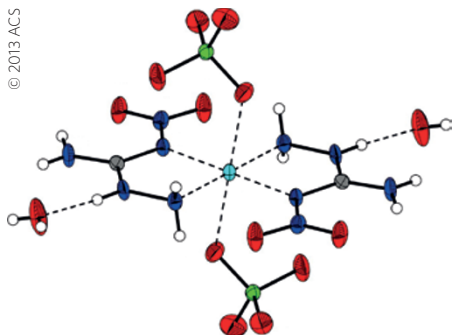


## ENERGETIC MATERIALS

### Bang go the complexes

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Primary explosives are high-energy materials that are typically used in small amounts to trigger the detonation of larger quantities of more stable explosives that are easier to store and handle. Not only is accidental detonation of these highly

sensitive materials a major concern, but toxicity can also be a problem, such as in the case of the commonly used lead azide. In an effort to improve the safety of these primary explosives, researchers are making and studying a range of different high-energy metal–ligand complexes that are non-toxic and that can potentially be detonated in a more controlled fashion, such as with a short laser pulse.

Now, Thomas Klapötke and co-workers at the University of Munich have prepared and investigated the properties of a series of metal complexes incorporating nitrogen-rich 3-amino-1-nitroguanidine (ANQ) ligands. Starting from a selection of simple Co, Ni, Cu, Zn and Ag salts, a range of different metal–ANQ complexes were formed, with either chloride, nitrate or perchlorate anions. In the case of Co, Ni and Ag, ANQ complexes with dinitramide anions,  $(\text{NO}_2)_2\text{N}^-$ , were also prepared. In total, 17 different compounds were isolated

and all of their solid-state structures were characterized using single-crystal X-ray analysis. Tests revealed that the materials displayed a range of impact and friction sensitivities with, on average, the perchlorate salts being the most sensitive and, perhaps unsurprisingly, the chloride salts being the least sensitive (chloride is a non-energetic anion).

Some of the perchlorate, nitrate and dinitramide complexes underwent laser ignition tests in which small pressed pellets of the samples were exposed to a single 100- $\mu\text{s}$  pulse of a 940-nm-wavelength laser. Only the Co, Cu and Ag perchlorate complexes detonated under these conditions, with none of the nitrate or dinitramide materials showing any response to the laser pulse. Although the mechanism by which the laser irradiation causes these metal complexes to detonate is not known, this study does offer some clues and points to an electronic process rather than a thermal trigger. **SC**

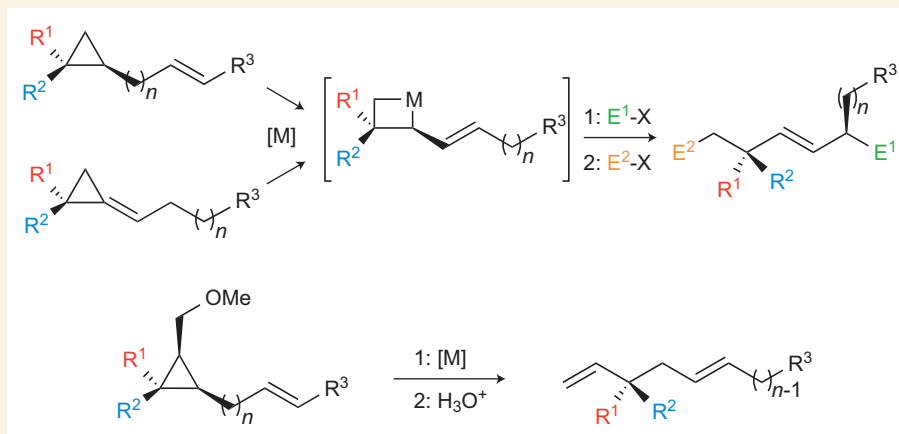
## ORGANOMETALLIC CHEMISTRY

### Activating in concert

*Nature* **505**, 199–203 (2014)

Making complex and highly functionalized molecules from simple, relatively unreactive substrates is a goal of many modern synthetic techniques. The development of protocols that activate C–H bonds for reaction have in recent years opened up new areas of substrate reactivity and led to new syntheses of useful compounds. Techniques to activate C–C bonds have seen much less development and are more limited in scope, often suffering from selectivity problems. Now, a group of researchers, led by Ilan Marek from the Israel Institute of Technology, have discovered a new reaction that combines both of these challenging approaches in a single transformation and allows chemoselective sequential functionalization of a reactive intermediate.

In the method a zirconium-based reagent is employed in the activation of unsaturated cyclopropanes. When the substrate is an  $\omega$ -ene-cyclopropane, the metal first activates the allylic C–H bond, before then carrying out a reversible ‘walk’ along the adjacent carbon chain (pictured, top). Once the metal reaches the cyclopropane, it irreversibly and selectively inserts into a C–C bond of the ring. This doubly activated organozirconium intermediate can then be quenched by successive additions of electrophiles. The first equivalent of



electrophile reacts at the activated allylic carbon, which occurs diastereoselectively in enantiopure substrates, and the second at the metallated carbon of the now-fragmented cyclopropane. The technique is not limited to  $\omega$ -ene-cyclopropanes; the same reactive organozirconium intermediate can be generated from alkylidenecyclopropane substrates, which can be easily prepared in enantiopure form. Because of the doubly activated nature of the reactive intermediate and the chemoselectivity of its reaction with electrophiles, a diverse range of acyclic and highly substituted

molecules can be prepared from simple hydrocarbon substrates.

Marek and co-workers also report another mode of reactivity for unsaturated cyclopropanes (pictured, bottom). With a methoxymethyl substituent on the cyclopropane ring, a fragmentation mechanism from the metallated intermediate occurs giving acyclic unconjugated dienes with high selectivity for the *E* isomer. Owing to its selectivity, potential diversity, and wide application to substrates, the reported reaction is likely to find wide use. **PM**