

Titanium tales

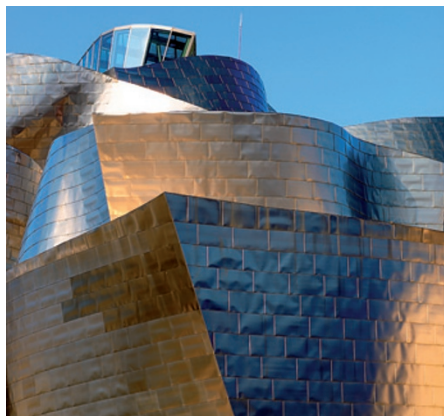
From toothpaste to Tebbe reagents, **Michael Tarselli** takes a look at the many different faces of titanium.

While writing, I stare through lenses held in place by lightweight and durable titanium frames. We adorn ourselves with titanium in many different ways, whether in earrings, marriage bands, or certain pins and fasteners used to hold together broken bones. You might brush your teeth with TiO₂-whitened paste, and that same glimmering white pigment can be found in the paint on your bedroom walls or the coatings on your pharmaceuticals. Single-crystal titania semiconductors will soon find homes in solar panels and tablet computers. Titanium has even been shot into space, built into the heat-resistant hull of NASA's Space Shuttle¹.

Element 22 is found almost everywhere — it ranks ninth in abundance among elements in the Earth's crust. A ubiquitous element demands a strong name, and titanium is fittingly named for the Titans, the ancient Greek immortals. Titanium's tough to isolate: you'll never find it in its metallic state in nature. Only in the past century has the pure metal become readily available; two common refinement processes require heating to around 300 °C with alkali-metal reductants.

Titanium (*s²d²*) lives on the outer fringes of the periodic table's 'd block', which includes redox champions such as manganese and chromium. Certainly no slouch when it comes to redox chemistry, titanium is commonly found in +2, +3 or +4 oxidation states, carrying heteroatoms (such as N, S and O) along for the ride.

Most organic chemists know titanium from TiCl₄, the prototypical Lewis acid involved in everything from aldol reactions to sugar deprotection. Prefer radical chemistry? Drop down one reduction level to TiCl₃, and you get pinacol adducts from imines and carbonyls. Titanium's rich coordination chemistry shows up best in 'half-sandwich' complexes, which can simultaneously tie up three ligands and unite them into short oligomers. Add another arene, and we're talking titanocenes — you'll find the Tebbe and Petasis reagents, two such



The titanium-clad Guggenheim Museum, Bilbao.

complexes used for olefination, in many synthetic laboratories.

Titanium works pretty well as a Lewis acid when starved of all four valence electrons. But, what if you give a few electrons back? Although attractive to heteroatoms in the +4 oxidation state, titanium(II) has a 'softer side' — it coordinates to alkynes and carbonyls, creating *umpolung* dianions. The Kulinkovich reaction, which generates cyclopropyl alcohols from aldehydes treated with a 'low-valent' titanium(II) reagent, kicked off a renaissance in titanium-coupling chemistry. Several research groups (including those of Micalizio, Cha and Panek) have utilized this unique reactivity to stitch together a wide array of alkaloids² and polyketides.

It's hardly surprising that such a well rounded metal has played its part in Nobel-worthy research. Ziegler and Natta's titanocene-based olefin polymerization catalysts cost little but exhibit high activity, such that polyethylene soda bottles and trash cans have traces of catalyst embedded in their walls — no sense in recovering the few nanograms of easily made complex! Sharpless's titanium-promoted epoxidation proved that single-enantiomer products could be generated from chiral catalysts. Even the early days of olefin metathesis used titanium carbenoids, long before the

now familiar molybdenum and ruthenium systems. Titanium may even make a name for itself in silicon metathesis — scientists in Japan and France recently characterized stable silacyclobutenes³.

The low cost and high abundance of titanium obviates any guilt over throwing away the relatively non-toxic salts produced as by-products in the reactions described above. However, new evidence suggests that this perspective might not be so simple: a recent *Analytical Chemistry* review⁴ investigates bio-accumulation and negative impacts on soil and water biomass imparted by varying doses of nanoparticulate titanium dioxide.

To limit environmental problems further down the road, we could translate stoichiometric titanium reactions into catalytic ones, much like earlier efforts for its transition metal cousins iron and copper. One 'green' approach to water purification uses photocatalysis: on ultraviolet light irradiation, doped TiO₂ catalysts form reactive oxygen species, which tear apart bacteria and biotoxins present in drinking water. Variants that utilize visible light⁵ are just starting to emerge. Several groups have also recently tackled multicomponent reactions in which titanium catalysts quickly stitch together drug-like molecules.

From pharmaceuticals to paint and from chemistry to jewellery, titanium pops up everywhere. In a numerical twist of fate, this year element 22 celebrates 222 years since its discovery. So raise a titanium silicate-coated champagne glass, and enjoy some titania-frosted cake. Delicious! □

MICHAEL A. TARSELLI is at Biomedisyn Corporation, 11 Research Dr., Woodbridge, Connecticut 06525, USA.
e-mail: mtarselli@biomedisyn.com

References

- <http://history.nasa.gov/SP-4221/ch8.htm>
- Yang, D. & Micalizio, G. C. *J. Am. Chem. Soc.* **134**, 15237–15240 (2012).
- Lee, V. Y. *et al. J. Am. Chem. Soc.* **135**, 2987–2990 (2013).
- Maurer-Jones, M. A., Gunsolus, I. L., Murphy, C. J. & Haynes, C. L. *Anal. Chem.* **85**, 3036–3049 (2013).
- Likodimos, V. *et al. Ind. Eng. Chem. Res.* <http://dx.doi.org/10.1021/ie3034575> (2013).

