

László Kürti and John R. Falck of the University of Texas Southwestern Medical Center and Daniel H. Ess of Brigham Young University had previously explored reactions using the aminating agent *O*-(2,4-dinitrophenyl)hydroxylamine, which they now use for aziridination. They also found that a rhodium catalyst and 2,2,2-trifluoroethanol solvent are essential. Their approach works on hindered olefins and doesn't disturb sensitive functional groups. The method isn't enantioselective yet, Kürti says, but the team is using the Ess lab's density functional theory calculations to hunt for the right catalyst for that job.—CD

RADICAL APPROACH TO BETTER BATTERIES

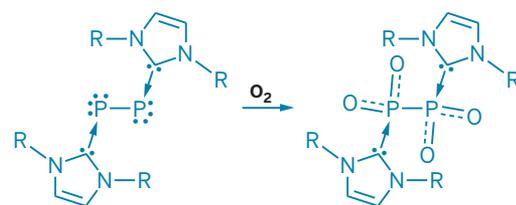
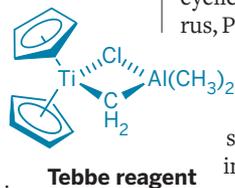
Energy storage is among today's greatest technical challenges, and chemists are playing a leading role by developing new materials to improve battery technology for automotive and power grid applications. In one of the latest advances, an academia-industry team has designed a high-performance battery that uses nascent silicon and heavier group 14 radical compounds as anode materials (*Angew. Chem. Int. Ed.* 2013, DOI: 10.1002/anie.201308302). The

researchers, led by Akira Sekiguchi of the University of Tsukuba and Hideyuki Nakano of Toyota Central R&D Labs, both in Japan, have been exploring new materials for making lithium-free batteries. In the current work, they focused on crystals of the radical compounds $(R_2R'Si)_3Si^{\bullet}$, where $R = \textit{tert}$ -butyl and $R' = \textit{methyl}$, were used to make a battery anode.

crystals of the radical compounds $(R_2R'Si)_3E^{\bullet}$, where $R = \textit{tert}$ -butyl, $R' = \textit{methyl}$, and $E = \text{Si, Ge, or Sn}$. They mixed the radical compounds with carbon black to make anodes and then paired the anodes with a graphite cathode. During the charge-discharge cycle, the radicals are reduced to form anions and then oxidized to re-form radicals. The anodes have a larger energy density than standard dual graphite batteries, with the silicon radical providing the best performance. "This is a nice example of a potential application for compounds that were hardly believed to exist at ambient conditions 10 years ago," Sekiguchi says.—SR

STRUCTURE FINALLY RESOLVED FOR THE FAMOUS TEBBE REAGENT

The Tebbe reagent has been renowned for decades for its utility as a methylene-transfer reagent. Although DuPont chemist Frederick N. Tebbe first isolated the titanocene-aluminum complex in 1974, it has eluded definitive structural characterization because of its high reactivity, chemists believe. Researchers at Indiana University led by Rick Thompson and Daniel J. Mindiola, both now at the University of Pennsylvania, have solved the structure of the Tebbe reagent cocrystallized with an inert impurity (*Organometallics* 2013, DOI: 10.1021/om401108b). The project began when Thompson was a graduate teaching assistant for an advanced undergraduate inorganic chemistry lab in which the students had to prepare and use the Tebbe reagent. Thompson noticed indications of an impurity and pursued an analysis that culminated in the crystal structure, Mindiola says. The geometry of the reagent complex is largely as Tebbe predicted and studies of other compounds had indicated, with a $(C_5H_5)_2Ti$ group bridged to an $Al(CH_3)_2$ fragment through Cl and CH_2 groups. In the impurity, the bridging CH_2 is replaced by a second Cl. What surprised Mindiola and colleagues was the impurity, which makes up 40 to 50% of their crystallized reagent samples and had gone unrecognized in the past, even though Tebbe had predicted it.—JK



R = diisopropylphenyl

to stabilize diphosphorus tetroxide, P_2O_4 , the long-sought phosphorus analog of the rocket propellant N_2O_4 (*J. Am. Chem. Soc.* 2013, DOI: 10.1021/ja411667f). Robinson's group had previously used bulky *N*-heterocyclic carbene ligands to tame diphosphorus, P_2 , which itself is normally a transient species, unlike the ubiquitous N_2 . The researchers used the carbene-stabilized diphosphorus complex to split O_2 , forming a compound containing P_2O_4 . This method suggests a new strategy to probe the chemistry of the highly reactive simple phosphorus oxides, Robinson says, and it could lead to useful reagents for synthesizing phosphorus-containing molecules.—SR

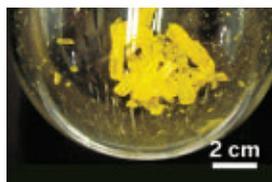
OPTICAL SENSOR PROVIDES A COLORFUL WAY TO DETECT H₂

The last thing anyone wants nearby when there's a hydrogen gas leak is a hot object with a lot of electrical connections. But the electronic H_2 sensors widely used in the chemical industry typically operate at temperatures between 100 and 300 °C and are hard-wired into electronic displays. Bernard Dam and Peter Ngene of Delft University of Technology, in the Netherlands, and coworkers have developed an optical sensor that more safely indicates the presence of H_2 with a simple color change that's visible to the naked eye (*Adv. Funct. Mater.* 2013, DOI: 10.1002/adfm.201303065). The device is built with thin films of yttrium and palladium. Upon absorption of H_2 , the nanocrystalline yttrium layer becomes transparent while the underlying palladium layer remains metallic and reflective. Refraction of light by the different yttrium-hydrogen adducts that form changes the sensor color to indicate the amount of H_2 present. Because the sensor is selective and sensitive even in the presence of water and oxygen, which bedevil conventional H_2 sensors, it could also be used to detect H_2 in human breath, which can indicate malabsorption of lactose or sucrose in the intestines during digestion.—CB

CHEMISTS TRAP SIMPLE PHOSPHORUS OXIDE

Although phosphorus resides immediately below nitrogen on the periodic table, the chemical behavior of the two elements is unexpectedly quite different. For example, when it comes to forming oxides, some of the most fundamental of chemical compounds, nitrogen readily forms linear NO , NO_2 , and N_2O_x ($x = 1, 3, 4, 5$), whereas phosphorus forms cage-like P_4O_6 and P_4O_{10} . Simpler phosphorus oxides such as PO and PO_2 are highly reactive and have only been studied in the gas phase or at cryogenic temperatures. Gregory H. Robinson, Yuzhong Wang, and coworkers at the University of Georgia have now found a way

COURTESY OF AKIRA SEKIGUCHI



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