

The newly discovered architecture of a copper-nitrenoid complex could revolutionize chemical synthesis

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Betley and his team of collaborators have characterized the architecture of a copper-nitrenoid complex, a catalyst hunted for over a half century. Credit: Harvard University

To make soap, just insert an oxygen atom into a carbon-hydrogen bond. The recipe may sound simple. But carbon-hydrogen bonds, like gum

stuck in hair, are difficult to pull apart. Since they provide the foundation for far more than just soap, finding a way to break that stubborn pair could revolutionize how chemical industries produce everything from pharmaceuticals to household goods.

Now, researchers at Harvard University and Cornell University have done just that: For the first time, they discovered exactly how a reactive copper-nitrene catalyst—which like the peanut butter used to loosen gum's grip on hair, helps nudge a chemical reaction to occur—could transform one of those strong carbon-hydrogen bonds into a carbon-nitrogen [bond](#), a valuable building block for chemical synthesis.

In a paper published in *Science*, Kurtis Carsch, a Ph.D. student in the Graduate School of Arts and Sciences at Harvard University, Ted Betley, the Erving Professor of Chemistry at Harvard, Kyle Lancaster, Associate Professor of Chemistry at Cornell University, and their team of collaborators, not only describe how a reactive copper-nitrene catalyst performs its magic, but also how to bottle the tool to break those stubborn [carbon-hydrogen bonds](#) and make products like solvents, detergents, and dyes with less waste, energy, and cost.

Industries often forge the foundation of such products (amines) through a multi-step process: First, raw alkane materials are converted to reactive molecules, often with high-cost, sometimes noxious catalysts. Then, the transformed substrate needs to exchange a chemical group, which often requires a whole new catalytic system. Avoiding that intermediate step—and instead instantly inserting the desired function directly into the starting material—could reduce the overall materials, energy, cost, and potentially even the toxicity of the process.

That's what Betley and his team aimed to do: Find a catalyst that could skip chemical steps. Even though researchers have hunted for the exact make-up of a reactive copper-nitrene catalyst for over a half century and

even speculated that copper and nitrogen might be the core of the chemical tool, the exact formation of the pair's electrons remained unknown. "Electrons are like real estate, man. Location is everything," Betley said.

"The disposition of electrons in a molecule is intimately tied to its reactivity," said Lancaster, who, along with Ida DiMucci, a graduate student in his lab, helped establish the inventories of electrons on the copper and the nitrogen. Using X-ray spectroscopy to find energies where photons would be absorbed—the mark of an electron's absence—they found two distinct holes on the nitrogen.

"This flavor of nitrogen—in which you have these two electrons missing—has been implicated in reactivity for decades, but nobody has provided direct experimental evidence for such a species."

They have now. Typically, if a copper atom binds to a nitrogen, both give up some of their electrons to form a covalent bond, in which they share the electrons equitably. "In this case," Betley said, "it's the nitrogen with two holes on it, so it has two free radicals and it's just bound by a lone pair into the copper."

That binding prevents the volatile nitrene from whizzing off and performing destructive chemistry with whatever gets in its way. When someone gets a cut on their leg, for example, the body sends out a reactive oxygen species, similar to these nitrene radicals. The [reactive oxygen species](#) attacks invading parasites or infectious agents, but they can damage DNA, too.

So, to contain the reactive nitrene, first-author Carsch built a massive cage in the form of a ligand. The ligand—like organic shrubbery surrounding the copper nitrene pair—keeps the catalyst intact. Cut back that shrubbery and introduce another substance—like a carbon-hydrogen

bond—and the fiery nitrene gets to work.

Betley calls the catalyst a skeleton key, a tool with the potential to unlock bonds that would otherwise be too strong to use in synthesis. "Hopefully, we can generate these chemical species that are now going to be so reactive that they render the most inert kind of substances we have around us as something we can play with," he said. "That would be really, really powerful." Since the building blocks—like copper and amines—are abundant and cheap, the skeleton key could unlock more practical ways to make pharmaceuticals or household products.

When Carsch first made the molecule, "he was literally bounding with joy," Betley said. "I was like, 'OK, settle down.'" But the results got more interesting: the nitrene reacts better than expected even though "the molecule has no right to be stable," and the bonding structure looked different than any of the designs proposed during the last six decades of research. "Had we proposed it at the outset, I think people would have scoffed at us."

Even though Betley chased this elusive species—what Lancaster calls "big game hunting"—ever since he launched his lab in 2007, he cares less about his win and more about his collaborators. "I get all my enjoyment from seeing Kurtis and my other students get super fired up about what they've actually been able to make." Carsch faced both critics and chemical walls but persisted in his hunt nonetheless. "I'm glad he's stubborn, as stubborn as I am," Betley said. They both might be as stubborn as the bonds they can now break.

At Cornell, when Lancaster and fifth-year graduate student DiMucci confirmed the findings, he "sent a rather colorful email" to the Betley team. But he, too, credits his collaborators. DiMucci spent seven days at the Stanford Synchrotron Radiation Lightsource analyzing the catalyst's electronic structure with their team. "Without their new experimental

capabilities," Lancaster said, "we really would not have had the signal to noise and the low background that made identifying this thing pretty easy."

Next, the team could draw inspiration from this new design to build catalysts with even broader-reaching applications, like mirroring nature's way of converting dangerous methane into methanol. "A real holy grail would be to say, 'OK, that C-H bond there, that particular one in this molecule, I want to turn that into a C-N bond or a C-O bond,'" Lancaster said. That may be a distant goal, but his so-called "dream team" could be the right one to hunt down the solution.

More information: "Synthesis of a copper-supported triplet nitrene complex pertinent to copper-catalyzed amination" *Science* (2019).
[science.sciencemag.org/cgi/doi ... 1126/science.aax4423](https://science.sciencemag.org/cgi/doi/10.1126/science.aax4423)

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