

Spotlights on Recent JACS Publications

■ CATCHING GOLD ATOMS ON THE RUN WITH A MOLECULAR DRAGNET

Gold nanocrystals have become popular catalysts for a variety of oxidation and reduction reactions, many of which have high commercial significance. The smallest nanocrystals tend to have higher catalytic activity, but also have a pronounced drawback: Over time, they sacrifice atoms to bigger nanocrystals, eventually losing their effectiveness.

Seeking a way to prevent this attrition, a group led by Niklas Nilius, Siegfried Blechert, and Joachim Sauer has developed tris(phenylthio)benzene molecules that trap individual gold atoms as they escape nanocrystal surfaces (DOI: 10.1021/ja300304s). The researchers find that applying a layer of these organic molecules successfully traps gold atoms at the surface of bulk gold crystals, preventing them from associating with larger nanocrystals. Scanning tunneling microscopy images show that the tris(phenylthio)benzene molecules generally clumped together in pairs, with each dimer capturing six gold atoms. However, at very cold temperatures, single molecules captured six gold atoms apiece.

In a scenario closer to real-world use, the researchers also tested their molecules with gold nanoparticles on an aluminum oxide surface. Tests showed that the molecules again successfully trapped gold atoms, leading to the formation of new ultrasmall nanocrystals. The researchers suggest that these molecular dragnets effectively steer the distribution of gold nanoparticles in a way that maintains strong catalytic activity.
Christen Brownlee

■ COPPER EASES THE WAY TO BUILDING BICYCLIC COMPOUNDS

Xiang-Ping Hu and co-workers have found a way to synthesize optically active bicyclo[*n*.3.1] frameworks that are part of a large variety of natural and bioactive compounds, including those with antidepressant, antimicrobial, antifungal, and anti-inflammatory activities (DOI: 10.1021/ja303129s). These bicyclo[*n*.3.1] ring systems can serve as key building blocks for organic chemistry, and this new process is efficient and uses mild conditions.

Hu and co-workers use a copper(II) catalyst and a chiral ferrocene-based ligand to produce bicyclo[*n*.3.1]alkane frameworks from propargyl esters and enamines. Their method for cycloaddition is both diastereo- and enantioselective. The reaction is also tolerant to variations in the two reagents, as the researchers successfully used a number of phenyl-substituted propargyl acetates and several cyclic enamines to synthesize a range of bicyclo[*n*.3.1] framework structures.

The authors' work is a significant addition to the small pool of available catalytic asymmetric methods for synthesizing optically active bicyclo[*n*.3.1] frameworks, which may be incorporated into bioactive compounds.
Yun Xie, Ph.D.

■ ELECTRONIC STRUCTURE OF AROMATIC AZABORINE COMPOUNDS

Anna Chrostowska, Shih-Yuan Liu, and co-workers have synthesized and characterized three azaborines that are isostructural and isoelectronic with either benzene or toluene, in that they are six-membered aromatic rings with boron and nitrogen in place of one carbon each (DOI: 10.1021/ja303595z). The researchers extensively characterize the molecular orbitals of these new compounds using ultraviolet photoelectron spectroscopy (UV-PES) and compare them with the all-carbon analogues.

These measurements are used in combination with calculations to predict the highest occupied molecular orbital energies, molecular dipole moments, maximum UV-vis absorption wavelengths, and other physical properties. The researchers verify the theoretical predictions using a variety of techniques including electrochemistry, UV-vis spectroscopy, and thin-layer chromatography, and they find good agreement between theory and experiment.

Recently there has been a resurgence of interest in developing boron-nitrogen-containing heterocycles that mimic other aromatic molecules. The authors suggest that this work opens up new possibilities for structural diversity that may impact research in the biomedical field and materials science by facilitating the development of molecules or materials with new properties.
Polly Berseth, Ph.D.

■ METALLOFULLERENES PURIFIED BY FILTRATION

Metal atoms trapped inside hollow carbon cages could be useful materials for electronics or biomedicine. However, these metallofullerenes have not found widespread use, possibly because they are difficult to purify on a large scale. Several rounds of time-consuming chromatography yield less than 10% of the product on a production scale.

Kazuhiko Akiyama, Hisanori Shinohara, and co-workers isolate metallofullerenes with 99% yield and purity via filtration following a 10-min reaction with titanium tetrachloride (DOI: 10.1021/ja3030627). Intact metallofullerenes collect as a solid, while empty carbon cages remain suspended in solution. The new purification method works for 10 different metal atoms and a variety of cage sizes.

Using atomic spectrometry measurements of the solids trapped on the filter, the researchers measured 18–19 titanium atoms surrounding each cage. They suspect that TiCl₄, which is a liquid at room temperature, diffuses through the impure metallofullerene solution and surrounds the metal-filled cages. Charge transfer between the titanium atoms and the metal-containing cage stabilizes this complex.

That critical charge transfer leads the researchers to believe that all metallofullerenes, regardless of interior metal or cage size, with a first oxidation potential around 0.5–0.6 V can be purified using this method.
Melissae Fellet

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■ FINDING ABLE ABELSON INHIBITORS

Abelson tyrosine kinase (Abl) is an enzyme that plays important roles in cell growth and signaling processes. However, an alternate form of the protein, called BCR-Abl, has been implicated in leukemia. To facilitate discovery of allosteric inhibitors of BCR-Abl, Daniel Rauh and co-workers developed an assay capable of detecting small molecules that cause changes in the conformation of Abl (DOI: 10.1021/ja303858w).

BCR-Abl inhibitors are promising anticancer drugs, but most directly target the enzymatically active part of the protein, and unfortunately many stop working as the cancer evolves. One strategy for circumventing this issue is to use inhibitors that bind to other parts of the protein, so-called allosteric inhibitors, which work by causing changes in the conformation of the protein. In combination with traditional inhibitors, this approach has been successful in treating certain types of leukemia.

The assay developed by the researchers uses a modified form of Abl that has a strategically placed fluorescent molecule attached to it. Conformational changes in the protein triggered by an allosteric inhibitor alter the fluorescent properties of the enzyme complex, providing a way to detect such inhibitors. This assay offers a valuable tool for discovery of specialized Abl inhibitors with therapeutic potential for leukemia. Identification of additional allosteric inhibitors of BCR-Abl may lead to increasingly effective treatment strategies for leukemia.
Eva J. Gordon, Ph.D.

■ FRUSTRATED LEWIS PAIR COMPOUNDS ARE TOTALLY RADICAL

Long-lived or persistent radicals are important chemical tools due to their ability to act as reagents for widely used radical-based polymerizations. The type of radical employed can affect the size distribution of molecules in the reaction mixture, thereby affecting the properties of the final polymeric or composite material.

A group led by Timothy Warren, Armido Studer, Stefan Grimme, and Gerhard Erker has discovered a new and effective radical system, namely FLP-NO radicals that were formed by addition of a frustrated Lewis pair (FLP) compound to nitric oxide (NO) (DOI: 10.1021/ja302652a). Illustrating their high reactivity, FLP-NO adducts are capable of abstracting hydrogen atoms from a variety of substrates. FLP compounds, which contain both a Lewis acid and base that cannot combine due to their steric bulkiness, are highly reactive compounds coming to the forefront of small-molecule activation chemistry.

The new FLP-NO radicals described in this article showed higher reactivity in hydrocarbon functionalization chemistry than the most commonly used radical initiator TEMPO, suggesting that FLP-NO radicals are a valuable addition to the current library of persistent aminoxyl radicals. In addition, the easily prepared compounds could potentially be synthesized with a specific application or polymer in mind, resulting in tailor-made radical reagents and a more direct route to desired and useful polymers and materials.
Leigh Krietsch Boerner, Ph.D.