

Spotlights on Recent JACS Publications

■ STRONG REDUCING AGENT FROM A METAL–METAL QUADRUPLE BOND

Stoichiometric reducing agents have been important tools for studying and understanding electronic structure and bonding in myriad chemical systems. Dennis L. Lichtenberger, Carlos A. Murillo, and colleagues report the general synthesis and photoelectron spectra of two new compounds with tungsten–tungsten quadruple bonds that add to the family of strong reducing agents for such work (DOI: 10.1021/ja408291k).

These compounds are thermally stable and easy to synthesize in high yields and good purity. Modification of the bicyclic guanidinate ligands significantly increases the solubility of the compounds in nonpolar solvents, thereby increasing the number of potential chemical systems in which the ditungsten compounds could be applied.

The new tungsten compounds set a record for the lowest ionization energies of any laboratory-prepared molecules. The low ionization energy and the stability over a range of oxidation states—properties that are mediated by the bicyclic guanidinate ligand—make the compounds potentially useful reagents for further application in organometallic, enzymatic, and organic electronic systems.

Sonja Krane, Ph.D.

■ HYBRID ULTRATHIN FILMS CAN HANDLE THE HEAT

As temperatures rise, the performance of membranes for separating gas molecules on the basis of size typically breaks down as a result of increased macromolecular dynamics that compromise the material's sieving abilities. Now researchers led by Nieck E. Benes present a new method for creating ultrathin membranes that can separate gases at temperatures up to 300 °C (DOI: 10.1021/ja410047u).

The unprecedented characteristics of these membranes are thanks to the hybrid organic–inorganic nature of the hypercross-linked films, which are made up of inorganic silicon oxide cage molecules known as polyhedral oligomeric silsesquioxane (POSS), linked in a periodic network by organic aromatic imide bridges. Unlike the syntheses of other nanoengineered materials that have been demonstrated for high-temperature separations to date, the two-step synthetic process for generating the polyPOSS-imide films is suitable for large-scale, defect-free production.

The simple and reliable synthetic route makes the films compatible with industrial-scale applications that require the separation of hot gases, such as large-scale chemical processes and the development of advanced energy production technologies.

Christine Herman, Ph.D.

■ 37 STEPS TO A DAPHNIPHYLLUM ALKALOID

Isolated in 2008, (–)-calyciphylline N belongs to the *Daphniphyllum* alkaloid family that comprises more than 180 known members to date. Despite the diverse biological activities of these natural products—examples include cytotoxic

agents, tubulin polymerization inhibitors, and vasorelaxants—synthetic studies on the *Daphniphyllum* alkaloids are very limited. Now, Artem Shvartsbart and Amos B. Smith, III, have accomplished the first total synthesis of (–)-calyciphylline N, meeting the challenge presented by the structural complexity (DOI: 10.1021/ja411539w).

Out of the six contiguous chiral carbon centers in (–)-calyciphylline N, three are quaternary bridgehead carbons. In addition, the molecule's central bicyclo[2.2.2]octane core is fused with two complicated ring systems. The researchers first construct the bicyclic core using a highly diastereoselective Diels–Alder reaction, generating four chiral centers in a single step. Equally noteworthy is the chemo- and diastereoselective hydrogenation of the fully substituted, extremely hindered diene ester moiety, which furnishes the last two stereogenic centers.

This total synthesis not only provides access to structurally intricate (–)-calyciphylline N, with a longest linear sequence of 37 steps starting from a simple chiral phenylethanol, but also opens up a new synthetic avenue to other congeners in the *Daphniphyllum* alkaloid family.

Xin Su, Ph.D.

■ CONNECTING PROTEINS AND CARBOHYDRATES WITH SULFUR

Many proteins are adorned with carbohydrate groups, and these groups often bestow important properties onto the proteins upon which they reside. Though carbohydrates are typically linked to the protein surface through an oxygen or a nitrogen atom, Wilfred A. van der Donk and co-workers discover an enzyme—only the second identified to date—that connects the two biomolecules via the sulfur atom of the amino acid cysteine (DOI: 10.1021/ja411159k).

This novel enzyme, called ThuS, was discovered during the authors' efforts to identify new antibiotics by mining the genome of *Bacillus thuringiensis*, a soil-dwelling bacterium with pesticidal activity. They show that ThuS can link carbohydrates to peptides through either an oxygen or a sulfur atom. Notably, ThuS is the first glycosyltransferase identified that can execute both types of linkages.

Further development and investigation into the mechanism of action of ThuS will offer insight into the biosynthesis and biological activity of other sulfur-linked glycopeptides. In addition, ThuS is a valuable new tool for the synthesis of novel glycopeptides for a variety of biotechnological and therapeutic applications.

Eva J. Gordon, Ph.D.

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