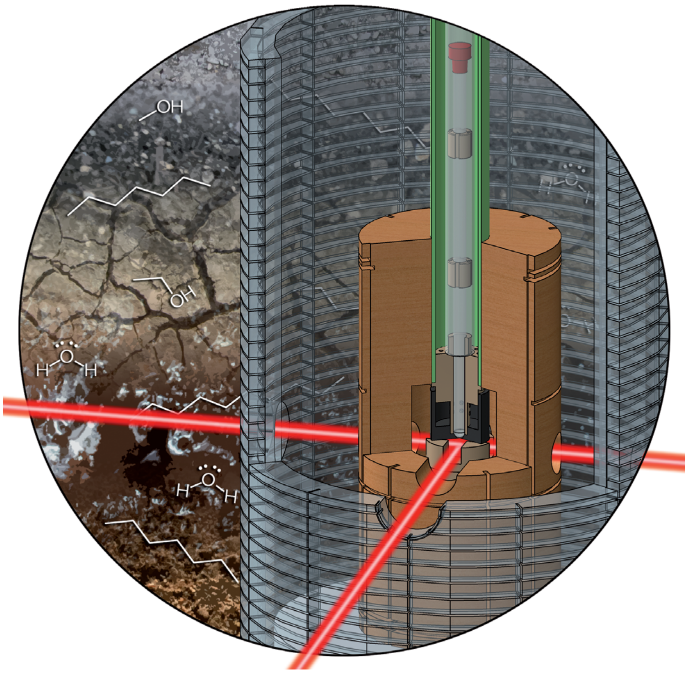
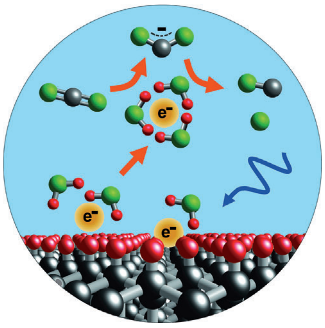
An optical magnetometer …

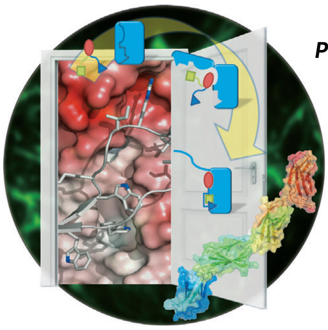


… used for making ultra-low-field NMR measurements of relaxation and diffusion has the chemical sensitivity required to distinguish between hydrocarbons and water in Earth's magnetic field (0.5 G). P. J. Ganssle, A. Pines et al. describe in their Communication on page 9766 ff., this important proof-of-concept for the commercial applicability of these robust, portable NMR sensors, particularly in the context of oil-well logging.

Photochemistry

The efficient and selective reduction of CO_2 to CO using solvated electrons, generated by illumination of inexpensive diamond substrates with UV light, is described by R. J. Hamers and co-workers in their Communication on page 9746 ff.



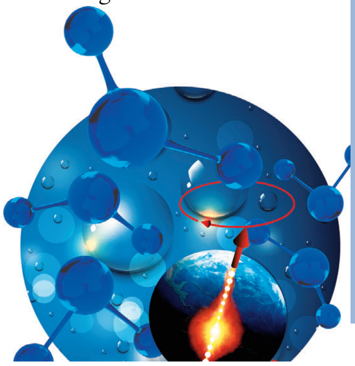


Protein–Protein Interactions

An unusual protein–protein interaction is described by J. Y. Suh and co-workers in their Communication on page 9784 ff. The binding of an aptide to fibronectin extradomain B involves partial unfolding to expose the binding surface.

High-Pressure NMR Spectroscopy

W. H. Casey and co-workers describe in their Communication on page 9788 ff. a simple NMR probe that allows analysis at geochemical pressures. A wide variety of NMR-active nuclei can be measured with as little as 10 μL of sample.



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Author Profile

"My favorite scientific principle is thermodynamics. You can't beat it.
My favorite quote is "It is not even wrong!" (attr. Wolfgang Pauli). …"
This and more about Andrew I. Cooper can be found on page 9702.

News

M. Möller

F. R. Wurm

S. Seiffert

K. Müllen

Obituaries

Carlos F. Barbas III passed away on June 24, 2014. He was a gifted "singular" scientific force with the ability to master both fundamental chemistry and biology at the same time to make revolutionary advances in both disciplines. He was the pioneer of enamine and imine-based catalysis, and his paradigm-changing approaches to catalytic asymmetric synthesis reinvigorated widespread interest in catalysis based on small organic molecules.

Books

Bioinorganic Chemistry | Dieter Rehder | *reviewed by F. Zelder* ______ **9706**

Highlights

Cycloadditions

H.-U. Reissig,* R. Zimmer _ **9708 – 9710**

Münchnones—New Facets after 50 Years

Developed and named 50 years ago in Munich, the mesoionic münchnones have had an astonishing career. New multicomponent reactions and enantioselective cycloadditions are discussed. They demonstrate the versatility of the münchnone approach to nitrogen heterocycles.

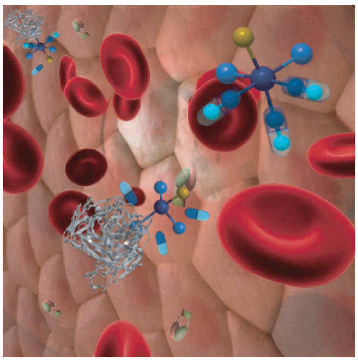
Minireviews

Bioinorganic Chemistry

S. García-Gallego,
G. J. L. Bernardes* ______ **9712 – 9721**

Carbon-Monoxide-Releasing Molecules for the Delivery of Therapeutic CO In Vivo

On target: Carbon-monoxide-releasing molecules (CORMs) are promising agents for the treatment of several diseases. CORMs are particularly good for enabling CO delivery in a controlled manner without affecting oxygen transport by hemoglobin. Significant progress in the methods for CO detection in live cells and the understanding of the reactivity of CORMs in vivo provides insights into CO biology and the design of safer, and more selective and efficient CORMs for clinical use.



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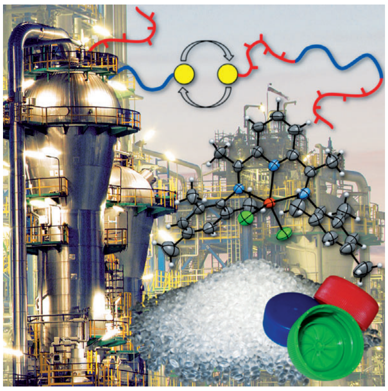
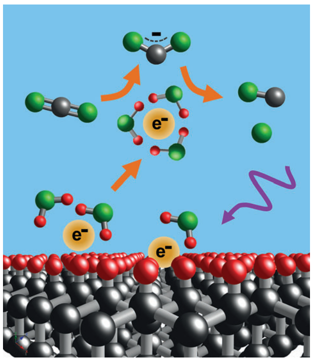
Reviews

"Post-metallocene" polymerization catalysis research ranges from fundamental mechanistic studies by catalyst design to material properties of polyolefins. A common goal of these studies is the creation of practically useful new materials or processes. A comprehensive overview of post-metallocene polymerization catalysts that have been put into practice is provided. The decisive properties for this success of a given catalyst structure are delineated.



Polyolefins

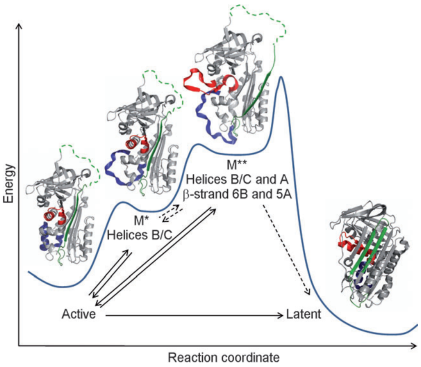
Communications



Diamond in the rough: Illumination of diamond substrates leads to emission of electrons into aqueous media. The solvated electrons are potent reducing agents and induce the direct one-electron reduction of CO_2 to $CO_2^{\bullet-}$, which then forms CO. This approach represents a new concept in catalysis by directly releasing electrons into reactant liquids.

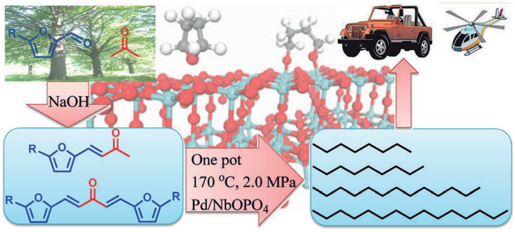
Photochemistry

Frontispiece



Serpin proteins are prone to pathological conformational change, for instance by conversion into an inactive, so-called latent form. By using advanced hydrogen/deuterium-exchange mass spectrometry, transient unfolding of a serpin is shown under native conditions. Based on these observations, a new mechanism (see picture) is proposed.

Protein Dynamics



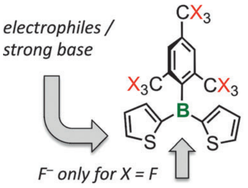
Fueling fuel production: Biomass conversion into liquid fuel depends on the design of multifunctional catalysts. In the direct conversion of furan-based aldol adducts into liquid alkanes over a Pd/$NbOPO_4$ catalyst under mild conditions (see scheme), NbO_x species played an important role in C–O bond cleavage.

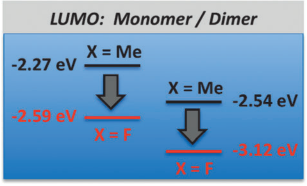
Biomass Conversion

Lewis Acids

X. Yin, J. Chen, R. A. Lalancette,
T. B. Marder,* F. Jäkle* ____ **9761 – 9765**

Highly Electron-Deficient and Air-Stable Conjugated Thienylboranes





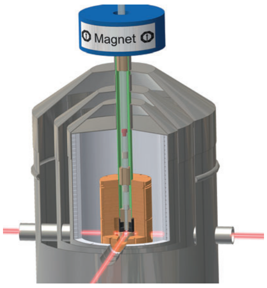
The bigger the better: Sterically demanding 2,4,6-tri-*tert*-butylphenyl (Mes*) or 2,4,6-tris(trifluoromethyl)phenyl (^{F}Mes) groups do not prevent but rather promote coplanarity and enhance electronic communication within conjugated thienylboranes. ^{F}Mes exerts a strong electron-withdrawing effect which results in significant lowering of the LUMO energy level and high Lewis acidity toward fluoride anions, while ensuring stability in air and towards acid or base.

NMR Spectroscopy

P. J. Ganssle,* H. D. Shin, S. J. Seltzer,
V. S. Bajaj, M. P. Ledbetter, D. Budker,
S. Knappe, J. Kitching,
A. Pines* ____ **9766 – 9770**

Ultra-Low-Field NMR Relaxation and Diffusion Measurements Using an Optical Magnetometer

Front Cover



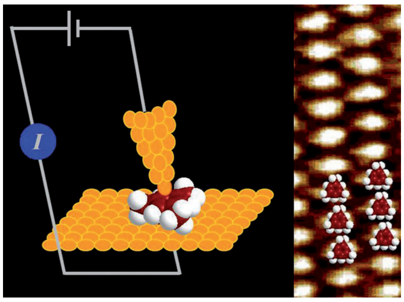
Portable NMR: NMR relaxometry and diffusometry can be highly effective in applications where high-resolution NMR spectroscopy is unnecessary or impractical, as is the case in the emerging field of portable chemical characterization. A proof-of-concept experiment is presented that demonstrates the use of high-sensitivity optical magnetometers as detectors for ultra-low-field NMR relaxation and diffusion measurements.

Molecular Electronics

S. Afsari, Z. Li, E. Borguet* **9771 – 9774**

Orientation-Controlled Single-Molecule Junctions

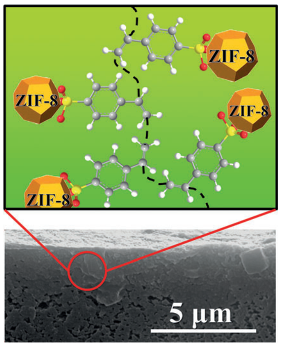
The conductivity of a single aromatic ring, perpendicular to its plane, is determined (see picture; I = current). The formation of highly ordered structures of mesitylene oriented parallel to an Au (111) plane enables direct contact between a scanning tunneling microscopy tip and the π-system of mesitylene to create highly conductive Au/aromatic/Au junctions under ambient conditions.



Membrane Preparation

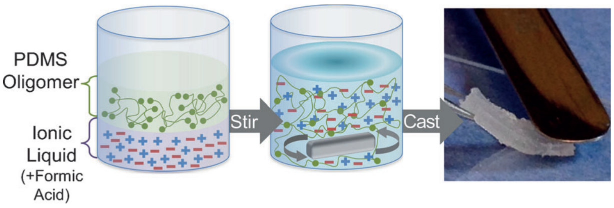
R. Zhang, S. Ji, N. Wang, L. Wang,
G. Zhang, J.-R. Li* ____ **9775 – 9779**

Coordination-Driven In Situ Self-Assembly Strategy for the Preparation of Metal–Organic Framework Hybrid Membranes



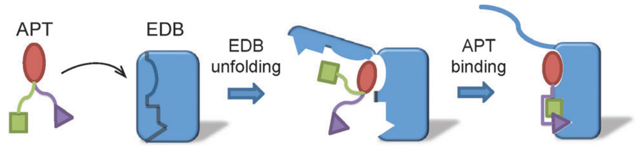
Mopping up the mess: A hybrid membrane composed of the metal–organic framework (MOF) ZIF-8 and poly(sodium 4-styrenesulfonate) was prepared by a coordination-driven in situ self-assembly method. The MOF particles were well-dispersed in the polymer in the resulting stable membrane (see picture), which showed excellent performance in the nanofiltration and separation of dyes from water.

Solid Electrolytes



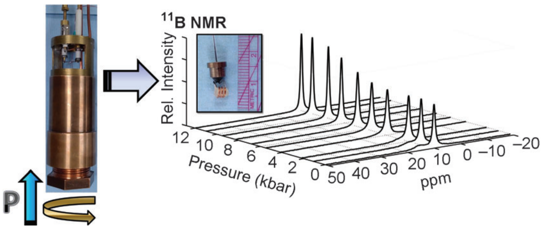
Supportive, despite their differences: The immiscibility of poly(dimethylsiloxane) (PDMS) and ionic liquids (ILs) has been overcome by a simple sol–gel reaction (see picture) to create PDMS-supported ILs (ionogels) with IL loadings of up to 80% by mass. The ionogels exhibited high ionic conductivity and excellent mechanical behavior, with an elastic modulus of approximately 60 kPa without fatigue over 5000 cycles, even at elevated temperatures.

Protein–Protein Interactions



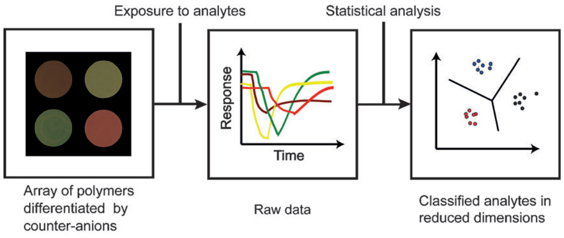
Unfold and hold: It is known that protein–protein interactions can involve coupled folding and binding, but coupled unfolding and binding is not well characterized. An unusual protein–protein interaction is described in which the binding of an aptide (APT) to fibronectin extradomain B (EDB) involves partial unfolding to expose the binding surface. The structural and energetic details were determined by NMR spectroscopy and thermodynamic analysis.

High-Pressure NMR Spectroscopy



A non-magnetic piston-cylinder pressure cell has been developed for solution-state NMR spectroscopy up to 20 kbar for aqueous geochemical applications. ^{11}B NMR spectroscopic investigations into the H_3BO_3–catechol equilibrium demonstrates a large pressure-driven exchange rate. The success of these experiments suggests that this probe design can be applied to a wide variety of NMR-active nuclei.

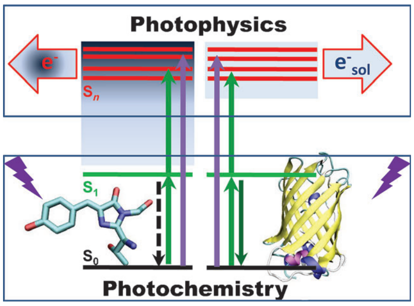
Polymer Sensors



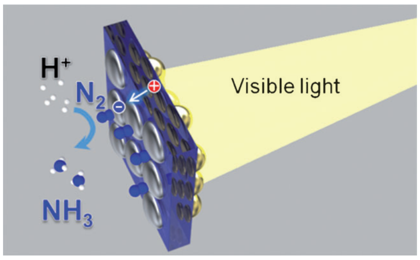
A sensor array comprising a conjugated cationic polymer combined with various counteranions has been developed. This simple approach allows the creation of polymer formulations able to detect vapors of industrially relevant amines in low ppm concentrations by fluorescence quenching measurements. Furthermore the array's response is useful to identify the nature of the analyte through pattern-based recognition algorithms.

Photophysics

Higher electronically excited states of the green fluorescent protein chromophore anion have been probed directly by action absorption spectroscopy. The high density of these UV molecular resonances in the UV makes electron detachment in the gas phase efficient. Quantum calculations show this electronic band inside the protein to be resonant with the quasi-continuum of a solvated electron, thus suggesting its major role in the photophysics in the UV region.

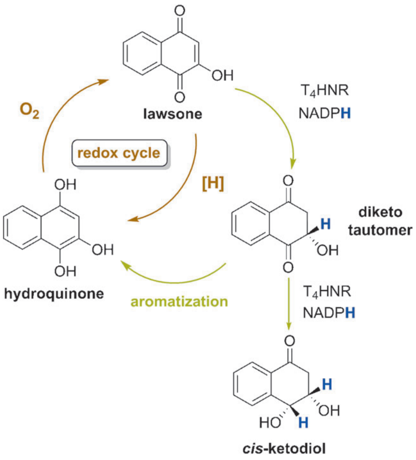


Nitrogen Photofixation



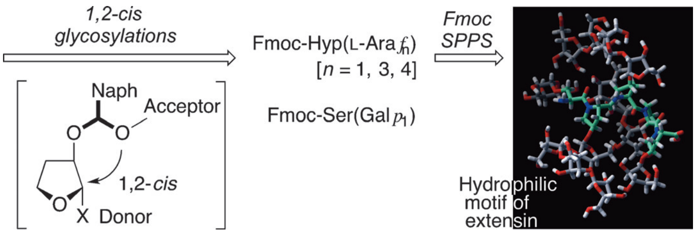
See the light of day: A plasmon-induced ammonia synthesis technique that responds to visible light and is based on a strontium titanate ($SrTiO_3$) photoelectrode loaded with gold nanoparticles has been developed. It is deduced that plasmon-induced charge separation at the Au/$SrTiO_3$ interface promotes oxidation in the anodic chamber and subsequent nitrogen reduction on the cathodic side.

Biocatalysis



Breaking the cycle: In studies on the reduction of 2-hydroxynaphthoquinones to the stable 1,4-diketo tautomeric form of hydronaphthoquinones and their further reduction by fungal tetrahydroxynaphthalene reductase, diketo tautomers emerge as true intermediates in biosynthesis. Their formation breaks the (redox) cycle, thus protecting the cell from stress-related redox events.

Glycopeptides

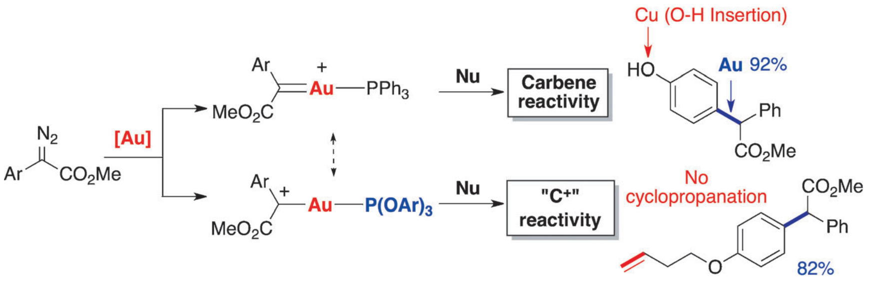


Just a phase: Stereoselective synthesis of one of the highly glycosylated hydrophilic motifs of extensins has been completed. Key steps were a 2-naphthylmethyl ether-mediated intramolecular aglycon delivery to the stereoselective construction of the Ser(Galp$_1$) and Hyp(Araf$_n$) ($n = 1, 3, 4$) fragments and Fmoc solid-phase peptide synthesis (SPPS) for the highly glycosylated pentapeptide motif.

Gold–Carbenoids

Y. Xi, Y. Su, Z. Yu, B. Dong, E. J. McClain,
Y. Lan,* X. Shi* ———— **9817 – 9821**

Chemoselective Carbophilic Addition of α-Diazoesters through Ligand-Controlled Gold Catalysis

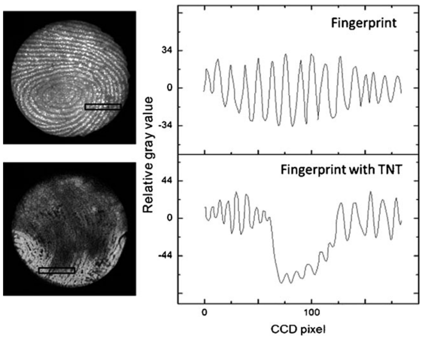


Carbocation or carbene? The chemoselective addition of arenes and 1,3-diketones to α-aryldiazoesters was achieved through ligand-controlled gold catalysis. The gold catalyst with electron-deficient phosphite as the ancillary ligand exclusively gave the carbophilic addition products, thus representing a new and efficient approach to form “carbophilic carbocations”, which selectively react with carbon nucleophiles.

Luminescence Imaging

J. Tan, L. Xu, T. Li, B. Su,
J. Wu* ———— **9822 – 9826**

Image-Contrast Technology Based on the Electrochemiluminescence of Porous Silicon and Its Application in Fingerprint Visualization

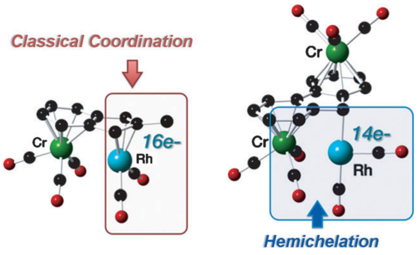


Fit for a modern Sherlock: Electrochemiluminescence by porous silicon (pSi) has a regular dynamic process involving activation, strong emission, and fading. This process can be perturbed by chemicals adsorbed on the pSi surface. The contrast in luminescence intensity between adjacent areas with different surface chemistry enabled the visualization of latent fingerprints and a trinitrotoluene (TNT) residue in a fingerprint with high resolution (see picture).

Metal–Metal Interactions

C. Werlé, C. Bailly, L. Karmazin-Brelot,
X.-F. Le Goff, M. Pfeffer,*
J.-P. Djukic* ———— **9827 – 9831**

First Stabilization of 14-Electron Rhodium(I) Complexes by Hemichelation

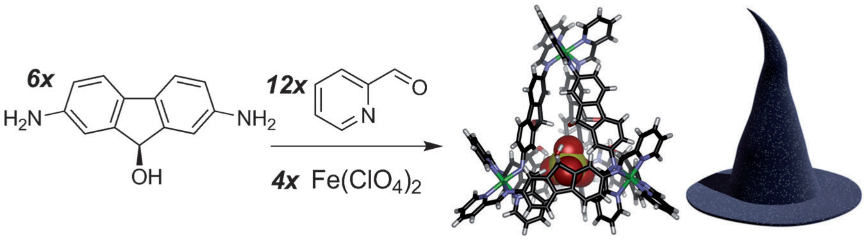


Touching from a distance: The syntheses of unprecedented T-shaped 14-electron Rh^I hemichelates is made possible by choosing the *anti*-[(η^6:η^6-fluorenyl){Cr(CO)$_3$}$_2$]-based benzylic anion as an ambiphilic hemichelating ligand, and treating it with [{Rh(nbd)Cl}$_2$] (nbd = norbornadiene) or [{Rh(CO)$_2$Cl}$_2$].

Self-Assembly

M. C. Young, L. R. Holloway,
A. M. Johnson,
R. J. Hooley* ———— **9832 – 9836**

A Supramolecular Sorting Hat: Stereocontrol in Metal–Ligand Self-Assembly by Complementary Hydrogen Bonding



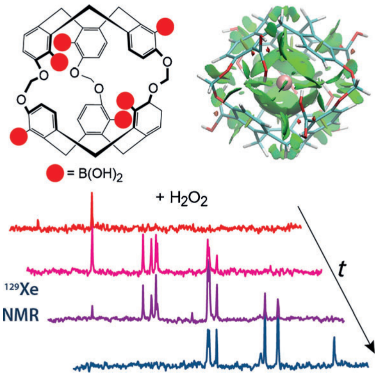
Abracadabra: The stereoselective self-assembly of an unsymmetrical metal–ligand cage can be controlled by self-complementary hydrogen bonding between alcohol-containing ligands as well as between ligands and suitable anion guests.

Noncovalent Interactions

E. Dubost, J.-P. Dognon,* B. Rousseau, G. Milanole, C. Dugave, Y. Boulard, E. Léonce, C. Boutin, P. Berthault* ______ 9837 – 9840

Understanding a Host–Guest Model System through ^{129}Xe NMR Spectroscopic Experiments and Theoretical Studies

How hosts handle a noble guest: A combination of NMR spectroscopy and quantum chemistry enabled thorough analysis of the noncovalent interactions inside a xenon–host complex. The validation of this approach with a family of cryptophane hosts derived by treatment of the structure shown with H_2O_2 paves the way for the design of potent smart hyperpolarized ^{129}Xe NMR sensors.

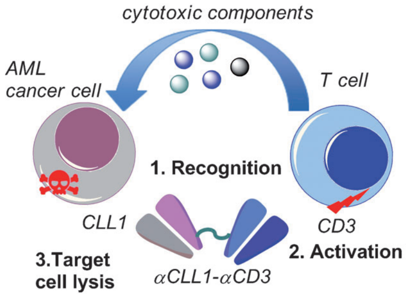


Cancer Immunotherapy

H. Lu, Q. Zhou, V. Deshmukh, H. Phull, J. Ma, V. Tardif, R. R. Naik, C. Bouvard, Y. Zhang, S. Choi, B. R. Lawson, S. Zhu, C. H. Kim,* P. G. Schultz* _ 9841 – 9845

Targeting Human C-Type Lectin-like Molecule-1 (CLL1) with a Bispecific Antibody for Immunotherapy of Acute Myeloid Leukemia

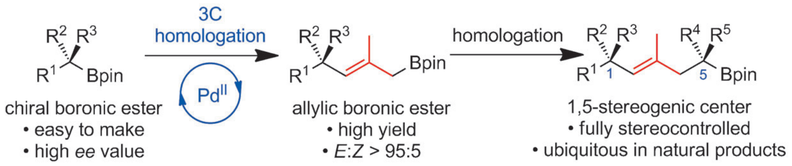
A bispecific antibody, αCLL1-αCD3, was synthesized using a genetically encoded unnatural amino acid, and shown to recruit cytotoxic T cells to CLL1-positive cells. The reported results validate the clinical potential of CLL1 as an AML-specific antigen for the generation of bispecific antibodies for the treatment of acute myeloid leukemia (AML).



Homologation

P. J. Unsworth, D. Leonori, V. K. Aggarwal* ______ 9846 – 9850

Stereocontrolled Synthesis of 1,5-Stereogenic Centers through Three-Carbon Homologation of Boronic Esters

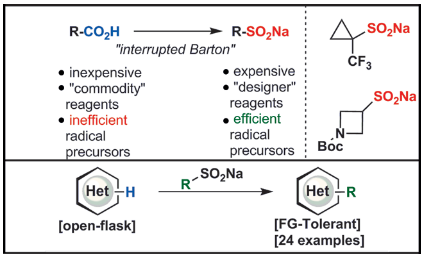


Three more: The 3C homologation of chiral pinacol boronic esters gives di- or trisubstituted allylic boronic esters with high yield and *E* selectivities. The combination of this method with lithiation–borylation enables the synthesis of alkyl chains that bear 1,5-stereogenic centers. The utility of the process was demonstrated in a formal synthesis of (+)-jaspakinolide.

C–H Functionalization

R. Gianatassio, S. Kawamura, C. L. Eprile, K. Foo, J. Ge, A. C. Burns, M. R. Collins, P. S. Baran* ______ 9851 – 9855

Simple Sulfinate Synthesis Enables C–H Trifluoromethylcyclopropanation

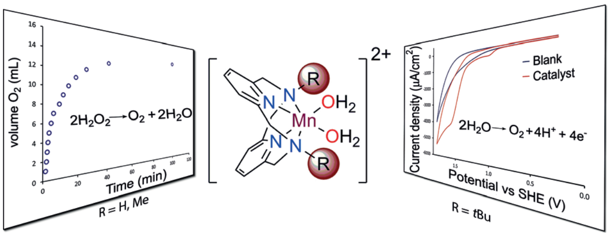


An interrupted Barton decarboxylation reaction has been used to convert readily available carboxylic acids into sulfinate salts (see scheme). Ten new sulfinate reagents were created and the reactivity of six of them towards C–H functionalization was tested on a range of heterocycles. The simplicity of this approach (a cheap industrial oxidant, simple solvent, and no metals) is a clear advantage over other radical donors.

Water Oxidation

W.-T. Lee, S. B. Muñoz, III, D. A. Dickie,
J. M. Smith* ———— **9856–9859**

Ligand Modification Transforms a Catalase Mimic into a Water Oxidation Catalyst

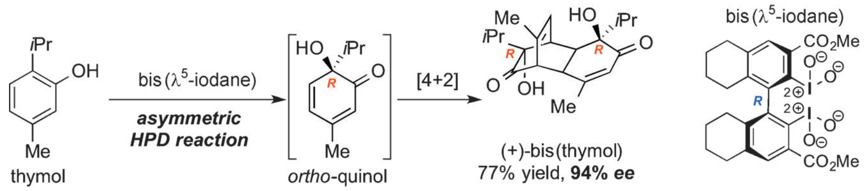


Ligand-controlled switch: Simple modification of the substituent on a pyridinophane macrocycle ligand converts the corresponding Mn^{II} complex from a hydrogen peroxide disproportionation catalyst into a water oxidation catalyst. Preliminary results indicate that the catalyst is mononuclear.

Asymmetric Synthesis

C. Bosset, R. Coffinier, P. A. Peixoto,
M. El Assal, K. Miqueu,
J.-M. Sotiropoulos, L. Pouységu,*
S. Quideau* ———— **9860–9864**

Asymmetric Hydroxylative Phenol Dearomatization Promoted by Chiral Binaphthylic and Biphenylic Iodanes

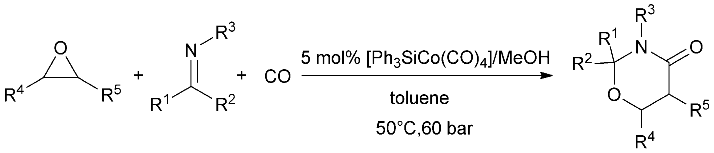


The selective oxygenation of iodobinaphthyls and iodobiphenyls afforded either λ^3- or λ^5-iodanes, which were evaluated for their capacity to promote asymmetric intermolecular hydroxylative phenol dearomatizations (HPDs). Most remarkably, a C_2-symmetrical biphenylic λ^5-iodane induced the HPD reaction/[4+2] cyclodimerization cascade of thymol into bis(thymol) with enantiomeric excesses of up to 94 %.

Cycloaddition

L. Liu, H. Sun* ———— **9865–9869**

[HCo(CO)$_4$]-Catalyzed Three-component Cycloaddition of Epoxides, Imines, and Carbon Monoxide: Facile Construction of 1,3-Oxazinan-4-ones



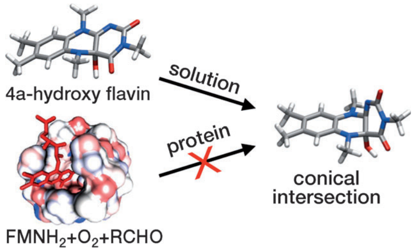
Cobalt and CO: The title reaction is described to proceed in the presence of [HCo(CO)$_4$] as the catalyst. The reaction occurs for a wide variety of imines and various substituted epoxides, thus providing an efficient and atom-economic route to 1,3-oxazinan-4-ones, with various substitution patterns, from simple and readily available starting materials.

Flavin Fluorescence

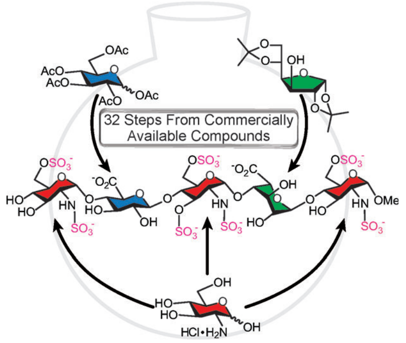
S. Gozem, E. Mirzakulova, I. Schapiro,
F. Melaccio, K. D. Glusac,*
M. Olivucci* ———— **9870–9875**

A Conical Intersection Controls the Deactivation of the Bacterial Luciferase Fluorophore

How nature lights up flavins: 4a-hydroxy flavins display weak fluorescence and ultrafast excited-state decay in solution, but exhibit strong fluorescence when produced in a protein cavity. A joint experimental and theoretical study explains the fluorescence properties of these flavin adducts in terms of a deactivation pathway mediated by a conical intersection that becomes inaccessible in sterically constrained environments.

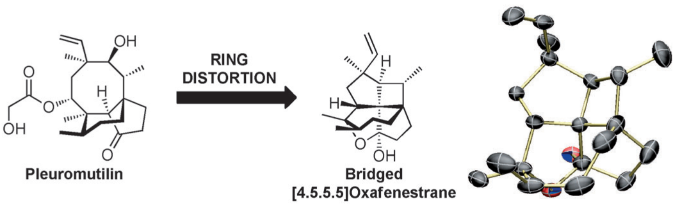


Carbohydrates



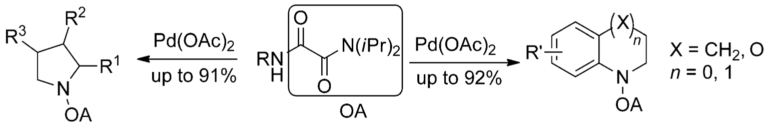
Working against the clot: The synthetic anticoagulant fondaparinux, a pentasaccharide based on the antithrombin-binding domain of heparin, was prepared in a concise and efficient manner in the shortest route reported to date. The application of one-pot strategies, the use of common intermediates, and the efficient preparation of monosaccharide building blocks from commercial sources are key features of this approach.

Strained Polycycles



Fenestranes are highly strained molecules possessing a quaternary carbon atom with bonds that deviate from the canonical tetrahedral geometry. The natural product pleuromutilin can be used as a starting material for the synthesis of bridged [4.5.5.5]- and [4.5.7.5]oxafenestranes through a carbocation rearrangement cascade. X-ray crystallography shows that these compounds exhibit significant planarization of the central tetracoordinate carbon center.

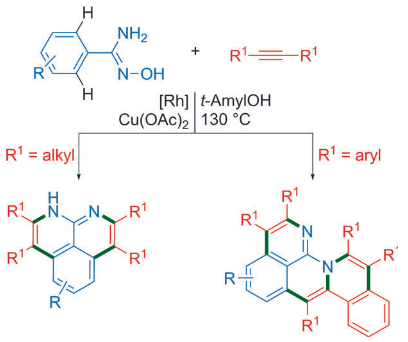
C–H Activation



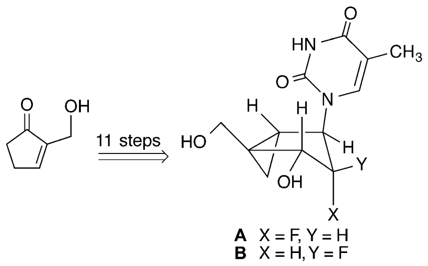
Remote access: The first application of an oxalyl amide to direct C–H functionalizations at remote positions is reported. The results show both C(sp^2)–H and C(sp^3)–H bonds at δ- and ε-positions are effectively activated, thus giving tetrahydroquinolines, benzomorpholines, pyrrolidines, and indolines in moderate to excellent yields by palladium-catalyzed intramolecular C–H amination.

Multiple C–H Activation

Activated and annulated: A rhodium-catalyzed one-pot synthesis of highly substituted polyheteroaromatic compounds from *N*-hydroxybenzamidines and alkynes is described. This reaction likely proceeds through multiple C–H bond activation and annulation.



Modified Nucleosides



The power of conviction: The efficient synthesis, antiviral activity, and duplex-stabilizing properties of both isomers, **A** and **B**, of the 2′-fluoro analogue of N-methanocarbathymidine (N-MCT) are reported. Incorporation of the fluorine substituent at the 2′-position of the N-MCT scaffold was found to have a strong positive effect on duplex thermal stability.

M. E. Jung,* T. A. Dwight, F. Vigant, M. E. Østergaard, E. E. Swayze, P. P. Seth ———— **9893 – 9897**

Synthesis and Duplex-Stabilizing Properties of Fluorinated N-Methanocarbathymidine Analogues Locked in the C3′-*endo* Conformation

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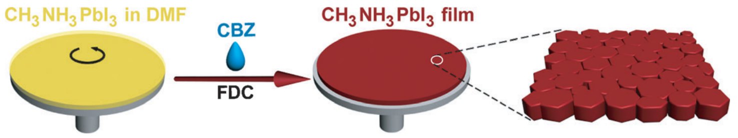
Perovskite Solar Cells



Fast and thin: Flat, uniform thin films of $CH_3NH_3PbI_3$ perovskites have been produced by a fast, one-step procedure involving spin-coating of a DMF solution of $CH_3NH_3PbI_3$ and immediate exposure to chlorobenzene to induce crystallization. Planar heterojunction solar cells made with these films gave a maximum power conversion efficiency of 16.2%.

M. D. Xiao, F. Z. Huang, W. C. Huang, Y. Dkhissi, Y. Zhu, J. Etheridge, A. Gray-Weale, U. Bach, Y.-B. Cheng,* L. Spiccia* ———— **9898 – 9903**

A Fast Deposition-Crystallization Procedure for Highly Efficient Lead Iodide Perovskite Thin-Film Solar Cells

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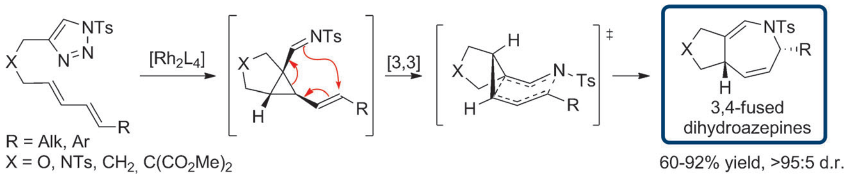
Heterocycles



A general method for the formation of fused dihydroazepines from 1-sulfonyl-1,2,3-triazoles bearing a tethered diene is reported. The process involves an intramolecular cyclopropanation of an α-imino rhodium(II) carbenoid, leading to a transient 1-imino-2-vinylcyclopropane intermediate which rapidly undergoes a 1-aza-Cope rearrangement to generate the products in moderate to excellent yields. Ts = 4-toluenesulfonyl.

E. E. Schultz, V. N. G. Lindsay, R. Sarpong* ———— **9904 – 9908**

Expedient Synthesis of Fused Azepine Derivatives Using a Sequential Rhodium(II)-Catalyzed Cyclopropanation/1-Aza-Cope Rearrangement of Dienyltriazoles

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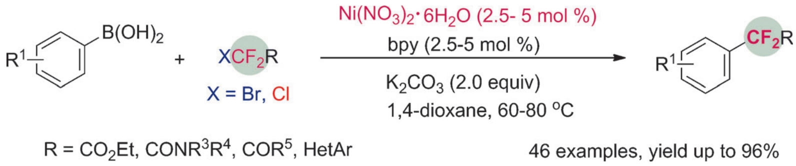
Synthetic Methods



Simple and easy: The first example of a nickel-catalyzed difluoroalkylation of aryl boronic acids with functionalized difluoromethyl bromides and chlorides has been developed. This cross-coupling process features a broad substrate scope, a cheap catalyst, and excellent functional-group compatibility.

Y.-L. Xiao, W.-H. Guo, G.-Z. He, Q. Pan, X. Zhang* ———— **9909 – 9913**

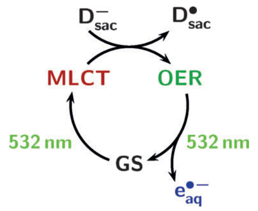
Nickel-Catalyzed Cross-Coupling of Functionalized Difluoromethyl Bromides and Chlorides with Aryl Boronic Acids: A General Method for Difluoroalkylated Arenes

Sustainable Chemistry

M. Goez,* C. Kerzig,
R. Naumann ______________ **9914 – 9916**

An “All-Green” Catalytic Cycle of Aqueous Photoionization

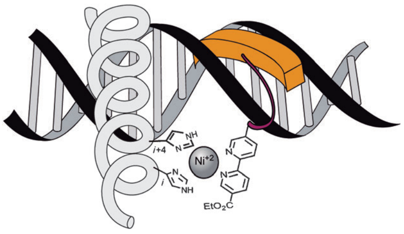
Green light and a cheap, even bioavailable, sacrificial donor produce hydrated electrons in the displayed catalytic cycle. The catalyst is a popular metal complex functioning as a “container” for a radical anion. The cycle could open a pathway toward the solar-driven reductive detoxification of halogenated organic waste. D^{-}_{sac} = MeOPhO^{-}; $D^{\bullet}_{sac}$ = MeOPhO$^{\bullet}$; MLCT = $^{*}[\mathrm{Ru^{III}(bpy)_2(bpy^{\bullet-})}]^{2+}$; OER = $[\mathrm{Ru^{II}(bpy)_2(bpy^{\bullet-})}]^{+}$; GS = $[\mathrm{Ru^{II}(bpy)_3}]^{2+}$; bpy = 2,2′-bipyridine.



Self-Assembly

M. I. Sánchez, J. Mosquera,
M. E. Vázquez,*
J. L. Mascareñas* ____________ **9917 – 9921**

Reversible Supramolecular Assembly at Specific DNA Sites: Nickel-Promoted Bivalent DNA Binding with Designed Peptide and Bipyridyl–Bis(benzamidine) Components



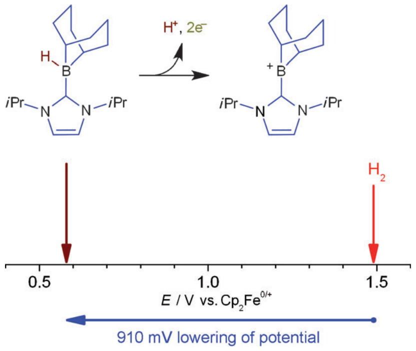
Nickel(II) salts promote the assembly of a bis(histidine)-modified peptide that is derived from a bZIP transcription factor and a bipyridine-substituted bis(benzamidine) unit at specific DNA sites. This supramolecular system features some key properties of naturally occurring DNA-binding proteins, such as bivalence, selectivity, responsiveness to external agents, and reversibility.

Electrocatalysis

E. J. Lawrence, T. J. Herrington,
A. E. Ashley,*
G. G. Wildgoose* ____________ **9922 – 9925**

Metal-Free Dihydrogen Oxidation by a Borenium Cation: A Combined Electrochemical/Frustrated Lewis Pair Approach

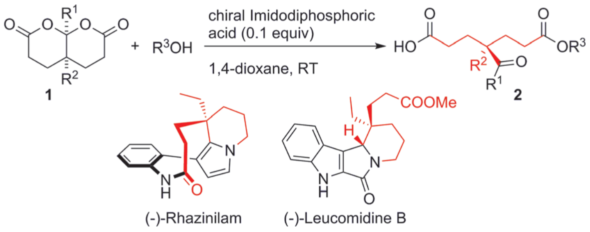
The potential that is required for nonaqueous H_2 oxidation at a carbon electrode can be significantly reduced by using a borenium cation in a combined electrochemical/frustrated Lewis pair approach. This system exhibits faster electrode kinetics, increased stability to electrogenerated protons, and improved catalyst recycling over a previously reported system that is based on the borane Lewis acid $B(C_6F_5)_3$.



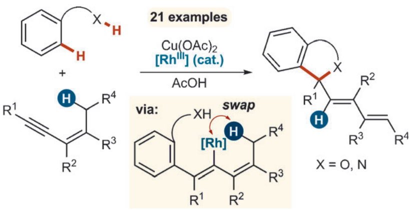
Organocatalysis

J.-B. Gualtierotti, D. Pasche, Q. Wang,
J. Zhu* ______________ **9926 – 9930**

Phosphoric Acid Catalyzed Desymmetrization of Bicyclic Bislactones Bearing an All-Carbon Stereogenic Center: Total Syntheses of (−)-Rhazinilam and (−)-Leucomidine B



Breaking symmetry: Achiral bislactones (**1**) undergo desymmetrization by reaction with alcohol in the presence of chiral imidodiphosphoric acids. The monoacids **2**, having an all-carbon stereogenic center, were obtained in good to excellent yields and enantioselectivities. Concise total syntheses of (−)-rhazinilam and (−)-leucomidine B were subsequently developed using **2** as a common starting material.

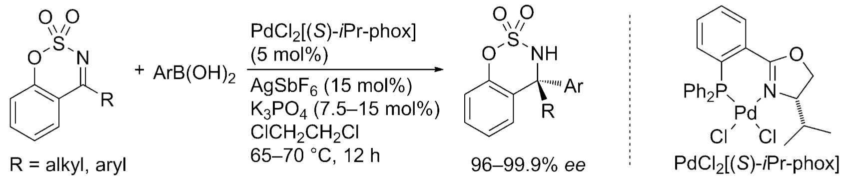


When two become one: 1,3-Enynes containing allylic hydrogen atoms *cis* to the alkyne are shown to act as one-carbon partners, rather than two-carbon partners, in various rhodium-catalyzed oxidative annulations. The mechanism of these unexpected transformations is proposed to occur through double C–H activation, involving a hitherto rare example of the 1,4-migration of a Rh^{III} species.

C–H Functionalization

D. J. Burns, H. W. Lam* —— **9931–9935**

Catalytic 1,4-Rhodium(III) Migration Enables 1,3-Enynes to Function as One-Carbon Oxidative Annulation Partners in C–H Functionalizations

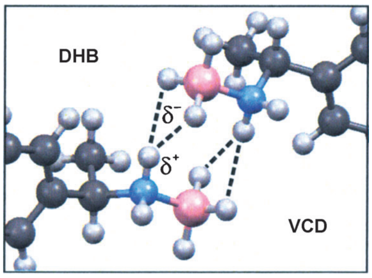


Chiral cyclic sulfamidates are obtained by the asymmetric addition of arylboronic acids to six-membered cyclic *N*-sulfonyl ketimines. A cationic palladium complex with a chiral phosphine-oxazoline ligand (*i*Pr-phox) shows high catalytic activity and enantioselectivity to give the products in high yields with 96–99.9% *ee*. The cyclic sulfamidates exhibit a tetrasubstituted stereogenic center with an amino group and a triaryl or alkyldiaryl group as substituents.

Asymmetric Catalysis

C. Jiang, Y. Lu,* T. Hayashi* **9936–9939**

High Performance of a Palladium Phosphinooxazoline Catalyst in the Asymmetric Arylation of Cyclic *N*-Sulfonyl Ketimines

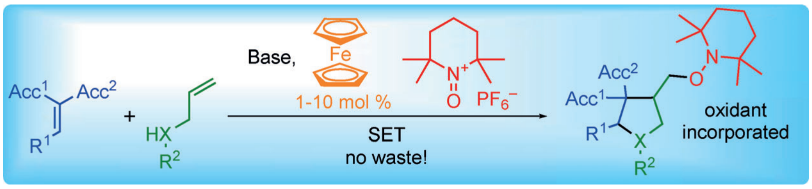


A chiral amine–borane is investigated by vibrational circular dichroism (VCD) spectroscopy. By comparison of experimental and calculated spectra, a unique VCD pattern associated with the formation of dihydrogen-bonded dimers in solution is identified. Different dihydrogen binding arrangements in solution and in the solid state are characterized.

Dihydrogen Bonding

C. Merten,* C. J. Berger, R. McDonald, Y. Xu* —— **9940–9943**

Evidence of Dihydrogen Bonding of a Chiral Amine–Borane Complex in Solution by VCD Spectroscopy



Making waste a functionality: Oxidative electron-transfer-mediated anion–radical transformations are rendered catalytic by employing a 2,2,6,6-tetramethyl-*N*-oxopiperidinium salt and ferrocene. The method provides an asymmetric approach to highly functionalized cyclopentane and pyrrolidine derivatives. At the same time the co-generated reduced species TEMPO serves as a useful oxygenating functionality.

Single-Electron-Transfer Catalysis

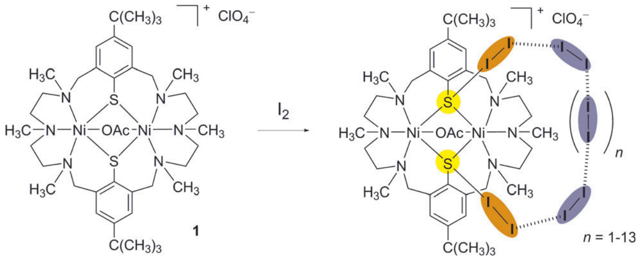
F. Kafka, M. Holan, D. Hidasová, R. Pohl, I. Císařová, B. Klepetářová, U. Jahn* —— **9944–9948**

Oxidative Catalysis Using the Stoichiometric Oxidant as a Reagent: An Efficient Strategy for Single-Electron-Transfer-Induced Tandem Anion–Radical Reactions

Iodine Adsorption

M. Golecki, N. Beyer, G. Steinfeld,
V. Lozan, S. Voitekhovich, M. Sehabi,
J. Möllmer, H.-J. Krüger,
B. Kersting* ______________ **9949 – 9952**

Adsorption of I_2 by Macrocyclic Polyazadithiophenolato Complexes Mediated by Charge-Transfer Interactions

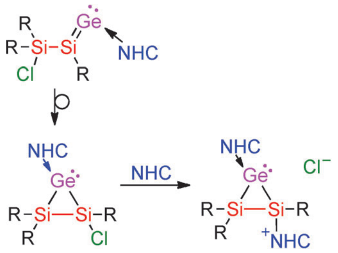


Seeing I to I: The macrocyclic complex $[Ni_2(L)(OAc)]ClO_4$ (**1**) adsorbs up to 17 molar equivalents (> 270 wt %) of iodine, although it does not exhibit permanent porosity. IR and crystallographic studies reveal that two I_2 molecules are captured by means of thiophenolate→I_2 charge-transfer interactions, which enable the diffusion and sorption of further I_2 molecules in a polyiodide-like network.

Group 14 Chemistry

A. Jana, I. Omlor, V. Huch, H. S. Rzepa,
D. Scheschkewitz* __________ **9953 – 9956**

N-Heterocyclic Carbene Coordinated Neutral and Cationic Heavier Cyclopropylidenes



He is heavy and he's my brother: NHC-coordinated cyclopropenylidene analogues with molecular scaffolds exclusively formed by heavier Group 14 elements are accessible from the corresponding vinylidene isomers by exchange of the NHC ligand for a smaller NHC. The residual chloride in one of these heavier cyclic carbenes can be expelled by a second equivalent of NHC to generate cationic derivatives of the imidazolium type.

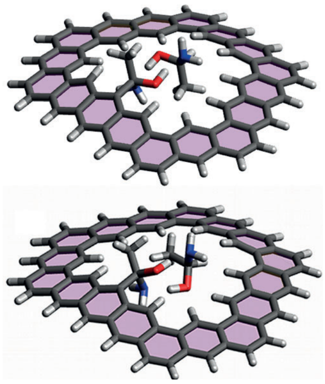
Chiral Separation

A. W. Hauser,* N. Mardirossian,
J. A. Panetier, M. Head-Gordon, A. T. Bell,
P. Schwerdtfeger* __________ **9957 – 9960**

Functionalized Graphene as a Gatekeeper for Chiral Molecules: An Alternative Concept for Chiral Separation

Inside Cover

Selective entry: A mixture of enantiomers can be separated with functionalized nanoporous graphene. Density functional calculations indicate that a "bouncer" molecule attached to the pore rim prevents the passage of the undesired enantiomer while letting its mirror image through.



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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The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.

Angewandte Corrigendum

Crowdsourcing Natural Products Discovery to Access Uncharted Dimensions of Fungal Metabolite Diversity

L. Du, A. J. Robles, J. B. King,
D. R. Powell, A. N. Miller,
S. L. Mooberry,*
R. H. Cichewicz* ———— 804–809

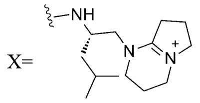
Angew. Chem. Int. Ed. **2014**, *53*

DOI: 10.1002/anie.201306549

The structures of compounds **5** and **6** in Figure 1 of this Communication were drawn incorrectly. The correct structures are shown below.

Efrapeptin F (**5**): Ac-Pip-Aib-Pip-Aib-Aib-Leu-ßAla-Gly-Aib-Aib-Pip-Aib-Ala-Leu-Iva-X

Efrapeptin G (**6**): Ac-Pip-Aib-Pip-Iva-Aib-Leu-ßAla-Gly-Aib-Aib-Pip-Aib-Ala-Leu-Iva-X



Angewandte Corrigendum

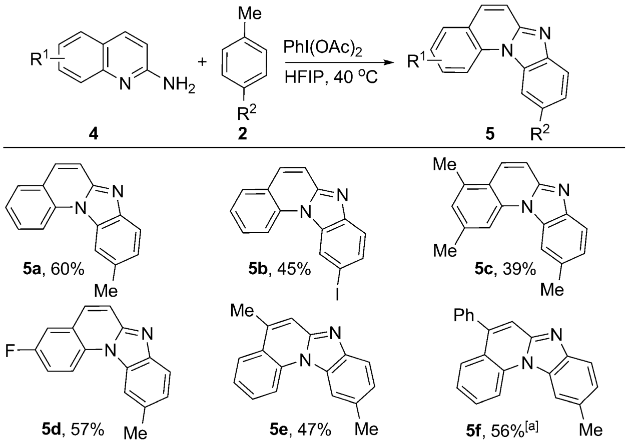
Metal-Free Annulation of Arenes with 2-Aminopyridine Derivatives: The Methyl Group as a Traceless Non-Chelating Directing Group

S. Manna, K. Matcha,
A. P. Antonchick* ———— 8163–8166

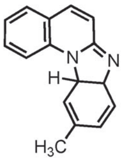
Angew. Chem. Int. Ed. **2014**, *53*

DOI: 10.1002/anie.201403712

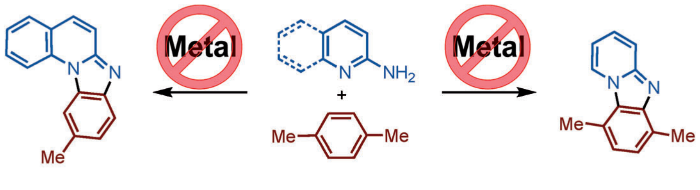
In this Communication, the structures of products **5** in Scheme 3 and intermediate **20** in Scheme 4 are incorrect with regard to the position of the substituent (R^2) on the imidazole-fused aromatic ring. The same mistake also occurs in the table-of-contents picture and for the structures of products **5** in the Supporting Information; these must be corrected accordingly. Corrected versions of Scheme 3, the structure of intermediate **20**, and the table-of-contents picture are provided below.



Scheme 3. Scope of application of the methyl-directed reaction. Reaction conditions: **4** (0.2 mmol), **2** (1.0 mmol), $PhI(OAc)_2$ (0.6 mmol total; added in 0.2 mmol portions every 6 h) in HFIP at 40 °C for 18 h. [a] $PhI(OAc)_2$ (0.8 mmol) used, reaction time 24 h.



20



The authors apologize for any confusion or inconvenience this error may have caused.