Replacing noble metals with nickel

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Credit: Washington University in St. Louis

Chemical synthesis can transform commodity chemicals into complex life-saving drugs, household products, or advanced materials. But this "alchemy" can also produce huge amounts of toxic waste or require harsh and dangerous conditions—and often relies on expensive and rare heavy metals to spark reactions.

In recent reports in the journals Dalton Transactions and the *Journal of the American Chemical Society*, the research team of Liviu Mirica, associate professor of chemistry in Arts & Sciences, has developed novel methods for generating the buildings blocks of important compounds with the common metal nickel.

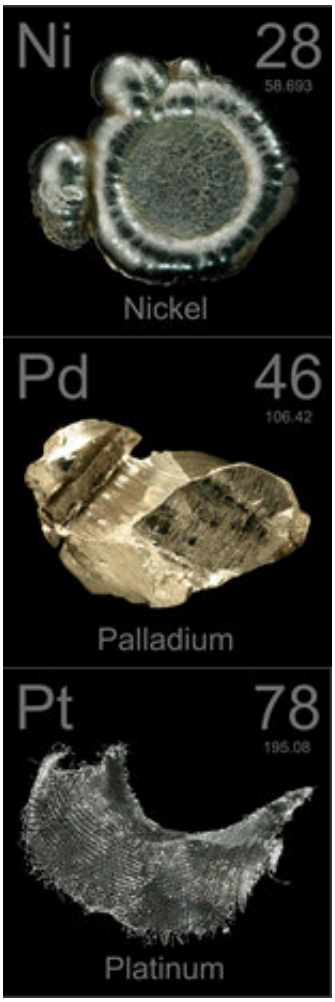
The work expands scientists' toolbox for nickel-based chemistry and contributes to the movement of "green chemistry" toward a 21st century of sustainable synthesis.

"Chemistry is 'greener', or more environmentally friendly, when chemical transformations are more efficient, fewer side products are produced, and most importantly the synthesis process creates less waste," Mirica said.

Toward this end, his lab researches how to elegantly create new compounds in as few steps as possible and with more sustainable catalysts, like nickel.

Using metals to goose carbon chemistry

Joining carbon atoms together in new combinations is the foundation of organic chemistry. But some carbon atoms are very stable. Those in carbon-hydrogen (C-H) bonds, for example, are considered unreactive and it can be difficult to coax them to create a new carbon-carbon (C-C) bond. So chemists like Wen Zhou, the postdoctoral scholar who is the first author of the two recent reports, rely on metals to "activate the bond," and make it more reactive. A metal atom, with its complex and diverse array of electrons, can help shuffle carbons around to make new compounds.



Nickel's position in the periodic table, in the same group as the expensive metals palladium and platinum, hints that it shares chemical properties with them. Credit: Washington University in St. Louis

The rare metals palladium and platinum have been used for decades for this reason, but they are expensive. Nickel, in the same chemical group, could be used for similar reactions if its properties were understood better.

"It turns out nickel is quite a bit more reactive than palladium," Mirica said.

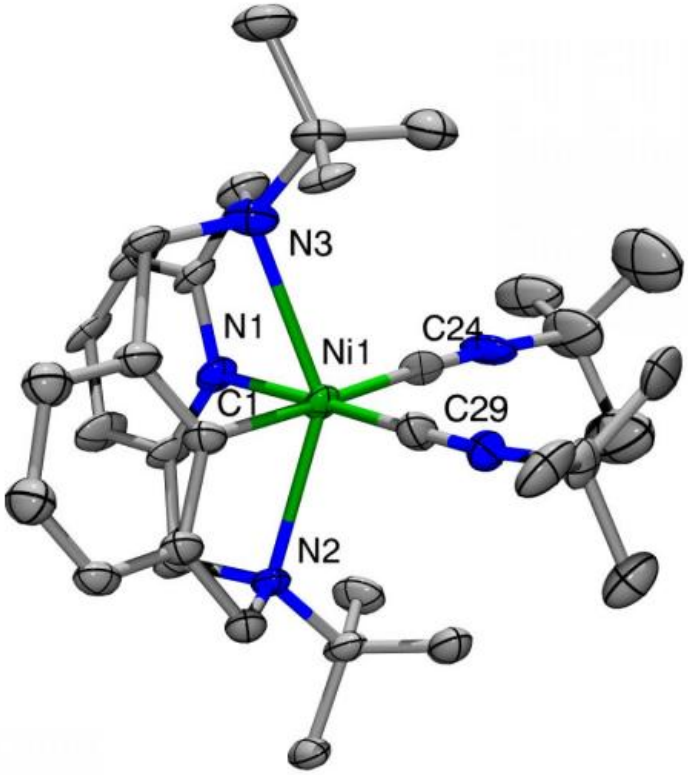
This greater reactivity allows reactions to proceed quickly and easily, but requires controlling the chemistry tightly to avoid producing unwanted side products.

A four-toothed chemical assistant

The scientists' key development was the creation of a new four-pronged molecule, known as a tetradentate ligand, which acts like the pocket of a baseball glove to grasp the nickel atom. When carbon-containing compounds also bind to the nickel center, the electrons can reshuffle to form a new C-C bond.

"These new ligands are able to stabilize the nickel center in different oxidation states, while also promoting rapid C-C bond formation reactivity," Zhou said.

The right balance of stability and reactivity allowed the scientists to create new bonds with cheap, safe and abundant nitriles, a class of carbon-containing compounds that can be turned into a whole range of useful chemical groups in simple synthetic steps.



Key innovation in nickel-based green chemistry is a four-pronged molecule (N1, N2,N3 and C24) that holds a nickel atom (Ni1) in such a way that it can participate in the bonding of two carbon atoms (C1 and C29). When an oxidant is added, the Ni center joins C1 and C29 together to create a new molecule. Credit: Washington University in St. Louis

The new ligand also gave the scientists the opportunity to explore nickel(III), a little-understood "oxidation state" of nickel missing three electrons (by convention, reactions that remove electrons are called oxidation reactions). The combination of nickel(III) and the new ligand promoted a reaction with two carbons, essentially condensing several steps into one.

And the final reaction took place in just a few minutes at room temperature, while similar reactions with other metals might need high temperatures, harsh conditions for hours or days.

Still, the novel ligand the scientists developed requires its own complicated synthesis and specialized conditions to produce. Zhou wants to learn how to condense the process down further, into something that could be scaled up one day, while expanding the type of new bonds that can be promoted by nickel.

"We want to simplify the system," Zhou said. "This ligand is pretty big and kind of hard to synthesize. However, it provided us insight into how to stabilize nickel(III) and now we're working on developing simpler systems that can perform similar reactions."

The hope is nickel could replace the rare and pricey heavy metals that have been used for years in the chemical industry and research labs like Mirica's.

"In the past, people have used platinum for catalyzing various difficult reactions, but it's very expensive," Zhou said. For example, his platinum wedding ring cost more than $100 a gram.

"Then people switched to palladium—an excellent catalyst for a large number of chemical reactions. But still palladium is not ideal because it's also a precious metal and is found in limited quantity."

Shuffling around for a five-cent coin to make his point, Zhou said, "For nickel, you know how cheap it is."

More information: Wen Zhou et al. Oxidatively-induced aromatic cyanation mediated by Ni(), *Dalton Trans.* (2016). DOI: 10.1039/c6dt00064a

Wen Zhou et al. Aromatic Cyanoalkylation through Double C–H Activation Mediated by Ni(III), *Journal of the American Chemical Society* (2016). DOI: 10.1021/jacs.6b02405