

Cyclobutane derivatives made from [2+2] cycloaddition of feedstock alkenes and an iron-based catalyst

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(Phys.org)—Substituted cyclobutanes, four-membered carbon rings with substituents on some of the carbon atoms, can be made with regio- and stereo-selectivity through various methods, including photochemistry. But because these methods often require activated alkenes, there are limits to the varieties of substituted cyclobutanes that are synthetically available. There has been much interest in making cyclobutanes from simple, unactivated, alkenes that are often used in industrial processes using a reaction that is analogous to a [4+2] Diels Alder cycloaddition reaction. While this is thermodynamically feasible, until now, it has not been realized.

Jordan M. Hoyt, Valerie A. Schmidt, Aaron M. Tondreau, and Paul J. Chirik from Princeton University have overcome this obstacle by designing transition-metal based catalysts that successfully promote the formation of regio- and stereo-selective cyclobutanes via the [2+2] cycloaddition of unactivated alkenes under mild conditions. Their work appears in *Science*.

They exacted this process by applying prior research using iron- or cobalt-based catalysts with redox active pyridine(diimine) ligands that they had used to make other cyclic compounds to industrial alkenes. For the [2+2] cycloaddition to work, they needed to tweak the peripheral atoms on the catalyst complex to target their desired reaction pathway. Their synthetic goals were to prevent β -hydrogen elimination and

promote C-C reductive elimination to obtain the desired cyclobutane, and to design a catalyst that was broadly useful for a several types of alkenes. They were successful in both of these.

The pyridine(diimine) ligand is adjustable by changing the substituents on the imines as well as changing those on the aryl groups. Specifically, they changed the methyl groups to ethyl groups on the imines to prevent imine dissociation, and thus preventing the unwanted β -hydrogen elimination reaction. They also replaced the isopropyl groups on the aryl rings with cyclopentyl, which are bulky groups that also constrain the ligand system.

By tweaking these organic features on the iron-based catalyst, Hoyt, et al. were able to preferentially react simple alkenes, such as propene, to form 1,2-disubstituted cyclobutane products. After tweaking their catalyst, such that the imine substituents were covalently attached to the central pyridine, thus making a more rigid structure, they were also able to react dienes with alkenes to form 1,3-disubstituted cyclobutane products. Both reactions types were done under relatively mild conditions (neat, 23°C, 48 hours) and are scalable.

According to principle investigator, Dr. Paul Chirik, "Our method is exciting because we can use an earth abundant metal to catalyze a [reaction](#) of overabundant hydrocarbons like butadiene and propylene and convert them into a core structure in organic chemistry that has not been adequately explored. The chemistry of simply four-membered rings has been largely unavailable because of the lack of synthetic access."

More information: "Iron-catalyzed intermolecular [2+2] cycloadditions of unactivated alkenes" *Science*, [DOI: 10.1126/science.aac7440](https://doi.org/10.1126/science.aac7440)

ABSTRACT

Cycloadditions, such as the [4+2] Diels-Alder reaction to form six-membered rings, are among the most powerful and widely used methods in synthetic chemistry. The analogous [2+2] alkene cycloaddition to synthesize cyclobutanes is kinetically accessible by photochemical methods, but the substrate scope and functional group tolerance are limited. Here, we report iron-catalyzed intermolecular [2+2] cycloaddition of unactivated alkenes and cross cycloaddition of alkenes and dienes as regio- and stereoselective routes to cyclobutanes. Through rational ligand design, development of this base metal-catalyzed method expands the chemical space accessible from abundant hydrocarbon feedstocks.

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