHCs bound in SAMs prepared using traditional methods, shown in Figure 1b. Indeed, STM-BJ measurements of monolayers assembled on Au surfaces from solutions of free NHCs, or from the vapor phase using NHC–CO2 adduct precursors, did not yield reproducible conductance results.

Figure 2a presents the molecular structure of the precursors NHCl1–CuCl, NHCl1–AgCl, and NHCl1–AuCl, as determined by single-crystal X-ray diffraction (SCXRD). Details of the STM-BJ measurements in an ionic environment have been described previously and are outlined in the Experimental Section. Briefly, the measurements are performed using an insulated Au STM tip, with an exposed area of ~1 μm², and an Au substrate with an area larger than 1 cm². When a bias is applied, a dense double layer of charge builds up around the small area of the coated tip while a sparse double layer is formed on the large-area, uncoated substrate. Previous studies have demonstrated that, under these conditions, redox-active compounds such as ferrocene or molecular clusters can be oxidized or reduced in the junction under positive or negative tip biases, respectively.

When we use this approach with NHCl1–MCl in propylene carbonate (PC), we can form electrically conducting NHC-bound single-molecule junctions by applying a negative (i.e.,
[NHCl\textsubscript{1}−AuPPh\textsubscript{3}]\textsubscript{a}[BF\textsubscript{4}]), is analogous to NHCl\textsubscript{1}−AuCl, but the Cl\textsuperscript{−} ligand is replaced with a weakly coordinating BF\textsubscript{4}− anion and PPh\textsubscript{3}, which is known to dissociate from Au complexes upon junction formation.\textsuperscript{3} The conductance of [NHCl\textsubscript{1}−AuPPh\textsubscript{3}]\textsubscript{a}[BF\textsubscript{4}] is close to that of NHCl\textsubscript{1}−AuCl, indicating that the molecular junction does not form by binding through the Cl atom to the Au electrode (i.e., NHCl\textsubscript{1}−Au−Cl−electrode). The second complex, bis(diethyl(4-(methylthio)phenyl)phosphine)AuCl ([(4-MeSPh)Et\textsubscript{2}P]AuCl), is used to confirm that junctions formed via in situ reduction of gold chloride complexes are analogous to those formed by directly binding the free linker to the electrode. In this experiment, we replace the highly reactive NHCl with a diethyl(aryl)phosphine group, which can be measured in the form of a metal chloride complex or as the free phosphine using the STM-BJ technique. In agreement with our premise, the conductance of the [(4-MeSPh)Et\textsubscript{2}P]AuCl complex agrees well with that of the free phosphine.

To gain a deeper understanding of electron transport across the NHCl−electrode interface, we investigate how the conductance of NHCl-bound single-molecule junctions changes with increasing molecular length. For this, we synthesized a new series of asymmetric oligophenylene derivatives. As in the previous design, each molecule is terminated by a SMe group on one end and a benzannulated NHCl−AuCl group on the other. Figure 3a shows the molecular structure of NHCl\textsubscript{0}−AuCl, NHCl\textsubscript{1}−AuCl, and NHCl\textsubscript{2}−AuCl.

Figure 2. (a) Molecular structure of NHCl\textsubscript{1}−MCl, as determined by SCXRD. Color code: black, C; blue, N; yellow, S; green, Cl; orange, Cu; gray, Ag; gold, Au. Hydrogens are omitted. (b) Sample conductance versus displacement traces of NHCl\textsubscript{1}−AuCl, offset laterally for clarity. The plateau at ∼3 × 10\textsuperscript{−4} G\textsubscript{0} results from the single-molecule junction. (c) Logarithmically binned 1D conductance histograms (100 bins/decade) of NHCl\textsubscript{1}−MCl junctions, each composed of at least 2 000 traces without data selection. All measurements are in PC at a tip bias of −720 mV.

Figure 3. (a) Molecular structure of NHCl\textsubscript{n}−AuCl (n = 0, 1, and 2), as determined by SCXRD. Note that the structure for NHCl\textsubscript{1}−AuCl is repeated from Figure 2a for completeness. (b) Logarithmically binned 1D conductance histograms (100 bins/decade) of NHCl\textsubscript{n}−AuCl, each composed of at least 2 000 traces obtained without data selection. All measurements are performed in PC at a tip bias of −360 mV. (Inset) Semilogarithmic plot of the conductance histogram peak value as a function of the number of phenylene units in the backbone of NHCl\textsubscript{n}−AuCl.
NHC2–AuCl, as determined by SCXRD. As with the NHC1–MCl series, molecular junctions only form under reducing conditions in PC. Figure 3b presents the 1D conductance histograms of all three molecules (2D conductance–displacement histograms are presented in Figure S10). Each histogram shows a clear peak below $G_0$ and the conductance decreases with increasing molecular length. The inset of Figure 3b shows a semilogarithmic plot of the conductance values, obtained from a Gaussian fit to the histogram as a function of the number of phenylene units $n$ in the molecular backbone. An exponential fit to the data with $G \sim e^{-\beta n}$ gives a conductance decay $\beta = 1.8$ per phenylene. This $\beta$ value is in good agreement with that reported for oligophenylene molecular junctions with other linkers.2,34

To support these measurements, we perform DFT-based atomistic calculations of NHC1–M and NHCn–Au junctions (see Experimental Section). These junctions are modeled with both NHC and SMe groups bound to undercoordinated metal atoms on the electrode surface (Figure 4a and Figure S11).30,35 The atomic simulations underscore the strength of the NHC contact, regardless of the undercoordinated metal M: the computed binding energies of the NHC to the undercoordinated metal M are 1.6–2.0 eV (Table S2), comparable to reported binding energies of NCs to Au(111) surfaces (1.5–1.75 eV),12,30 and significantly higher than those calculated for thiolate-based Au–S bonds.36,37 For the NHCn–Au series, the calculated binding energy of the molecule in the junction is $\sim 2.7$ eV and is essentially independent of the number of phenylene units $n$ (Table S2). The NHC contact is responsible for most of the binding ($\sim 2.0$ eV), while the contribution of the Au–SMe bond is smaller ($\sim 0.7$ eV), in agreement with previous calculations.38

DFT-based transport calculations are subsequently applied to establish the role the NHC contact plays in the transport properties of NHC1–M and NHCn–Au junctions. Figure 4b presents the calculated transmissions as a function of energy relative to Fermi level ($E_F$) for all three types of NHC1–M junction. For each junction type, the high-transmission peak closest to $E_F$ derives from the lowest unoccupied molecular orbital (LUMO). A peak with lower transmission originating from a $\delta$-localized metal–molecule state is observed at ca. $-1.5$ $V$, which has previously been attributed to the Au–S gateway state.39 The precursor metal atom M introduces only minor changes in the transmission function, but it modulates the low-bias conductance. In agreement with the measurements, we find a slightly lower conductance for Ag and Cu precursors than for Au. The position of the occupied resonance and resulting zero-bias conductance follow the trend in the position of the d-states in Au, Ag, and Cu.30

Analysis of the transmission functions of the NHCn–Au junctions reveal that the LUMO and other empty molecular states derive mainly from the NHC unit while the SMe group contributes to the occupied state around $-1.5$ eV (Figures S12 and S13). The computed conductance for the NHCn–Au junctions decreases exponentially as $n$ increases. An exponential fit to the calculated values yields a decay constant $\beta \approx 1.6$ per phenylene (Figure S14), slightly lower than the experimental $\beta$. This difference is in line with the general trends of DFT-based calculations.27

The projection of the electronic coupling matrices of the NHC/SMe contacts (top/bottom contacts in Figure 4a) for the NHC1–Au junction onto the HOMO and LUMO (Figure 4c) reveals the role the NHC plays in the transport characteristics (see Supporting Information for details). The low transmission observed when the NHC or SMe contacts are projected onto the HOMO (left panel in Figure 4c) illustrates the poor electronic coupling of this state to the electrodes. By contrast, when the coupling matrix of the NHC–Au contact is projected onto the (NHC-derived) LUMO, the total transmission is almost recovered (right panel in Figure 4c). This demonstrates the excellent conducting properties of the NHC linker and quantifies the electronic coupling of the NHC-derived state to the electrode. In agreement with this finding, we see that current is carried by a single transmission channel, shown in Figure 4d at the LUMO energy, which resembles the LUMO of the isolated molecule (see Figure S15).

CONCLUSION

By designing a series of metal NHC complexes that can be electrochemically reduced in situ at the STM tip to form the NHC–electrode contact, we have demonstrated the first single-molecule study of electron transfer across an NHC–metal interface. Experimental and theoretical data indicate that the NHC conducts primarily through the LUMO. Given that many types of carbenes can form stable metal complexes, our in situ electrochemical approach opens the door to exploring the electronic properties of a wide range of carbene–electrode interfaces beyond NHCs. Remarkably, our method also introduces a unique strategy to manipulate the conductance of a single-molecule junction through in situ formation of heterometallic electrode contacts. Our results thus chart a clear path to define the final electrode structure down to the atomic
level, through a combination of careful molecular design and synthetic electrochemistry.

**ASSOCIATED CONTENT**

# Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b05184.

Additional data, synthetic methods, and characterization (PDF)

- $C_{14}H_{30}AuClN_2S$ (CIF)
- $C_{20}H_{24}AuClN_2S$ (CIF)
- $C_{26}H_{28}AuClN_2S$ (CIF)
- $C_{40}H_{40}AgClN_2S_2$ (CIF)
- $C_{20}H_{28}CICuN_2S$ (CIF)
- $C_{22}H_{34}AuClP_2S_2$ (CIF)

**AUTHOR INFORMATION**

**Corresponding Authors**

*lv2117@columbia.edu
*zxvquez@fzu.cz
*xr2114@columbia.edu

**ORCID**

Giacomo Lovat: 0000-0001-8926-005X
Héctor Vázquez: 0000-0002-3865-9922
Latha Venkataraman: 0000-0002-6957-6089
Xavier Roy: 0000-0002-8850-0725

**Author Contributions**

$^\dagger$E.A.D. and M.S.I. contributed equally to this work.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We are grateful to N. R. Papior for useful discussion. This work was supported in part by the Center for Precision Assembly of Superstatic and Superatomic Solids at Columbia University, an NSF MRSEC (DMR-1420634). Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund for partial support of this research (ACS PRF no. 57062-DNI10). Part of this work was also supported by the U.S. Air Force Office of Scientific Research (AFOSR) Grant no. FA9550-18-1-0020. Single-crystal X-ray diffraction analysis was performed at the Shared Materials Characterisation Laboratory (SMCL) at Columbia University. Use of the SMCL was made possible by funding from Columbia University, E.M. and H.V. thank the Purkyně Fellowship program of the Czech Academy of Sciences and the Czech Science Foundation (15-19672S). Computational resources were provided by the National Grid Infrastructure MetaCentrum and the “Projects of Large Research, Development, and Innovations Infrastructures” program (CESNET LM2015042 and LM2015087). M.S.I. was supported primarily by a Marie Skłodowska Curie Global Fellowship (MOLCLICK: 657247) within the Horizon 2020 Program.

**REFERENCES**