AMINO ACIDS ANCHOR NOVEL C–H OLEFINATION

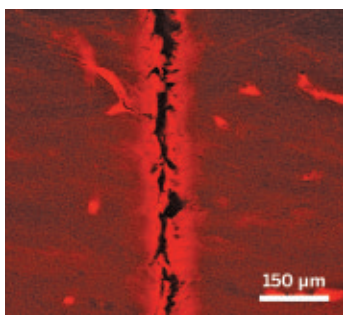
With the help of amino acid ligands, a team at Scripps Research Institute has developed a versatile way to functionalize C–H bonds on aromatic rings with olefins (*Science*, DOI: 10.1126/science.1182512). The process might come in handy for synthesizing natural products and drugs. Chemists traditionally have turned to the palladium-catalyzed Mizoroki-Heck reaction to forge C–C bonds between aromatic rings and olefins, but the process requires an aryl halide, which isn't always easy to make. As an alternative, palladium-catalyzed C–H olefination has been plagued by limited substrate scope or a requirement for stoichiometric palladium. In contrast, the new olefination by Jin-Quan Yu and colleagues works on a variety of substrates and uses catalytic amounts of palladium. The researchers attribute the versatility to amino acid ligands, which enhance the catalyst's reactivity and selectivity.—CD

CATALYST COMBO FOR CYCLOHEXANONE

Researchers at the Chinese Academy of Sciences' Institute of Chemistry, in Beijing, have found that combining two common catalysts can produce the industrially important chemical intermediate cyclohexanone at higher yields and lower temperatures than do current methods (*Science* **2009,** *326,* 1250). Tao Jiang and colleagues used a palladium nanoparticle catalyst on a solid support and the Lewis acid catalyst $AlCl_3$ to hydrogenate phenol to cyclohexanone. The reaction, when carried out at 50 °C and 1 megapascal of H_2, proceeds with essentially 100% yield and selectivity. Cyclohexanone is the starting material used in the synthesis of materials such as nylon. Hydrogenating phenol via a palladium catalyst is a key industrial route to cyclohexanone, but it typically requires high temperatures (150–300 °C) and suffers from low yields. Scientists have searched for catalysts to improve the reaction, but they have had trouble preventing continued hydrogenation of cyclohexanone into cyclohexanol. Interactions between the Lewis acid and cyclohexanone might inhibit the excess hydrogenation into cyclohexanol.—EKW

ILLUMINATING TINY BONE BREAKS

The first luminescent lanthanide contrast agent capable of imaging microcracks in bone has been developed by chemists in Ireland (*J. Am. Chem. Soc.,* DOI: 10.1021/ja908006r). The cyclen-based europium compound could be used for bone structure analysis, lighting up barely visible fractures caused by repetitive loading and stress. Trinity College Dublin's Thorfinnur Gunnlaugsson and coworkers constructed the contrast agent so that it contains three iminodiacetate moieties hanging off the cyclen ring. These groups selectively bind to exposed calcium sites in the damaged bone's hydroxyapatite matrix, and a covalently linked naphthalene antenna sensitizes europium to its excited state. The researchers were able to differentiate polished and scratched bone four hours after exposure to the complex using confocal fluorescence laser-scanning microscopy. Gunnlaugsson tells C&EN that his group is currently developing the imaging agent for use in living systems.—BH

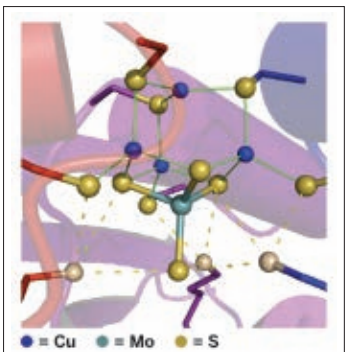


J. AM. CHEM. SOC.

A europium imaging agent lights up a microcrack in a cow bone.

NEW METALLOPROTEIN CLUSTER DISCOVERED

Crystallographic analysis of tetrathiomolybdate (TM) interacting with the yeast metallochaperone protein Atx1 has revealed a copper-molybdenum cluster never before seen in metalloproteins (*Science,* DOI: 10.1126/science.1179907). Atx1 is related to the human protein Atox1, which forms a complex with Wilson disease protein in order to transfer copper. TM is used to inhibit several copper enzymes, but the structures of the complexes are not yet known. Thomas V. O'Halloran of Northwestern University and coworkers expected that TM would inhibit Atx1 by removing copper from its binding site and forming a polymeric copper-molybdenum sulfide precipitate. Instead, the copper remains in its binding site and forms part of a nest-shaped cluster that consists of four Cu^+, a single MoS_4^{2-}, and three pairs of sulfur atoms from two Atx1 cysteines involved in copper binding. In a gel-based assay, the researchers show that TM inhibits Atx1's copper chaperone activity.—CHA



SCIENCE

NESTING MoS_4^{2-} **forms a nest-shaped cluster with Atx1.**

UREA-RNA DISRUPTION

Scientists have made a fundamental advance in biochemistry by using simulations to discover a new type of interaction between urea and RNA (*J. Am. Chem. Soc.,* DOI: 10.1021/ja9057951v). Urea has long been used to denature proteins, and it was recently found to destabilize RNA. Studies have shown that urea disrupts proteins by interacting with their peptide backbones and hydrophobic side chains, but the mechanism by which it aggravates RNA remained unknown. A team led by Devarajan (Dave) Thirumalai of the University of Maryland, College Park, and Alexander D. MacKerell Jr. of the University of Maryland, Baltimore, now reports all-atom molecular dynamics simulations that reveal how urea hydrogen bonds and stacks with RNA's bases, making normal interaction between bases impossible. "The microscopic mechanism of chemical denaturants has bedeviled the protein- and RNA-folding fields for decades," comments Tobin R. Sosnick of the University of Chicago. "The stacking interaction is unexpected and an important insight."—SB