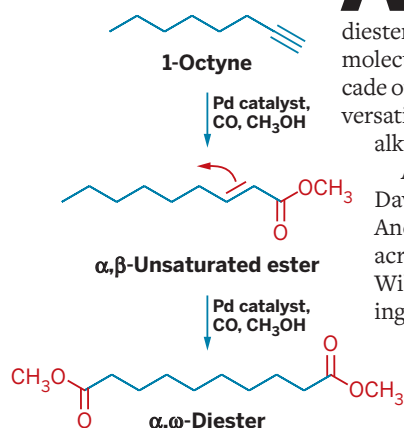


EXTENDING ALKYNE VERSATILITY

ORGANIC INTERMEDIATES: Selective cascade isomerization reaction converts alkynes into α,ω -diesters

A **COLLABORATIVE** academic-industry research team in the U.K. has devised a method to convert the terminal triple bond of an alkyne into a diester with the two ester groups at opposite ends of the molecule. This unusual reaction, made possible by a cascade of double-bond isomerization steps, provides new versatility in preparing chemical intermediates from alkynes, which are popular chemical feedstocks.

A team including A. Alberto Núñez Magro and David J. Cole-Hamilton of the University of St. Andrews, in Scotland, and Graham R. Eastham of acrylic polymer producer Lucite International, in Wilton, England, made the discovery when exploring methoxycarbonylation reactions (*Chem. Sci.*, DOI: 10.1039/cosco0276c). In these reactions, carbon monoxide and methanol are added sequentially to a carbon-carbon double or triple bond to form an ester.



Cole-Hamilton's group found that the palladium catalyst used for the reaction is highly selective for producing linear esters rather than branched esters, which are the usual products of alkyne carbonylations. Lucite also uses this catalyst, which features a customized phosphinomethylbenzene ligand, to make methyl propanoate from ethylene as part of a commercial route to methyl methacrylate monomer.

In the new reaction, the first step is the methoxycarbonylation of an alkyne to form an α,β -unsaturated ester, Cole-Hamilton explains. The ester's carbon-carbon double bond then isomerizes stepwise to each carbon along the molecule's chain, a process his group has observed before with unsaturated esters. When the double bond reaches the end of the chain—the thermodynamically least-favored position for the double bond—it's trapped by a second methoxycarbonylation step, thereby forming an α,ω -diester.

Although alkoxycarbonylation reactions to prepare esters are well-known, the new one boasts "very high linear selectivity, as well as the unprecedented second step to give α,ω -diesters," says Chao-Jun Li of McGill University, in Montreal, who specializes in alkyne-based coupling reactions. "This work provides a nice alternative to the less-atom-economical Wittig reaction and Heck-type reactions," Li notes. "Furthermore, the diesters are highly useful, for example, in polymer synthesis."—STEVE RITTER

MULTIMETAL ORGANIC COMPLEXES

SYNTHESIS: Method couples various metals in predetermined sequences

M **AKING MOLECULES** that contain multiple metal atoms and more than one type of metal is notoriously tough. But that's exactly what a research team based in Japan and the U.S. has done.

The researchers have devised a method to string metal-containing molecular segments in specific sequences and lengths to form surface-tethered metal-organic complexes, including one with three types of metals and a total of six metal atoms (*J. Am. Chem. Soc.*, DOI: 10.1021/

ja1097644). Complexes of this type may mediate highly selective catalytic reactions or "cascading reactions."

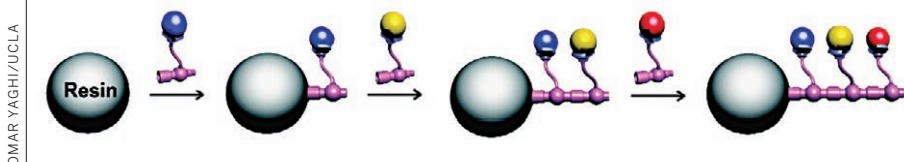
The underlying design strategy is an adaptation of the Merrifield solid-phase peptide synthesis, according to Omar M. Yaghi of UCLA, who led the study.

To make the complexes, Yaghi, Kentaro Tashiro of the National Institute for Materials Science, in Tsukuba, Japan; and coworkers functionalized tyrosine with a multidentate ligand and reacted the product with platinum, rhodium, or ruthenium. Then they attached one of those building blocks to a polymeric resin and linked additional building blocks to the surface-bound unit to tailor-make products featuring a desired number of metal atoms in a particular sequence. For example, they prepared one of the complexes by coupling units containing Rh, Pt, Ru, Pt, Rh, Pt—in that order.

"The idea of extending the Merrifield solid-phase synthesis to metal-coordination complexes to create predetermined and varying metal sequences is brilliant," says Northwestern University's Mercurio G. Kanatzidis, a materials chemistry specialist.

This technique has the potential to inspire broad-based activity in tailor-made complexes for specific applications, Kanatzidis says. "I am curious to see how people will use this approach. Who knows," he laughs, "finally we may be able to synthesize the Co-Ca-Co-La molecule."—MITCH JACOBY

METALATED Metal-organic complexes featuring several types of metal atoms (blue, yellow, red) arranged in targeted sequences can be prepared from functionalized tyrosine building blocks (pink) via a method similar to solid-phase peptide synthesis.



OMAR YAGHI/UCLA