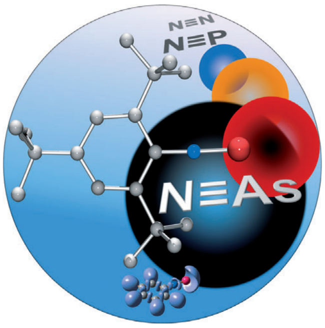
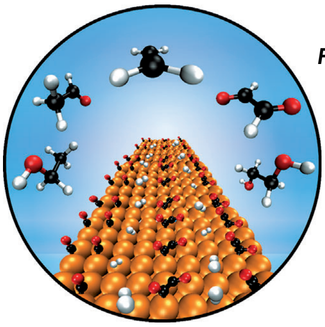
A rare pearl ...

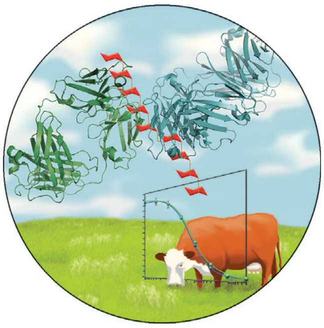
… of a neutral silicon atom in the formal oxidation state zero seems to evolve best in the oyster-like coordination environment of a bidentate N-heterocyclic carbene ligand. In their Communication on page 7147 ff., M. Driess and co-workers present the strikingly facile formation of this silicon pearl, which belongs to the novel class of theoretically predicted compounds termed silylones. (Graphics: Wernerwerke.)

As–N Triple Bonds
More than 150 years after the discovery of stable diazonium salts, a heavy arsenic analogue has been isolated. In their Communication on page 7126 ff., A. Schulz et al. describe the electronic structure of arsa-diazonium salts and their use in 3+2 cycloaddition reactions.





From CO to C_2
By using DFT calculations, F. Calle-Vallejo and M. T. M. Koper elucidate a mechanism for the electroreduction of CO to C_2 species on Cu(100) in their Communication on page 7282 ff. They also show why the process is pH-independent.



Universal Antigen
The O-antigen of infectious *Brucella* bacteria can be in either A- or M-antigenic forms. In their Communication on page 7181 ff., D. R. Bundle et al. describe a nonasaccharide glycoconjugate that encompasses both antigenic features.

How to contact us:

Editorial Office:
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

Reprints, E-Prints, Posters, Calendars:
Carmen Leitner
E-mail: chem-reprints@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-327

Copyright Permission:
Bettina Loycke
E-mail: rights-and-licences@wiley-vch.de
Fax: (+49) 6201–606-332
Telephone: (+49) 6201–606-280

Online Open:
Margitta Schmitt, Carmen Leitner
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

Subscriptions:
www.wileycustomerhelp.com
Fax: (+49) 6201–606-184
Telephone: 0800 1800536 (Germany only)
+44(0) 1865476721 (all other countries)

Advertising:
Marion Schulz
E-mail: mschulz@wiley-vch.de
jspiess@wiley-vch.de
Fax: (+49) 6201–606-550
Telephone: (+49) 6201–606-565

Courier Services:
Boschstrasse 12, 69469 Weinheim

Regular Mail:
Postfach 101161, 69451 Weinheim

Angewandte Chemie International Edition is a journal of the Gesellschaft Deutscher Chemiker (GDCh), the largest chemistry-related scientific society in continental Europe. Information on the various activities and services of the GDCh, for example, cheaper subscription to *Angewandte Chemie International Edition*, as well as applications for membership can be found at **www.gdch.de** or can be requested from GDCh, Postfach 900440, D-60444 Frankfurt am Main, Germany.

Service

Author Profile

“My greatest achievement has been getting paid to do what I do.
Guaranteed to make me laugh is the comedy series “Absolutely Fabulous”. …”
This and more about Xile Hu can be found on page 7070.

News


H. L. Anderson


G. C. Lloyd-Jones


P. O’Brien


C. J. Schofield


D. W. Stephan


K. C. Nicolaou

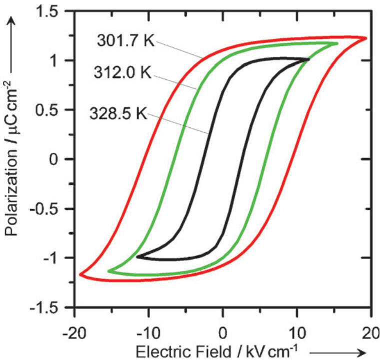

G. Férey


K. Meerholz

Books

Correspondence

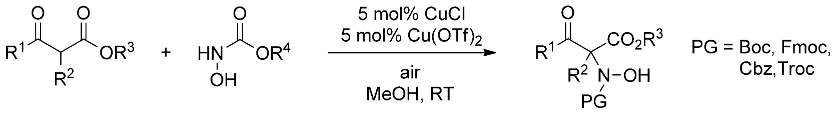
Phase Transitions



Ferroelectric properties verified: Recent results presented for the complex of imidazole and L-tartaric acid are based on improper analysis and interpretation of the experimental dielectric and crystallographic data. In particular, it has now been shown that a ferroelectric-to-paraelectric phase transition in this compound occurs at 351 K, namely at a temperature 100 K higher than reported previously.

Highlights

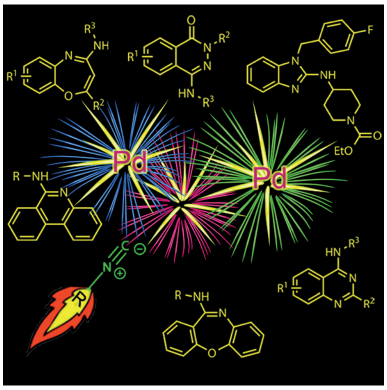
Nitroso Aldol Reactions



Lewis acid and oxidation catalysis are merged in the reaction discussed here, which provides access to diversely substituted *N*-hydroxycarbamates (see scheme). This reaction highlights the potential of nitrosoformates as electrophilic amination reagents as well as the benefits of aerobic oxidation for the formation of highly reactive species.

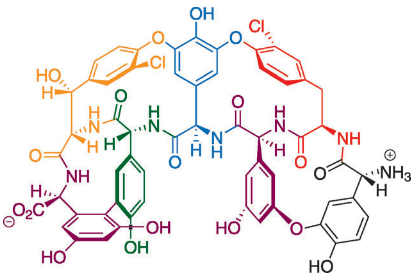
For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. 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.

Minireviews



R you in? Isocyanides (R-NC) have recently gained attention as novel, versatile C_1 building blocks in palladium catalysis. This Minireview highlights the recent progress in palladium-catalyzed reactions involving isocyanide insertion (imidoylative cross-couplings), thus illustrating their potential for the rapid construction of a variety of heterocycles and functional groups.

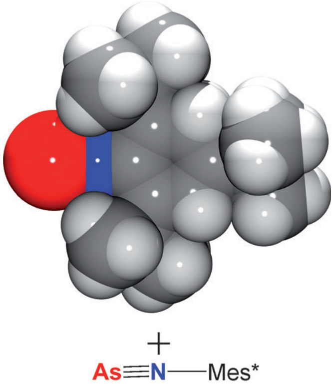
Reviews



Microbes have a remarkable capacity to build amino acid frameworks that are not incorporated into proteins. This Review summarizes the biosynthetic routes to and metabolic logic for the major classes of the noncanonical amino acid building blocks that end up in both nonribosomal peptide frameworks and in hybrid nonribosomal peptide/polyketide scaffolds.

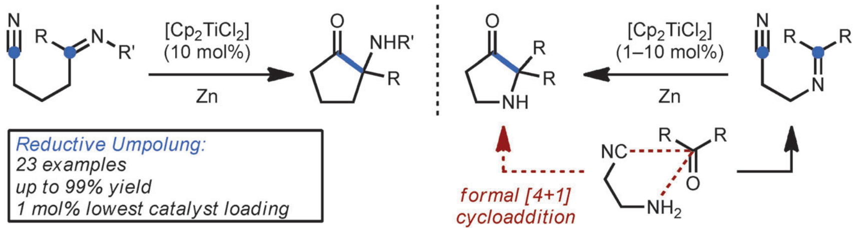
Communications

Arsenic triply bound: Arsa-diazonium salts containing a cation with an arsenic–nitrogen triple bond ([R-N≡As]$^+$), which is stable at room temperature, are isolated and fully characterized for the first time. Analogous to the diazonium salts, arsa-diazonium salts can be used in [3+2] dipolar cycloaddition reactions with azides to prepare arsenic analogues ($RAsN_4$) of pentazoles (RN_5).



Frontispiece


Fruitful Research
www.angewandte.com
Angewandte Chemie
125 YEARS
GDCh
A Journal of Gesellschaft Deutscher Chemiker



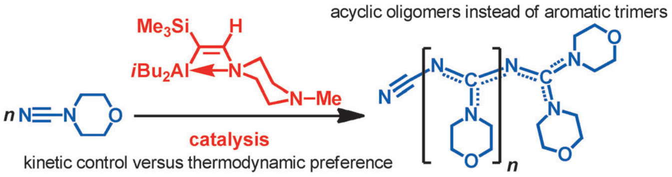
Have it both ways: α-Aminated ketones can be prepared by the titanium(III)-catalyzed reductive radical cyclization of iminonitriles. Depending on the position of the nitrile at the imine carbon or nitrogen, cyclic aminoketones or pyrrolidin-3-ones with a tetrasubstituted α-carbon can be formed in up to quantitative yield. In the latter case, the imine condensation and Ti^{III} catalysis correspond to a formal [4+1] cycloaddition.

Redox Umpolung

G. Frey, H.-T. Luu, P. Bichovski, M. Feurer, J. Streuff* ______ **7131 – 7134**

Convenient Titanium(III)-Catalyzed Synthesis of Cyclic Aminoketones and Pyrrolidinones—Development of a Formal [4+1] Cycloaddition

---



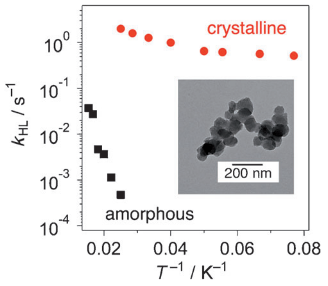
Put in chains: Acyclic oligomers and not the thermodynamically strongly preferred aromatic trimers are formed on treatment of cyanamides with catalytic quantities of an Al–N based Lewis pair (see scheme; $n=0$ to >22). These oligomers have delocalized electronic systems in their backbone and are long-sought nitrogen-containing analogues of polyethyne.

Lewis Pairs

T. Holtrichter-Rößmann, J. Isermann, C. Rösener, B. Cramer C.-G. Daniliuc, J. Kösters, M. Letzel, E.-U. Würthwein,* W. Uhl* ______ **7135 – 7138**

An Aluminum–Nitrogen Based Lewis Pair as an Effective Catalyst for the Oligomerization of Cyanamides: Formation of Acyclic C=N Oligomers Instead of Thermodynamically Favored Cyclic Aromatic Trimers

---



A switch in time: A fast precipitation technique was used to prepare 75 nm Fe^{II} spin-crossover nanocrystals. Their photoswitching dynamics, based on the light-induced excited spin-state trapping effect, has been investigated by means of optical spectroscopy. A significant variation of the switching proprieties is observed compared to similar but amorphous nanoparticles.

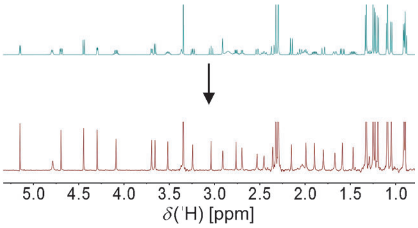
Spin-Crossover Nanoparticles

P. Chakraborty, M.-L. Boillot, A. Tissot,* A. Hauser* ______ **7139 – 7142**

Photoinduced Relaxation Dynamics in Iron(II) Spin-Crossover Nanoparticles: The Significance of Crystallinity

---

Shift work: The new NMR technique, instant homonuclear decoupling, which is achieved by slice-selective homo-decoupling during acquisition, yields pure-shift NMR spectra (see picture) which can be recorded like regular 1D spectra. No special data processing is necessary and this approach can also be easily adapted for the direct dimension of two- and multidimensional spectra, giving improved resolution.



NMR Spectroscopy

N. H. Meyer, K. Zangger* __ **7143 – 7146**

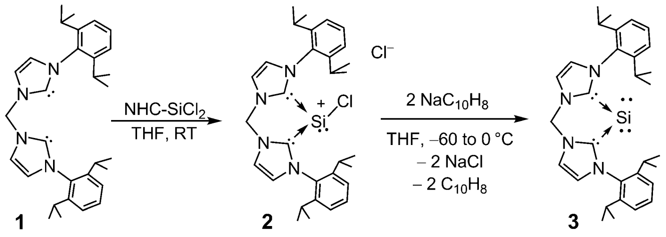
Simplifying Proton NMR Spectra by Instant Homonuclear Broadband Decoupling

Silicon Chemistry

Y. Xiong, S. Yao, S. Inoue, J. D. Epping,
M. Driess* ________________ **7147 – 7150**

A Cyclic Silylone ("Siladicarbene") with an Electron-Rich Silicon(0) Atom

Front Cover

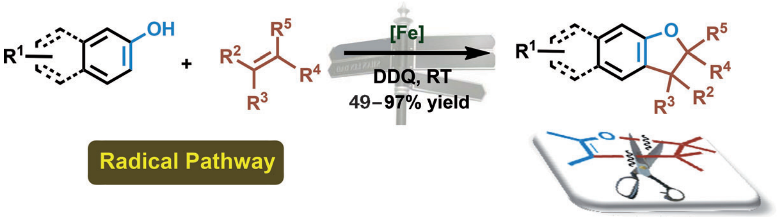


King of donor: The chelating bis(carbene) **1** enabled the synthesis of the new silyliumylidene salt **2**. This salt can be dechlorinated with sodium naphthalenide to give the first cyclic siladicarbene **3**, which bears a single Si^0 atom with strikingly high basicity. The small C-Si-C angle of 89.1° and the average C–Si distance of 1.869 Å are consistent with results from theoretical calculations, which revealed that **3** is best described as a silylone.

Oxidative Radical Coupling

Z. Huang, L. Jin, Y. Feng, P. Peng, H. Yi,
A. Lei* ________________ **7151 – 7155**

Iron-Catalyzed Oxidative Radical Cross-Coupling/Cyclization between Phenols and Olefins

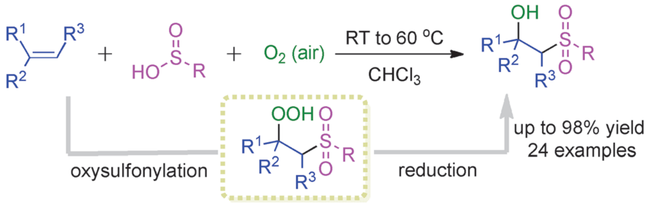


Selectively free: A highly efficient and selective iron-catalyzed oxidative radical cross-coupling/cyclization to prepare dihydrobenzofurans under mild conditions had been established. Phenols and olefins are directly utilized as clean nucleophiles. Mechanistic investigations revealed that the reaction proceeds through a radical pathway, and the high selectivity is due to the Lewis acid.

Dioxygen Activation

Q. Lu, J. Zhang, F. Wei, Y. Qi, H. Wang,
Z. Liu, A. Lei* ________________ **7156 – 7159**

Aerobic Oxysulfonylation of Alkenes Leading to Secondary and Tertiary β-Hydroxysulfones

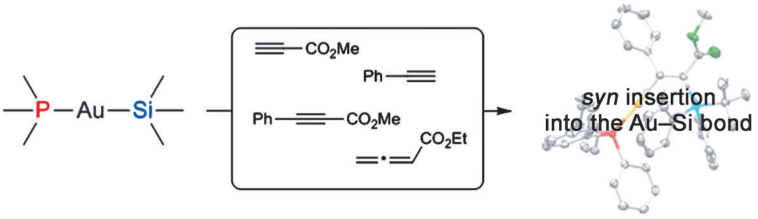


New channel! A novel and attractive dioxygen activation by sulfinic acids was explored that is capable of performing efficiently without the assistance of transition metals or radical initiators. This reaction furnishes secondary and tertiary β-hydroxysulfones under mild conditions; β-hydroperoxysulfone was isolated as an important intermediate.

Gold Complexes

M. Joost, P. Gualco, S. Mallet-Ladeira,
A. Amgoune,*
D. Bourissou* ________________ **7160 – 7163**

Direct *syn* Insertion of Alkynes and Allenes into Au–Si Bonds

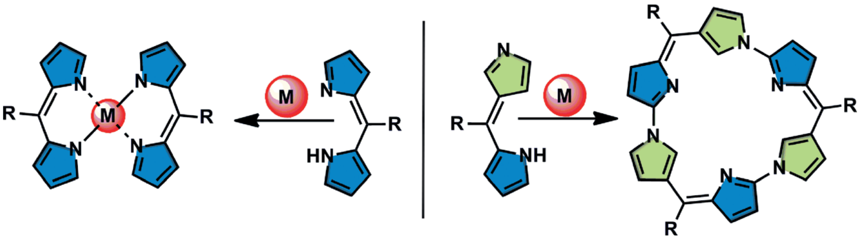


Complete control: Alkynes and allenes are shown to insert into Au–Si bonds with complete stereocontrol and in most cases complete regiocontrol. The ensuing β-silyl vinylgold complexes have been characterized by spectroscopic and crystallographic means. These results provide unequivocal evidence for *syn* insertion reactions at gold.

Porphyrinoids

S. C. Gadekar, B. K. Reddy,
V. G. Anand* ______ **7164 – 7167**

Metal-Assisted Cyclomerization of N-Confused Dipyrrins into Expanded Norroles

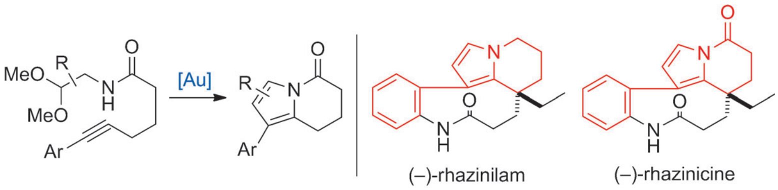


Neoconfusion: In contrast to metal ligation by dipyrrin (see scheme, left), N-confused dipyrrin undergoes cyclomerization with various metal salts to form NCNCNC and NCNCNCNC expanded norroles (see scheme, right), novel isomers of 24π rosarin and 32π octaphyrin with C–N linked bipyrrole units with near-planar conformations in the solid state. They also exhibit paratropic ring-current effects typical of antiaromatic porphyrinoids.

Natural Products

K. Sugimoto, K. Toyoshima, S. Nonaka,
K. Kotaki, H. Ueda,
H. Tokuyama* ______ **7168 – 7171**

Protecting-Group-Free Total Synthesis of (−)-Rhazinilam and (−)-Rhazinicine using a Gold-Catalyzed Cascade Cyclization

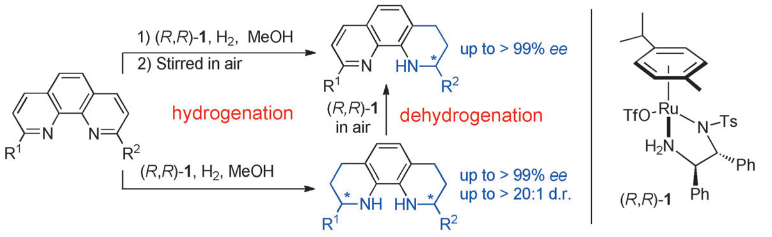


‘Rhaz’zmatazz: A total synthesis of (−)-rhazinilam and the first asymmetric total synthesis of (−)-rhazinicine were accomplished by using constructing the indolizinone core through the gold-catalyzed cyclization of a fully elaborated linear ynamide. The scope and generality of this cascade reaction for the construction of highly substituted indolizinones were also investigated.

Synthetic Methods

T. L. Wang, F. Chen, J. Qin, Y.-M. He,
Q.-H. Fan* ______ **7172 – 7176**

Asymmetric Ruthenium-Catalyzed Hydrogenation of 2- and 2,9-Substituted 1,10-Phenanthrolines

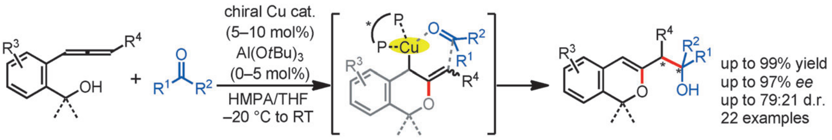


A ‘Phen’atic: The title reaction proceeds in the presence of the chiral cationic ruthenium diamine catalyst (*R*,*R*)-**1** (Tf = trifluoromethanesulfonyl, Ts = 4-toluenesulfonyl). Both chiral 1,2,3,4-tetrahydro- and 1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline derivatives could be obtained in high yields with excellent enantio- and diastereoselectivity.

Asymmetric Catalysis

J. Kawai, P. K. Chikkade, Y. Shimizu,*
M. Kanai* ______ **7177 – 7180**

In Situ Catalytic Generation of Allylcopper Species for Asymmetric Allylation: Toward 1*H*-Isochromene Skeletons



Stay active: Allylcopper species can be generated in situ through catalytic intramolecular oxycupration of allenic alcohol. The allylcopper can react with various aldehydes and a ketone to give 1*H*-isochromene derivatives in an enantioselective manner (see scheme; HMPA = hexamethylphosphoramide, THF = tetrahydrofuran). The protocol is atom-economical, highly regioselective, stereoconvergent, and tolerant to free hydroxy groups.

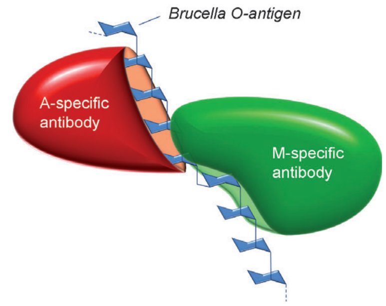
Brucellosis Detection

J. Guiard, E. Paszkiewicz, J. Sadowska,
D. R. Bundle* ______________ **7181 – 7185**

Design and Synthesis of a Universal Antigen to Detect Brucellosis

Back Cover

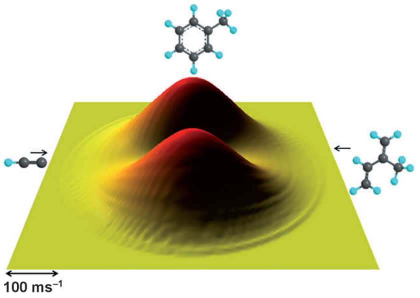
Upgrading diagnostics: A universal antigen has been prepared for the detection of brucellosis caused by any *Brucella* species that express a smooth lipopolysaccharide. This nonasaccharide, which encompasses *Brucella* A- and M-antigenic determinants, is uniquely available only by chemical synthesis.



Gas-Phase Chemistry

B. B. Dangi,* D. S. N. Parker, R. I. Kaiser,
A. Jamal, A. M. Mebel ______ **7186 – 7189**

A Combined Experimental and Theoretical Study on the Gas-Phase Synthesis of Toluene under Single Collision Conditions

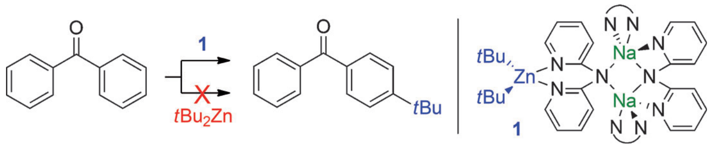


Reaction dynamics: Crossed molecular beam experiments and ab initio electronic structure calculations on the reaction of the ethynyl radical with isoprene are reported. The picture shows a flux contour map of the reaction of [D$_1$]ethynyl with isoprene forming [D$_1$]toluene and atomic hydrogen at a collision energy of 51.3 kJ mol^{-1}.

Homogeneous Catalysis

D. R. Armstrong, J. A. Garden,
A. R. Kennedy, R. E. Mulvey,*
S. D. Robertson ______________ **7190 – 7193**

Modifying Alkylzinc Reactivity with 2,2′-Dipyridylamide: Activation of *t*Bu–Zn Bonds for *para*-Alkylation of Benzophenone

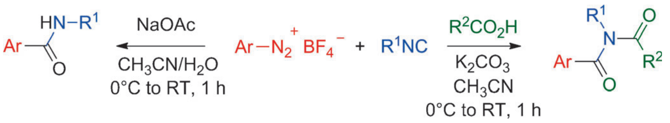


Undercover agent: Masquerading as a simple donor-acceptor complex (**1**), sodium amide substoichiometrically activates *t*Bu$_2$Zn for the challenging 1,6-addition of a *tert*-butyl group to benzophenone. In contrast, the nonactivated *t*Bu$_2$Zn is ineffectual.

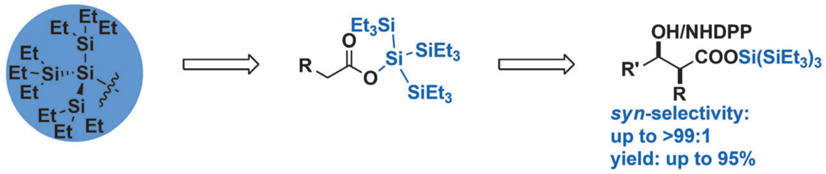
Synthetic Methods

U. M. V. Basavanag, A. Dos Santos,
L. El Kaim,* R. Gámez-Montaño,*
L. Grimaud* ______________ **7194 – 7197**

Three-Component Metal-Free Arylation of Isocyanides



Mumm's the word: The title reaction can be performed by the addition of isocyanides to benzenediazonium salts in the presence of sodium or potassium carboxylates. The reaction involves nitrilium intermediates which may be trapped by water or carboxylic acids to form amides and imides, respectively, after Mumm rearrangement.



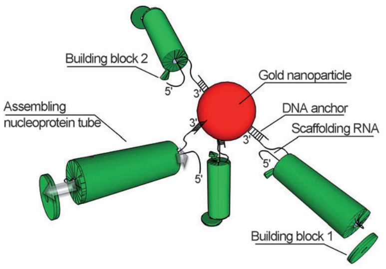
Silyl superpowers: The supersilyl group was investigated as a superior carboxylic acid protecting group. Supersilyl esters were also utilized as stable carboxylic acid synthetic equivalents in highly stereoselective aldol and Mannich reactions (see scheme). The value of this method lies in easy photodeprotection and in the rapid synthesis of polyketide subunits.

Synthetic Methods

J.-J. Tan, M. Akakura,
H. Yamamoto* ———— **7198 – 7202**

The Supersilyl Group as a Carboxylic Acid Protecting Group: Application to Highly Stereoselective Aldol and Mannich Reactions

---



Twinkle, twinkle little star: Directed self-assembly of bioinorganic hybrid nanostars with a high protein surface area was achieved by encapsidating immobilized RNA on metal beads with a plant viral protein. The selectivity of RNA hybridization to oligodeoxynucleotides exposed on the gold allowed the simultaneous fabrication of star colloids with distinct predetermined arm-length distributions in single-batch processes.

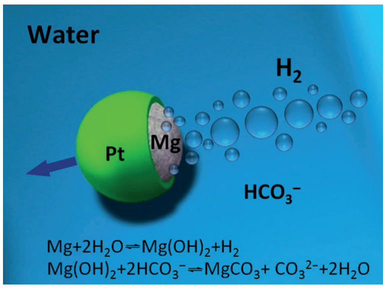
Self-Assembled Nanostructures

F. J. Eber, S. Eiben, H. Jeske,
C. Wege* ———— **7203 – 7207**

Bottom-Up-Assembled Nanostar Colloids of Gold Cores and Tubes Derived From Tobacco Mosaic Virus

---

Get your motor running: A hemocompatible Mg/Pt Janus micromotor is propelled by hydrogen bubbles generated by the magnesium–water reaction (see picture). Aqueous $NaHCO_3$ reacts with the $Mg(OH)_2$ passivation layer on the Mg surface to form water-soluble $MgCO_3$ and expose the active metal. Since the micromotor is biocompatible, it has potential applications in drug delivery and cell separation.

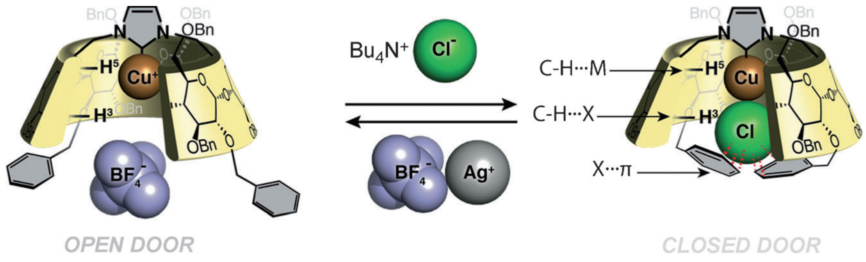


Micromotors

F. Mou, C. Chen, H. Ma, Y. Yin, Q. Wu,
J. Guan* ———— **7208 – 7212**

Self-Propelled Micromotors Driven by the Magnesium–Water Reaction and Their Hemolytic Properties

---



Don't slam the door! Cyclodextrins capped with an N-heterocyclic carbene (ICyDs) entrapped metal ions within their cavity through a novel set of interactions, including X···π, which enabled the cavity to be closed by ligand exchange (see scheme; Bn = benzyl). Although insulated from an electrode, the deeply buried metal ions retained catalytic activity. The cavity influenced the regio- and stereochemical outcome of the catalyzed reactions.

Metallocavitands

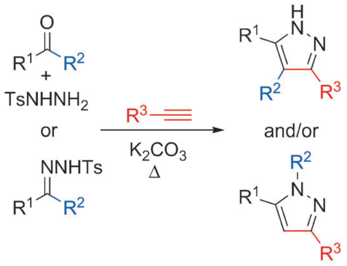
M. Guitet, P. Zhang, F. Marcelo, C. Tugny,
J. Jiménez-Barbero, O. Buriez, C. Amatore,
V. Mouriès-Mansuy, J.-P. Goddard,
L. Fensterbank, Y. Zhang, S. Roland,
M. Ménand, M. Sollogoub* **7213 – 7218**

NHC-Capped Cyclodextrins (ICyDs): Insulated Metal Complexes, Commutable Multicoordination Sphere, and Cavity-Dependent Catalysis

Synthetic Methods

M. C. Pérez-Aguilar,
C. Valdés* ______ **7219–7223**

Regioselective One-Step Synthesis of Pyrazoles from Alkynes and N-Tosylhydrazones: [3+2] Dipolar Cycloaddition/[1,5] Sigmatropic Rearrangement Cascade



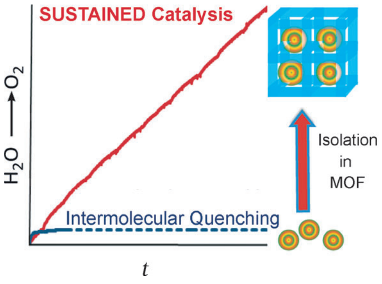
Rearrangement under control: A wide variety of 3,4,5- and 1,3,5-trisubstituted pyrazoles can be prepared from tosylhydrazones of ketones and terminal alkynes through the title reaction sequence (see scheme; Ts = 4-toluenesulfonyl). The rearrangement, and therefore, the regioselectivity of the reaction is controlled by the nature of the substituents of the tosylhydrazone.

Heterogeneous/Homogeneous Catalysis

B. Nepal, S. Das* ______ **7224–7227**

Sustained Water Oxidation by a Catalyst Cage-Isolated in a Metal–Organic Framework

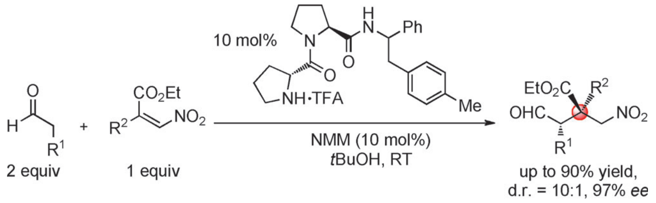
Keep 'em separated: Pores of a MOF were used to isolate a highly reactive water-oxidation catalyst ($Mn^{III}(\mu\text{-}O)_2Mn^{IV}$; spheres in picture). The resulting construct shows highly sustained water oxidation, with minimized intermolecular degradative side-reactions. This system provides a simple path to extend the lifetime of reactive catalysts without compromising their molecular definition and reactivity.



Asymmetric Catalysis

R. Kastl, H. Wennemers* ______ **7228–7232**

Peptide-Catalyzed Stereoselective Conjugate Addition Reactions Generating All-Carbon Quaternary Stereogenic Centers

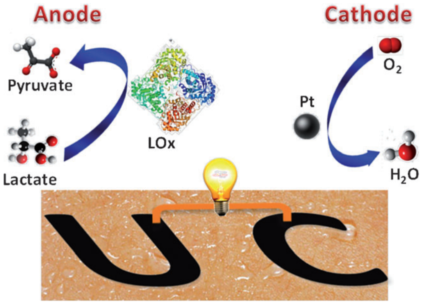


A powerful catalyst: Quaternary stereogenic centers adjacent to tertiary stereocenters were formed with high diastereoselectivities and enantioselectivities in conjugate addition reactions between aldehydes and β,β-disubstituted nitroolefins by using a peptidic catalyst (see scheme). γ-Amino acids and heterocyclic compounds bearing quaternary stereogenic centers are easily accessible from the products.

Biofuel Cells

W. Jia, G. Valdés-Ramírez, A. J. Bandodkar,
J. R. Windmiller, J. Wang* ______ **7233–7236**

Epidermal Biofuel Cells: Energy Harvesting from Human Perspiration

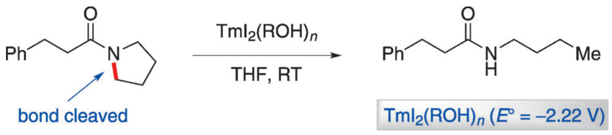


No sweat, no gain: Flexible biofuel cells functionalized with lactate oxidase (LOx) and platinum as anode and cathode materials harvested biochemical energy from human perspiration (see picture). Substantial power was generated from human sweat in real-life scenarios.

Thulium Diiodide

M. Szostak,* M. Spain,
D. J. Procter* ______ 7237 – 7241

Uncovering the Importance of Proton Donors in TmI_2-Promoted Electron Transfer: Facile C−N Bond Cleavage in Unactivated Amides

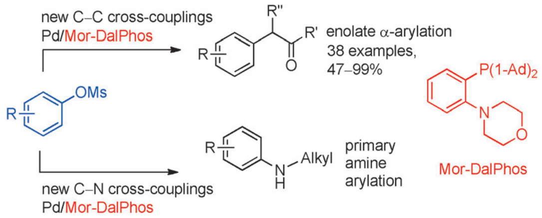


Nonclassical lanthanide(II) iodides are modern reagents for the development of challenging electron-transfer processes. It was demonstrated that alcohols are critical for the formation of a thermodynamically more powerful reductant from TmI_2 (thulium diiodide), the first nonclassical lanthanide(II) iodide in the series (TmI_2, DyI_2, NdI_2). The $TmI_2(ROH)_n$ reagent promotes an unprecedented cleavage of the σ C−N bond in amides.

Synthetic Methods

P. G. Alsabeh,
M. Stradiotto* ______ 7242 – 7246

Addressing Challenges in Palladium-Catalyzed Cross-Couplings of Aryl Mesylates: Monoarylation of Ketones and Primary Alkyl Amines

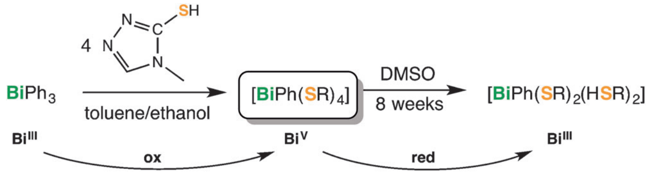


Mor(DalPhos) for Me(sylates): Described are the first examples of ketone mono-α-arylation and primary aliphatic amine monoarylation employing aryl methanesulfonate coupling partners. A range of functionalized aryl mesylates were employed with dialkyl ketones, and also with primary and secondary amines as well as the otherwise challenging coupling partners acetone and methylamine. Ad = adamantyl.

Coordination Chemistry

A. Luqman, V. L. Blair, A. M. Bond,
P. C. Andrews* ______ 7247 – 7251

Formation of Bismuth(V) Thiolates: Protolysis and Oxidation of Triphenylbismuth(III) with Heterocyclic Thiols



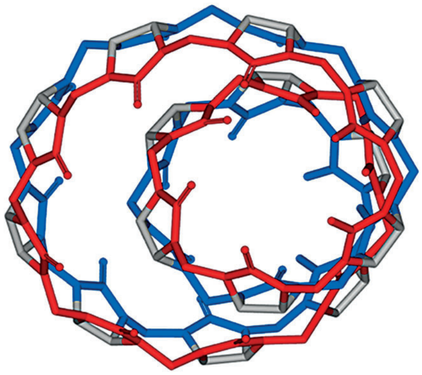
Stressing bismuth: Two monophenyl tetrathiolato Bi^{V} complexes, $[BiPh(SR)_4]$, have been prepared upon treating $BiPh_3$ in toluene/ethanol under reflux conditions with an excess of N-heterocyclic thiols (see scheme), indicating oxidation of the bismuth center. Crystallization from DMSO over several months leads to reduction of bismuth back to Bi^{III} through protonation of two of the thiolato ligands.

Macrocyclic Hosts

X.-J. Cheng, L.-L. Liang, K. Chen, N.-N. Ji, X. Xiao, J.-X. Zhang, Y.-Q. Zhang, S.-F. Xue, Q.-J. Zhu, X.-L. Ni,*
Z. Tao* ______ 7252 – 7255

Twisted Cucurbit[14]uril

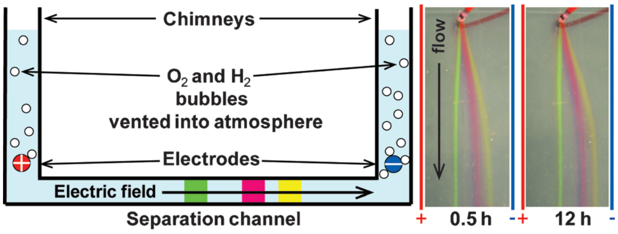
All in a twist: The largest cucurbit[*n*]uril, namely tQ[14] (see picture; colors indicate sides of the molecule) contains 14 normal glycoluril units linked by 28 methylene bridges. However, it contains a 360° twist. As a consequence, it does not have a normal cavity like the most cucurbit[*n*]urils, and instead has a folded, figure-of-eight conformation.



In-Flow Purification

F. J. Agostino, L. T. Cherney, V. Galievsky,
S. N. Krylov* ______ **7256 – 7260**

Steady-State Continuous-Flow Purification by Electrophoresis



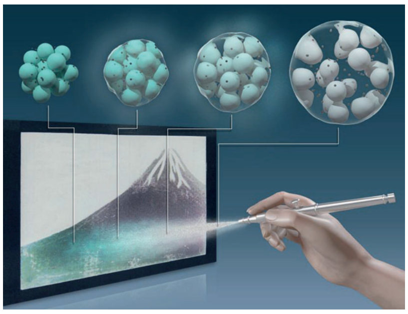
Bubble and sweep: Free-flow electrophoresis (FFE) could allow continuous-flow purification of products from continuous-flow microsynthesis. However, gas bubbles distort the separation. An open-electrolyte FFE system avoids this problem. Electrodes placed in chimneys open to the atmosphere mean bubbles are vented directly from the system and cannot enter the separation channel (see picture).

Pigments

Y. Takeoka,* S. Yoshioka,* A. Takano,
S. Arai, K. Nueangnoraj, H. Nishihara,
M. Teshima, Y. Ohtsuka,
T. Seki ______ **7261 – 7265**

Production of Colored Pigments with Amorphous Arrays of Black and White Colloidal Particles

Sprayed: Pigments with various angle-independent colors were prepared by a spray method (see picture), which is a remarkably simple method using submicrometer-sized silica particles and carbon black. The use of a polyelectrolyte that adheres to the particles can stabilize the structure of the colloidal amorphous arrays to create highly stressable, non-fading pigments.

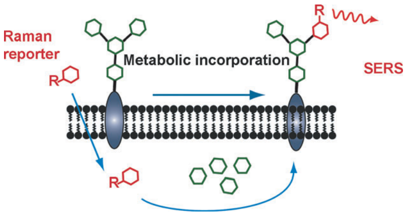


Detection of Glycans

L. Lin, X. Tian, S. Hong, P. Dai, Q. You,
R. Wang, L. Feng, C. Xie, Z. Q. Tian,*
X. Chen* ______ **7266 – 7271**

A Bioorthogonal Raman Reporter Strategy for SERS Detection of Glycans on Live Cells

Direct detection of glycans on live cells using surface-enhanced Raman scattering (SERS) has been shown. A bioorthogonal Raman reporter was directly installed onto the monosaccharide analogs. Once metabolically incorporated into cell surface glycans, the Raman reporter was detected using SERS (see picture).

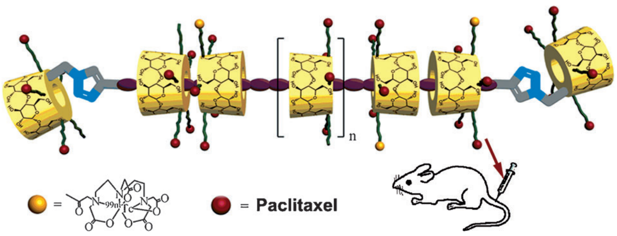


Inside Cover

Polyrotaxanes

S. L. Yu, Y. J. Zhang, X. Wang, X. Zhen,
Z. H. Zhang, W. Wu,*
X. Q. Jiang* ______ **7272 – 7277**

Synthesis of Paclitaxel-Conjugated β-Cyclodextrin Polyrotaxane and Its Antitumor Activity

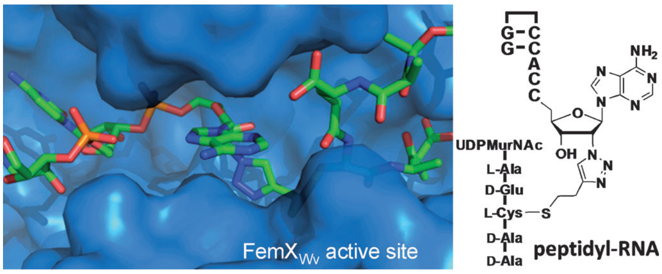


Cap it all: A β-cyclodextrin polyrotaxane was synthesized by using poly(propylene glycol) as the axle and β-cyclodextrin as the end cap. An antitumor agent, paclitaxel, was conjugated to it. The drug-conjugated polyrotaxane penetrates deep into tumors, impedes tumor growth, and prolongs the life of tumor-bearing mice better than Taxol.

RNA–Protein Complexes

M. Fonvielle, I. Li de La Sierra-Gallay, A. H. El-Sagheer, M. Lecerf, D. Patin, D. Mellal, C. Mayer, D. Blanot, N. Gale, T. Brown, H. van Tilbeurgh, M. Ethève-Quelquejeu,* M. Arthur* ________ 7278 – 7281

The Structure of FemX$_{Wv}$ in Complex with a Peptidyl-RNA Conjugate: Mechanism of Aminoacyl Transfer from Ala-tRNA^{Ala} to Peptidoglycan Precursors



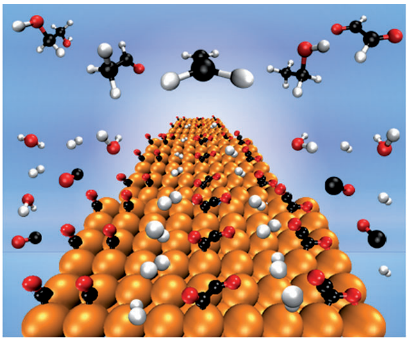
To gain insight into the catalytic mechanism of non-ribosomal amino acid transferases, peptidyl-RNA conjugates were synthesized for co-crystallization with FemX$_{Wv}$ of *Weissella viridescens*, which transfers L-Ala from Ala-tRNA^{Ala} to the peptidoglycan precursor UDP-MurNAc-pentapeptide. The structure of the resulting complex and mutational studies revealed the mechanism by which FemX$_{Wv}$ binds its substrates for substrate-assisted catalysis and stabilization of the tetrahedral intermediate.

CO Reduction Mechanism

F. Calle-Vallejo, M. T. M. Koper* ________ 7282 – 7285

Theoretical Considerations on the Electroreduction of CO to C$_2$ Species on Cu(100) Electrodes

Inside Back Cover

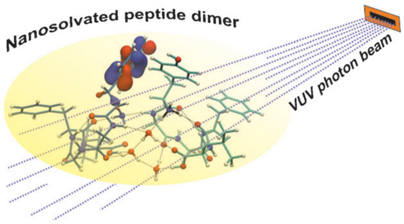


CO-products: DFT calculations are used to construct a mechanism for the electrochemical reduction of CO on Cu(100) that agrees with the experimental observations (see picture) of pH independence in the formation of C$_2$ species. The rate-determining step is an electron-transfer-mediated CO dimerization. Ethylene, acetaldehyde, and ethanol are formed through a common pathway, and adsorbed ethylene oxide is one of the reaction intermediates.

Nanosolvation

A. R. Milosavljević,* V. Z. Cerovski, F. Canon, L. Nahon, A. Giuliani* ________ 7286 – 7290

Nanosolvation-Induced Stabilization of a Protonated Peptide Dimer Isolated in the Gas Phase

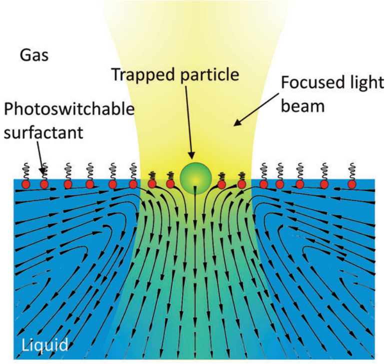


A dash of water: Nanosolvation of a leucine–enkephalin peptide dimer by only three water molecules has a dramatic impact on its stability to VUV photon irradiation. A drastic reduction of the fragmentation abundance of the hydrated protonated peptide dimer precursor, isolated in the gas phase, was observed. Calculations show that hydration in fact stabilizes the dimer structure.

Marangoni Tweezers

S. N. Varanakkottu, S. D. George, T. Baier, S. Hardt,* M. Ewald, M. Biesalski ________ 7291 – 7295

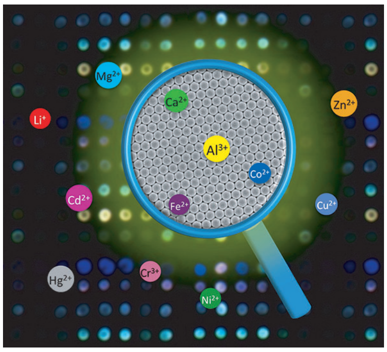
Particle Manipulation Based on Optically Controlled Free Surface Hydrodynamics



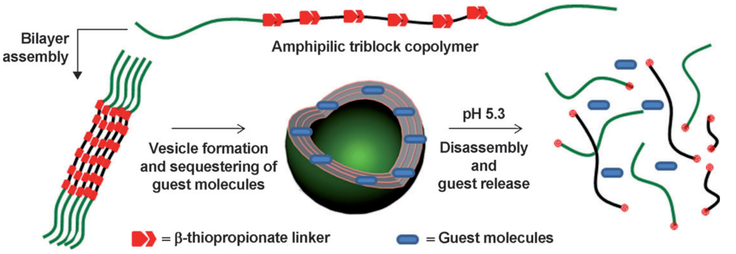
Microparticle manipulation: The photoisomerization of surfactants adsorbed at a gas–liquid interface drives a Marangoni flow that can be used for the trapping and manipulation of small particles. By switching the laser wavelength, a flow either into or away from the focal spot can be induced. The picture shows a microparticle trapped in the focal region by the inflow.

Photonic Crystals

Twelve metal ions are analyzed by a microchip that was developed for high-performance recognition and analysis. The microchip enhances fluorescence at multiple channels and improves the discriminability of multi-analyte testing. The facile fabrication of the microchip and insights into sensing efficiency will be of great importance for the development of advanced discriminant analysis for complex analytes.

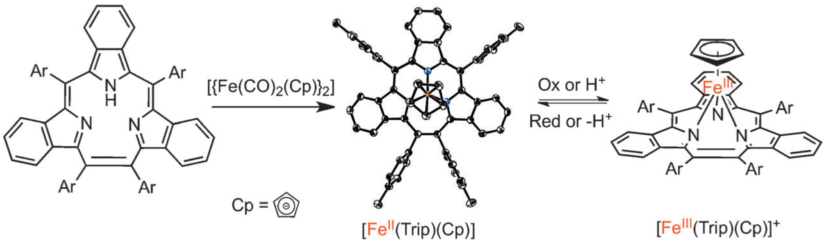


Polymersomes



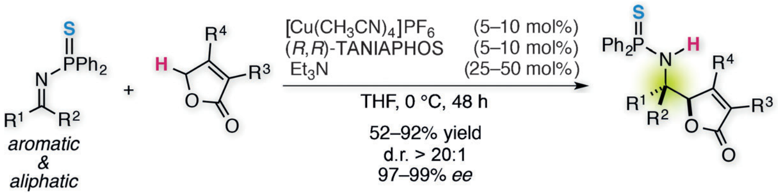
An amphiphilic triblock copolymer segmented by an acid-labile β-thiopropionate linker was synthesized from a dithiol, a diacrylate, and an acrylate-terminated hydrophilic polymer in two steps in one pot. It showed spontaneous vesicular assembly, and the stimuli-responsive disassembly at mild acidic pH values resulted in sustained release of noncovalently encapsulated guest molecules.

Metalloporphyrinoids

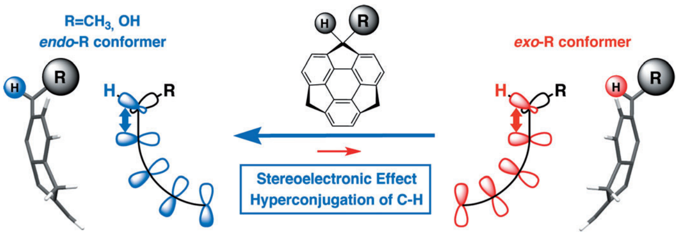


A semiferrocene complex with a [14]triphyrin(2.1.1) (TriP) ligand has been synthesized. The structure and properties are characterized by X-ray crystallographic analysis, UV/Vis spectroscopy, and variable-temperature ^{1}H NMR spectroscopy. The Fe^{II} and Fe^{III} complexes are electrochemically reversible.

Asymmetric Catalysis



A cooperative catalyst consisting of a soft Lewis acid and a hard Brønsted base promoted the title reaction. The *N*-thiophosphinoyl group on the ketimines was critical to surpass the high activation barrier through the soft–soft interaction of sulfur and copper. Mannich adducts with a tetrasubstituted stereogenic center were produced with excellent diastereo- and enantioselectivities. TANIAPHOS = ferrocenyl ligand.



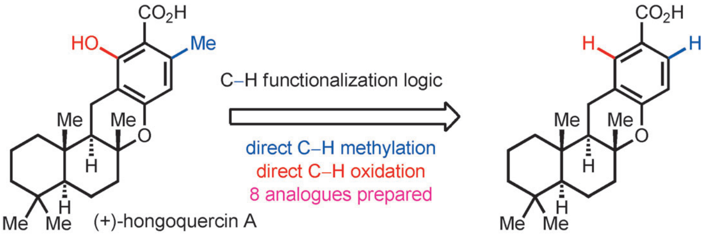
Throwing a curve: The first example of a through-bond stereoelectronic effect for curved aromatic compounds is described for buckybowls, that is, benzylic-substituted sumanenes. Methyl- and hydroxy-sumanene favor the *endo*-R conformer because of a difference in the strength, between the conformers, of the hyperconjugation of the benzylic C–H bond with the bowl.

Through-Bond Interactions

S. Higashibayashi,* S. Onogi,
H. K. Srivastava, G. N. Sastry,
Y.-T. Wu, H. Sakurai* ______ **7314 – 7316**

Stereoelectronic Effect of Curved Aromatic Structures: Favoring the Unexpected *endo* Conformation of Benzylic-Substituted Sumanene

---



The specifics: A synthesis of the sesquiterpenoid antibiotic (+)-hongoquercin A using sequential site-specific C–H methylation and oxidation reactions is described. A key advancement toward this goal was the development of a ligand-accelerated C–H methylation reaction, and enabled the generation of a library of eight structurally diverse analogues.

Synthesis Design

B. R. Rosen, L. R. Simke, P. S. Thuy-Boun,
D. D. Dixon, J.-Q. Yu,*
P. S. Baran* ______ **7317 – 7320**

C–H Functionalization Logic Enables Synthesis of (+)-Hongoquercin A and Related Compounds

---

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).

This article is available online free of charge (Open Access).

This article is accompanied by a cover picture (front or back cover, and inside or outside).

Angewandte Corrigendum

After further analysis, the authors of this Communication found that the electron diffraction pattern in Figure 5 b has unusual spacings and may not correspond to the materials investigated. As this diffraction pattern is incidental to the main theme of the manuscript, the conclusions and main findings remain unaffected.

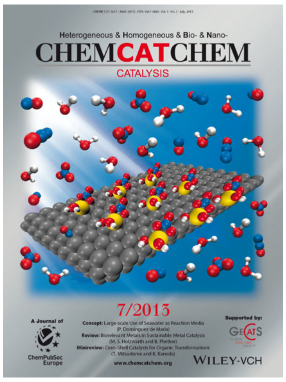
A Supramolecular Complex in Small-Molecule Solar Cells based on Contorted Aromatic Molecules

S. J. Kang, J. B. Kim, C.-Y. Chiu, S. Ahn,
T. Schiros, S. S. Lee, K. G. Yager,
M. F. Toney, Y.-L. Loo
C. Nuckolls* ______ **8594–8597**

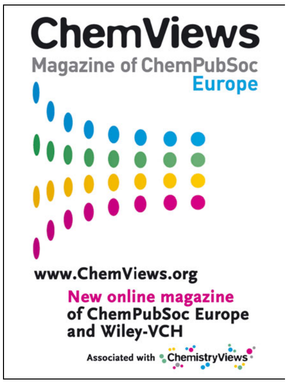
Angew. Chem. Int. Ed. **2012**, *51*

DOI: 10.1002/anie.201203330


CHEMISTRY
AN ASIAN JOURNAL
7/08 2013


CHEMCATCHEM
CATALYSIS
7/2013


CHEMPLUSCHEM
CENTERING ON CHEMISTRY
6/2013


ChemViews
Magazine of ChemPubSoc Europe
www.ChemViews.org
New online magazine of ChemPubSoc Europe and Wiley-VCH
Associated with ChemistryViews


THE RIGHT CHEMISTRY