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

*H. Jiang, P. Elsner, K. L. Jensen, A. Falcicchio, V. Marcos, K. A. Jørgensen**
Achieving Molecular Complexity by Organocatalytic One-Pot Strategies: A Fast Entry for the De Novo Synthesis of Sphingoids, Amino Sugars, and Polyhydroxylated α-Amino Acids

*T. J. Kucharski, Z. Huang, Q.-Z. Yang, Y. Tian, N. C. Rubin, C. D. Concepcion, R. Boulatov**
Kinetics of Thiol/Disulfide Exchange Correlates Weakly with the Restoring Force in the Disulfide Moiety

*W. Xu, X. Xue, T. Li, H. Zeng, X. Liu**
Ultrasensitive and Selective Colorimetric DNA Detection by Nicking Endonuclease-Assisted Nanoparticle Amplification

H. Ueda, H. Satoh, K. Matsumoto, K. Sugimoto, T. Fukuyama, H. Tokuyama**
Total Synthesis of (+)-Haplophytine

G. A. Zelada, J. Riu, A. Düzgün, F. X. Rius**
Immediate Detection of Living Bacteria at Ultra-Low Concentrations Using a Carbon-Nanotube-Based Potentiometric Aptasensor

*K. Fuchibe, T. Kaneko, K. Mori, T. Akiyama**
Expedient Synthesis of N-Fused Indoles: A C–F Activation and C–H Insertion Approach

A. Giannis, P. Heretsch, V. Sarli, A. Stößel*
Synthesis of Cyclopamine Using a Biomimetic and Diastereoselective Approach

*W. A. Chalifoux, R. McDonald, M. J. Ferguson, R. R. Tykwinski**
***tert*-Butyl Endcapped Polyynes: Crystallographic Evidence of Reduced Bond-Length Alternation**

*W. Cheng, L. Ding, S. Ding, Y. Yin, H. Ju**
A Facile Electrochemical Cytosensor Array for Dynamic Analysis of Carcinoma Cell Surface Glycans

Author Profile

"The most important future applications of my research are to the training of young minds. My favorite piece of research is a living work in progress. …"
This and more about Jay S. Siegel can be found on page 6194.

News


R. Zare


K. Suzuki


S. J. Lippard

Books

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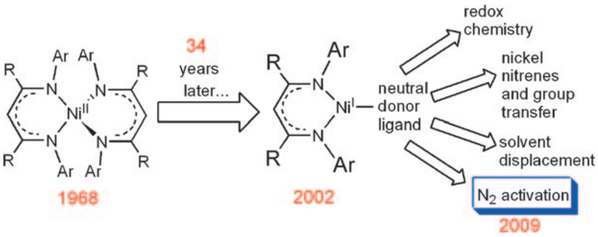
Highlights

Coordination Chemistry

D. J. Mindiola* ______ **6198 – 6200**

Nacnac ... Are You Still There? The Evolution of β-Diketiminate Complexes of Nickel



A long time coming: In 1968, the first nickel(II) β-diketiminate complexes were prepared. It took over 30 years to find the right steric conditions to afford unsaturated nickel(I) scaffolds of the type $[(\{ArNC(tBu)\}_2CH)Ni{-}L]$ (see scheme, L = neutral ligand). Ultimately, the right combination of ingredients resulted in formation of the dinitrogen complexes $[\{(\{ArNC(tBu)\}_2CH)Ni\}_2(\mu_2,\eta^1{:}\eta^1\text{-}N_2)]^{x-}$ ($x = 0, 1, 2$).

Carboxylations

A. Correa, R. Martín* ______ **6201 – 6204**

Metal-Catalyzed Carboxylation of Organometallic Reagents with Carbon Dioxide

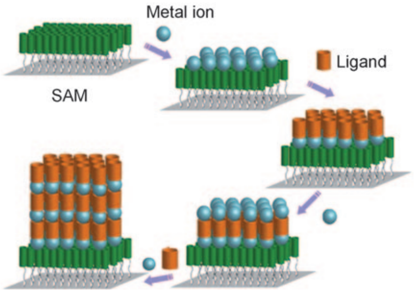
$$R{-}M \;+\; CO_2 \xrightarrow{[M'] \text{ (cat.)}} R{-}CO_2H$$

On course for a C_1 source: Highly functionalized carboxylic acids can be conveniently prepared from the carboxylation of organometallic reagents using carbon dioxide as the sole source of carbon. Given the sustainable nature of using carbon dioxide as a C_1 source, these novel methods could revolutionize approaches towards the elaboration of complex organic molecules and will probably find industrial applications.

Coordination Polymers

R. A. Fischer,* C. Wöll ______ **6205 – 6208**

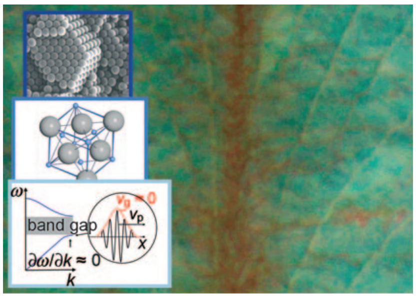
Layer-by-Layer Liquid-Phase Epitaxy of Crystalline Coordination Polymers at Surfaces



Topping it off: Layer-by-layer growth was used to produce a highly oriented crystalline surface coordination polymer made up of copper dithiooxamide complexes (see scheme; SAM = self-assembled monolayer). This example demonstrates that layer-by-layer growth in the liquid phase can produce a highly crystalline system even in difficult cases.

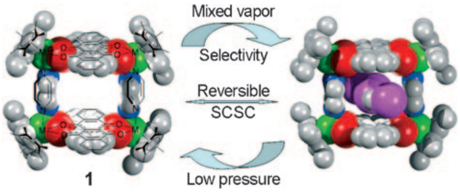
For the USA and Canada: ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Wiley-VCH, 111 River Street, Hoboken, NJ 07030. Annual subscription price for institutions: US$ 7225/6568 (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.

Reviews



Like a rainbow: Owing to their periodic nature, which leads to opalescence, opals are a prototype for photonic crystals. Such crystals are formed by microstructuring or by self-assembly, as are opals. Self-assembly can lead to a number of defects that may make applications difficult but also lead to interesting functional properties.

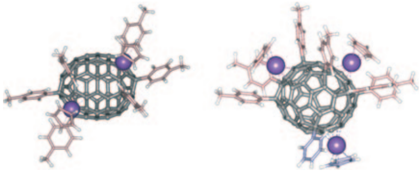
Communications

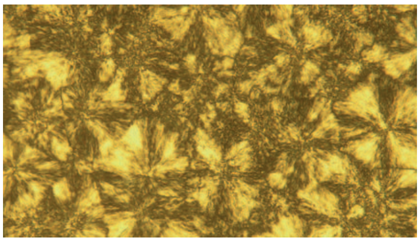


1

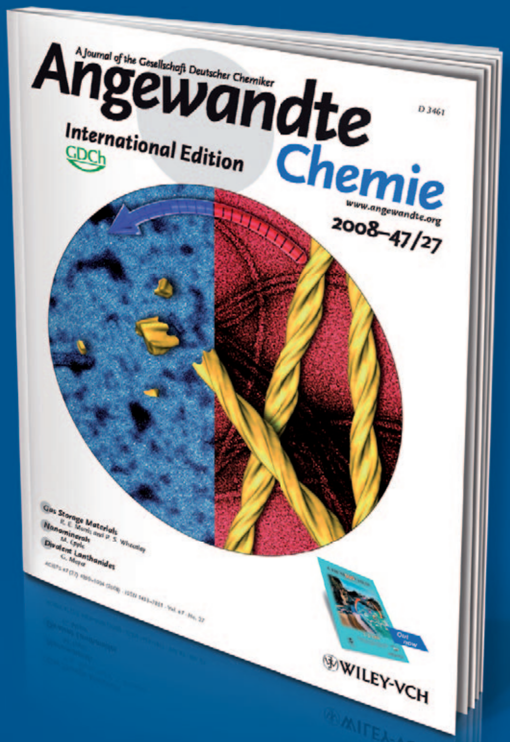
Gone up in frames: Organometallic “molecular splints” with half-sandwich Ir and Rh corners are synthesized, characterized, and studied for reversible trapping of halocarbons. Complex **1** (M = Ir, Rh) selectively recognizes CH_2Cl_2 and $ClCH_2CH_2Cl$ molecules with retention of crystallinity. These complexes undergo reversible single-crystal to single-crystal structural transformations that are induced by solvent exchange.

Buckyballs with studs: [70]Fullerene has been converted into di- and trinuclear complexes $[M_2(C_{70}Ar_6)Cp_2]$, $[M_2(C_{70}Ar_7H)Cp_2]$, and $[M_3(C_{70}Ar_7)Cp_3]$ (M = Fe, Ru; Ar = aryl; Cp = C_5H_5; see picture, M purple, C pink, blue, gray) in which the metal atoms interact electronically through the [70]fullerene π-conjugated system. The structures and the electrochemical properties of these complexes suggest their use in molecular electronics.





Molten proteins: Warming a freeze-dried powder of a stoichiometric ferritin–polymer ionic construct produces a solvent-free liquid protein that exhibits viscoelastic and thermotropic liquid-crystalline properties at 30 °C (see polarized-light micrograph), and transforms into a Newtonian fluid above 40 °C.


A Journal of the Gesellschaft Deutscher Chemiker
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GDCh
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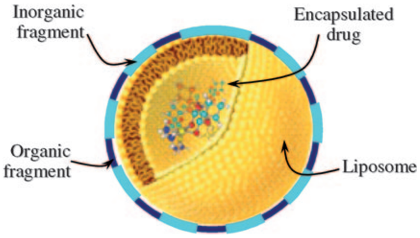
Drug Delivery Systems

A. Corma,* U. Díaz, M. Arrica, E. Fernández, Í. Ortega ______ 6247 – 6250

Organic–Inorganic Nanospheres with Responsive Molecular Gates for Drug Storage and Release

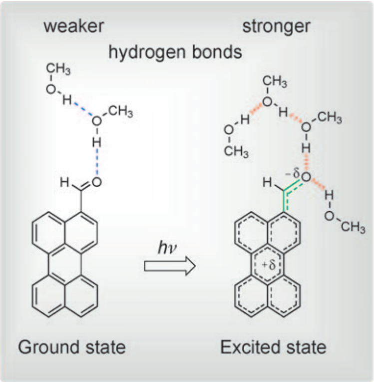


Catch and release: Bridged silsesquioxanes act as organic–inorganic precursors for nanospheres to encapsulate bioactive molecules for drug-delivery applications. The nanosystems (see picture) are constructed from an liposomal core containing bioactive molecules and an network shell formed by silica and organic ester fragments that can act as responsive molecular gates.

Femtochemistry

O. F. Mohammed, O.-H. Kwon, C. M. Othon, A. H. Zewail* 6251 – 6256

Charge Transfer Assisted by Collective Hydrogen-Bonding Dynamics

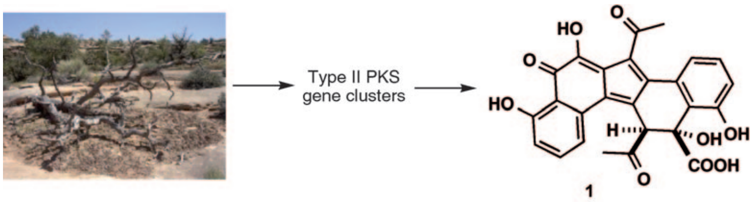


Bipolar disorder: Femtosecond spectroscopy of samples in protic and aprotic solvents of similar polarities reveals that charge-transfer processes are substantially facilitated by the formation of solute–solvent hydrogen-bond networks (see picture). This notion of molecular-specific interactions is not part of the continuum dielectric models of solvation and should be of significance to biological processes such as those of enzymes.

Natural Products

R. W. King, J. D. Bauer, S. F. Brady* ______ 6257 – 6261

An Environmental DNA-Derived Type II Polyketide Biosynthetic Pathway Encodes the Biosynthesis of the Pentacyclic Polyketide Erdacin



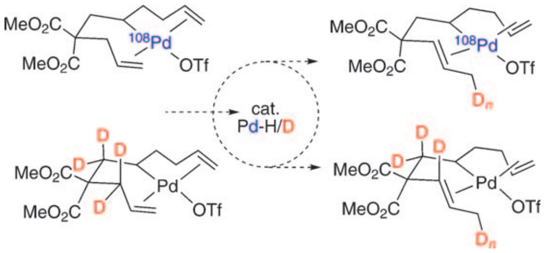
1

A down to earth approach: Environmental (from desert soil) DNA derived cosmid clones containing type II polyketide synthase genes were screened for their ability to produce clone-specific metabolites in *Streptomyces*. One of the *Streptomyces* recombinants produces erdacin (**1**), a polyketide with a previously unknown pentacyclic structure.

Reaction Mechanism

L. A. Evans, N. Fey, G. C. Lloyd-Jones,* M. P. Muñoz, P. A. Slatford 6262 – 6265

Cryptocatalytic 1,2-Alkene Migration in a σ-Alkyl Palladium Diene Complex

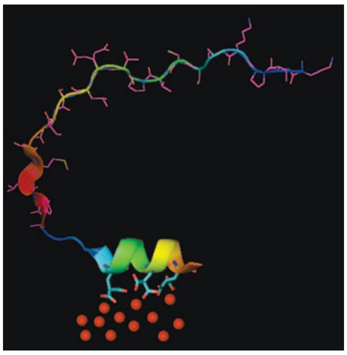


Not so simple: A combination of ^{2}H, ^{13}C, and ^{108}Pd labels shows that the alkene migration in a σ-alkyl palladium diene complex induced by trifluoromethanesulfonic acid is not intramolecular or acid-mediated, but instead requires a self-generated palladium hydride species (see scheme; Tf = triflate).

Modular Peptide Growth Factor

J. S. Lee, J. S. Lee, A. Wagoner-Johnson, W. L. Murphy* ______ 6266 – 6269

Modular Peptide Growth Factors for Substrate-Mediated Stem Cell Differentiation

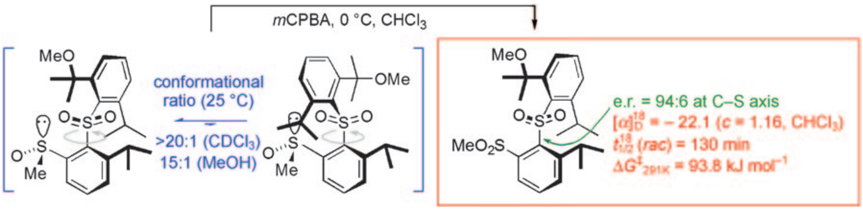


The sequence specificity of the binding of a modular peptide growth factor (eBGa3) that contains a BMP2-derived sequence and a mineral-binding sequence inspired by osteocalcin to calcium ions of hydroxyapatite (HA) may be attributed in part to evolution of an α-helical structure in the presence of HA, which allows for registration of γ-carboxylated glutamic acid residues in the peptide (cyan) with calcium atoms (orange) in the HA crystal lattice.

Atropisomeric Sulfur Compounds

J. Clayden,* J. Senior, M. Helliwell ______ 6270 – 6273

Atropisomerism at C–S Bonds: Asymmetric Synthesis of Diaryl Sulfones by Dynamic Resolution Under Thermodynamic Control



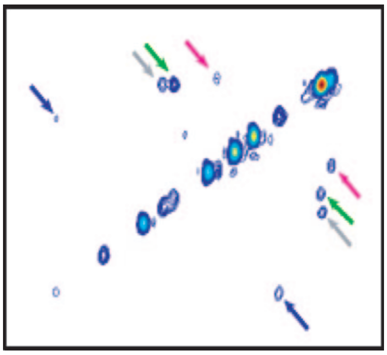
A powerful conformational preference exhibited by a diaryl sulfone axis lying *ortho* to a sulfinyl substituent enabled the dynamic resolution of atropisomeric diaryl sulfones under thermodynamic control (see scheme; e.r. = enantiomeric ratio). These compounds are the first resolvable compounds exhibiting atropisomerism at C–S bonds.

NMR Spectroscopy

A. Herrera,* E. Fernández-Valle, R. Martínez-Álvarez, D. Molero, Z. D. Pardo, E. Sáez, M. Gal 6274 – 6277

Real-Time Monitoring of Organic Reactions with Two-Dimensional Ultrafast TOCSY NMR Spectroscopy

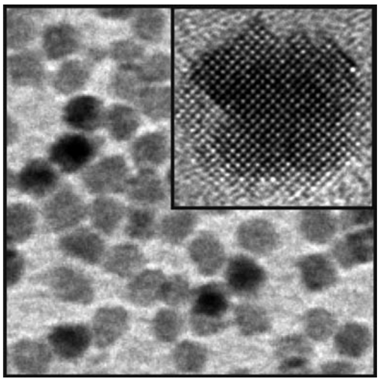
A quick look reveals all: A two-dimensional ultrafast TOCSY experiment in one scan is presented and used to study the synthesis of pyrimidine from an aliphatic ketone, a nitrile, and Tf$_2$O. 525 two-dimensional TOCSY experiments were recorded, and the reactants, intermediates, and products could be monitored (see picture; blue = product; gray, green, and pink = intermediates).



MgO Nanocrystals

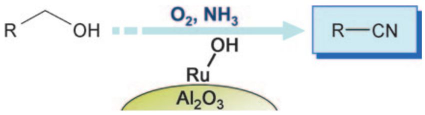
H. R. Moon, J. J. Urban, D. J. Milliron* ______ 6278 – 6281

Size-Controlled Synthesis and Optical Properties of Monodisperse Colloidal Magnesium Oxide Nanocrystals

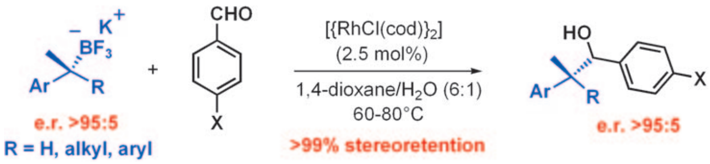


MgO gets discrete: Monodisperse nanocrystals of the alkaline earth metal oxide MgO can be prepared by direct colloidal synthesis (see image). Diameter control (2–8 nm) is achieved by incorporating catalytic amounts of water into the organic reaction medium. Although trioctylphosphine oxide is present during the reaction, the resulting nanocrystals are capped primarly by benzyl ether. Blue luminescence is observed with a quantum yield up to approximately 20%.

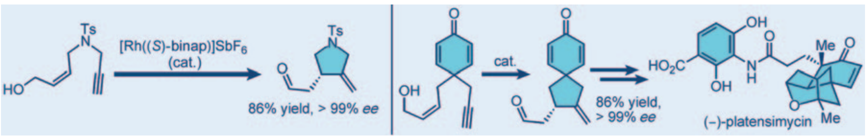
Mark and destroy: Arsenic sulfide nanoclusters passivated by ethylenediamine derivatives can form a fluorescent, pH-responsive nanosized colloidal hydrogel in water (see scheme). Besides acting as a fluorescent label, the arsenic sulfide nanogel exhibits remarkable cytotoxicity on certain cancer cells (OVCAR-3 and HeLa).



In full support: A supported ruthenium hydroxide, Ru(OH)$_x$/Al$_2$O$_3$, served as an efficient heterogeneous catalyst for the aerobic oxidative synthesis of nitriles directly from primary alcohols (or aldehydes) and ammonia. The retrieved catalyst could be reused without a significant loss of its catalytic performance.



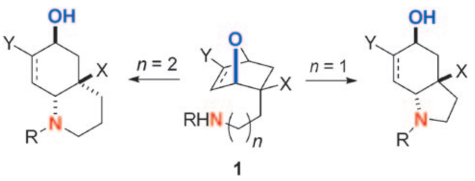
Take your new partner by the hand: Chiral secondary and tertiary alkyl trifluoroborate salts undergo rhodium-catalyzed 1,2-addition to aldehydes with complete stereoretention (handedness) in all cases, enabling the creation of quaternary stereogenic centers with essentially perfect enantioselectivity (see scheme; cod = cycloocta-1,5-diene).



Rh built: The title reaction is described and applied to a formal total synthesis of (−)-platensimycin (see scheme; Ts = *para*-toluenesulfonyl, binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthalene).

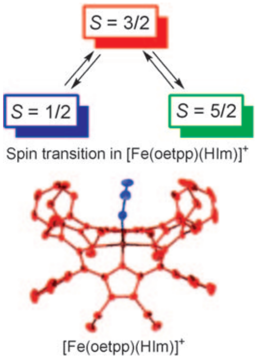
Contents

Synthetic Methods



With remarkable ease, even saturated [2.2.1]oxabicyclic systems of type **1** underwent Lewis acid mediated nucleophilic ring opening to provide rapid access to densely functionalized perhydroindoles ($n=1$) and perhydroquinolines ($n=2$, see scheme). Both amines and amides are suitable nucleophiles for this efficient transformation with broad substrate scope.

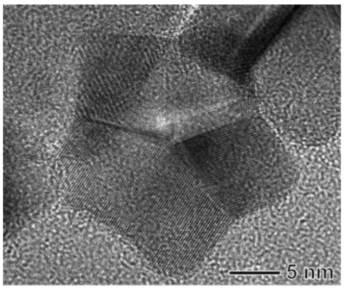
Protein Models



Saddle in a spin: The saddle-shaped octaethyltetraphenylporphyrin–imidazole complex $[\mathrm{Fe^{III}(oetpp)(HIm)}]^+$ adopts an essentially pure intermediate-spin state between 298 and 173 K in CD_2Cl_2 solution, the conditions under which the NMR spectra are recorded. This complex has shown, however, a novel spin transition from $S=3/2$ to $S=5/2$ and $S=1/2$ below 70 K. Thus, the complex exists as an equilibrium mixture of three spin isomers at 4 K.

Nanocrystals

Identical or fraternal? Palladium–platinum alloy nanocrystals with well-defined twinned structures (see picture) were synthesized by co-reducing Pd and Pt salts. The evolution of twinned morphologies involves coalescence between initially formed small particles under the slow reduction process. Manipulation of the reduction kinetics allows ready control over crystallinity, and thus shape, of the nanocrystals.



Sn–Sn Bond Formation

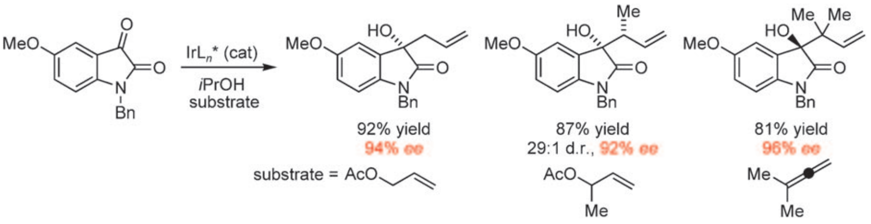
$$2\,t\mathrm{Bu_2SnH_2} \xrightarrow[\mathrm{C_6D_6}]{\text{catalyst}/h\nu\ \text{or}\ \Delta} \mathrm{H}t\mathrm{Bu_2Sn\text{-}Sn}t\mathrm{Bu_2H}$$

Tin–tin bonds are formed in the title reaction, which provides $t\mathrm{Bu_2HSn{-}SnH}t\mathrm{Bu_2}$ in high yield. The reaction is either photochemically catalyzed by the iron complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Me]$ or its molybdenum analogue $[(\eta^5\text{-}C_5H_5)\text{-}Mo(CO)_3Me]$ or thermally catalyzed by $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)Me]$ or its analogue $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)Me]$.

Synthetic Methods

J. Itoh, S. B. Han,
M. J. Krische* ______ 6313–6316

Enantioselective Allylation, Crotylation, and Reverse Prenylation of Substituted Isatins: Iridium-Catalyzed C—C Bond-Forming Transfer Hydrogenation

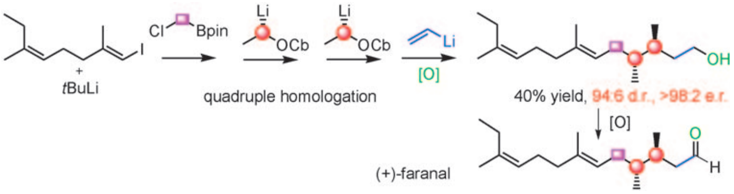


Oxindoles with a twist: Transfer hydrogenation of substituted isatins in the presence of allyl acetate, α-methyl allyl acetate, or 1,1,-dimethylallene using an cyclometalated iridium catalyst, provides products of carbonyl allylation, crotylation, and reverse prenylation, respectively, in highly enantiomerically enriched form. These studies represent the first use of activated ketones as electrophilic partners in asymmetric C—C bond-forming transfer hydrogenation.

Assembly-Line Synthesis

G. Dutheuil, M. P. Webster,
P. A. Worthington,
V. K. Aggarwal* ______ 6317–6319

Stereocontrolled Synthesis of Carbon Chains Bearing Contiguous Methyl Groups by Iterative Boronic Ester Homologations: Application to the Total Synthesis of (+)-Faranal

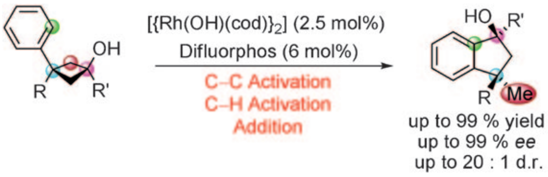


Adding links to the chain: A quadruple homologation of a boronic ester converts a simple vinyl iodide into a complex precursor to faranal with very high levels of diastereo- and enantiocontrol. This enables the synthesis of (+)-faranal to be completed in just six steps and 18% overall yield from propyne.

Asymmetric Catalysis

T. Seiser, O. A. Roth,
N. Cramer* ______ 6320–6323

Enantioselective Synthesis of Indanols from *tert*-Cyclobutanols Using a Rhodium-Catalyzed C—C/C—H Activation Sequence

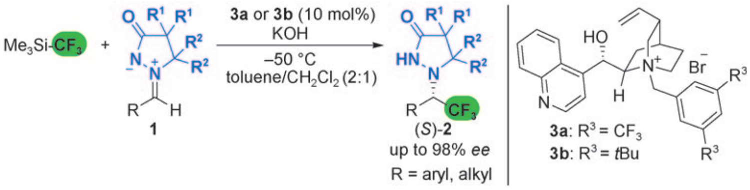


Activation! An enantioselective activation of *tert*-cyclobutanols by a chiral rhodium(I) complex has been developed. The resulting reactive organometallic species lead (presumably by a C—H activation pathway) to aryl rhodium intermediates that provide substituted indanol derivatives in excellent enantio- and diastereoselectivities (see scheme).

Trifluoromethylation

H. Kawai, A. Kusuda, S. Nakamura,
M. Shiro, N. Shibata* ______ 6324–6327

Catalytic Enantioselective Trifluoromethylation of Azomethine Imines with Trimethyl(trifluoromethyl)silane

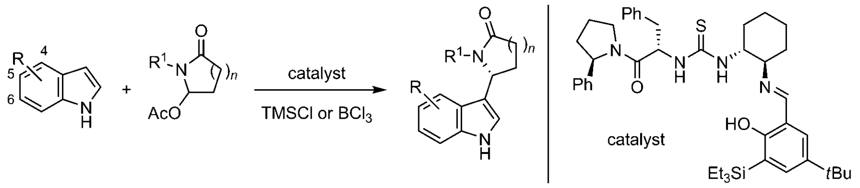


It's a cinch! The title reaction with azomethine imines **1** uses an operationally simple procedure, based on the combination of the bromide salt of cinchona alkaloids (**3**) and KOH. The procedure is reliable and general. Trifluoromethyl-substituted amines can be accessed by a two-step deprotection of the product (*S*)-**2**.

Organocatalysis

E. A. Peterson,
E. N. Jacobsen* ______________ **6328 – 6331**

Enantioselective, Thiourea-Catalyzed Intermolecular Addition of Indoles to Cyclic *N*-Acyl Iminium Ions



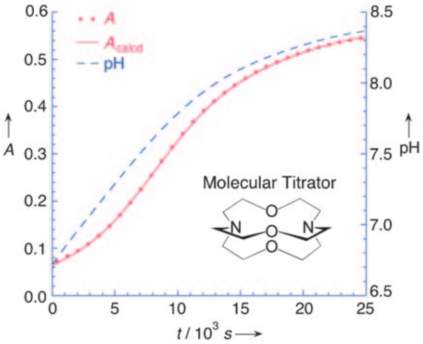
Fair game for indoles, *N*-acyl iminium ion intermediates underwent intermolecular addition by these nucleophiles under the catalysis of a chiral thiourea Schiff base derivative. A variety of functionalized indole frameworks were assembled with high enantioselectivity from simple precursors by this method (see scheme; TMS = trimethylsilyl; R = H, Me, vinyl, OMe, F, Cl, Br; R^1 = benzyl, methyl; n = 1,2).

Molecular Devices

G. Alibrandi,* C. Lo Vecchio,
G. Lando ______________ **6332 – 6334**

[1.1.1]Cryptand: A Molecular Automatic Titrator

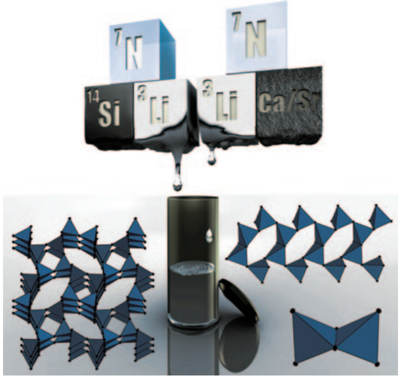
Old dog, new tricks! The pH value of a solution changes slowly and irreversibly over time when [1.1.1]cryptand is used as an automatic molecular titrator. The pK_a value of phenol red was determined spectrophotometrically in a completely automatic run, without the need for external input adjustments (see picture, A = absorption, A_{calcd} = theoretical absorption). The experiment is proposed as a model for the automatic determination of thermodynamic parameters.



Nitridosilicates

S. Pagano, S. Lupart, M. Zeuner,
W. Schnick* ______________ **6335 – 6338**

Tuning the Dimensionality of Nitridosilicates in Lithium Melts

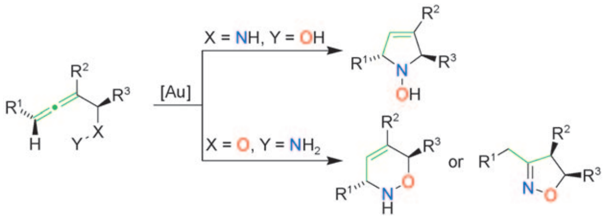


Convenient access to nitridosilicates with the whole range of dimensionality known for silicates is provided by synthesis in molten lithium in welded-shut tantalum ampoules. For example, $Li_4Ca_3Si_2N_6$ consists of edge-sharing "bow-tie" $[Si_2N_6]^{10-}$ units, $LiCa_3Si_2N_5$ has an edge-sharing double-chain and channels occupied by Li^+ ions, and $Li_2Sr_4Si_4N_8O$ exhibits a zeolite-analogous structure due to inclusion of Li_2O (see picture).

Gold Catalysis

C. Winter, N. Krause* ______ **6339 – 6342**

Structural Diversity through Gold Catalysis: Stereoselective Synthesis of *N*-Hydroxypyrrolines, Dihydroisoxazoles, and Dihydro-1,2-oxazines



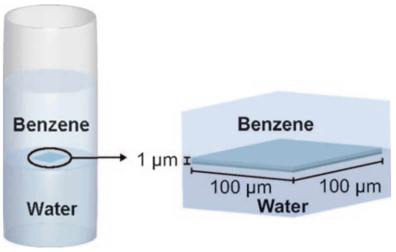
The power of gold: Three chiral heterocycles are obtained by highly efficient regio- and stereoselective gold-catalyzed cycloisomerization of allenic hydroxylamine derivatives (see scheme). In all cases, the nitrogen atom acts as the nucleophile and attacks the allene in a 5- or 6-*endo* cyclization. The regioselectivity is controlled by careful choice of the gold precatalyst and of the protecting group for the nitrogen atom.

Interface Analysis

J. Lambert, R. Hergenröder, D. Suter,
V. Deckert* ———— **6343 – 6345**

Probing Liquid–Liquid Interfaces with Spatially Resolved NMR Spectroscopy

En route to nanometer resolution: Spatially resolved NMR spectroscopy is used to directly probe liquid–liquid interfaces with exceptionally high spatial resolution in one selected dimension. The novel technique is a first step towards NMR spatial resolution in the nanometer range.

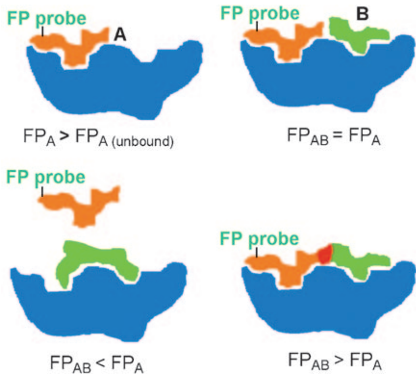


Dynamic Ligation Screening

M. F. Schmidt, A. El-Dahshan, S. Keller,
J. Rademann* ———— **6346 – 6349**

Selective Identification of Cooperatively Binding Fragments in a High-Throughput Ligation Assay Enables Development of a Picomolar Caspase-3 Inhibitor

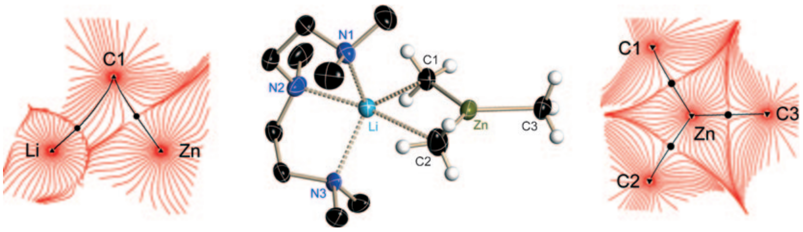
Putting the pieces together: A chemically reactive fluorescence polarization (FP) probe can be use to detect positively cooperative fragments through the over-additive binding of their ligation products. For confirmation, an stable derivative of the ligation product was prepared and found to be significantly more active than all previously reported caspase-3 inhibitors.



Lithium Zincates

S. Merkel, D. Stern, J. Henn,
D. Stalke* ———— **6350 – 6353**

Solvent-Separated and Contact Ion Pairs of Parent Lithium Trimethyl Zincate

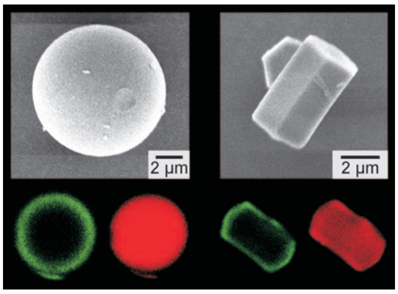


In the contact ion pair (CIP) of the trimethyl zincate with a lithium cation, no additional amide ligand is required to bridge the two metal atoms and to activate the bridging Zn–C bond. Topological analysis of the Li–C bond shows that it is as important as a Li–N donor bond to preserve the CIP in solution. A smaller donor base gives the solvent-separated ion pair in which all Zn–C bonds are equal.

Mesoporous Materials

N. Gartmann,
D. Brühwiler* ———— **6354 – 6356**

Controlling and Imaging the Functional-Group Distribution on Mesoporous Silica



In, out, shake it all about: The distribution of fluorescence-labeled amino groups on mesoporous silica was imaged by confocal laser scanning microscopy. The mobility of the aminosilane precursor determines the degree of external vs. pore-surface functionalization. This observation was used to develop a simple and general method for the modification of external mesoporous silica surfaces.

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).

Contents

Service

Corrigendum

Intermolecular Double Prins-Type Cyclization: A Facile and Efficient Synthesis of 1,6-Dioxecanes

P. R. Ullapu, S.-J. Min, S. N. Chavre, H. Choo, J. K. Lee, A. N. Pae, Y. Kim, M. H. Chang, Y. S. Cho* — **2196–2200**

Angew. Chem. Int. Ed. **2009**, *48*

DOI 10.1002/anie.200804576

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