



New Application Developments in PGMs – April 2009

Arene choreography: Palladium

Science, 03 April 2009

<http://www.sciencemag.org/content/vol324/issue5923/twil.dtl>

Selective substitution of benzene derivatives is a key component of pharmaceutical and fine chemicals synthesis. In general, the easiest positions to modify are the ring carbons directly adjacent to or across from electron-rich substituents already present. Electron-withdrawing groups, in contrast, tend to reduce inherent reactivity toward further substitution, thus hampering direct synthetic strategies for a wide range of desirable products. Zhang et al. have addressed this challenge through careful ligand design in palladium-catalyzed addition (via C-H activation) of unsaturated esters to electron-poor arenes to yield olefin-substituted products. The optimal, pyridine-based ligand was sufficiently electron-rich to facilitate reoxidation of the metal after an addition cycle, but also strategically bulky so as to hinder coordination of a second such ligand after the first had bound, thereby leaving a site open for the weakly coordinating arene substrate. The catalyst selectively appended acrylate and cinnamate derivatives at the meta position (two carbons away) of nitro-, trifluoromethyl-, and ester-substituted arenes. More conventional, directed palladium-catalyzed addition facilitated further substitution at the ring carbons in between. The method complements a recently reported meta-selective arylation employing a copper catalyst.

Pd(II)-catalyzed olefination of electron-deficient arenes using 2,6-dialkylpyridine ligand

Jake Yeston

Consecutive thermal hydrogen and light-induced oxygen evolution from water promoted by a ruthenium complex

Science, 03 April 2009

<http://www.sciencemag.org/cgi/content/abstract/324/5923/74>

Discovery of an efficient artificial catalyst for the sunlight-driven splitting of water into dioxygen and dihydrogen is a major goal of renewable energy research. We describe a solution-phase reaction scheme that leads to the stoichiometric liberation of dihydrogen and dioxygen in consecutive thermal- and light-driven steps mediated by mononuclear, well-defined ruthenium complexes. The initial reaction of water at 25°C with a dearomatized ruthenium (II) [Ru(II)] pincer complex yields a monomeric aromatic Ru(II) hydrido-hydroxo complex that, on further reaction with water at 100°C, releases H₂ and forms a cis dihydroxo complex. Irradiation of this complex in the 320-to-420-nanometer range liberates oxygen and regenerates the starting hydrido-hydroxo Ru(II) complex, probably by elimination of hydrogen peroxide, which rapidly disproportionates. Isotopic labeling experiments with H₂¹⁷O and H₂¹⁸O show unequivocally that the process of oxygen-oxygen bond formation is intramolecular, establishing a previously elusive fundamental step toward dioxygen-generating homogeneous catalysis.

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New dye design for solar cells: Ruthenium

Chemistry World, 06 April 2009

<http://www.rsc.org/chemistryworld/News/2009/April/06040902.asp>

A new type of dye could improve the lifespan of dye-sensitised solar cells - low-cost photovoltaic cells that can convert sunlight into electricity and thought to be some of the most promising for widespread use. Designed by Swiss and Japanese researchers, the dye has a light to electric conversion efficiency of 10.1 per cent, making it competitive with the best available.

Dye-sensitised solar cells (DSSCs) use dyes to capture energy from sunlight and convert it into electric current. Standard devices contain the ruthenium-based dye N719, which is considered one of the most efficient. But the lifespan of N719, and therefore most DSSCs, is limited by thiocyanate (SCN) ligands that reduce the chemical stability of the dye.

Hayley Birch

Bubbles turn on chemical catalysts

ScienceNews, 06 April 2009

http://www.sciencenews.org/view/generic/id/42507/title/Bubbles_turn_on_chemical_catalysts

Scientists have figured out a new way to strong-arm some catalysts, tying the chemical compounds down and then, as needed, unleashing them with brute force. The research, published online April 6 in Nature Chemistry, could lead to coatings that heal when scratched or new fluids for making moldings or microchips. The work also offers a way to monitor stress in materials found in products such as bike helmets.

A catalyst's job is to speed up or slow down a reaction in everything from car engines to cells. But to do so, an area known as the active site has to be exposed. In materials science, catalysts are often spurred into action with heat, UV light or a change in pH. In the new study scientists used the ultrasonic force released by bursting bubbles to unleash two catalysts that had been bound in chains of polymers.

Torn catalysts help polymers heal themselves

RSC, 06 April 2009

<http://www.rsc.org/chemistryworld/News/2009/April/06040904.asp>

Catalysts that are activated by a mechanical force tearing them in two have been designed by Dutch scientists. The team's ultimate goal is to develop these catalysts for use in self-healing materials where damaging the materials - by tearing, scratching or bending - automatically triggers the start of the repair process.

The team, led by Rint Sijbesma from the Eindhoven University of Technology, have made a series of metal-based latent catalysts that are completely unreactive until activated. To activate them, ultrasound is applied to mechanically break the bond between the metal and one of its polymer chain-based ligands. 'The ligand is pulled off the metal to activate the catalyst,' explains Sijbesma.

Nina Notman

Weizmann institute scientists develop a unique approach for splitting water into hydrogen and oxygen

Weizmann Institute of Science, 06 April 2009

http://wis-wander.weizmann.ac.il/site/en/weizman.asp?pi=371&doc_id=5517

The design of efficient systems for splitting water into hydrogen and oxygen, driven by sunlight is among the most important challenges facing science today, underpinning the long term potential of hydrogen as a clean, sustainable fuel. But man-made systems that exist today are very inefficient and often require additional use of sacrificial chemical agents. In this context, it is important to establish new mechanisms by which water splitting can take place.

Now, a unique approach developed by Prof. David Milstein and colleagues of the Weizmann Institute's Organic Chemistry Department, provides important steps in overcoming this challenge. During this work, the team demonstrated a new mode of bond generation between oxygen atoms and even defined the mechanism by which it takes place. In fact, it is the generation of oxygen gas by the formation of a bond between two oxygen atoms originating from water molecules that proves to be the bottleneck in the water splitting process. Their results have recently been published in Science.

Ripping into a catalyst

Ars technical, 08 April 2009

<http://arstechnica.com/science/news/2009/04/ripping-into-a-catalyst.ars>

One of the more fun "don't try this at home" (that also rates a "stand well back") cocktail-chemistry reactions is the creation and ignition of thermite. The very violent, spectacular reaction is fairly simple from a chemistry standpoint: it switches aluminum for the iron in rust, leaving behind aluminum oxide, iron, and a lot of energy. During the reaction, temperatures as high as 4,500°F are easily reached. While the reaction is highly exothermic—as evidenced by those temperatures—it faces a huge activation barrier. Aluminum and rust can sit together until the end of time without doing anything.

Nature Chemistry, 2009. DOI: [10.1038/NCHEM.167](https://doi.org/10.1038/NCHEM.167)

Mechanical Force Activates Catalyst: Ruthenium

Chemical & Engineering News, 13 April 2009

<http://pubs.acs.org/cen/news/87/i15/8715notw4.html>

Ultrasound turns on silver- and ruthenium-based catalysts

Chemists are intrigued by the possibilities of the new mechanical approach, which was developed by chemistry professor Rint P. Sijbesma and coworkers at Eindhoven University of Technology, in the Netherlands. "Coupling catalyst activity to a mechanical force is in principle completely orthogonal to the use of light, heat, or chemical activation," says Stephen L. Craig, a chemist at Duke University. One can imagine systems of multiple catalysts where one catalyst can be controlled specifically by force while others are controlled by more conventional stimuli, he says.

Sijbesma and postdocs Alessio Piermattei and Karthikeyan Sivasubramanian report two different metal-carbene catalysts that can be activated by mechanical force. They demonstrate that ultrasound-generated force triggers a silver-based catalyst to perform transesterification and a ruthenium-based catalyst to facilitate olefin metathesis (Nature Chem., DOI: 10.1038/nchem.167).

Rachel Petkewich

Osmium and pyridine ring together

RSC, 14 April 2009

<http://www.rsc.org/chemistryworld/News/2009/April/14040902.asp>

Organic chemists in China have found a way to put osmium into a pyridine ring - leading to the synthesis of the first metallapyridinium complex. The reaction makes use of the classic ring-forming Diels-Alder reaction, so there is great potential to extend this process to other metals and compounds, the researchers say.

Trapping metals in aromatic rings is a field of intense study - and although there are many examples of metallabenzenes, hetero-aromatic rings containing both metal atoms and nitrogen or oxygen atoms are rare. Although the new method is not yet refined, it could provide access to interesting new metallacycles.

Lewis Brindley

Straight route to nanorings: Ruthenium

Chemical & Engineering News, 14 April 2009-04-20

<http://pubs.acs.org/cen/news/87/i16/8716notw7.html>

NANOSCALE RINGS have been a challenging architecture to synthesize. Now, Caltech and University of California, Berkeley, chemists report a direct catalytic route for making these rings, which could have applications in drug delivery or organic photovoltaic devices (J. Am. Chem. Soc., DOI: 10.1021/ja901658c).

Grant Willson, a chemistry and chemical engineering professor at the University of Texas, Austin, says the new catalytic method exemplifies "the ability of chemists to control not only the sequence connectivity of atoms in molecules, but the way in which the resulting molecules form themselves into three-dimensional shapes."

Rachel Petkewich

Process for producing hydrogen peroxide and its use: Palladium

CAS Patent Watch, 13 April 2009

<http://www.cas.org/pwatch/041309.html>

Preferably, the noble metal is Pd, Au, or a Pd-Au mixt. The noble metal is reduced with hydrogen. The noble metal is supported on a carrier, such as silica, alumina, titania, aluminosilicates, silica-titanias, zeolites, clays, carbons, or ion exchangers. The thiol is tethered to the carrier. The thiol or thiolate improves the hydrogen peroxide yield.

Chiral metals shape up for catalysis: Palladium

Chemistry World, 19 April 2009

<http://www.rsc.org/chemistryworld/News/2009/April/19040902.asp>

Dutch and Israeli scientists have found a way to induce the chirality usually only found in organic materials in palladium. They say palladium and other so-called chirally imprinted metals will have widespread application in chiral catalysis.

Reducing a metal salt in the presence of a cinchona alkaloid dopant gives a chirally imprinted metallo-organic hybrid material that is catalytically active and shows moderate enantioselectivity in hydrogenation.

A route for making ethylene glycol (EG) without starting from ethylene is under development: Rhodium

Patent Watch, 20 April 2009

http://portal.acs.org/portal/PublicWebSite/patent/archive/WPCP_012744

Lenero and colleagues at Shell are working on a different route to EG—one that does not begin with ethylene. Their method proceeds by hydroformylating formaldehyde to give glycolaldehyde, which can undergo hydrogenolysis to make EG. The first step is the difficult part, and the key to this invention is an improved catalyst for the hydroformylation step.

Catalytic process for preparing glycolaldehyde from synthesis gas and formaldehyde: Rhodium

Patent Watch, 20 April 2009

<http://www.cas.org/pwatch/042009.html>

Glycolaldehyde is prep'd. by reacting formaldehyde with hydrogen and carbon monoxide in the presence of a catalyst compn. which is based on (a) a source of rhodium, and (b) a ligand of general formula R^1PR^2 .

Jeffrey S. Plotkin

Planting the seeds for nanoparticle growth: Palladium

Chemie, DE, 22 April 2009

<http://www.chemie.de/news/e/99887/>

Toshiharu Teranishi and co-workers from the University of Tsukuba, Ibaraki, have developed a seed-mediated growth strategy to make flower- and dumbbell-shaped heterostructured nanoparticles. The group demonstrated that the resulting heterostructured nanoparticles consisted of metal sulphide building blocks.

CdPd sulfide heterostructured nanoparticles with metal sulfide seed-dependent morphologies

Chem. Commun., 2009

<http://dx.doi.org/10.1039/b902189b>

Image: <http://www.rsc.org/ejga/CC/2009/b902189b-ga.gif>

Seed-mediated growth synthesis has provided us with anisotropically phase-segregated CdPd sulfide heterostructured nanoparticles with seed-dependent morphologies and crystal structures.

Nonacetone routes to phenol continue to be developed: Palladium

Patent Watch, 27 April 2009

http://portal.acs.org/portal/PublicWebSite/patent/archive/WPCP_012799

T.-J. Chen and colleagues at ExxonMobil Chemicals disclose a catalyst that facilitates the hydroalkylation of benzene to cyclohexylbenzene (CHB, **1**) in good selectivity.



In one example, two catalysts, each composed of 2 g of 0.3 wt% Pd supported on γ -Al₂O₃, were prepared. One catalyst (A) was copelletized with 1.6 g of MCM-49 catalyst, whereas the other sample (B) was copelletized with 4.8 g of MCM-49. The Al/Pd mol ratios were 50:1 and 150:1 in catalysts A and B, respectively.

Both catalysts were tested under the same conditions. Benzene was fed at a rate of 0.08 mL/min and hydrogen was fed at 10 mL/min. The reaction temperature was 150 °C, and the gauge pressure was 1034 kPa. Both catalysts gave about the same conversion (42.5–43.5%), but selectivity to CHB was much better with catalyst B (78%); catalyst A gave only 70.8% selectivity. The major byproducts in both cases were dicyclohexylbenzene and lower amounts of cyclohexane.

Production of cyclohexylbenzene by hydroalkylation of benzene in presence of metal and aluminosilicate molecular sieve

CAS Patent Watch, April 27, 2009

<http://www.cas.org/pwatch/042709.html>

Jeffrey S. Plotkin

Use carbon nanotube catalysts to convert synthesis gas to diesel fuel: Ruthenium

Noteworthy Chemistry, 27 April 2009

http://portal.acs.org/portal/PublicWebSite/noteworthy/archive/WPCP_012798

The Fischer–Tropsch (FT) synthesis is a key step in using synthesis gas (syngas) to transform nonpetroleum feedstocks to hydrocarbon fuels. Ruthenium-based FT catalysts are the basis of recent studies of syngas conversion. Building on this research, Q. Zhang, Y. Wang, and co-workers at Xiamen University (China) report that ruthenium nanoparticles supported on carbon nanotubes (CNTs) provide excellent selectivity for producing the C₁₀–C₂₀ hydrocarbon fraction used routinely for diesel fuels.

W. Jerry Patterson

Should you choose an enol triflate or an enol tosylate as the substrate for a palladium catalyzed amidation?

Noteworthy Chemistry, 27 April 2009

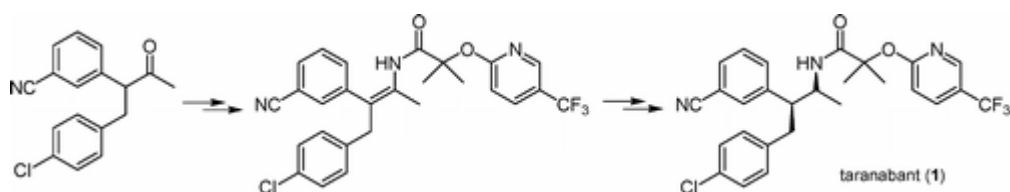
http://portal.acs.org/portal/PublicWebSite/noteworthy/archive/WPCP_012798

D. E. Wallace, K. R. Campos, C. S. Shultz, and coauthors at Merck Research Laboratories (Rahway, NJ) and Solvias AG (Basel, Switzerland)

New efficient asymmetric synthesis of taranabant, a CB1R inverse agonist for the treatment of obesity

Org. Process Res. Dev., 2009

<http://dx.doi.org/10.1021/op800270e>



Taranabant (1) is a cannabinoid-1 receptor (CB1R) inverse agonist that was recently in late-stage clinical development for the treatment of obesity. The previously employed synthesis exhibited a number of shortcomings for continuing development, and in this paper we report an improved synthesis of the target molecule that is suitable for large-scale implementation. Palladium-catalyzed amidation of an enol tosylate afforded a stereodefined tetrasubstituted enamide, and asymmetric hydrogenation thereof provided the target molecule.

Will Watson

New Scientist: Press 'print' for a light-emitting T-shirt: Ruthenium

New Scientist, 29 April 2009, Magazine Issue 2706

<http://www.newscientist.com/article/mg20227066.000-press-print-for-a-lightemitting-tshirt.html>

DNP Develops Light Emitting Material Printable on Paper, Cloth

Tech-On!, Mar 31, 2009

http://techon.nikkeibp.co.jp/english/NEWS_EN/20090331/168045/

Michael Fitzpatrick

Fluorophores join forces for cell imaging: Ruthenium

Chemical Biology, 30 April 2009

http://www.rsc.org/Publishing/Journals/cb/Volume/2009/6/Ruthenium_probe.asp

Images: http://www.rsc.org/images/b900290a-400-FOR-TRIDION_tcm18-151557.jpg

Nicholas Turro at Columbia University, New York, and coworkers developed the fluorescent probe, RuEth,

<http://www.rsc.org/publishing/journals/prospect/cheminfo.asp?XMLID=7&compoundtext=RuEth&MSID=b900290a> which can be used to image RNA-rich regions in cells.

Paul Cooper

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