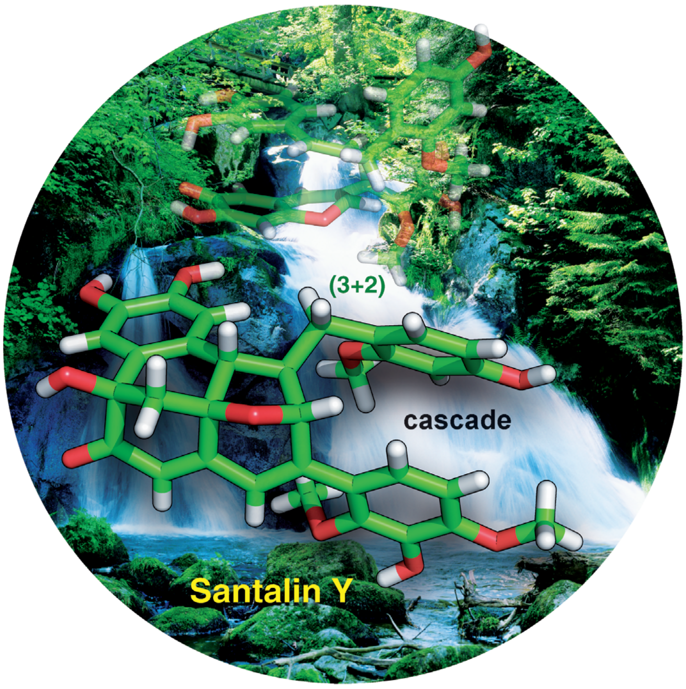
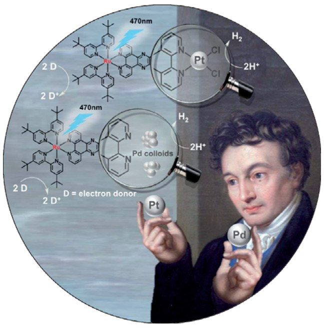
Santalin Y ...

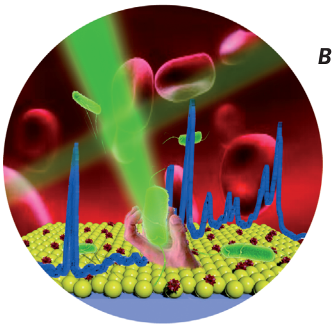


... , a complex yet racemic natural product, has been prepared by a biomimetic total synthesis. D. J. Tantillo, D. Trauner et al. propose in their Communication on page 5079 ff. that the key step is a cascade involving a (3 + 2) cycloaddition and a Friedel–Crafts ring closure, which generates the unique oxafenestrane framework of santalin Y and sets its five stereocenters in one operation. The Triberg Falls in the background, located in the Black Forest, are Germany's longest with 163 m.

Photocatalytic H_2 Production

In their Communication on page 5044 ff., S. Rau et al. investigate the mechanisms of the photocatalytic hydrogen production at Ru–Pd and Ru–Pt centers. Whereas Pd forms metal colloids as the initial step, Pt shows no change in the coordination sphere.





Bacterial Detection

The use of a multifunctional surface-enhanced Raman scattering chip for the simultaneous capture, detection, and inactivation of bacteria in real systems is described by Y. He and co-workers in their Communication on page 5132 ff.

Asymmetric Catalysis

The iron(II)-catalyzed asymmetric transfer hydrogenation of C=O bonds is described by A. Mezzetti et al. in their Communication on page 5171 ff. With the robust, highly active N_2P_2 macrocyclic catalysts, a wide scope of substrates can be hydrogenated.

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Editorial

"... The Bürgenstock program always allows for important scientific discussion. It is clear that this meeting is valuable for the scientific community as it is on one hand important for its deep historical significance, and on the other hand crucial for what it preserves of great scientific tradition for future generations. Every meeting contained a lesson learned and further brought together the family of stereochemists ..."
Read more in the Editorial by Jay S. Siegel.

Service

Author Profile

*„When I'm frustrated, I play the guitar.
I can never resist any new and fascinating scientific discovery ...“*
This and more about Pi-Tai Chou can be found on page 4998.

News


P. Simon


M.-P. Teulade-Fichou


S. Arseniyadis


W. Drenckhan


H. Kabbour


M. Scheer


L. A. Oro

Obituaries

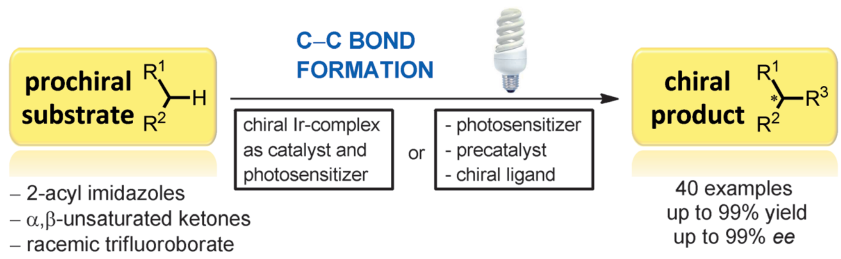
Carl Djerassi died at the age of 91 on January 30, 2015. He is best known for developing the synthetic hormone used to the present day in the oral contraceptive commonly known as The Pill. Djerassi's other achievements include the use of mass spectrometry in organic chemistry, and extensive research on antibiotics and marine natural products. He was also an author of plays, poems, and short stories, including *Oxygen*, written together with Roald Hoffmann.

Books

For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. US mailing agent: SPP, PO Box 437, Emigsville, PA 17318. Periodicals postage paid at Emigsville, PA. US POSTMASTER: send address changes to *Angewandte Chemie*, John Wiley & Sons Inc., C/O The Sheridan Press, PO Box 465, Hanover, PA 17331. Annual subscription price for institutions: US$ 11.738/10.206 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Highlights

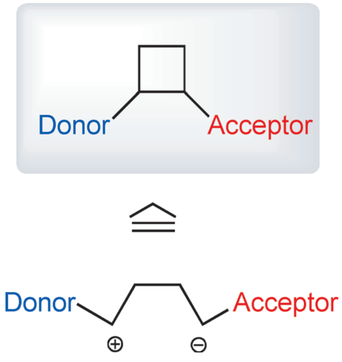
Asymmetric Synthesis



Dual role for catalysts: Novel routes for the generation of asymmetric stereocenters using photoredox catalysis were recently developed. Different chiral catalytic systems allowed new C–C bonds to form in good yields and enantioselectivities using a mild methodology in which light is used as the energy source.

Cycloaddition

The analogy goes further: Following the often-studied donor–acceptor-substituted cyclopropanes, the corresponding cyclobutane derivatives were employed for the ring-strain-driven stereoselective syntheses of carbo- and heterocycles.



Essays

Bürgenstock Conference

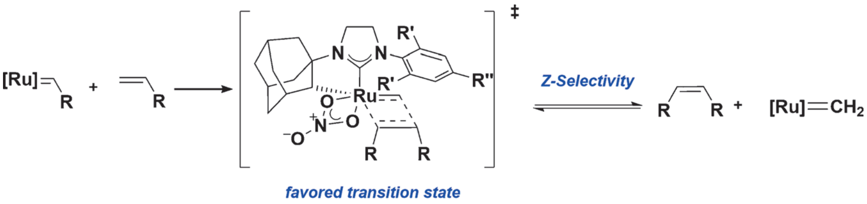
The secret of success: This year the famous “Bürgenstock Conference” will take place for the 50th time. This conference has become internationally one of the, if not the, most highly regarded conference in chemistry, chemical biology, and physical chemistry. What are the success factors of this conference? These as well as a number of perhaps more hidden figures and facts are discussed.

Minireviews

Olefin Cross Metathesis

M. B. Herbert,
R. H. Grubbs* ________ **5018 – 5024**

Z-Selective Cross Metathesis with Ruthenium Catalysts: Synthetic Applications and Mechanistic Implications



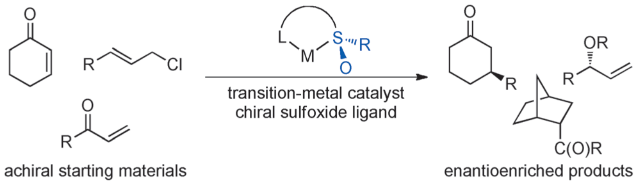
Zo Zelective: After the initial discovery that ruthenium alkylidene catalysts with cyclometalated NHC ligands could enable the *Z*-selective homodimerization of terminal olefins, research into forming more complex products containing internal *Z*-double bonds has moved at a fast pace. This Minireview serves as a guide for the use of these catalysts and similarly powerful *Z*-selective ruthenium catalysts for the formation of complex cross products with *Z*-olefins.

Reviews

Asymmetric Synthesis

B. M. Trost,* M. Rao ______ **5026 – 5043**

Development of Chiral Sulfoxide Ligands for Asymmetric Catalysis



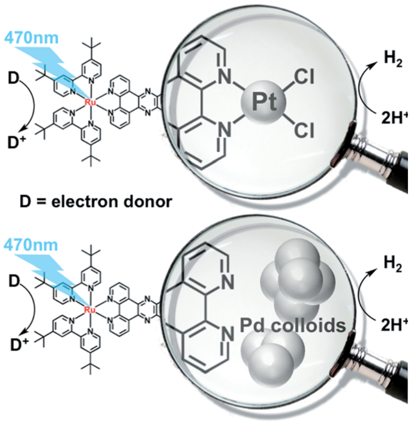
Auspicious ligands: Sulfoxides with chirality at the sulfur atom have mainly been used as chiral auxiliaries for diastereoselective reactions and have only recently emerged as a versatile class of chiral ligands. In this Review, the development of chiral sulfoxide ligands for asymmetric catalysis is discussed, and metal–sulfoxide bonding and strategies for the synthesis of enantiopure sulfoxides are described.

Communications

Photocatalytic H_2 Production

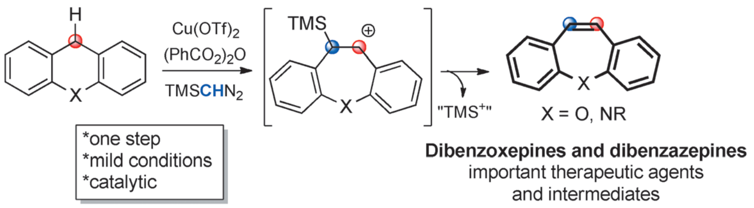
M. G. Pfeffer, B. Schäfer, G. Smolentsev, J. Uhlig, E. Nazarenko, J. Guthmuller, C. Kuhnt, M. Wächtler, B. Dietzek, V. Sundström, S. Rau* ______ **5044 – 5048**

Palladium versus Platinum: The Metal in the Catalytic Center of a Molecular Photocatalyst Determines the Mechanism of the Hydrogen Production with Visible Light



Show your metal: The mechanism of the visible light-driven hydrogen production with an intramolecular photocatalyst depends on the nature of the catalytically active metal center. In Ru–M systems, where M = Pt or Pd, palladium forms metal colloids as initial step, whereas platinum shows a high stability and there is no change in the $(N^\wedge N)PtCl_2$ coordination sphere.

Frontispiece



Cut a long story short: Tricyclic dibenzoxepines and dibenzazepines are important therapeutic agents for pharmaceuticals, but their syntheses are generally rather tedious. A copper(I)-catalyzed oxidative C−H bond functionalization and ring expansion sequence with TMSCHN$_2$ has been developed to yield these important derivatives in a facile and straightforward way.

Synthetic Methods

T. Stopka, L. Marzo, M. Zurro, S. Janich, E.-U. Würthwein, C. G. Daniliuc, J. Alemán,* O. G. Mancheño* ________ **5049 – 5053**

Oxidative C−H Bond Functionalization and Ring Expansion with TMSCHN$_2$: A Copper(I)-Catalyzed Approach to Dibenzoxepines and Dibenzoazepines

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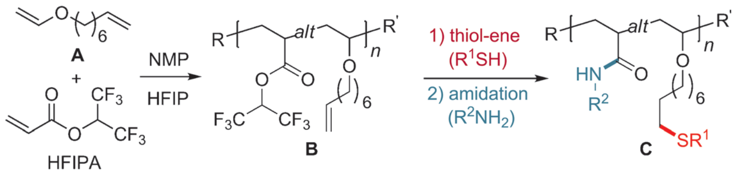

Alternating through double click: The title reaction of **A** with hexafluoroisopropyl acrylate (HFIPA) provides alternating polymer **B**, which can be chemically modified using two orthogonal polymer-analogous reactions. With this method, a small library of fifteen functionalized alternating copolymers was prepared.

Sequence-Controlled Polymerization

M. Tesch, J. A. M. Hepperle, H. Klaasen, M. Letzel, A. Studer* ______ **5054 – 5059**

Alternating Copolymerization by Nitroxide-Mediated Polymerization and Subsequent Orthogonal Functionalization

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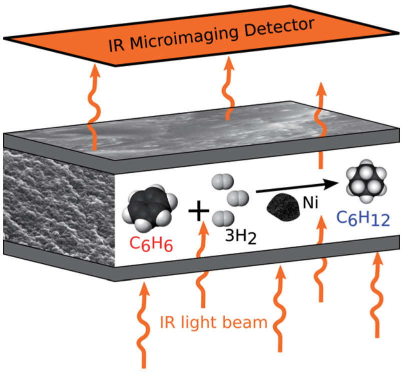

At a glance: Microimaging by IR microscopy is used to record the evolution of the concentration profiles of reactant and product molecules during catalytic reaction. The method is thus shown to allow a one-shot determination of effectiveness factors.

In Situ Spectroscopy

T. Titze, C. Chmelik, J. Kullmann, L. Prager, E. Miersemann, R. Gläser, D. Enke, J. Weitkamp, J. Kärger* _____ **5060 – 5064**

Microimaging of Transient Concentration Profiles of Reactant and Product Molecules during Catalytic Conversion in Nanoporous Materials

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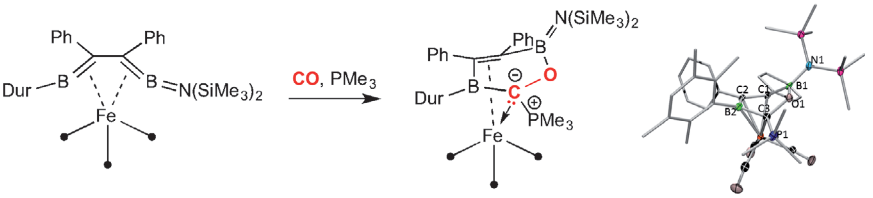


Ringing the changes: A 1,4-dibora-1,3-butadiene iron complex was successfully synthesized through the stoichiometric reaction of iron bis(borylene) with diphenylacetylene. This complex was treated with CO and PMe$_3$, thereby leading to the formation of an unusual six-membered B$_2$C$_3$O ylidic ring bound to both the PMe$_3$ group and zerovalent iron center. The reaction is a very rare example of the incorporation of both atoms of CO into a ring system.

Cyclization with CO

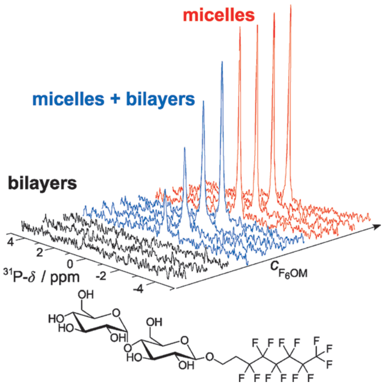
H. Braunschweig,* Q. Ye, M. A. Celik, R. D. Dewhurst, K. Radacki _ **5065 – 5068**

Cyclization of a 1,4-Diborabutadiene Ligand with Both Atoms of CO

Membrane Proteins

E. Frotscher, B. Danielczak, C. Vargas, A. Meister, G. Durand, S. Keller* ______ **5069 – 5073**

A Fluorinated Detergent for Membrane-Protein Applications

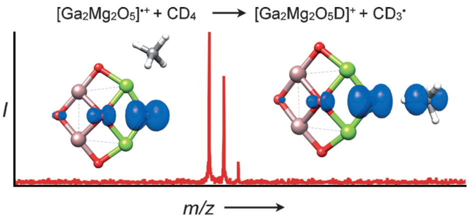


Mild thing: Mild detergency is required for a surfactant to chaperone the functional refolding of membrane proteins into liposomes. In contrast with other surfactants carrying a lipophobic fluorinated chain, a fluorinated octyl maltoside derivative meets this condition and solubilizes phospholipid vesicles in a detergent-like but gentle fashion.

Methane Activation

J. Li, X.-N. Wu, M. Schlangen, S. Zhou, P. González-Navarrete, S. Tang, H. Schwarz* ______ **5074 – 5078**

On the Role of the Electronic Structure of the Heteronuclear Oxide Cluster $[Ga_2Mg_2O_5]^{\bullet +}$ in the Thermal Activation of Methane and Ethane: An Unusual Doping Effect



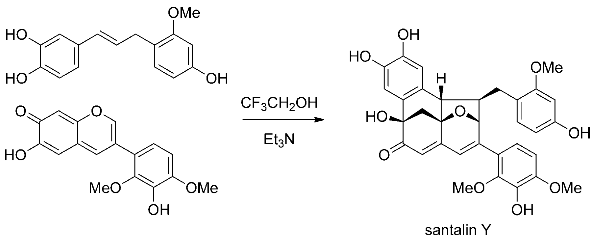
Bridging oxygen: A combination of mass spectrometry and quantum chemical calculations shows that $[Ga_2Mg_2O_5]^{\bullet +}$, bearing an unpaired electron at a bridging oxygen atom, is capable of activating the C−H bond of methane. The roles of spin density and charge distributions in hydrogen-atom transfer processes provide important guidance for the rational design of catalysts.

Biomimetic Synthesis

S. Strych, G. Journot, R. P. Pemberton, S. C. Wang, D. J. Tantillo,* D. Trauner* ______ **5079 – 5083**

Biomimetic Total Synthesis of Santalin Y

Front Cover

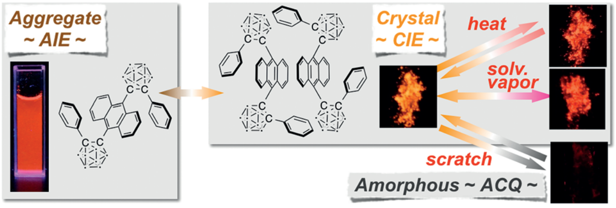


High five! The five stereocenters of santalin Y, a complex yet racemic natural product, were installed in a single operation. Quantum chemical computations point to a concerted 1,3-dipoar cycloaddition that involves a “vinylogous oxidopyrylium species” as the key step.

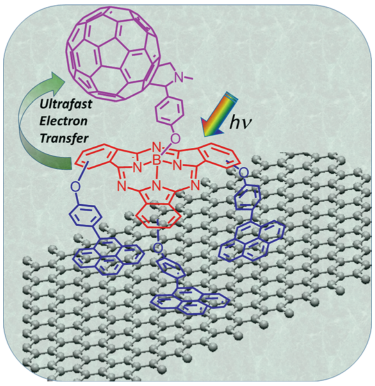
Aggregation

H. Naito, Y. Morisaki,* Y. Chujo* ______ **5084 – 5087**

o-Carborane-Based Anthracene: A Variety of Emission Behaviors

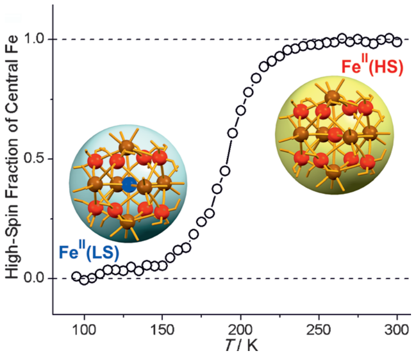


Multiple personalities: Single crystals of *o*-carborane-based anthracene were obtained. In the crystal, the anthracene ring is highly distorted because of the formation of a π-stacked dimer. The crystals exhibit a variety of emission behaviors such as aggregation-induced emission (AIE), crystallization-induced emission (CIE), aggregation-caused quenching (ACQ), vapochromism, thermochromism, and mechanochromism.



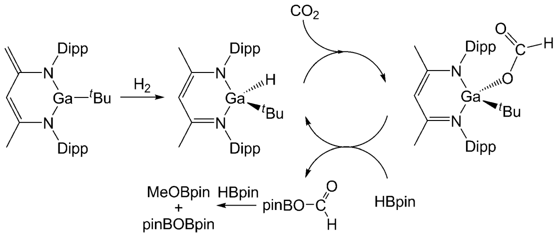
In a split second: Ultrafast photochemical charge separation in multimodular donor–acceptor systems, composed of three units of pyrene, a subphthalocyanine, and a fullerene hybridized on graphene through π–π stacking interactions, is demonstrated using femtosecond transient spectroscopy. The present hybrids may have use as materials for fast-responding optoelectronic devices and in light energy harvesting applications.

Donor–Acceptor Systems



Selective switching: A single Fe^{II} ion embedded in the center of nanosized $\{Fe_9Re_6\}$ cyanido-bridged cluster exhibits a complete thermally induced spin-crossover phase transition between a paramagnetic high-spin (HS; $S=2$) and diamagnetic low-spin state (LS; $S=0$). The HS and LS states dominate at high and low temperatures, respectively (see picture; sphere colors: red = Fe^{II}(HS), blue = Fe^{II}(LS), brown = Re^{V}).

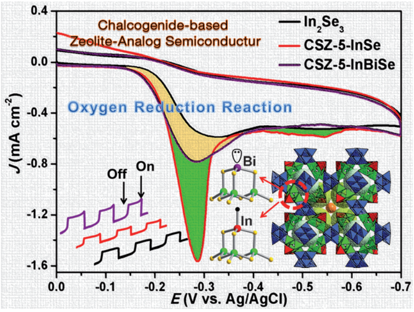
Spin Crossover



A single-component ambiphilic Group 13 system has been developed, capable of the cooperative activation of protic, hydridic, and apolar H–X bonds. The hydride complex derived from the activation of H_2 catalyzes the selective transformation of CO_2 to a methanol derivative, representing the first example of such a reduction process catalyzed by a molecular gallium complex.

Group 13 Metal Catalysis

Zeolitic architecture: An interrupted chalcogenide-based zeolite-analogue semiconductor with an entirely new boracite-related framework and specific sites at the interrupted section is reported. The specific indium sites serving as effective electrocatalytic active centers for the oxygen reduction reaction are atomically precisely doped by trivalent bismuth ions.



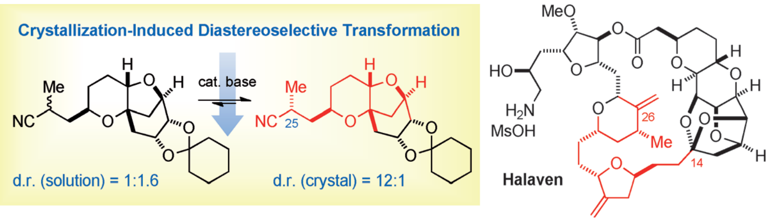
Mesoporous Materials

Asymmetric Synthesis

F. Belanger, C. E. Chase, A. Endo, F. G. Fang,* J. Li, S. R. Mathieu, A. Z. Wilcoxen, H. Zhang ____ **5108–5111**

Stereoselective Synthesis of the Halaven C14–C26 Fragment from D-Quinic Acid: Crystallization-Induced Diastereoselective Transformation of an α-Methyl Nitrile

Inside Cover

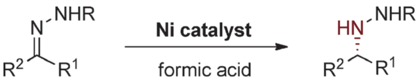


Crystallization-induced diastereoselective transformation of an α-methyl nitrile completes an entirely non-chromatographic synthesis of the halichondrin B C14–C26 stereochemical array. All four stereogenic centers in the Halaven C14–C26 fragment were assembled on a crystalline polycyclic template derived from the single chiral source D-quinic acid.

Asymmetric Hydrogenation

H. Xu, P. Yang, P. Chuanprasit, H. Hirao,* J. Zhou* ____ **5112–5116**

Nickel-Catalyzed Asymmetric Transfer Hydrogenation of Hydrazones and Other Ketimines

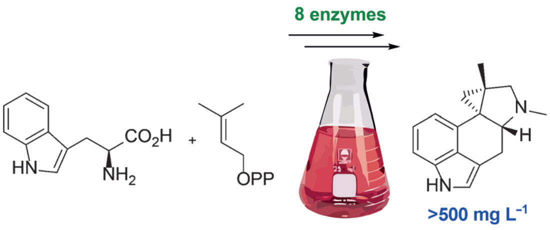


Cheap and abundant nickel was used for the catalytic transfer hydrogenation of hydrazones and related compounds (see scheme; R = acyl, aryl; R^1 = alkyl, CF_3; R^2 = aryl, alkyl). The nickel/binapine catalyst may exert stereocontrol through weak attractive interactions, thus behaving like an enzyme.

Biosynthesis

D. Jakubczyk, L. Caputi, A. Hatsch, C. A. F. Nielsen, M. Diefenbacher, J. Klein, A. Molt, H. Schröder, J. Z. Cheng, M. Naesby,* S. E. O'Connor* ____ **5117–5121**

Discovery and Reconstitution of the Cycloclavine Biosynthetic Pathway—Enzymatic Formation of a Cyclopropyl Group



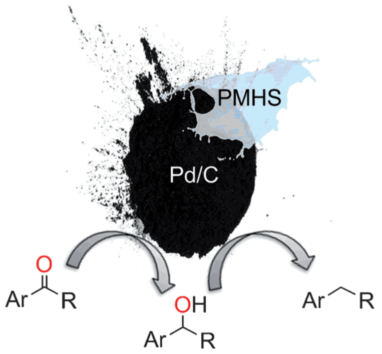
Who's responsible for the ring? The biosynthetic pathway of the ergot alkaloid cycloclavine (see scheme) was discovered and reconstituted in yeast at titers of $>500\,\mathrm{mg\,L^{-1}}$. A yeast-based expression platform and in vitro biochemical experiments enabled the identification of the enzyme that catalyzes the unprecedented rearrangement of a biosynthetic intermediate to form the cyclopropyl moiety of cycloclavine.

Heterogeneous Catalysis

A. Volkov, K. P. J. Gustafson, C.-W. Tai, O. Verho,* J.-E. Bäckvall,* H. Adolfsson* ____ **5122–5126**

Mild Deoxygenation of Aromatic Ketones and Aldehydes over Pd/C Using Polymethylhydrosiloxane as the Reducing Agent

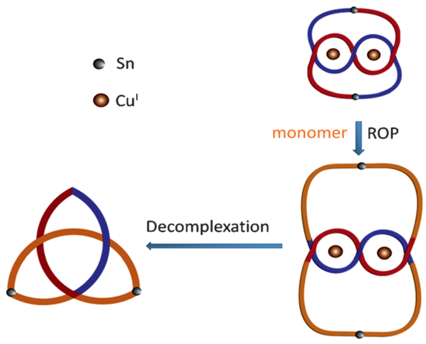
O, Farewell! Heterogeneous Pd/C was found to be an efficient and recyclable catalyst for the title reaction. The robustness of the catalytic system was demonstrated by the high-yielding reduction of ethyl vanillin, which was conducted on a 30 mmol scale in an open-to-air set-up at room temperature.



Knotted Polymers

P.-F. Cao, J. Mangadlao,
R. Advincula* ______ **5127 – 5131**

A Trefoil Knotted Polymer Produced through Ring Expansion



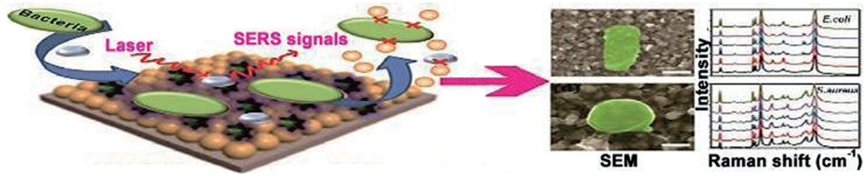
Knot a problem: A synthetic strategy is reported for the production of a trefoil knotted polymer from a Cu$^{\mathrm{I}}$-templated helical knot precursor through ring expansion. The expected changes in the properties of the knotted polymer compared to a linear analogue, namely reduced hydrodynamic radius and lower intrinsic viscosity, together with atomic force microscopy images of individual molecular knots, confirmed the formation of a trefoil knotted polymer.

Bacterial Detection

H. Wang, Y. Zhou, X. Jiang, B. Sun, Y. Zhu,
H. Wang, Y. Su, Y. He* ______ **5132 – 5136**

Simultaneous Capture, Detection, and Inactivation of Bacteria as Enabled by a Surface-Enhanced Raman Scattering Multifunctional Chip

Inside Back Cover

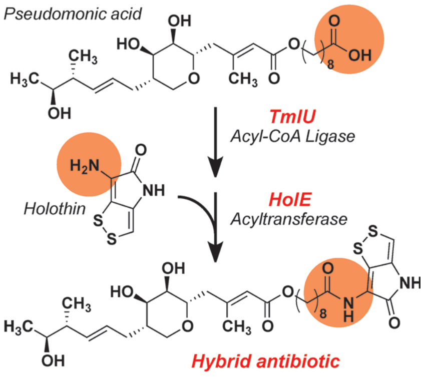


No chip off the old block: A multifunctional platform was developed for the simultaneous capture, sensing by surface-enhanced Raman scattering (SERS), and inactivation of bacteria (see picture). The SERS chip featured excellent reproducibility, good bacterial-capture efficiency, high sensitivity, and a high antibacterial rate, and was found to be suitable for capturing and discriminating bacteria in real systems.

Biosynthesis

Z. D. Dunn, W. J. Wever, N. J. Economou,
A. A. Bowers, B. Li* ______ **5137 – 5141**

Enzymatic Basis of “Hybridity” in Thiomarinol Biosynthesis

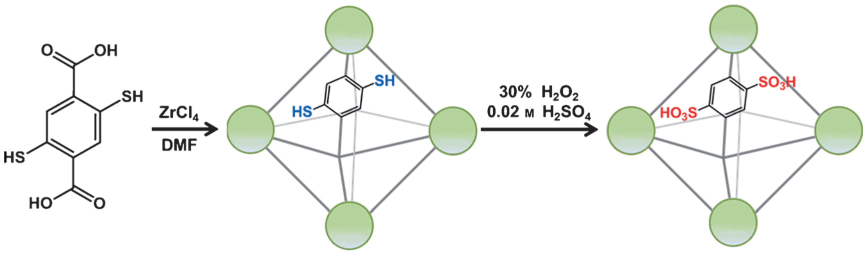


The biosynthetic mechanism responsible for generating the antibiotic thiomarinol was elucidated. In contrast to previous hypotheses, TmlU acts as a CoA-ligase and works in tandem with a second enzyme, acyltransferase HolE, to link two antimicrobial warheads pseudomonic acid and holothin, creating a hybrid antibiotic (see scheme).

Proton-Conducting Materials

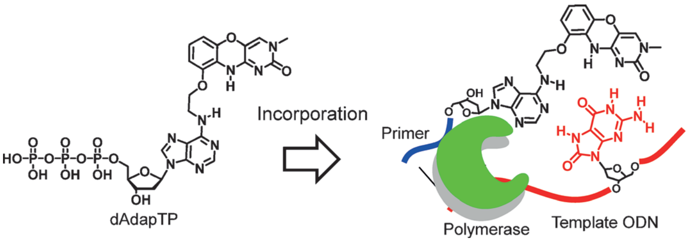
W. J. Phang, H. Jo, W. R. Lee, J. H. Song,
K. Yoo, B. Kim, C. S. Hong* **5142 – 5146**

Superprotonic Conductivity of a UiO-66 Framework Functionalized with Sulfonic Acid Groups by Facile Postsynthetic Oxidation



Decorated for honorable conductivity: The postsynthetic oxidation of a thiol-laced UiO-66-type framework generated sulfonic acid groups covalently linked to the backbone of the system (see picture; green circles are Zr–O nodes). The oxidized material exhibited stable superprotonic conductivity of 8.4×10^{-2} S cm^{-1} at 80 °C and 90% relative humidity.

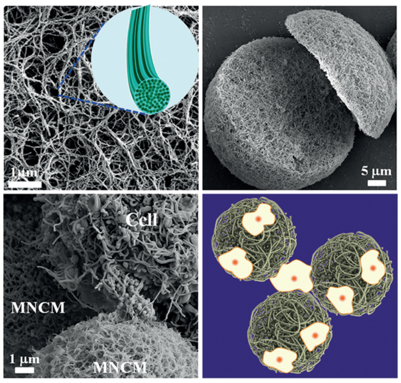
DNA Damage



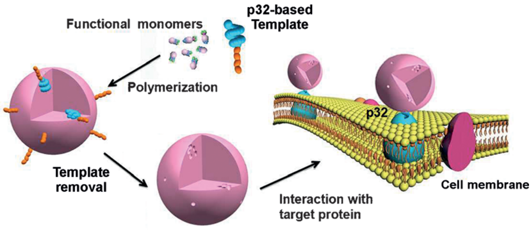
One is not like the other: The triphosphate of Adap (dAdapTP) was synthesized and used in single nucleotide primer extension reactions with the Klenow Fragment. Based on the extension efficiency, dAdapTP showed excellent discrimination between 8-oxo-dG and dG in the template ODNs. The sequence-specific detection of 8-oxo-dG in human telomeric DNA sequences extracted from H_2O_2-treated HeLa cells was also performed by an enzymatic incorporation reaction with dAdapTP.

Biomedical Materials

Nimbly weaved: Chitin chains rapidly self-assembled into nanofibers in aqueous NaOH/urea solution by a thermally induced method. Subsequently, the nanofibers formed weaved chitin microspheres (NCM) having a uniform architecture throughout. Cells could adhere to the nanofibrous NCM, which indicates the great potential of the NCM for cell microcarriers.



Drug Delivery

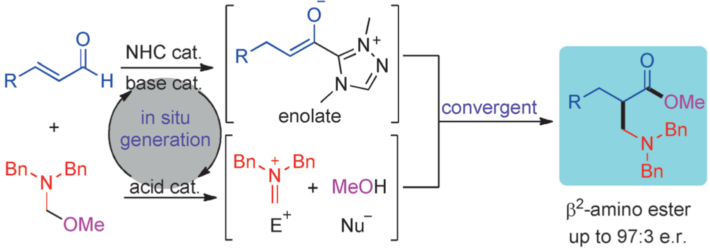


Magic bullet: A peptide served as an "indirect" targeting ligand to mediate active tumor-targeted drug delivery. A disulfide-linked α-helix containing peptide, apamin, was used to mimic the extracellular, structured N-terminal part of the protein p32. The combination with surface molecular imprinting produced a nanocarrier that recognizes p32-positive tumors in vivo.

Organocatalysis

J. Xu, X. Chen, M. Wang, P. Zheng, B.-A. Song, Y. R. Chi* ——— 5161 – 5165

Aminomethylation of Enals through Carbene and Acid Cooperative Catalysis: Concise Access to β^2-Amino Acids

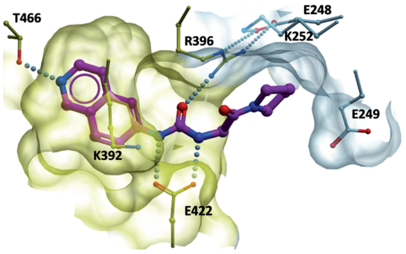


Harmonious cooperation: An N-heterocyclic carbene (NHC) and (in situ generated) Brønsted acid cooperatively catalyze the aminomethylation of α,β-unsaturated aldehydes. This cooperative catalytic reaction provides a redox neutral strategy for quick access to β^2-amino esters in an enantioselective manner.

Chemical Probes

H. Ü. Kaniskan, M. M. Szewczyk, Z. Yu, M. S. Eram, X. Yang, K. Schmidt, X. Luo, M. Dai, F. He, I. Zang, Y. Lin, S. Kennedy, F. Li, E. Dobrovetsky, A. Dong, D. Smil, S.-J. Min, M. Landon, J. Lin-Jones, X. P. Huang, B. L. Roth, M. Schapira, P. Atadja, D. Barsyte-Lovejoy, C. H. Arrowsmith, P. J. Brown, K. Zhao,* J. Jin,* M. Vedadi* ——— 5166 – 5170

A Potent, Selective and Cell-Active Allosteric Inhibitor of Protein Arginine Methyltransferase 3 (PRMT3)



High selectivity: The first PRMT3 chemical probe, SGC707, was discovered by structure-based optimization. SGC707 is a potent PRMT3 inhibitor with outstanding selectivity. The mechanism of action studies and crystal structure of the PRMT3–SGC707 complex confirm the allosteric inhibition mode. SGC707 engages PRMT3 and potently inhibits its methyltransferase activity in cells. It is also bioavailable and suitable for animal studies.

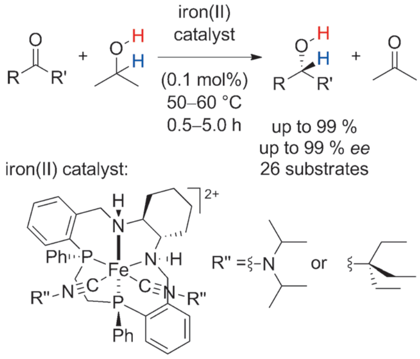
Asymmetric Catalysis

R. Bigler, R. Huber, A. Mezzetti* ——— 5171 – 5174

Highly Enantioselective Transfer Hydrogenation of Ketones with Chiral (NH)$_2$P$_2$ Macrocyclic Iron(II) Complexes

Back Cover

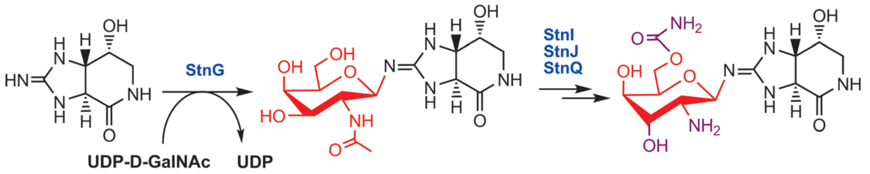
Paying the iron price: Bis(isonitrile) iron(II) complexes with a C_2-symmetric diamino (NH)$_2$P$_2$ macrocyclic ligand efficiently catalyze the hydrogenation of polar bonds of a broad scope of substrates (ketones, enones, imines) in high yield (up to 99.5%), excellent enantioselectivity (up to 99% *ee*), and with low catalyst loading (generally 0.1 mol%).



Biosynthesis

Z. Guo, J. Li, H. Qin, M. Wang, X. Lv, X. Li, Y. Chen* ——— 5175 – 5178

Biosynthesis of the Carbamoylated D-Gulosamine Moiety of Streptothricins: Involvement of a Guanidino-*N*-glycosyltransferase and an *N*-Acetyl-D-gulosamine Deacetylase

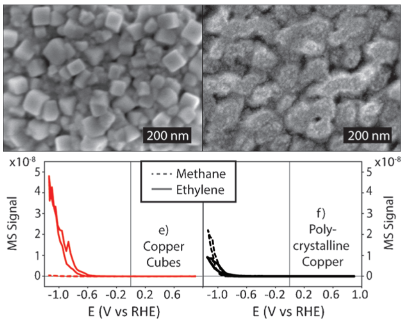


The dynamic duo: Two novel enzymes, StnG and StnI, have been found to be involved in the biosynthetic pathway of the carbamoylated D-gulosamine moiety in streptothricins. StnG is a GT-A fold glycosyltransferase that catalyzes the unprecedented attachment of a sugar to the imine nitrogen atom of a guanidine group; StnI catalyzes the deacetylation of the *N*-acetyl-D-gulosamine moiety.

Electrocatalysis

F. S. Roberts, K. P. Kuhl,
A. Nilsson* ______________ **5179 – 5182**

High Selectivity for Ethylene from Carbon Dioxide Reduction over Copper Nanocube Electrocatalysts

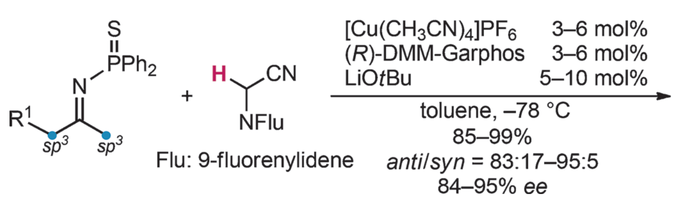


Cubic nanostructures formed on a polycrystalline copper surface give high selectivity for ethylene formation from carbon dioxide electroreduction. The nanocubes are easily synthesized in situ, and online electrochemical mass spectrometry is used to compare the reactivity to other copper single-crystal surfaces.

Asymmetric Catalysis

S. Lin, Y. Kawato, N. Kumagai,*
M. Shibasaki* ______________ **5183 – 5186**

Catalytic Asymmetric Mannich-Type Reaction of *N*-Alkylidene-α-Aminoacetonitrile with Ketimines

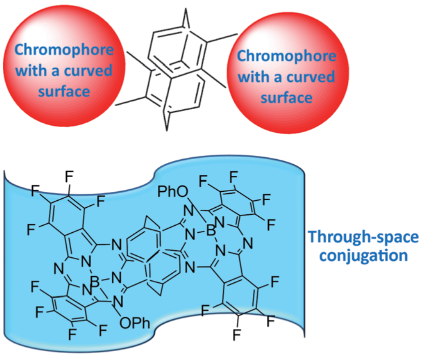


Getting in key: A soft Lewis acid/hard Brønsted base cooperative catalyst allows for efficient stereoselectives coupling of *N*-alkylidene-α-aminoacetonitrile and aliphatic ketimines to access vicinal diamines bearing consecutive tetra- and trisubstituted stereogenic centers. The use of a soft Lewis basic thiophosphinoyl group on the ketimines is key to promoting the reaction with as little as 3 mol% catalyst loading.

Paracyclophanes

Q. Liu, S. Shimizu,
N. Kobayashi* ______________ **5187 – 5191**

Cyclophanes Containing Bowl-Shaped Aromatic Chromophores: Three Isomers of *anti*-[2.2](1,4)Subphthalocyaninophane

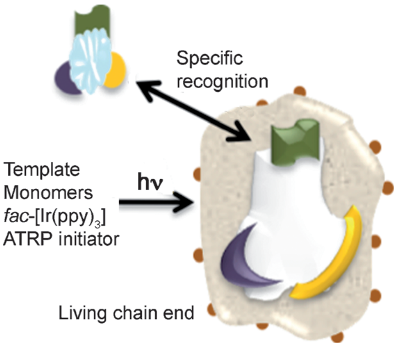


Bending the rules: A transannular interaction between two bowl-shaped π-conjugated systems was investigated in the designed subphthalocyaninophane (see scheme). The extension of π conjugation along the long axis of the molecule led to redshifting, broadening, and splitting of the Q band in the UV/Vis absorption spectrum. ^{1}H NMR spectra showed significant differences between the *endo* and *exo* faces of the subphthalocyanine units.

Polymers

Z. Adali-Kaya, B. Tse Sum Bui,
A. Falcimaigne-Cordin,
K. Haupt* ______________ **5192 – 5195**

Molecularly Imprinted Polymer Nanomaterials and Nanocomposites: Atom-Transfer Radical Polymerization with Acidic Monomers

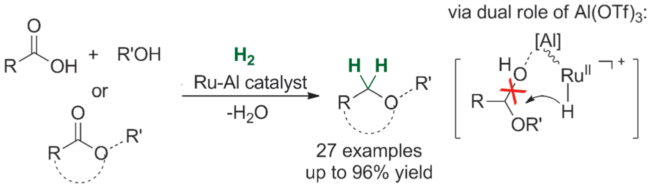


Read the small (im)print: Molecularly imprinted polymers (MIPs) are artificial receptors which can be tailored to bind target molecules specifically. The title reaction is compatible with acidic monomers, for their synthesis as monoliths, thin films and nanoparticles. This paves the way for surface modification and lithographic patterning of MIPs and their postfunctionalization from living chain-ends. ppy = 2-phenylpyridine.

Homogeneous catalysis

Y. Li, C. Topf, X. Cui, K. Junge, M. Beller* ———— 5196 – 5200

Lewis Acid Promoted Ruthenium(II)-Catalyzed Etherifications by Selective Hydrogenation of Carboxylic Acids/Esters

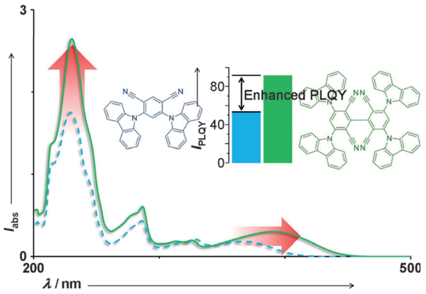


An assist from Al: A bifunctional catalyst system consisting of a Ru/phosphine complex and aluminum triflate allows selective hydrogenation of esters to ethers. A variety of lactones were reduced to the desired products in good yields. The catalyst further provides a general method for the reduction of linear esters and reductive etherification of carboxylic acids with alcohols.

Fluorescence

Y. J. Cho, S. K. Jeon, B. D. Chin, E. Yu, J. Y. Lee* ———— 5201 – 5204

The Design of Dual Emitting Cores for Green Thermally Activated Delayed Fluorescent Materials

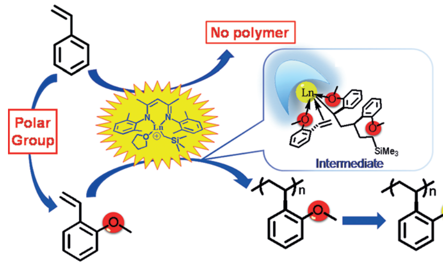


Coupled emitter units: The design of dual emitting cores for thermally activated delayed fluorescent (TADF) materials is reported. The strategy can be used to improve the quantum efficiency of TADF emitters (see picture; PLQY = photoluminescence quantum yield).

Polymers

D. Liu, C. Yao, R. Wang, M. Wang, Z. Wang, C. Wu, F. Lin, S. Li, X. Wan, D. Cui* ———— 5205 – 5209

Highly Isoselective Coordination Polymerization of *ortho*-Methoxystyrene with β-Diketiminato Rare-Earth-Metal Precursors

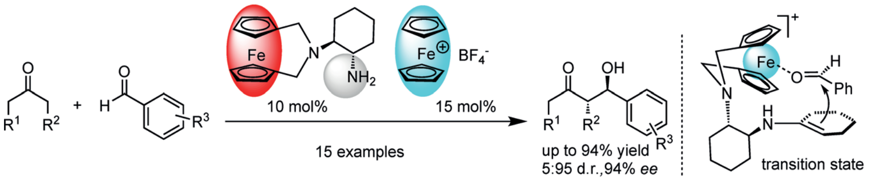


Name your poison: The title reaction has been achieved for the first time by using a β-diketiminato cationic rare-earth-metal species. High activity and excellent isoselectivity are observed. The Lewis-basic methoxy group does not poison the Lewis-acidic metal center but activates the polymerization through σ-π chelation to the active species.

Asymmetric Catalysis

Q. Zhang, X. Cui,* L. Zhang, S. Luo,* H. Wang, Y. Wu* ———— 5210 – 5213

Redox Tuning of a Direct Asymmetric Aldol Reaction

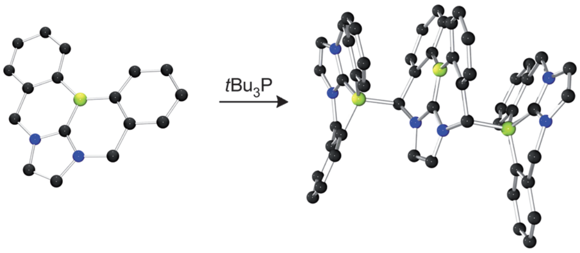


Stay tuned: A redox tuning strategy has been developed for asymmetric aminocatalysis using a chiral ferrocenophane. Under redox control, the catalyst catalyzes the asymmetric aldol reaction at room temperature with excellent yield and good stereoselectivity. Moreover, the catalyst is recyclable.

Boron–Carbene Adducts

J. M. Farrell, D. W. Stephan* **5214 – 5217**

Planar N-Heterocyclic Carbene Diarylborenium Ions: Synthesis by Cationic Borylation and Reactivity with Lewis Bases



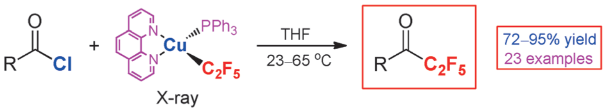
Boron in action: Singly or doubly ring closed NHC–borenium salts (NHC = N-heterocyclic carbene) are prepared by dehydrogenative cationic borylation. Treatment of the planar doubly ring closed product (see picture, left) with tBu$_3$P leads to the formation of an unusual *trans* C_2-symmetric oligomeric borenium salt (right). Atom colors: C, black; N, blue; B, yellow.

VIP

Pentafluoroethylation

L. I. Panferova, F. M. Miloserdov, A. Lishchynskyi, M. Martínez Belmonte, J. Benet-Buchholz, V. V. Grushin* **5218 – 5222**

Well-Defined CuC_2F_5 Complexes and Pentafluoroethylation of Acid Chlorides

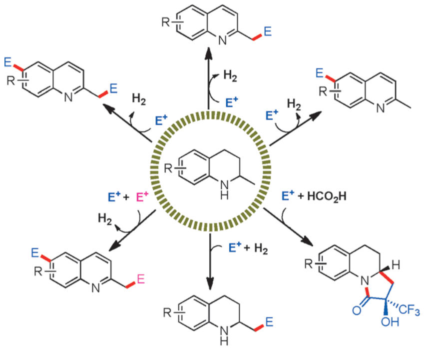


Four well-defined CuC_2F_5 complexes have been prepared and fully characterized, with [(phen)Cu(PPh$_3$)C$_2$F$_5$] (phen = 1,10-phenanthroline) proving to be a remarkably efficient fluoroalkylating agent for a broad variety of acid chlorides (see scheme). The procedure represents the first general method for the one-step conversion of RCOCl into valuable pentafluoroethyl ketones.

C–H Functionalization

D. Talwar, A. Gonzalez-de-Castro, H. Y. Li, J. L. Xiao* **5223 – 5227**

Regioselective Acceptorless Dehydrogenative Coupling of N-Heterocycles toward Functionalized Quinolines, Phenanthrolines, and Indoles

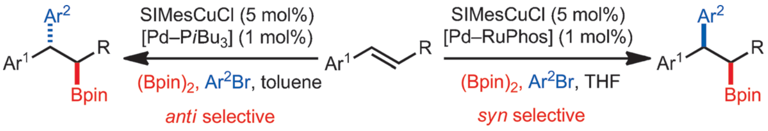


Regioselectively functionalized quinolines, phenanthrolines, and indoles are obtained by dehydrogenation of N-heterocycles in the presence of electrophiles. This reaction produces H_2 as the only byproduct under mild conditions.

Cross-Coupling

K. M. Logan, K. B. Smith, M. K. Brown* **5228 – 5231**

Copper/Palladium Synergistic Catalysis for the *syn-* and *anti-*Selective Carboboration of Alkenes

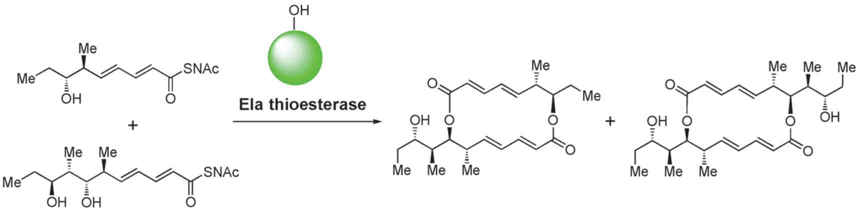


The diastereoselective carboboration of 1,2-disubstituted styrenes with aryl/vinyl bromides and (Bpin)$_2$ proceeds with high diastereoselectivities and yields. The formation of either diastereomer of the product from a single alkene isomer is determined by the reaction conditions. The method thus provides access to a diverse range of structures from simple starting materials.

Biosynthesis

Y. Zhou, P. Prediger, L. C. Dias,
A. C. Murphy, P. F. Leadlay* **5232 – 5235**

Macrodiolide Formation by the Thioesterase of a Modular Polyketide Synthase

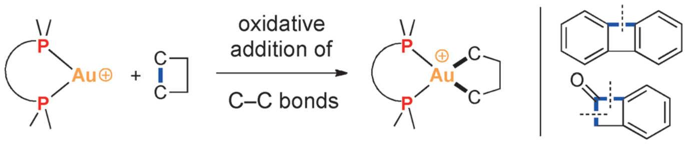


Think again: The thioesterase/cyclase enzyme of the elaiophylin polyketide synthase catalyzes symmetric diolide formation in vitro from a synthetic pentaketide substrate by an iterative mechanism. Unexpectedly, a tetraketide that is not itself a substrate can be co-opted in the presence of the pentaketide to produce an asymmetric macrodiolide.

Gold Chemistry

M. Joost, L. Estévez, K. Miqueu,
A. Amgoune,*
D. Bourissou* ____________ **5236 – 5240**

Oxidative Addition of Carbon–Carbon Bonds to Gold



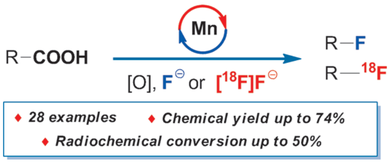
Gold(I) complexes ($[(DPCb)Au]^+$) readily insert into the four-membered rings of biphenylene and benzocyclobutenone. These transformations afforded well-defined cationic organogold(III) complexes that were isolated and fully characterized. $[(DPCb)Au]^+$ is the only complex to cleave selectively either the C(aryl)−C(O) or the C(alkyl)−C(O) bond of benzocyclobutenone under kinetic/thermodynamic control. DPCb = diphosphinocarborane.

Decarboxylative Fluorination

X. Huang, W. Liu, J. M. Hooker,
J. T. Groves* ____________ **5241 – 5245**

Targeted Fluorination with the Fluoride Ion by Manganese-Catalyzed Decarboxylation

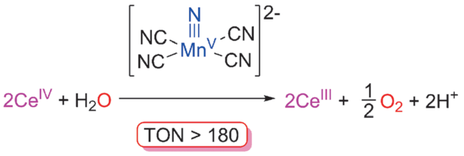
Nucleophile first: An efficient manganese porphyrin catalyzed decarboxylative fluorination reaction based on a nucleophilic fluorine source is described. The potential of the described method for use in PET imaging has been demonstrated by the successful ^{18}F labeling of various aliphatic carboxylic acids, representing the first decarboxylative ^{18}F labeling method with no-carrier-added [^{18}F]fluoride.



Water Oxidation

L. Ma, Q. Wang, W.-L. Man, H.-K. Kwong,
C.-C. Ko, T.-C. Lau* ________ **5246 – 5249**

Cerium(IV)-Driven Water Oxidation Catalyzed by a Manganese(V)–Nitrido Complex



High turnover: The study of manganese complexes as catalysts for the oxidation of water is of great interest as they can serve as models for the oxygen-evolving complex of photosystem II. The manganese(V)–nitrido complex $[Mn(N)(CN)_4]^{2-}$ was now shown to catalyze the oxidation of water by cerium(IV) with a turnover number (TON) of higher than 180.

Synthetic Methods

U. Orcel, J. Waser* ________ **5250 – 5254**

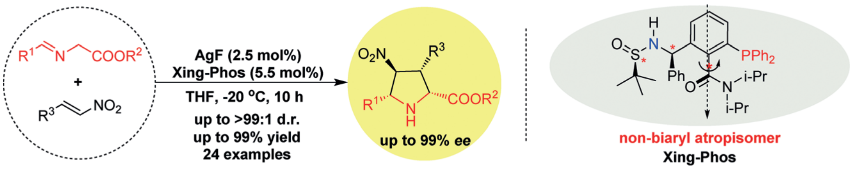
Palladium-Catalyzed Vicinal Amino Alcohols Synthesis from Allyl Amines by In Situ Tether Formation and Carboetherification

Just tether it! Vicinal amino alcohols are important structural motifs of bioactive compounds. An efficient method for their synthesis is based on the palladium-catalyzed oxy-alkynylation, oxy-arylation, or oxy-vinylation of allyl amines. High regio- and stereoselectivity were ensured through the in situ formation of a hemiaminal tether using the commercially available trifluoroacetaldehyde in its hemiacetal form.

Asymmetric Catalysis

X.-F. Bai, T. Song, Z. Xu, C.-G. Xia,* W.-S. Huang, L.-W. Xu* ____ **5255 – 5259**

Aromatic Amide-Derived Non-Biaryl Atropisomers as Highly Efficient Ligands in Silver-Catalyzed Asymmetric Cycloaddition Reactions



New chiral ligands: Optically pure aromatic amide-derived atropisomers were shown to be powerful phosphine ligands in the enantioselective silver-catalyzed [3+2] cycloaddition. This method provides a highly efficient strategy for the synthesis of optically pure nitro-substituted pyrrolidines with multiple stereogenic centers.

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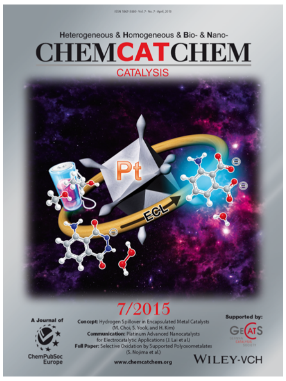

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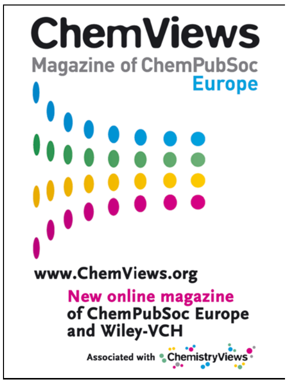

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