Angewandte
International Edition Chemie

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:

*H. Chinen, K. Mawatari, Y. Pihosh, K. Morikawa, Y. Kazoe, T. Tsukahara, T. Kitamori**
Enhancement of Proton Mobility in Extended-Nanospace Channels

*C. Parthier, S. Görlich, F. Jaenecke, C. Breithaupt, U. Bräuer, U. Fandrich, D. Clausnitzer, U. F. Wehmeier, C. Böttcher, D. Scheel, M. T. Stubbs**
The *O*-Carbamoyltransferase TobZ Catalyzes an Ancient Enzymatic Reaction

Editorial

"... The Spanish science system is still fragile, and financial support should be maintained as much as possible, even under the current critical economic conditions ..."
Read more in the Editorial by Nazario Martín.

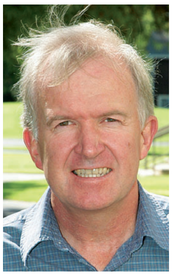
Author Profile

*"My favorite food is Japanese cuisine.
The most important thing I learned from my parents is a love for dedicated and reliable craftsmanship ..."*
This and more about François Diederich can be found on page 3302.

News

D. O'Hagan

A. L. Rheingold



P. P. Power

J. A. Ellman

C. A. Reed

S. Hanessian

M. Kira

E. Iglesia

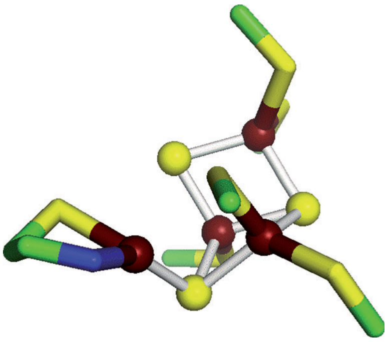
R. E. Schaak

Books

Highlights

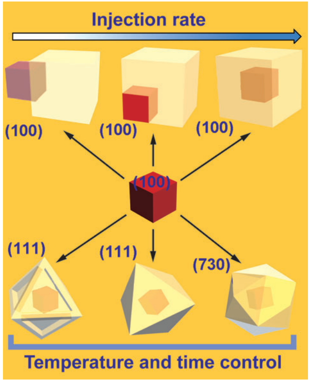
Hydrogenases

One S less: Recent crystallographic studies have revealed a new, oxygen-tolerant kind of iron–sulfur cluster [4Fe-3S], which contains only three rather than four sulfur atoms in its cage (see picture; yellow = S, red = Fe, blue = N, green = cysteine). It is proposed that the cluster's ability to transfer multiple electrons increases the oxygen tolerance by enabling the enzyme to reduce O_2 rapidly, converting the dioxygen into harmless water before it can damage the protein.



Nanomaterials

Morphologies à la carte: A kinetic control strategy has been utilized to fabricate bimetallic nanoparticles. Using cubic Pd nanocrystals as seeds and a syringe pump that enables precise control over precursor injection rate, it is possible to synthesize Pd–Ag bimetallic nanoparticles with tailored shapes (see picture: dimers, eccentric hybrid bars, and core–shell structures) and tunable localized surface plasmon resonances.



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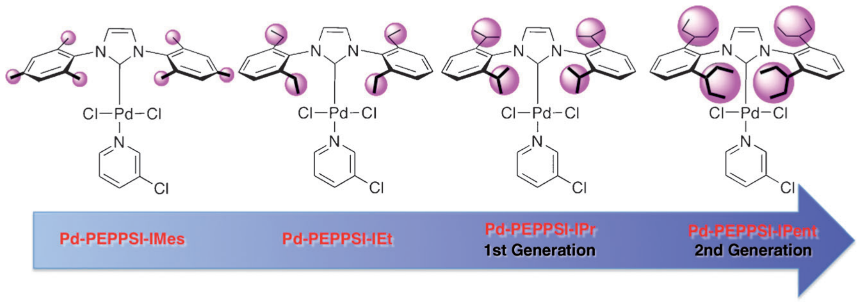
Reviews

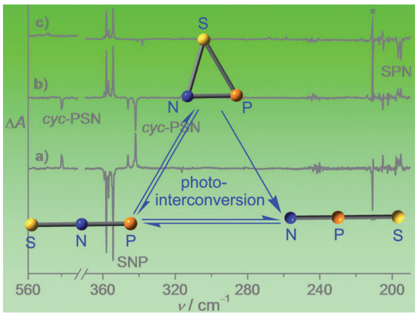
Cross-Coupling Catalysts



Adding fizz to catalysis: The Pd-PEPPSI series of catalysts (see scheme) is very active for the Suzuki–Miyaura, Negishi, Stille–Migita, aryl amination, and aryl sulfination reactions. The high reactivities of Pd-PEPPSI-IPr and Pd-PEPPSI-IPent catalysts with N-heterocyclic carbene (NHC) ligands are compared with other state-of-the-art catalysts. Pd-PEPPSI-IPent is shown to be one of the most active and general catalysts for cross-coupling reactions.

Communications

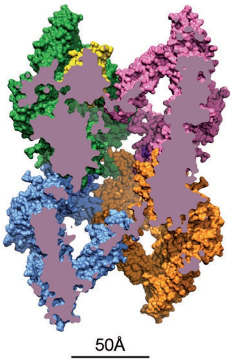
Small-Ring Systems



16-Electron triatomic ring: Novel thiazylidynephosphane (SNP) was produced by either flash vacuum pyrolysis (ca. 1000 °C) or laser photolysis (193 nm) of $SP(N_3)_3$. Its photointerconversion to cyclic thiazaphosphirine (*cyc*-PSN) and thiophosphoryl nitride (SPN) was found in Ar matrix at 16 K. *Cyc*-PSN is the first experimentally observed 16-electron cyclic triatomic molecule.

Molecular Biology

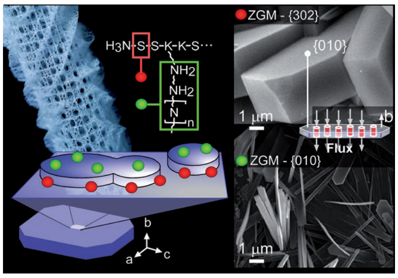
I'm your Venus: The crystal structure of the human methylamine-induced form of α_2-macroglobulin (α_2M) shows its large central cavity can accommodate two medium-sized proteinases (see structure, front part clipped off to better show central cavity). Twelve major entrances provide access for small substrates to the cavity and the still-active trapped "prey". The structure unveils the molecular basis of the unique "venus flytrap" mechanism of α_2M.



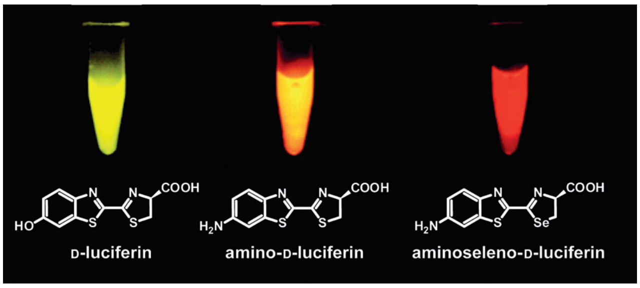
Zeolite Crystallization

Back Cover

Modified point of view: A bio-inspired approach was used to tailor silicalite-1 crystallization. Growth modifiers (ZGMs) with molecular recognition for binding to specific crystal faces produced drastic changes in zeolite crystal morphology. This facile approach offers an efficient method for tuning zeolite properties.



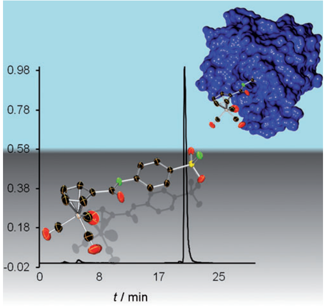
Bioluminescence



A selenium analogue of amino-D-luciferin, aminoseleno-D-luciferin, is synthesized and shown to be a competent substrate for the firefly luciferase enzyme. It has a red-shifted bioluminescence emission maximum at 600 nm (see scheme) and is suitable for bioluminescence imaging studies in living subjects.

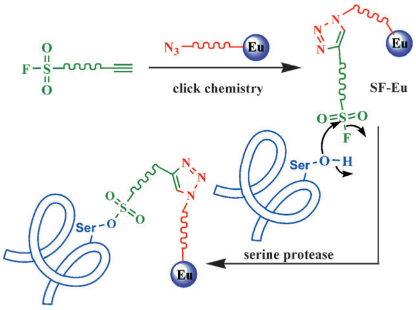
Bio-organometallic Chemistry

Enhanced receptor selectivity: Carbonic anhydrase inhibitors are relevant for both cancer diagnosis and therapy. Combining non-radioactive Re compounds with their radioactive ^{99m}Tc homologs enables the use of identical molecules for therapy and imaging (theragnostic). The syntheses and in vitro evaluation of $[(Cp\text{-}R)M(CO)_3]$ (Cp = cyclopentadienyl, M = Re, ^{99m}Tc) with R being a highly potent carbonic-anhydrase-targeting vector is reported (see picture).

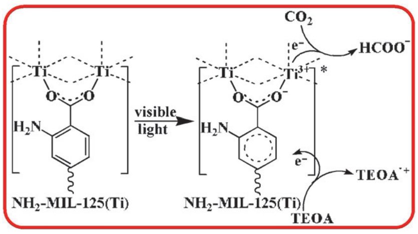


Protein Quantification

Click and analyze: The titled probe was synthesized by conjugating a sulfonyl fluoride and azido unit using click chemistry to give SF-Eu, which can react specifically with serine (Ser) in the active site of serine protease (SP). Combination of the method with ^{153}Eu-isotope dilution ICP/MS enables absolute protein quantification of active SPs in biological samples using only one $^{153}Eu(NO_3)_3$ isotopic standard.



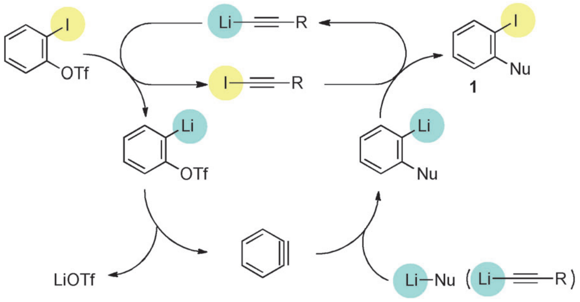
Let your light shine: The photocatalytic reduction of carbon dioxide to the formate anion under visible light irradiation is for the first time realized over a photoactive Ti-containing metal–organic framework, NH_2-MIL-125(Ti), which is fabricated by a facile substitution of ligands in the UV-responsive MIL-125(Ti) material (see scheme; TEOA = triethanolamine).



Photocatalysis

Y. Fu, D. Sun, Y. Chen, R. Huang, Z. Ding, X. Fu, Z. Li* ______ **3364 – 3367**

An Amine-Functionalized Titanium Metal–Organic Framework Photocatalyst with Visible-Light-Induced Activity for CO_2 Reduction



A fair exchange: In the title reaction, alkynyllithium serves as an initiator for benzyne generation through an iodine–lithium exchange (see scheme; Tf = trifluoromethanesulfonyl). When performed in the presence of stoichiometric amounts of a nucleophile, the generated benzyne undergoes attack by lithio nucleophiles to generate aryllithium, which is then iodinated by iodoalkyne to give the iodoarenes **1**.

Arynes

T. Hamura,* Y. Chuda, Y. Nakatsuji, K. Suzuki* ______ **3368 – 3372**

Catalytic Generation of Arynes and Trapping by Nucleophilic Addition and Iodination

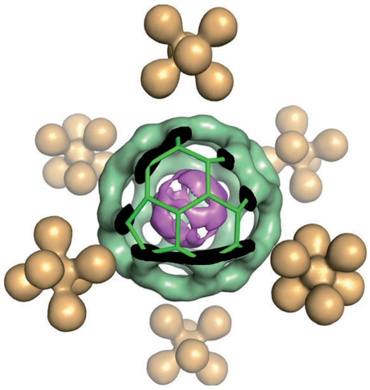
Neoclassical architecture: A new family of heteropolyoxometalates with "pagoda"-shaped building blocks $[Te_nW_{6n+3}O_{21n+12}]^{(6+2n)-}$ ($n = 1, 2, 3$) was discovered by adding $\{TeW_6O_{21}\}$ layers on a classic $\{TeW_9O_{33}\}$ fragment. Linking of the units allowed the generation of nanostructured clusters whose gross conformation is cation controlled. Studies of the redox behaviors of the multi-layered clusters indicate that the Te^{IV} template is redox-active.

Polyoxometalates

J. Gao, J. Yan, S. Beeg, D. L. Long,* L. Cronin* ______ **3373 – 3376**

Assembly of Molecular "Layered" Heteropolyoxometalate Architectures

Rock solid: Fullerene-encapsulated Li^+ ($Li^+@C_{60}$) is an alkaline cation owing to the spherical shape and positive charge. $Li^+@C_{60}$ crystallizes as a rock-salt-type crystal in the presence of PF_6^-. The orientations of C_{60} (green; see picture) and PF_6^- (orange) are perfectly ordered below 370 K, and Li^+ (purple) hops within the cage. At temperatures below 100 K two Li^+ units are localized at two polar positions within each C_{60}.



Fullerenes

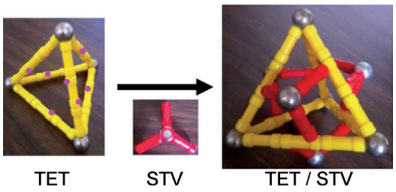
S. Aoyagi,* Y. Sado, E. Nishibori, H. Sawa, H. Okada, H. Tobita, Y. Kasama, R. Kitaura, H. Shinohara ___ **3377 – 3381**

Rock-Salt-Type Crystal of Thermally Contracted C_{60} with Encapsulated Lithium Cation

DNA Nanostructures

C. Zhang, C. Tian, F. Guo, Z. Liu, W. Jiang, C. Mao* ________ 3382 – 3385

DNA-Directed Three-Dimensional Protein Organization

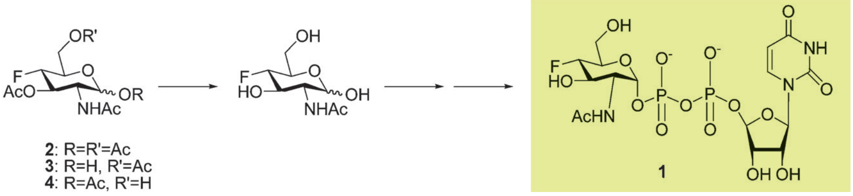


All bound together: Self-assembled symmetric DNA polyhedra were used to organize proteins in 3D space. Biotin moieties were incorporated into the self-assembled symmetric DNA polyhedra. Upon incubation with streptavidin (STV) protein, an STV protein became bound to each polyhedral face, thus resulting in well-structured DNA polyhedra/STV complexes (see picture, TET = tetrahedron). This strategy was also applied to different 3D DNA nanostructures and different proteins.

Sugar Derivatives

S.-I. Nishimura,* M. Hato, S. Hyugaji, F. Feng, M. Amano ________ 3386 – 3390

Glycomics for Drug Discovery: Metabolic Perturbation in Androgen-Independent Prostate Cancer Cells Induced by Unnatural Hexosamine Mimics



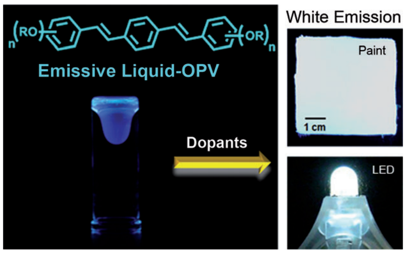
Inhibited: *N*-acetylglucosamine (GlcNAc) derivatives with a fluorine atom at the C4 position (**2**–**4**) were synthesized, and their ability to inhibit cancer-cell growth was investigated. The administration of these 4F-GlcNAc derivatives to cells led to the unnatural sugar nucleotide **1**. Furthermore, N-glycan profiles of cells were determined by using a glycoblotting-based enrichment analysis, which is suitable for high-throughput screenings for drug discovery.

Luminescent Liquids

S. Santhosh Babu, J. Aimi, H. Ozawa, N. Shirahata, A. Saeki, S. Seki, A. Ajayaghosh, H. Möhwald, T. Nakanishi* ________ 3391 – 3395

Solvent-Free Luminescent Organic Liquids

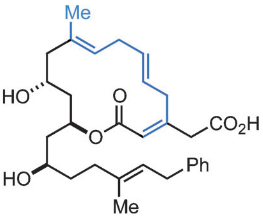
Illuminating! Isolation of a π-core by covalently attached flexible hydrocarbon chains has been employed to synthesize blue-emitting oligo(*p*-phenylenevinylene) (OPV) liquids with tunable viscosity and optical properties. A solvent-free, stable, white-light emitting ink/paint, which can be applied onto various surfaces and even onto LEDs, was made by blending of liquid OPVs with emissive solid dopants.



Ripostatin B (1)

P. Winter, W. Hiller, M. Christmann* ________ 3396 – 3400

Access to Skipped Polyene Macrolides through Ring-Closing Metathesis: Total Synthesis of the RNA Polymerase Inhibitor Ripostatin B



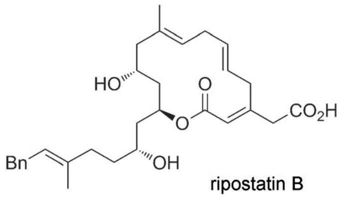
ripostatin B

Rip-Roaring! A convergent total synthesis of antibiotic ripostatin B was developed. A key step in the synthesis is a metathesis reaction allowing for a ring closure to the labile doubly skipped triene macrolide.

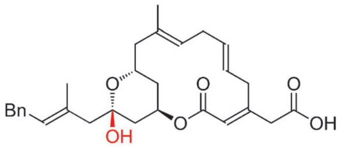
Ripostatin B (2)

W. Tang, E. V. Prusov* **3401–3404**

Total Synthesis of RNA-Polymerase Inhibitor Ripostatin B and 15-Deoxyripostatin A



ripostatin B



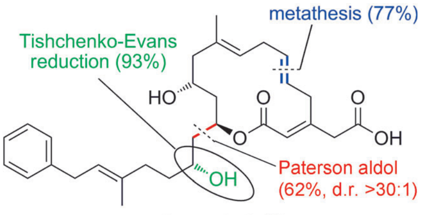
ripostatin A

Keep me skipped: A highly convergent total synthesis of ripostatin B, an inhibitor of the bacterial RNA polymerase, is described. The key steps to construct and avoid isomerization of the skipped triene are a double Stille cross-coupling reaction and a ring-closing metathesis. Furthermore, 15-deoxyripostatin A, a stable and conformationally locked analogue of ripostatin A (see scheme, 15-OH group red), was prepared and tested in vivo.

Ripostatin B (3)

F. Glaus, K.-H. Altmann* **3405–3409**

Total Synthesis of the Bacterial RNA Polymerase Inhibitor Ripostatin B



ripostatin B (**1**)

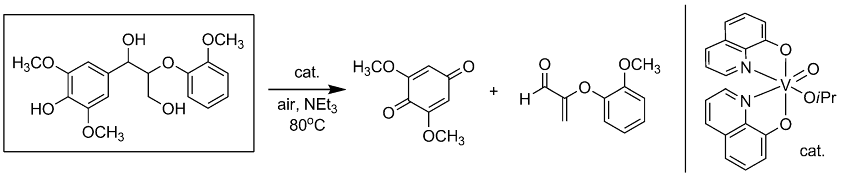
A modular and highly stereoselective synthesis of the title compound was developed. Key steps in the assembly of the carbon framework of ripostatin B (**1**; see scheme) were a stereoselective Paterson aldol reaction and a high-yielding ring-closing metathesis mediated by Grubbs first generation catalyst. The C15 hydroxy group was established through Tishchenko–Evans reduction in excellent yield and selectivity.

Oxidative Cleavage

S. K. Hanson,* R. Wu,
L. A. "Pete" Silks* **3410–3413**

C–C or C–O Bond Cleavage in a Phenolic Lignin Model Compound: Selectivity Depends on Vanadium Catalyst

Inside Cover

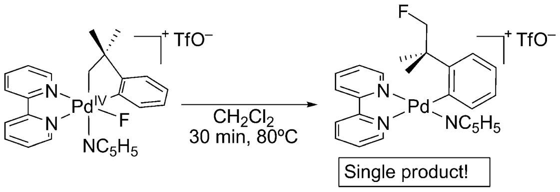


The aerobic oxidation of a phenolic lignin model compound with a vanadium catalyst results in the oxidative cleavage of the C–C bond between the aryl ring and the adjacent hydroxy-substituted carbon atom (see scheme). Labeling experiments indicate key mechanistic differences to a previously reported related C–O bond cleavage reaction. The selectivity in C–C versus C–O bond cleavage depends on the choice of the vanadium catalyst.

Fluorination

J. M. Racowski, J. B. Gary,
M. S. Sanford* **3414–3417**

Carbon(sp^3)–Fluorine Bond-Forming Reductive Elimination from Palladium(IV) Complexes

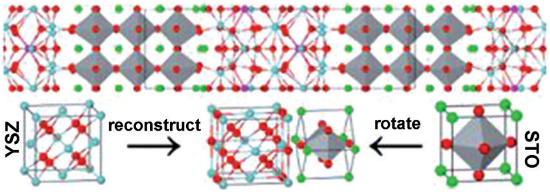


Pd^{IV}–fluoride complexes, some of which are remarkably insensitive to water, have been synthesized and used in the title reaction, which proceeds with high selectivity to give the product of the $C(sp^3)$–F coupling (see scheme, TfO = trifluoromethanesulfonate). Preliminary mechanistic studies implicate a pathway involving dissociation of pyridine followed by direct C–F coupling at the Pd center.

Solid-State Chemistry

M. S. Dyer, G. R. Darling, J. B. Claridge,
M. J. Rosseinsky* ________ 3418 – 3422

Chemical Bonding and Atomic Structure in Y_2O_3:ZrO_2-$SrTiO_3$ Layered Heterostructures

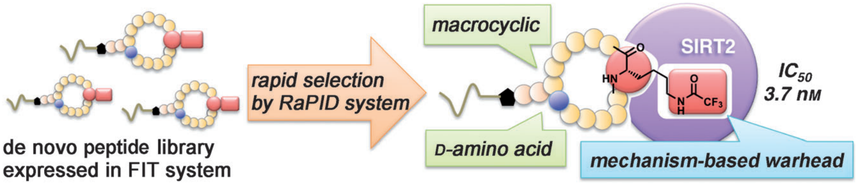


Repeating boundaries: The buried interfaces in artificial heterostructures produced by sequential deposition of nanosized units are critical to their properties. With density functional theory it was shown that in Y_2O_3:ZrO_2 (YSZ) and $SrTiO_3$ (STO) heterostructures reconstruction of the interfaces between the component units is required to access the most favorable structure (see picture).

Inhibitors

J. Morimoto, Y. Hayashi,
H. Suga* ________ 3423 – 3427

Discovery of Macrocyclic Peptides Armed with a Mechanism-Based Warhead: Isoform-Selective Inhibition of Human Deacetylase SIRT2

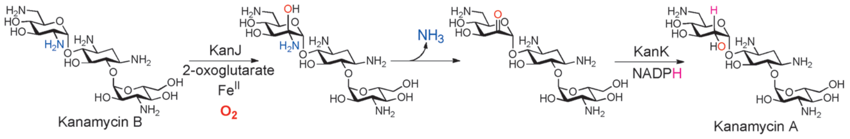


Designed to inhibit: By using the random nonstandard peptide integrated discovery (RaPID) system, highly potent isoform-selective inhibitors can be identified from a library of nonstandard macrocyclic peptides (see picture). These inhibitors, which contain a mechanism-based warhead residue, are active against the human deacetylase SIRT2, with IC_{50} values in the low nanomolar region.

Enzymes

H. Sucipto, F. Kudo,
T. Eguchi* ________ 3428 – 3431

The Last Step of Kanamycin Biosynthesis: Unique Deamination Reaction Catalyzed by the α-Ketoglutarate-Dependent Nonheme Iron Dioxygenase KanJ and the NADPH-Dependent Reductase KanK

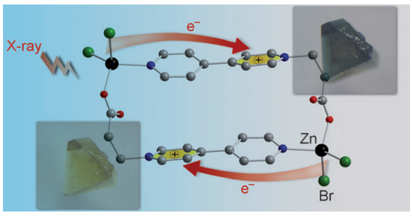


Mystery solved: Using heterologous expression, the activities of two enzymes exclusively belonging to the kanamycin biosynthetic pathway have been identified in vitro. A distinctive reaction mechanism (see scheme) to produce kanamycin is proposed and the previously unknown catalytic deamination activity of KanJ dioxygenase is uncovered.

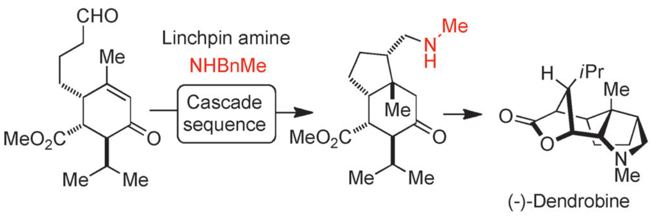
Photochromism

M.-S. Wang, C. Yang, G.-E. Wang, G. Xu,
X.-Y. Lv, Z.-N. Xu, R.-G. Lin, L. Z. Cai,
G.-C. Guo* ________ 3432 – 3435

A Room-Temperature X-ray-Induced Photochromic Material for X-ray Detection



A color change: X-ray-induced photochromic species are rare and can be used for detection of X-rays. A highly robust X-ray-sensitive material with the discrete structure of a metal–organic complex has been found to show both soft and hard X-ray-induced photochromism at room temperature (see picture). A new ligand-to-ligand electron-transfer mechanism was proposed to elucidate this photochromic phenomenon.



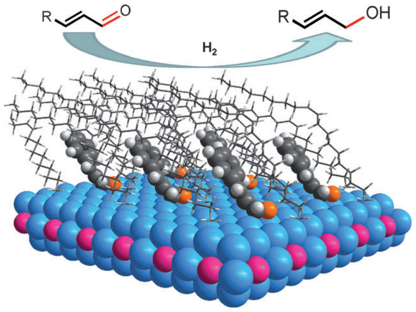
Cascading to alkaloids: An 18-step total synthesis of (−)-dendrobine is based on a reaction cascade with a key amine group (see scheme, Bn = benzyl). The amine is the initiator of the cascade and provides an efficient method for installing the stereocenters at C11 and C3. The overall transformation occurs stereoselectively only when the conversion is carried out without the isolation of intermediates.

Total Synthesis

L. M. Kreis, E. M. Carreira* **3436 – 3439**

Total Synthesis of (−)-Dendrobine

More Greasy, More Selective: Amine-capped Pt_3Co nanocatalysts were synthesized and used for the hydrogenation of cinnamaldehyde (CAL). Capping the catalysts with amines that contain long carbon chains results in an ordered surface "array" (see scheme), in which high selectivity towards C=O hydrogenation can be achieved because the C=C bond in CAL does not interact with the surface. The longer the carbon chains in the amine, the higher the selectivity.



Heterogeneous Catalysis

B. H. Wu, H. Q. Huang, J. Yang,
N. F. Zheng,* G. Fu* **3440 – 3443**

Selective Hydrogenation of α,β-Unsaturated Aldehydes Catalyzed by Amine-Capped Platinum-Cobalt Nanocrystals

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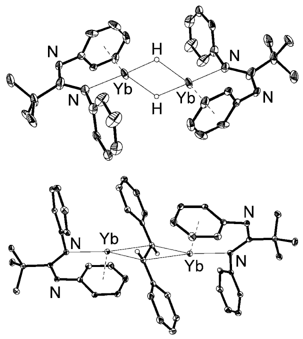

Addition of two Ln−H bonds of an Yb^{II} hydrido complex supported by bulky amidinate ligand to a C≡C bond lead to the formation of 1,2-dianionic bibenzyl fragment (see picture). Both Yb^{II} and hydrido centers are oxidized under the reaction conditions. The resulting Yb^{II}-η^6-arene interaction is surprisingly robust: the arene cannot be replaced from the metal coordination sphere when treated with Lewis bases.

Hydrides of Lanthanides

I. V. Basalov, D. M. Lyubov, G. K. Fukin,
A. S. Shavyrin,
A. A. Trifonov* **3444 – 3447**

A Double Addition of Ln−H to a Carbon–Carbon Triple Bond and Competitive Oxidation of Ytterbium(II) and Hydrido Centers

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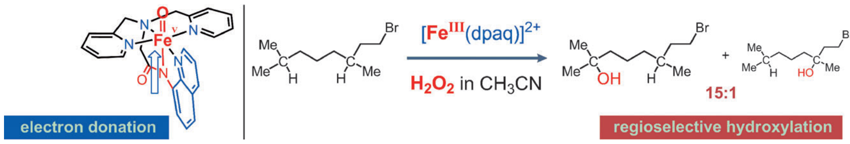


Selective oxidation: The success of the title reaction (see scheme) is caused by the strong electron donation from the amidate moiety of the dpaq ligand to the iron center (dpaq = 2-[bis(pyridin-2-ylmethyl)]amino-*N*-quinolin-8-yl-acetamidate). This process facilitates the O−O bond heterolysis of the intermediate $Fe^{III}OOH$ species to generate a selective oxidant without forming highly reactive hydroxyl radicals.

Hydroxylation

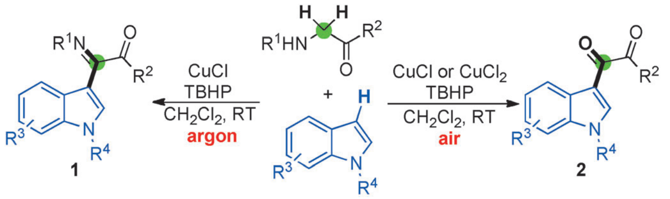
Y. Hitomi,* K. Arakawa, T. Funabiki,
M. Kodera **3448 – 3452**

An Iron(III)–Monoamidate Complex Catalyst for Selective Hydroxylation of Alkane C−H Bonds with Hydrogen Peroxide

Synthetic Methods

J.-C. Wu, R.-J. Song, Z.-Q. Wang,
X.-C. Huang, Y.-X. Xie,
J.-H. Li* ________ **3453 – 3457**

Copper-Catalyzed C—H Oxidation/
Cross-Coupling of α-Amino Carbonyl
Compounds

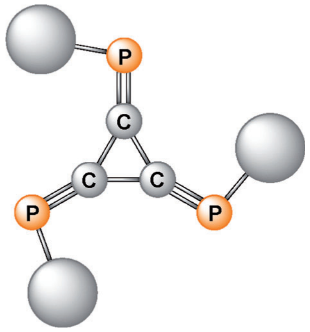


Keeping options open: The new and mild title reaction involving indoles selectively furnishes **1** and **2** with the aid of *tert*-butyl hydroperoxide (TBHP). The method represents the first example of a copper-catalyzed α arylation of α-amino carbonyl substrates leading to α-aryl α-imino and α-aryl α-oxo carbonyl compounds using a C—H oxidation strategy.

Radialene Chemistry

H. Miyake, T. Sasamori,*
N. Tokitoh* ________ **3458 – 3461**

Synthesis and Properties of
4,5,6-Triphospha[3]radialene



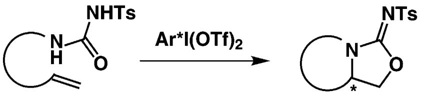
[3]Radialenes: 4,5,6-Tris(2,4,6-tri-*tert*-butylphenyl)phospha[3]radialene has been synthesized (see picture). The compound can be easily handled in air under ambient conditions, despite the [3]radialene moiety containing P═C bonds, and exhibits red-shifted absorption as well as high electron-accepting ability. The unique electronic properties are brought about by the synergistic effect of the [3]radialene framework and the phosphorus substitution.

Stereoselective Synthesis

U. Farid, T. Wirth* ________ **3462 – 3465**

Highly Stereoselective Metal-Free
Oxyaminations Using Chiral Hypervalent
Iodine Reagents

Inside Back Cover

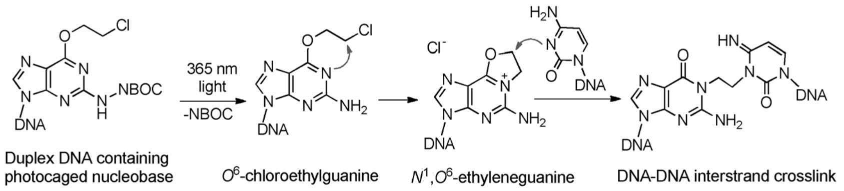


The ring and I: Hypervalent iodine compounds avoid the issues of toxicity or complicated ligands of many transition-metal-based systems. A highly enantioselective oxyamination of alkenes with *N*-sulfonyl ureas employing chiral, lactic acid-based hypervalent iodine reagents gives a facile synthesis of enantiomerically pure 2-arylproline derivatives (see scheme) for the first time.

Linking DNA

S. Hentschel, J. Alzeer, T. Angelov,
O. D. Schärer,
N. W. Luedtke* ________ **3466 – 3469**

Synthesis of DNA Interstrand Cross-Links
Using a Photocaged Nucleobase

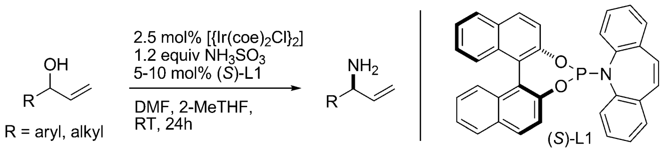


The missing linking: BCNU is a chemotherapy drug that generates an ethylene bridge between N^1 of deoxyguanosine and N^3 of deoxycytidine. No synthesis of a DNA containing this moiety has been reported until now. A new strategy uses a photocaged nucleobase that, when released, generates a highly reactive intermediate which cross-links the opposing DNA strand in a manner analogous to BCNU (see scheme, NBOC = *ortho*-nitrobenzyloxycarbonyl).

Enantioselective Allylic Amination

M. Lafrance, M. Roggen, E. M. Carreira* ____________ **3470 – 3473**

Direct, Enantioselective Iridium-Catalyzed Allylic Amination of Racemic Allylic Alcohols

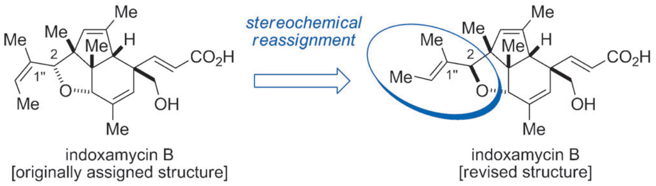


The direct route: Iridium-catalyzed direct conversion of branched allylic alcohols into enantioenriched branched primary allylic amines is highly regio- and enantioselective (see scheme; coe = cyclooctene).

Natural Product Synthesis

O. F. Jeker, E. M. Carreira* _ **3474 – 3477**

Total Synthesis and Stereochemical Reassignment of (±)-Indoxamycin B

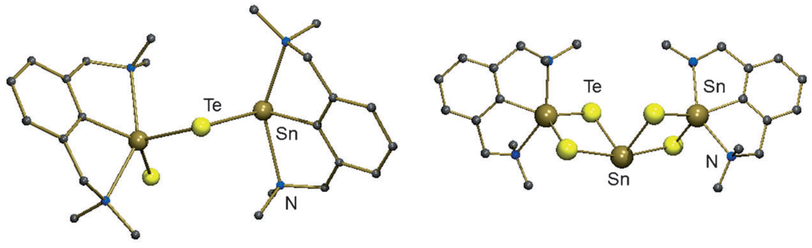


Revised version: The first total synthesis of indoxamycin B leads to a stereochemical reassignment of the natural product (see picture). The synthetic route features an efficient carboannulation sequence to rapidly access the dihydroindenone system. Moreover, a series of Au^I-catalyzed transformations served in the construction of the sterically congested core framework.

Organotin Compounds

M. Bouška, L. Dostál, Z. Padělková, A. Lyčka, S. Herres-Pawlis,* K. Jurkschat,* R. Jambor* ______________ **3478 – 3482**

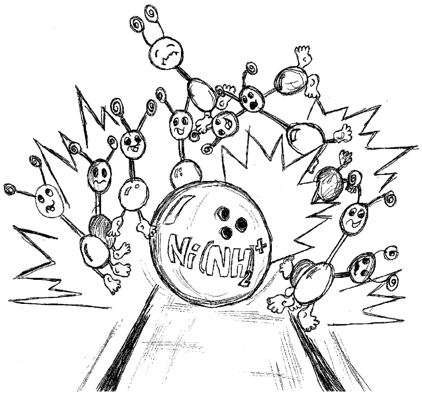
Intramolecularly Coordinated Organotin Tellurides: Stable or Unstable?



The step-wise oxidation of an organotin(I) compound with elemental tellurium gave a variety of unprecedented organotin tellurides containing tin atoms in the oxidation states +II and +IV (see examples).

Gas-Phase Reactions

Strike! While pure ammonia is out of luck, $Ni(NH_2)^+$ gets one strike after another at the "ethylene bowling championship". In fact, $Ni(NH_2)^+$ is so effective that no pin, not even at the neighboring lane, is safe from it.



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