

## New Application Developments in PGM – January 2009

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**Trifluorotoluene solvent improves a palladium-mediated cyclization**
*Noteworthy Chemistry*, January 5, 2009

http://portal.acs.org/portal/PublicWebSite/noteworthy/archive/WPCP_011559

As part of an effort to improve the synthesis of linezolid, an oxazolidinone antibacterial, M. Pamment and co-workers at Pfizer Global R&D (Ann Arbor, MI) studied the formation of a key oxindole intermediate. Fluoride displacement of the starting 3,4-difluoronitrobenzene with aqueous $MeNH_2$, followed by N-acylation with $ClCH_2COCl$, gave the oxindole precursor. Initial attempts to run the cyclization under literature-described conditions (80 °C, toluene solvent, Pd catalyst, and 1.5 equiv $Et_3N$) met with limited success.

A solvent screen showed that the reaction worked well in DMF or trifluorotoluene (TFT). When the reaction was run in TFT, complete conversion was achieved in 5 h. The product precipitated out of the reaction mixture, which minimized decomposition of the base-sensitive oxindole. A solvent switch to *i*-PrOH completed the precipitation of the product; it was then washed with water to remove inorganic salts and give the oxindole in 86% yield.

Ref.
Development of a Synthesis for a Long-Term Oxazolidinone Antibacterial
*Org. Process Res. Dev.*, 2008, **12**, (5), 884–887
http://pubs.acs.org/doi/abs/10.1021/op8001195

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**Japanese Researchers Pave Way for Artificial Photosynthesis**

http://techon.nikkeibp.co.jp/english/NEWS_EN/20081224/163313/

A Japanese research group saw its way clear to the practical application of ruthenium-rhenium (Ru-Re) supramolecular complex as a photocatalyst that uses sunlight to reduce CO2 to CO, which can be used as a chemical engineering material.

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**Olefin metathesis reactions can be run in water: Ruthenium**

http://portal.acs.org/portal/PublicWebSite/noteworthy/archive/WPCP_011673

Olefin metathesis is a powerful transformation in organic synthesis, but the reactions usually must be run in dry, degassed organic solvents to avoid catalyst deactivation. Because water is an environmentally benign solvent, D. Burtscher of the Polish Academy of Sciences (Warsaw) and K. Grela* at Warsaw University provide a mini-review of the role of water in olefin metathesis.

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**Bug enzyme generates fuel from water: Ruthenium**
tech - New Scientist, 13 January 2009

http://www.newscientist.com/article/dn16409-bug-enzyme-generates-fuel-from-water.html

Catalytic electrochemistry of a [NiFeSe]-hydrogenase on $TiO_2$ and demonstration of its suitability for visible-light driven $H_2$ production

http://dx.doi.org/10.1039/b817371k

A [NiFeSe]-hydrogenase able to produce $H_2$ in the presence of $O_2$ forms the basis of a hybrid enzyme–$TiO_2$ nanoparticle system with a co-attached synthetic Ru photosensitiser for visible-light driven $H_2$ production at room temperature from neutral water under non-strictly anaerobic conditions on the bench.

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**Clean Coupling: Rhodium**

http://www.sciencemag.org/content/vol323/issue5912/twil.dtl

Alcohol oxidation is a crucial step in the preparation of many drugs and fine chemicals, but it often requires large amounts of toxic reagents. Zweifel *et al.* present a rhodium catalyst that can dehydrogenatively couple a range of alcohols with water, methanol, or various amines (including ammonia, a generally recalcitrant substrate) to afford the corresponding acid, ester, or amide directly. The reactions proceed in a few hours at room temperature, driven by transfer of the liberated hydrogen to a cyclohexanone acceptor that can subsequently be recycled by reaction with hydrogen peroxide. Primary alcohols are oxidized selectively, and the catalyst tolerates olefin, thioether, and pyridine substituents. Simulations support a mechanism involving the transfer of a hydride to the Rh center, with accompanying protonation of a coordinated nitrogen ligand.

Synthetic Methods
Catalyzed Dehydrogenative Coupling of Primary Alcohols with Water, Methanol, or Amines
Theo Zweifel, Jean-Valère Naubron, Hansjörg Grützmacher
*Angewandte Chemie International Edition*, 2009, Volume 48, Issue 3, Pages 559-563
http://dx.doi.org/10.1002/anie.200804757

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**Tuning selectivity in catalysis by controlling particle shape: Platinum**
Nature Materials, 18 January 2009

http://www.nature.com/nmat/journal/vaop/ncurrent/abs/nmat2371.html

A catalytic process for the selective formation of cis olefins would help minimize the production of unhealthy trans fats during the partial hydrogenation of edible oils. Here we report on the design of such a process on the basis of studies with model systems. . .

**How natural oils can be hydrogenated without making unhealthy trans fats: Platinum**
EurekAlert!, 23-Jan-2009

http://www.eurekalert.org/pub_releases/2009-01/uoc--hno012309.php

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**Phase-Switching Catalysis: Rhodium**
Chemical & Engineering News: Latest News, January 22, 2009

http://pubs.acs.org/cen/news/87/i04/8704notw8.html

CO2-regulated solubility adds a new twist to catalyst recycling
Stephen K. Ritter
A pair of chemists in Scotland has come up with a neat trick for reversibly shuttling a homogeneous catalyst between the organic and aqueous phases in a biphasic solvent system by simply adding or removing carbon dioxide (Angew. Chem. Int. Ed., DOI: 10.1002/anie.200804729). . .

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**New Catalyst Paves the Path for Ethanol-Powered FuelCells: Platinum, Rhodium**
Brookhaven National Lab News, January 25, 2009

http://www.bnl.gov/bnlweb/pubaf/pr/PR_display.asp?prID=898

**Ternary Pt/Rh/SnO2 electrocatalysts for oxidizing ethanol to CO2**
Nature Materials, 25 January 2009

http://dx.doi.org/10.1038/nmat2359

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**Nano-tetherball biosensor precisely detects glucose: Palladium**
EurekAlert!, 22-Jan-2009

http://www.eurekalert.org/pub_releases/2009-01/pu-nbp012209.php

Nano-tetherball biosensor precisely detects glucose

Researchers have created a precise biosensor for detecting blood glucose and potentially many other biological molecules by using hollow structures called single-wall carbon nanotubes anchored to gold-coated "nanocubes."

The device resembles a tiny cube-shaped tetherball. Each tetherball is a sensor and is anchored to electronic circuitry by a nanotube, which acts as both a tether and ultrathin wire to conduct electrical signals, said Timothy Fisher, a Purdue University professor of mechanical engineering.

The technology, which detects glucose more precisely than any biosensors in development, also might be used in medicine to detect other types of biological molecules and in future biosensors for scientific research, said Marshall Porterfield, an associate professor of agricultural and biological engineering at Purdue . . .

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**Air Liquide Electronics Announce Major CapacityExpansion of TORUS Manufacturing at ALOHA TM Facility: Ruthenium**
ZoNano, January 22nd, 2009

http://www.azonano.com/news.asp?newsID=9557

Air Liquide Electronics ramps-up first mass production ruthenium CVD/ALD solution
Nanotechnology Now, January 22nd, 2009

http://www.nanotech-now.com/news.cgi?story_id=31966

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**Carbon nanotube memories speed up: Palladium**
nanotechweb.org, Jan 22, 2009

http://nanotechweb.org/cws/article/tech/37434
Researchers in Finland are the first to make nanotube field-effect transistor-based memories with an operating speed of just 100 ns – 105 times faster than the previous best such devices. This speed can compete with commercially available silicon-based flash memories with single-cell write and erase times of more than 100 microseconds.

cont . . .

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**Carbon-Nanotube Memory that Really Competes**
PhysOrg.com, January 26th, 2009
http://www.physorg.com/news152202897.html

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**Here's an improved process for a pharmaceutical intermediate: Rhodium**
Patent Watch, January 26, 2009

http://portal.acs.org/portal/PublicWebSite/patent/archive/WPCP_011715
M. Prashad and co-inventors describe an improved process for synthesizing compounds such as 1 that are used to prepare antibacterial agents. Alternative methods have safety problems because they use H2O2; they also create waste-disposal difficulties because of a nonselective debenzylation step.

**US2007179298:**
http://v3.espacenet.com/publicationDetails/biblio?KC=A1&date=20070802&NR=2007179298A1&DB=EPODOC&locale=en_GB&CC=US&FT=D

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**Identifying toxins: Platinum**
The Engineer, 27 January 2009

http://www.theengineer.co.uk/Articles/309784/Identifying+toxins.htm

Nelson's team developed a concept, now awaiting a patent, by which small platinum microelectrodes are fabricated on a wafer and tiny quantities of mercury are electrodeposited on the tip of each. A phospholipid monolayer can then be deposited on each of these and interrogated and imaged using atomic force microscopy techniques. Nelson founded a spinout called Organisense last March to manufacture these chips.

Andrew Nelson,
http://www.chem.leeds.ac.uk/People/Nelson2.html

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**Exploring the Ultimate Nanoscale for Future Electronics**
Azonano.com, 29 January 2009

The logic and memory functions of future electronic devices could shrink dramatically - to one or two nanometers (billionths of a meter) instead of the many tens of nanometers that characterize today's most advanced elements - if a way can be found to control domain walls, the ultrathin transition zones that separate regions of a material having different magnetic, electric, or other properties.

http://www.azonano.com/news.asp?newsID=9628

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**Single Nanocrystals of Platinum Prepared by Partial Dissolution of Au-Pt Nanoalloys**
Science, 30 January 2009

Precious metals in catalysts are often used in the form of nanoparticles, which increases the number of exposed surface atoms relative to the bulk material. Nanocrystals with well-defined surface planes and distinct edges can exhibit different or greater reactivity than less crystalline forms, but can be difficult to synthesize at sizes below 100 nanometers, and very small nanoparticles (below about 5 nanometers in diameter) are often rounded and less reactive. Schrinner *et al.* (p. 617) describe a route for converting nanoparticle alloys of gold and platinum, between 2 and 3 nanometers in diameter, into Pt nanocrystals. The particles were embedded in a polymer network on the surface of a latex particle, and a leaching reaction that removes gold proceeded slowly (over the course of hours) so that the particles formed single crystals. The network prevented the nanocrystals from agglomerating and was used as a support for the nanocrystals in hydrogenation reactions.

Vol. 323, no. 5914, pp. 617-620
http://dx.doi.org/10.1126/science.1166703

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**Nanocrystals get in shape for catalysis**
Chemistry World, 30 January 2009

New research in fine tuning the shape and size of nanoparticles could lead to important advances in catalysis, say scientists. Two independent groups of researchers have shown that the catalytic activities of tiny platinum crystals can be greatly enhanced by tightly controlling their shape and size.

Hayley Birch
http://www.rsc.org/chemistryworld/News/2009/January/30010903.asp

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