The functionalization of oxide surfaces through the covalent attachment of molecular monolayers has been intensively pursued, leading to very important advances in the fields of optoelectronics, biosensing, and catalysis. Different approaches were employed to achieve this goal, including the use of silanes, phosphonates, carboxylates, and thiols. N-Heterocyclic carbenes (NHCs) have been successfully employed in the modification of metal surfaces due to their capability of forming strong bonds to metallic centers. Furthermore, it is possible to tune the binding mode by carefully selecting the side groups. Less common is the attachment of NHC on semiconductors, and the direct binding of NHCs to metal oxides was not reported to date. In particular, mainly transition-metal NHC complexes were employed to functionalize metal oxide particles.

Many metal surfaces present a native oxide under ambient conditions, which can also participate in the adsorption of ligands. Among these metals, copper, an abundant and inexpensive first-row transition metal, is historically one of the most commonly employed in the development of technological applications. The functionalization of oxidized copper surfaces is challenging because the attachment of organic molecules leads to reduction. At the same time, many efforts have been made to avoid further oxidation of copper using thiols or, recently, NHC ligands. In photocatalysis, copper oxide is a widely used material and the attachment of organic molecules can be very beneficial.

In this work, we study the adsorption of a model NHC (1,3-bis(2,6-disopropylphenyl)imidazol-2-ylidine, IPr-NHC) molecule on a copper oxide layer grown on Cu(111) by means of low-temperature scanning tunneling microscopy (LT-STM), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT). We show that the IPr-NHC molecules strongly bind to the surface without distorting the long-range order of the oxide layer. Furthermore, we demonstrate that IPr-NHC forms a covalent bond with the oxygen atoms from the oxide layer, representing the first example of NHC attachment on a metal oxide where no metal complex is needed.

IPr-NHC molecules adsorb on the bare Cu(111) surface, forming a hexagonal lattice and well-defined structures such as the molecular islands in Figure 1a. This image corresponds to 0.25 ML of IPr-NHC on Cu(111). Occasionally, some molecules move during scanning (for example, the ones marked in Figure 1a), indicating a certain mobility under specific tunneling conditions. The formation of an oxide layer (Cu$_2$O) on Cu(111), as described in the Supporting Information (SI), results in a variety of structures depending on the amount of oxygen incorporated. In this case, most of the surface is covered by the “29” structure with some patches of the “41” structure. Both phases exhibit a characteristic row pattern. The evaporation of 0.05 ML (according to the calibration on bare Cu(111)) of IPr-NHC on the Cu$_2$O layer results in the arrangement shown in Figure 1b,c for the 29 and 41 phases, respectively. The observed arrangement on Cu$_2$O contrasts dramatically with the one on the bare Cu(111) surface. In particular, two properties for the arrangement on Cu$_2$O are worth mentioning: (1) The ligands do not form close-packed structures. (2) No molecular mobility is observed for a broad range of bias voltages (section C in the SI). Regarding the adsorption on the different oxide phases, the 41 regions present a higher coverage in comparison to the 29 regions, suggesting a certain difference in reactivity.

Figure 1d shows the Cu$_2$O surface after depositing 0.25 ML of IPr-NHC (coverage according to the calibration on the bare Cu(111)).
Cu(111) surface). A stripe pattern can be clearly recognized. The molecules arrange, forming rows especially in the regions with a lower density of molecules (orange lines). Interestingly, the distance between these rows matches the long lattice vector of the 29-CuO structure. The magnification shown in Figure 1e shows how the molecules are actually confined in the row pattern from the 29-CuO lattice, meaning that the molecular arrangement is strongly influenced by the substrate. In addition, the oxide structure is not distorted by the increased molecular coverage. The regions of the stripe pattern showing a higher density of molecules and poor order are, because of the relative quantity, probably related to the 41-CuO areas, indicating a lower site selectivity inside its unit cell.

The adsorption of IPr-NHC on CuO has been modeled by means of static structural relaxation with dispersion-corrected DFT. The complex potential energy surface was partially explored by studying three possible adsorption modes: chemisorption with the formation of a carbene−oxygen bond (NHC−O, Figure 2a,b), chemisorption with the formation of a carbene−Cu bond (NHC−Cu, Figure 2c,d), and aspecific physisorption (Figure 2e,f). The results are collected in Table 1. In NHC−O, the ligand binds to the support with a very large adsorption energy, \( D_e = -5.01 \) eV, and a C−O bond distance of 1.26 Å. The ligand is able to break a Cu−O bond in the oxidized overlayer, and the oxygen bond to the carbene center points outward from the surface. This structure may be a stable intermediate toward the reduction of the oxidized copper substrate by means of organic ligands. A less favorable though strongly bound configuration is obtained if IPr-NHC binds to a Cu atom from the CuO overlayer (\( D_e = -3.85 \) eV). Also in this case, a Cu−O bond is broken and the Cu atom is dragged out from the surface to bind the ligand (the C−Cu distance is 1.85 Å). It is interesting to compare these results with those obtained at the same level of calculations on the clean Cu(111) and Cu(100) surfaces, where IPr-NHC was found to attach to the surface with adsorption energies of as large as 3.7−4.20 eV while still being able to diffuse on the surface-forming islands and assembles.35 The remarkably larger \( D_e \) reported for the most stable structure, NHC−O, is a first hint explaining the nonmobile behavior of IPr-NHC on oxidized supports. A second, important aspect is that on Cu(111) the stable adsorption sites for the ligand are very close to each other, while in the present case a diffusion via desorption/readsorption necessarily implies the breaking of a strong C−O covalent bond. The least-stable configuration is the one envisaging only nonspecific dispersive interactions between the ligand and the surface, exerted by the large isopropylphenyl side substituents. This corresponds to a local minimum with \( D_e = -1.96 \) eV.

The role of the side substituents in terms of the additional stabilization of IPr-NHC is sizable in NHC−O and NHC−Cu as well, where the long-range dispersion accounts for 65 and 51% of \( D_e \). If phenyl (or smaller) groups are adopted instead of disisoproplyphenyl, then NHC−O and NHC−Cu binding modes display the same stability (section G in the S.I.),

| support  | bond     | \( D_e \) (eV) | bond length (Å) |
|----------|----------|----------------|-----------------|
| Cu(111)  | NHC−Cu   | -3.68          | 1.98            |
| CuO      | NHC−Cu   | -3.85          | 1.85            |
| CuO      | NHC−O    | -5.01          | 1.26            |
| CuO      | physisorption | -1.96       |                 |
highlighting the role of steric hindrance in determining the binding mode. Previous studies showed the strong influence of the side substituents in the binding mode of NHCs on metallic surfaces. While the diisopropylphenyl groups used in the present study lead to vertical adsorption, other side substituents favor a lying configuration, lifting a metallic atom from the substrate and forming mononuclear complexes. On polycrystalline copper oxide, a treatment with 1,3-diisopropylbenzimidazoliumhydrogen carbonate results in the formation of a cyclic urea and an NHC copper complex.

The formation of a covalent bond between IPr-NHC and the O atoms from the CuO is further supported by XPS measurements. Figure 3a,b show the O 1s spectra for the as-prepared CuO and for the IPr-NHC adsorbed on CuO, respectively. For the as-prepared CuO surface, the observed O 1s peak appears at 529.5 eV (Figure 3a), in agreement with previous studies. After the deposition of IPr-NHC, a new component at higher binding energy, 531.3 eV, appears (Figure 3b). In addition, the original peak found in the as-prepared CuO sample is now located at 529.7 eV. Our DFT calculations predict a shift of +0.6 eV toward higher binding energies. The XPS data corroborate this energy shift. Our study demonstrates that NHCs anchor strongly to the CuO layer, predicting a shift of the O 1s level toward higher binding energies.

The qualitative agreement between DFT and XPS data supports the idea of IPr-NHC ligands forming a covalent bond to oxygen atoms from the oxide layer. The formation of bonds between NHCs and oxygen atoms is well reported for the synthesis of cyclic ureas. In the present work, however, the binding oxygen atom preserves the bond with the oxide layer (Figure 2a,b). The binding oxygen atom thus acts as an anchor atom (section 1 in the S.I.), fixing the IPr-NHC molecule on the CuO layer. This strong attachment provides good thermal stability of the ligands, even at temperatures of up to 420 K (section 2 in the S.I.). Interestingly, the functionalization of oxide surfaces takes place normally with the NHC group forming a metal complex. In the present study, the carbene centers can bind directly to the O atoms from the CuO layer.

To conclude, IPr-NHC successfully attaches on a CuO layer grown on Cu(111). A strong interaction between the ligands and the substrate is supported by STM measurements, revealing a molecular arrangement governed by the CuO structure. DFT calculations found that the most stable molecular configuration for IPr-NHC on CuO/Cu(111) is one in which IPr-NHC binds covalently to an O atom from the CuO layer, predicting a shift of the O 1s level toward higher binding energies. The XPS data corroborate this energy shift. Our study demonstrates that NHCs anchor strongly to the CuO lattice through oxygen atoms from the oxidized surface, exhibiting thermal stability at temperatures of up to 420 K.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c06335.

Methods; copper oxide structures on Cu(111); STM of IPr-NHC on CuO at different bias voltages; apparent size of IPr-NHC from STM images; Cu 2p, CuLMM, C 1s, and N 1s XPS peaks; DFT calculations for different substituents; and thermal stability of IPr-NHC on CuO/Cu(111) (PDF)

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REFERENCES

(1) Pujari, S. P.; Scheres, L.; Marcelis, A. T. M.; Zuilhof, H. Covalent Surface Modification of Oxide Surfaces. Angew. Chem., Int. Ed. 2014, 53, 6322–6356.
(2) Dias, A.; Hussain, A.; Marcos, A.; Roque, A. Biotechnological perspective on the application of iron oxide magnetic colloids modified with polysaccharides. Biotechnology Advances 2011, 29, 142–155.
(3) Sui, R.; Lesage, K. L.; Carefoot, S. K.; Fürstenhaupt, T.; Rose, C. J.; Marnett, R. A. Selective Adsorption of Thiols Using Gold Nanoparticles Supported on Metal Oxides. Langmuir 2016, 32, 9197–9205.
(4) Le, M. N.; et al. Versatile Solution-Processed Organic–Inorganic Hybrid Superlattices for Ultraflexible and Transparent High-Performance Optoelectronic Devices. Adv. Funct. Mater. 2021, 31, 2103285.
(5) Wechsler, D.; Fernández, C. C.; Steinrück, H.-P.; Lytkench, O.; Williams, F. Covalent Anchoring and Interfacial Reactions of Adsorbed Porphyrins on Rutile TiO2(110). J. Phys. Chem. C 2018, 122, 4480–4487.
(6) Grimm, O. C.; Somaratne, R. M. D. S.; Wang, Y.; Kim, S.; Whitten, J. E. Thiol adsorption on metal oxide nanoparticles. Phys. Chem. Chem. Phys. 2021, 23, 8309–8317.
(7) Crudden, C. M.; Horton, J. H.; Ebralidze, I. I.; Zenkina, O. V.; McLean, A. B.; Drevniok, B.; She, Z.; Kraatz, H.-B.; Mosey, N. J.; Seki, T.; Keske, E. C.; Leake, J. D.; Rousins-Webb, A.; Wu, G. Ultra-stable self-assembled monolayers of N-heterocyclic carbenes on gold. Nat. Chem. 2014, 6, 409–414.
(8) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. An overview of N-heterocyclic carbenes. Nature 2014, 510, 485–496.
(9) Zhukhovitskiy, A. V.; MacLeod, M. J.; Johnson, J. C. Carbone Ligands in Surface Chemistry: From Stabilization of Discrete Elemental Allotropes to Modification of Nanoscale and Bulk Substrates. Chem. Rev. 2015, 115, 11503–11532.
(10) Wang, G.; Rühlung, A.; Amirjalya, S.; Knor, M.; Ernst, J. B.; Richter, C.; Gao, H.-J.; Timmer, A.; Gao, H.-Y.; Doltinsin, N. L.; Glorius, F.; Fuchs, H. Ballbot-type motion of N-heterocyclic carbenes on gold surfaces. Nat. Chem. 2017, 9, 152–156.
(11) Jiang, L.; Zhang, B.; Méard, G.; Seitsen, A. P.; Haag, F.; Allegretti, F.; Reichert, J.; Kuster, B.; Barth, J. V.; Papageorgiou, A. C. N-Heterocyclic carbenes on close-packed coinage metal surfaces: bis-carbene metal adatom bonding scheme of monolayer films on Au, Ag and Cu. Chem. Sci. 2017, 8, 8301–8308.
(12) Smith, C. A.; Narouz, M. R.; Lummis, P. A.; Singh, I.; Nazemi, A.; Li, C.-H.; Cruden, C. M. N-Heterocyclic Carbenes in Materials Chemistry. Chem. Rev. 2019, 119, 4986–5056.
(13) Koy, M.; Bellotti, P.; Das, M.; Glorius, F. N-Heterocyclic carbenes as tunable ligands for catalytic metal surfaces. Nat. Catal. 2021, 4, 352–363.
(14) Bellotti, P.; Koy, M.; Hopkinson, M. N.; Glorius, F. Recent advances in the chemistry and applications of N-heterocyclic carbenes. Nat. Rev. Chem. 2021, 5, 711–725.
(15) Bakker, A.; Timmer, A.; Kolodziecki, E.; Freitag, M.; Gao, H. Y.; Mönig, H.; Amirjalya, S.; Glorius, F.; Fuchs, H. Elucidating the Binding Modes of N-Heterocyclic Carbenes on a Gold Surface. J. Am. Chem. Soc. 2018, 140, 11889–11892.
(16) Franz, M.; et al. Controlled growth of ordered monolayers of N-heterocyclic carbenes on silicon. Nat. Chem. 2021, 13, 828–835.
(17) Schernich, S.; Laurin, M.; Lytkench, O.; Steinrück, H.-P.; Tsud, N.; Skála, T.; Prince, K. C.; Taccardi, N.; Matolín, V.; Wasserscheid, P.; Libuda, J. Functionalization of Oxide Surfaces through Reaction with 1,3-DialkyldimazolidiniumIonic Liquids. J. Phys. Chem. Lett. 2013, 4, 30–35.
(18) Shaikh, M.; Sahu, M.; Gavel, P. K.; Turpu, G. R.; Khilari, S.; Pradhan, D.; Ranganath, K. V. Mg-NHC complex on the surface of nanomagnesium oxide for catalytic application. Catal. Commun. 2016, 84, 89–92.
(19) Shaikh, M.; Sahu, M.; Khilari, S.; Kumar, A. K.; Maji, P.; Ranganath, K. V. S. Surface modification of polyhedral nanocrystalline MgO with imidazolium carboxylates for dehydrogenation reactions: a new approach. RSC Adv. 2016, 6, 82591–82595.
(20) Gürbüz, N.; Özdemir, I.; Seçkin, T.; Çetinkaya, B. Surface Modification of Inorganic Oxide Particles with a Carbene Complex of Palladium: A Recyclable Catalyst for the Suzuki Reaction. J. Inorg. Organomet. Polym. 2004, 14, 149–159.
(21) Ranganath, K. V. S.; Kleoegs, J.; Schäfer, A. H.; Glorius, F. Asymmetric Nanocatalysis: N-Heterocyclic Carbenes as Chiral Modifiers of Fe3O4/Pd nanoparticles. Angew. Chem., Int. Ed. 2010, 49, 7786–7789.
(22) Ranganath, K. V. S.; Schäfer, A. H.; Glorius, F. Comparison of Superparamagnetic Fe3O4-Supported N-Heterocyclic Carbene-Based Catalysts for Enantioselective Allylation. ChemCatChem. 2011, 3, 1889–1891.
(23) Ernst, J. B.; Muratsugu, S.; Wang, F.; Tada, M.; Glorius, F. Tunable Heterogeneous Catalysis: N-Heterocyclic Carbenes as Ligands for Supported Heterogeneous Ru/K-Al2O3 Catalysts To Tune Reactivity and Selectivity. J. Am. Chem. Soc. 2016, 138, 10718–10721.
(24) Ernst, J. B.; Schwermann, C.; Yokota, G.-i.; Tada, M.; Muratsugu, S.; Doltinsin, N. L.; Glorius, F. Molecular Adsorbates Switch on Heterogeneous Catalysis: Induction of Reactivity by N-Heterocyclic Carbenes. J. Am. Chem. Soc. 2017, 139, 9144–9147.
(25) Rafiee, F.; Mehdiyad, N. Palladium N-Heterocyclic Carbone Complex of Vitamin B1 Supported on Silica-Coated Fe3O4 Nanoparticles: A Green and Efficient Catalyst for C-C Coupling. Catal. Lett. 2018, 148, 1345–1354.
(26) Bullock, R. M.; Chen, J. G.; Gagliardi, L.; Chirik, P. J.; Farha, O. K.; Hendon, C. H.; Jones, C. W.; Keith, J. A.; Klosin, J.; Minteer, S. D.; Morris, R. H.; Radosovich, A. T.; Rauchfuss, T. B.; Strotman, N. A.; Vojodic, A.; Ward, T. R.; Yang, J. Y.; Surendranath, Y.; et al. Using nature’s blueprint to expand catalysis with Earth-abundant metals. Science 2020, 369, eabc3183.
Zemlyanov, D. Y. Trimethylaluminum and Oxygen Atomic Layer Deposition on Copper Oxide Surfaces and Layers. *Langmuir* 2016, 32, 3848–3857.

(29) Bergsman, D.; Liu, T.-L.; Closser, R. G.; Nardi, K. L.; Draeger, N.; Hausmann, D. M.; Bent, S. F. Formation and Ripening of Self-Assembled Multilayers from the Vapor-Phase Deposition of Dodecanethiol on Copper. Chem. Mater. 2018, 30, 5694–5703.

(30) Veinot, A. J.; Al-Rashed, A. A.; Padmos, J. D.; Singh, J.; Lee, D. S.; Narouz, M. R.; Lummis, P. A.; Baddeley, C. J.; Cruden, C. M.; Horton, J. H. N-Heterocyclic Carbene Reduce and Functionalize Copper Oxide Surfaces in One Pot. *Eur. J. Chem.* 2020, 26, 11431–11434.

(31) Petrovic, Z.; Metkios-Hukovic, M.; Babic, R. Modification of copper with self-assembled organic coatings. *Prog. Org. Coat.* 2008, 61, 1–6.

(32) Hosseinpour, S.; Hedberg, J.; Baldelli, S.; Leygraf, C.; Johnson, M. Initial Oxidation of Alkanethiol-Covered Copper Studied by Vibrational Sum Frequency Spectroscopy. *J. Phys. Chem. C* 2011, 115, 23871–23879.

(33) Berg, I.; Amit, E.; Hale, L.; Toste, F. D.; Gross, E. N-Heterocyclic Carbene Nanolayer for Copper Film Oxidation Mitigation. *Angew. Chem., Int. Ed.* 2022, 61, e202201093.

(34) Chen, T.-N.; Kao, J.-C.; Zhong, X.-Y.; Chan, S.-J.; Patra, A. S.; Lo, Y.-C.; Huang, M. H. Facet-Specific Photocatalytic Activity Enhancement of Cu2O Polyhedra Functionalized with 4-Ethynylpyridyl-amino-silane Resulting from Band Structure Tuning. *ACS Cent. Sci.* 2020, 6, 984–994.

(35) Navarro, J. J.; Das, M.; Tosoni, S.; Landwehr, F.; Koy, M.; Heyde, M.; Pacchioni, G.; Glorius, F.; Cuenya, B. R. Growth of N-Heterocyclic Carbene Assemblies on Cu(100) and Cu(111): from Single Molecules to Magic-Number Islands. *Angew. Chem., Int. Ed.* 2022, 61, e202202127.

(36) Jensen, F.; Besenbacher, F.; Stensgaard, I. Two new oxygen induced reconstructions on Cu(111). *Surf. Sci.* 1992, 269–270, 400–404.

(37) Matsumoto, T.; Bennett, R.; Stone, P.; Yamada, T.; Domen, K.; Bowker, M. Scanning tunneling microscopy studies of oxygen adsorption on Cu(111). *Surf. Sci.* 2001, 471, 225–245.

(38) Thirrien, A. J.; Zhang, R.; Lucci, F. R.; Marcinkowski, M. D.; Hensley, A.; McEwen, J.-S.; Sykes, E. C. H. Structurally Accurate Model for the “29”-Structure of CuxO/Cu(111): A DFT and STM Study. *J. Phys. Chem. C* 2016, 120, 10879–10886.

(39) Huang, M.; Zhong, Y.; Lu, S.; Guo, Q.; Yu, Y. Antimony allotropes fabricated on oxide layer of Cu(111). *Thin Solid Films* 2021, 727, 138669.

(40) Lovat, G.; Doud, E. A.; Lu, D.; Kladnik, G.; Inkpen, M. S.; Steigerwald, M. L.; Cvetko, D.; Hybertsen, M. S.; Morgante, A.; Roy, X.; Venkataraman, L. Determination of the structure and geometry of N-heterocyclic carbenes on Au(111) using high-resolution spectroscopy. *Chem. Sci.* 2019, 10, 930–935.

(41) Larrea, C. R.; Baddeley, C. J.; Narouz, M. R.; Mosey, N. J.; Horton, J. H.; Cruden, C. M. N-Heterocyclic Carbene Self-Assembled Monolayers on Copper and Gold: Dramatic Effect of Wingtip Groups on Binding, Orientation and Assembly. *ChemPhysChem* 2017, 18, 3536–3539.

(42) Shirley, D. A. High-Resolution X-Ray Photoemission Spectrum of the Valence Bands of Gold. *Phys. Rev. B* 1972, 5, 4709–4714.

(43) Moritani, K.; Okada, M.; Teraoka, Y.; Yoshigoe, A.; Kasai, T. Reconstruction of Cu(111) Induced by a Hyperthermal Oxygen Molecular Beam. *J. Phys. Chem. C* 2008, 112, 8662–8667.

(44) Gharchorlou, A.; Detwiler, M. D.; Gu, X.-K.; Mayr, L.; Klötzer, B.; Greesly, J.; Reifenberger, R. G.; Delgass, W. N.; Ribeiro, F. H.; Zemlyanov, D. Y. Trimethylaluminum and Oxygen Atomic Layer Deposition on Hydroxyl-Free Cu(111). *ACS Appl. Mater. Interfaces* 2015, 7, 16428–16439.

(45) Li, Y.; Chen, H.; Wang, W.; Huang, W.; Ning, Y.; Liu, Q.; Cui, Y.; Han, Y.; Liu, Z.; Yang, F.; Bao, X. Crystal-plane-dependent redox reaction on Cu surfaces. *Nano Research* 2020, 13, 1677–1685.

(46) Hayashida, K.; Tsuda, Y.; Yamada, T.; Yoshigoe, A.; Okada, M. Revisit of XPS Studies of Supersonic O2Molecular Adsorption on Cu(111): Copper Oxides. *ACS Omega* 2021, 6, 26814–26820.

(47) Li, D.; Olevier, T. Mechanism studies of oxidation and hydrolysis of Cu(I)−NHC and Ag−NHC in solution under air. *J. Organomet. Chem.* 2020, 906, 121025.

(48) Hussein, M. A.; Nguyen, T. V. Promotion of Appel-type reactions by N-heterocyclic carbenes. *Chem. Commun.* 2019, 55, 7962–7965.

(49) Kato, T.; Matsuoka, S.-i.; Suzuki, M. N-Heterocyclic carbene-mediated redox condensation of alcohols. *Chem. Commun.* 2016, 52, 8569–8572.

(50) Zeng, W.; Wang, E.; Qiu, R.; Sohail, M.; Wu, S.; Chen, F.-X. Oxygen-atom insertion of NHC−copper complex: The source of oxygen from N,N-dimethylformamide. *J. Organomet. Chem.* 2013, 743, 44–48.

(51) Tskhovrebov, A. G.; Solari, E.; Wodrich, M. D.; Scopelliti, R.; Severin, K. Covalent Capture of Nitrous Oxide by N-Heterocyclic Carbenes. *Angew. Chem., Int. Ed.* 2012, 51, 232–234.