VIP The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:

Author Profile

"My science "heroes" are my co-workers in my group. The biggest problem that scientists face is to keep an open and prepared mind …"
This and more about Annie Powell can be found on page 800.

News

C. Nájera

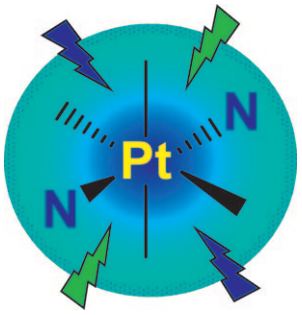
M. S. Sanford

V. M. Dong

Books

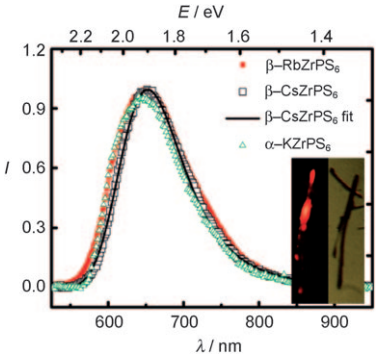
Contents

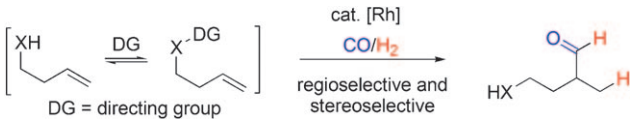
Highlights



The next generation: Classical Pt^{II} anticancer compounds contain *cis* diam(m)ine ligands and are activated by ligand-substitution reactions. Pt^{IV} diam(m)ine diazido dihydroxo complexes are nontoxic to cells until activated by light. Replacement of the diam(m)ine ligands in a *trans* configuration by pyridine gives a complex that is potently cytotoxic when irradiated with visible light and which has potential as a photochemotherapeutic agent.

Bright light! Semiconductor materials are playing an ever-increasing role in optical applications, but the number of systems used is limited. The $AZrPS_6$ class of compounds (A = K, Rb, Cs) shows extremely interesting optical properties (see picture) and could thus smooth the way to the use of more complex materials.





A designer phosphine ligand capable of bonding covalently to an olefin substrate directed rhodium-catalyzed hydroformylation to generate branched aldehydes with high regio- and enantioselectivity. The use of such scaffolding ligands opens up new directions in asymmetric synthesis.

For the USA and Canada:
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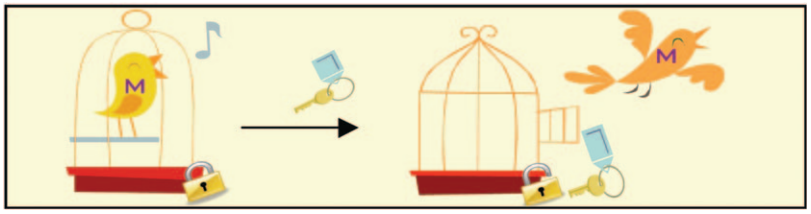
Minireviews

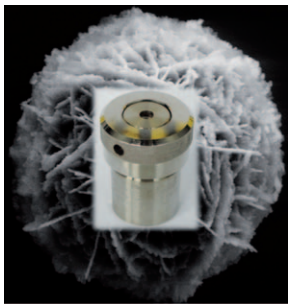


The key to the door: Photolabile metal cages utilize light as the "key" to unlock a change in the coordination environment around the metal center. These triggerable agents can be useful tools for manipulating the bioavailability of metals or their coordinating ligands in order to study biological pathways or for potential therapeutic purposes.

Photochemistry

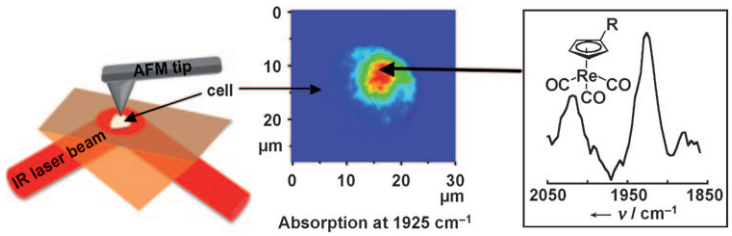
Reviews

Plans for profit: Oxide nanomaterials (see picture) offer a limitless spectrum of structures, properties, and applications. In recent years, new synthetic approaches have been developed to access them and the most sophisticated in situ monitoring techniques are applied to understand their growth processes. This Review shows how these developments open up new design perspectives for the technical application of oxide nanomaterials in all current fields.



Nanotechnology

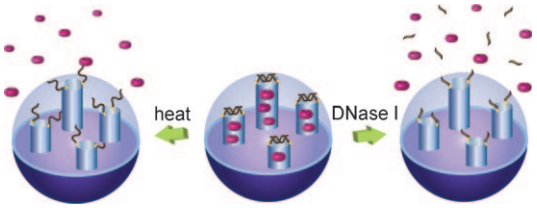
Communications



Some like it hot! The photothermally induced resonance technique, in which an AFM microscope is coupled to a tunable pulsed IR laser, allows IR mapping and gives access to local IR spectra at the subcellular level. A metal–carbonyl compound was internalized in cells and detected in the cell nucleus thanks to its IR signature. The local IR spectrum at the nucleus showed the characteristic IR bands of the $\{Re(CO)_3\}$ unit.

Subcellular IR Spectromicroscopy

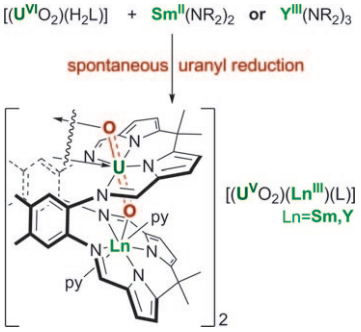
Contents



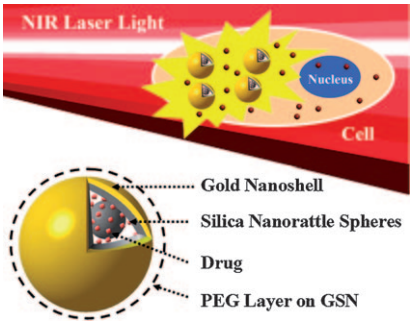
Blocked tubes: Attachment of self-complementary duplex DNA to the openings of mesoporous silica nanoparticles results in a cap for trapping guest molecules. The cargo can be released either by thermal stimuli or by the introduction of DNase I, both of which open the capping DNA structure (see picture).

Drug Delivery

Reducing the irreducible: Incorporation of a lanthanide cation into the vacant coordination pocket of a uranyl Pacman complex results in single electron reduction to form stable pentavalent uranyl–rare-earth complexes with uranyl–oxo–rare-earth bonds (see scheme; py = pyridine, R = $SiMe_3$).



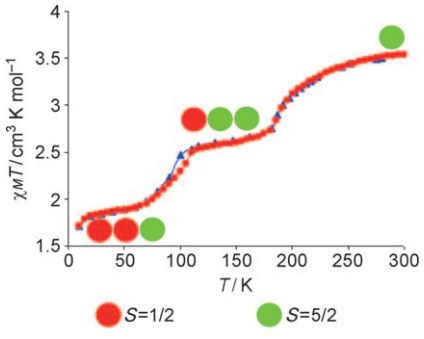
Uranyl Reduction



Magic bullets: A drug-loaded structure comprising a PEGylated (PEG = polyethylene glycol) gold nanoshell on silica nanorattle spheres (GSNs; see picture) combines remote-controlled photothermal therapy with chemotherapy. Tumor cells are killed with higher efficacy and less toxicity than the free drug.

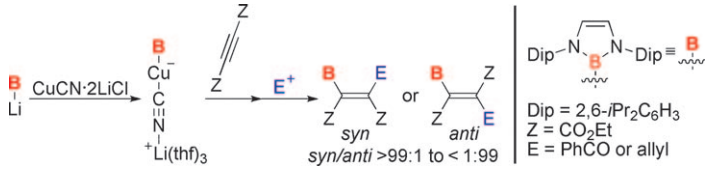
Nanomedicine

Stepping up: A two-step magnetic spin transition with accompanying structural phase transitions is reported for the first time for Fe^{III}. The transitions are observed at 187 K and 90 K on cooling with a hysteretic transition recorded upon heating during the first crossover at 106 K. The intermediate phase persists over 97 K and contains an unprecedented [HS-HS-LS] motif with tripling of the unit cell.



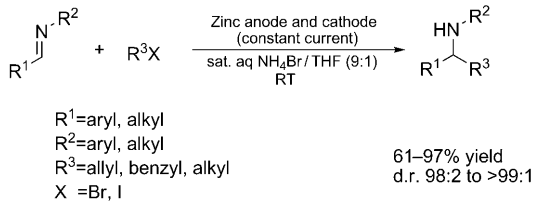
Two-Step Transitions

Contents



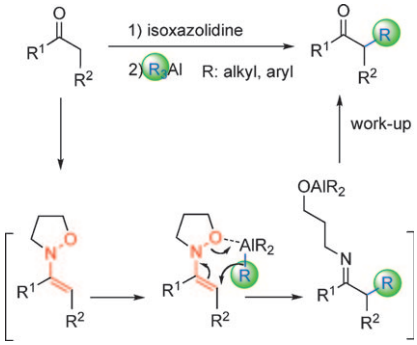
A key reactive species, lithium borylcyanocuprate, was isolated and fully characterized in a one-pot carboboration of alkynes. The carboboration involves a boryllithium, CuCN·2 LiCl, an ester-substituted alkyne, and an organic electrophile (see scheme). By changing the reaction temperature, the *syn*/*anti* ratio of the carboborated products can also be changed.

Borylcyanocuprates



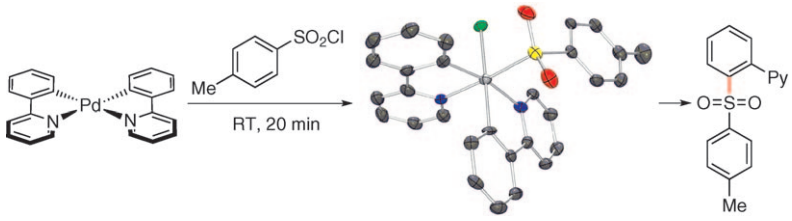
I zinc we're alone now: The title reactions were achieved in an undivided cell fitted with a pair of zinc electrodes in aqueous solution. A preliminary study on the relationship of reaction activity and surface morphology showed that the deposited zinc powders with nanoscale architectures had very high activity.

Electrochemistry



A new aspect of enamine chemistry: The formation of *N*-alkoxyenamines from ketones has led to an efficient umpolung reaction. The alkylation of *N*-alkoxyenamines with trialkylaluminum compounds proceeded smoothly and gave α-alkylated ketones (see scheme). This reaction offers a simple transformation of ketones into α-substituted ketones without the need to isolate enamines and intermediary imines.

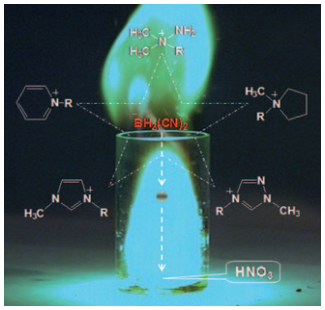
Umpolung Reaction



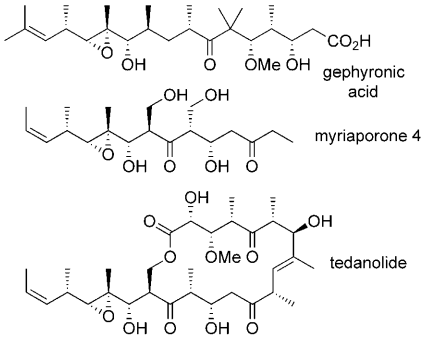
Sulfurin succotash: The oxidation of Pd^{II} complexes with sulfonyl chlorides leads to a series of stable palladium(IV) sulfinate complexes. These complexes undergo reductive elimination to afford products with C–S, C–C, and C–Cl bonds, as well as a desulfitated product (see scheme; Py = pyridyl, Pd gray, N blue, S yellow, O red).

C–S Bond Formation

Contents

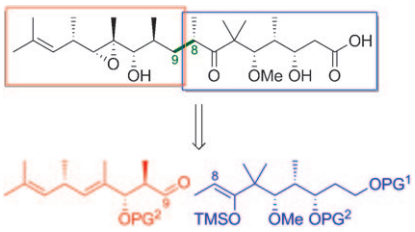


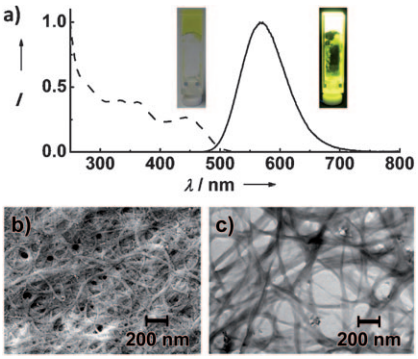
Explosive though stable: Dicyanoborate-based ionic liquids are hypergolic fuels in the presence of white fuming nitric acid as oxidizer (see high-speed picture of the ignition process). With long liquid ranges, low viscosities, and short ignition delay times, these thermally and hydrolytically stable ionic liquids appear to be very promising substitutes for hydrazine and its derivatives as bipropellants.



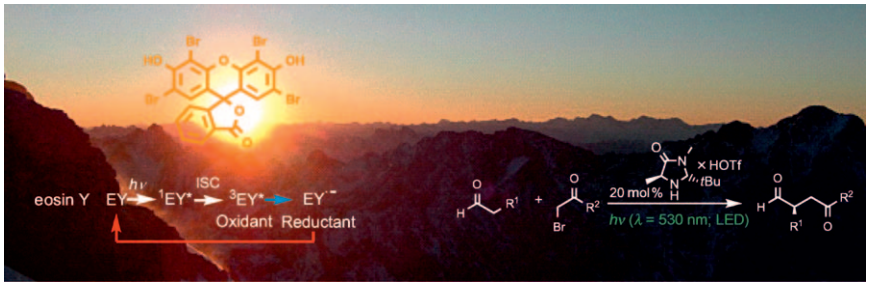
Solving the puzzle: The correct structure and configuration of the natural product gephyronic acid has been determined by NMR analysis and correlation with synthetic reference compounds, as well as with myriaporone 4 and tedanolide. Gephyronic acid, isolated from culture supernatants of *Archangium gephyra*, displays intriguing antibiotic activity.

19 steps in the longest linear sequence are required in the 27 step total synthesis of gephyronic acid. A key step is a diastereodifferentiating Mukaiyama aldol reaction of an aldehyde and an enolsilane (see picture, PG: protecting group). The strongly cytotoxic target compound is a structural relative of the polyketide tedanolide and was isolated from the myxobacterium *Archangium gephyra*.



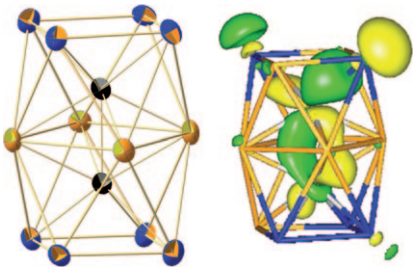


A platinum(II) emitter is able to self-assemble into gelating nanofibers, leading to an unprecedented 90% photoluminescence quantum yield. Electroluminescent devices processed in solution can be doped with the aforementioned complex. Picture: a) Emission (——) and excitation spectra (-----) and photos of the gel, b) REM, and c) TEM images of the nanofibers.



The dawn of old stars: Classic xanthene dyes like eosin Y (gr. εος = goddess of dawn) and green-light irradiation can replace precious metal complexes for the organocatalytic asymmetric α-alkylation of aldehydes, thus rendering the process purely organic.

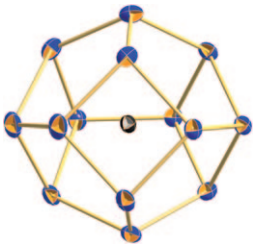
Photocatalysis



The birdcage: The title anion, which contains two endohedral d^{10} metal atoms, is the second known ternary cluster anion comprising only metal atoms (see picture: Sn orange, Sn/Bi blue, Ni black). The K([2.2.2]crypt) salt was obtained upon reaction of the binary precursor $[Sn_2Bi_2]^{2-}$ with $[Ni(cod)_2]$ in ethylenediamine/toluene by a complicated fragmentation/re-arrangement process. X-ray diffraction and DFT calculations confirm the composition of the anion.

Ternary Cluster Anions

La cage aux folles: The $[Eu@Sn_6Bi_8]^{4-}$ anion (see picture: Sn/Bi blue/orange, Eu black) is the first example of an intermetalloid cluster anion that embeds a lanthanide ion in the solid state. Magnetic measurements and calculations both point to an $S = 7/2$ ground state and indicate ionic interactions of the Eu^{II} ion with the main-group-metal cage. ESI mass spectrometry suggest that the cage forms from two seven-atom hemispheres.



Intermetalloid Clusters

Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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