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:

*Y. Muramatsu, T. Harada**
Catalytic Asymmetric Alkylation of Aldehydes with Grignard Reagents

*V. P. Denysenkov, D. Biglino, W. Lubitz, T. F. Prisner, M. Bennati**
Structure of the Tyrosyl Biradical in mouse R2 Ribonucleotide Reductase from High-Field PELDOR

*M. D. Eelman, J. M. Blacquiere, M. M. Moriarty, D. E. Fogg**
Shining New Light on an Old Problem: Retooling MALDI Mass Spectrometry for Organo-Transition-Metal Catalysis

L. Soderholm, P. M. Almond, S. Skanthakumar, R. E. Wilson, P. C. Burns**
The Structure of a 38-Plutonium Oxide Nanocluster: $[Pu_{38}O_{56}Cl_{54}(H_2O)_8]^{14-}$

*T. Dohi, M. Ito, K. Morimoto, M. Iwata, Y. Kita**
Single Electron Transfer Induced Oxidative Cross-Coupling of Arenes Leading to Biaryls by the Use of Organo-iodine(III) Oxidants

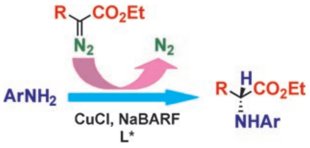
Y. Filinchuk, D. Chernyshov, A. Nevidomskyy, V. Dmitriev*
High-Pressure Polymorphism as a Step towards Destabilization of $LiBH_4$

News

Books

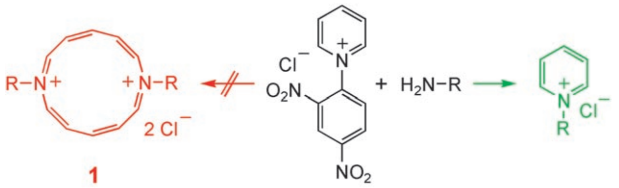
Highlights

Carbene Insertion



Back to copper: The Rh-catalyzed reactions of diazocarbonyl compounds with amines, leading to N–H insertion products, have found wide application. However, an enantioselective variant has remained elusive. A return to copper catalysis, first reported for carbene N–H insertions over 50 years ago, in the presence of chiral ligands and a large noncoordinating counterion, has resulted in enantioselective N–H insertion into anilines.

Correspondence



The 103-year-old reaction of *N*-(2,4-dinitrophenyl)pyridinium chloride with primary amines was rediscovered by two research groups recently. Since neither authors nor referees knew the pertinent literature, the products were assigned the structure of the diaza[12]annulenes **1**, although they are nothing but *N*-substituted pyridinium salts.

Essays

The dramatic societal upheavals and radical value shifts that occurred during the first half of the 20th century influenced every aspect of life, including the scientific and research systems. A biography of Heinrich Wieland, awarded the Nobel Prize for Chemistry in 1927, one embedded in a chronicle of the times, shows clearly how this one individual adapted to multiple drastic changes in his environment.

Reviews

$[B(CF_3)_4]^-$ $(CF_3)_3BC{\equiv}O$ $[(CF_3)_3BC{\equiv}As]^-$

Sought for weak coordination: The first synthesis of the $[B(CF_3)_4]^-$ ion by fluorination of the $[B(CN)_4]^-$ ion marks the beginning of a new development in the field of B-CF_3 chemistry. In concentrated sulfuric acid one of the CF_3 groups is transformed into a CO ligand. The borane carbonyl $(CF_3)_3BC{\equiv}O$ is a reactive species and excellent starting material for the synthesis of various $(CF_3)_3B$ compounds, for example, the pnicogeneethynyl complexes $[(CF_3)_3BC{\equiv}Pnic]^-$ (Pnic = N, P, As).

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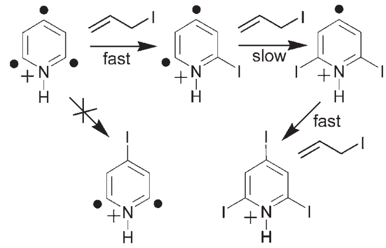
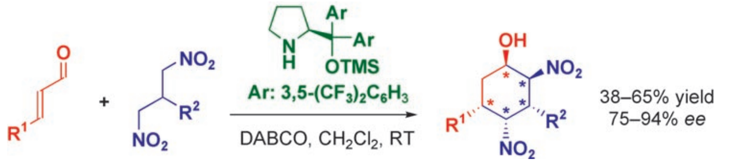
Communications

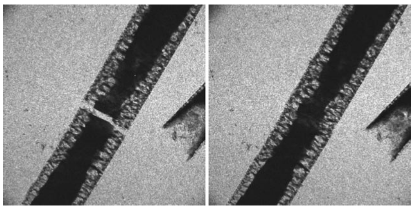


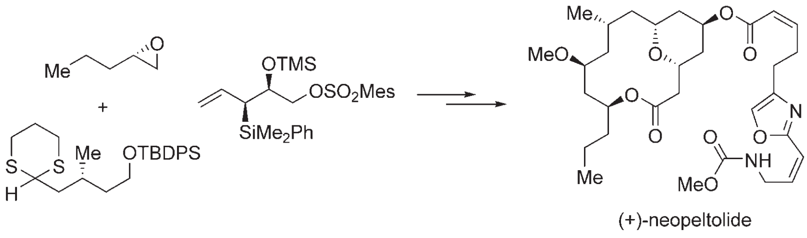
Tri-, bi-, and monoradicals: The reactivity of a σ,σ,σ-triradical, 2,4,6-tridehydropyridinium cation, was compared with that of related mono- and biradicals in a Fourier transform ion cyclotron resonance mass spectrometer. The triradical has a doublet ground state and contains three interacting radical sites. The reactivity of the triradical more closely resembles that of related monoradicals than related biradicals.



Give me five! An organocatalyzed two-component domino reaction has been developed in which two new C−C bonds and five stereocenters are created in a one-pot fashion (see scheme; DABCO = 1,4-diazabicyclo[2.2.2]octane, TMS = trimethylsilyl). The striking features of this transformation are the high preference for one diastereomer (out of 32 possible isomers) and enantioselectivities of up to 94 %.

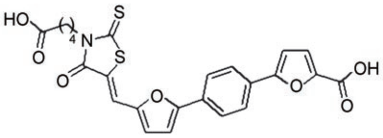
On again, off again: The reversible expansion and contraction of single crystals of [Cu(TCNQ)] induced by near-infrared laser pulses was studied with ultrafast electron microscopy (TCNQ = 7,7,8,8-tetracyanoquinodimethane). The crystal expands along the π-stacking axis of the TCNQ molecules, but not perpendicular to this axis, when exposed to light. The crystal returned to its original structure when the laser light was blocked.



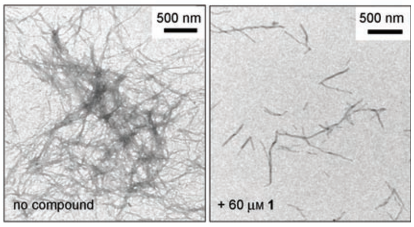


Take a closer look! The first enantioselective total synthesis, stereochemical reassignment, and absolute configuration of the metabolite neopeltolide is described (see picture). Synthetic highlights of this route include a modified Evans–Tishchenko reduction to introduce the C11 stereocenter, [4+2] annulation to construct the pyran system, and a Still–Gennari olefination to install the oxazole side chain.

Breaking up the crowd: The pathological aggregation of tau protein correlates closely with the progression of Alzheimer's disease. Rhodanine-based inhibitors of tau aggregation (e.g. **1**) have been identified, and it has been shown that tau aggregation in a cell model is reversible and can be inhibited by small molecules at nanomolar concentrations (see SEM images).



1



Aggregation Inhibitors

B. Bulic, M. Pickhardt, I. Khlistunova, J. Biernat, E.-M. Mandelkow, E. Mandelkow,* H. Waldmann* ______ **9215 – 9219**

Rhodanine-Based Tau Aggregation Inhibitors in Cell Models of Tauopathy

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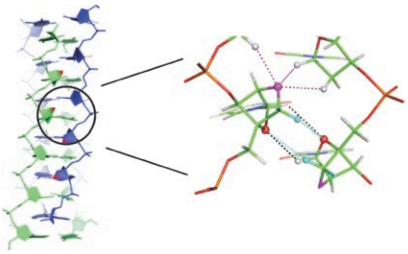
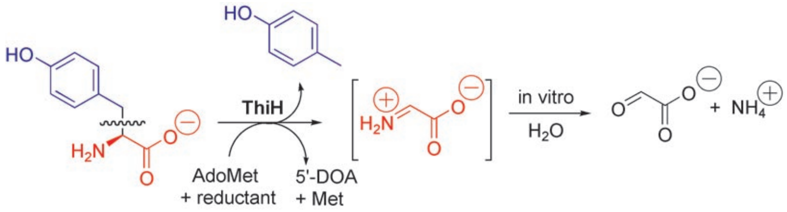
Dotting the i: The i-motif is a four-stranded DNA structure that consists of intercalated hemiprotonated C:C$^+$ base pairs. Although they contain 2′-*ribo* oxygen atoms, LNA-modified TC_5 oligonucleotides are also able to form stable tetrameric i-motif structures at low pH values (see view into one of the two narrow grooves of such a structure), as shown by a combination of CD, UV, and NMR spectroscopy.



DNA Structures

N. Kumar, J. T. Nielsen, S. Maiti,* M. Petersen* ______ **9220 – 9222**

i-Motif Formation with Locked Nucleic Acid (LNA)



In anaerobic organisms such as *E. coli* the tyrosine lyase ThiH is essential for the biosynthesis of the thiazole moiety of the vitamin thiamine. ThiH is a member of the "radical AdoMet" family. The products formed by cleavage of tyrosine in vitro have been identified and suggest a radical-mediated cleavage resulting in *p*-cresol and dehydroglycine which is hydrolyzed to glyoxylate.

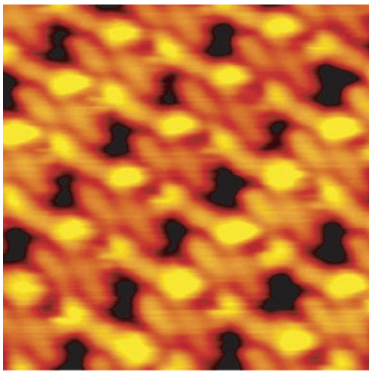
Thiamine Biosynthesis

M. Kriek, F. Martins, M. R. Challand, A. Croft, P. L. Roach* ______ **9223 – 9226**

Thiamine Biosynthesis in *Escherichia coli*: Identification of the Intermediate and By-Product Derived from Tyrosine

---

Getting a reaction: A condensation reaction occurs between a dialdehyde and an amine coadsorbed on a Au(111) surface in an ultrahigh vacuum. The self-assembled structures formed by the diimine reaction product on the surface have been investigated by scanning tunneling microscopy (see image). A solvent-free reaction path is proposed from DFT calculations.



Scanning Tunneling Microscopy

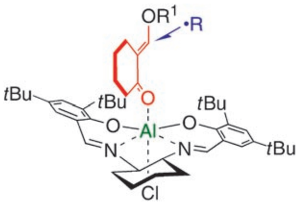
S. Weigelt, C. Busse, C. Bombis, M. M. Knudsen, K. V. Gothelf,* T. Strunskus, C. Wöll, M. Dahlbom, B. Hammer, E. Lægsgaard, F. Besenbacher, T. R. Linderoth* ______ **9227 – 9230**

Covalent Interlinking of an Aldehyde and an Amine on a Au(111) Surface in Ultrahigh Vacuum

Enantioselective Radical Reactions

M. P. Sibi,* S. Nad ________ **9231 – 9234**

Enantioselective Radical Reactions: Stereoselective Aldol Synthesis from Cyclic Ketones

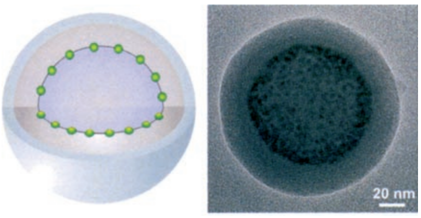


Radicalized aldols: Enones with a fixed *s-cis* geometry can undergo enantioselective radical reactions. The synthesis of aldol products derived from cyclic ketones in excellent yields and enantioselectivity demonstrates that *s-cis*-enones are excellent substrates for radical reactions. A tentative model to explain the stereochemical outcome of the reaction consists of nucleophilic radical addition to the *si* face (see picture).

Nanostructures

B. L. Sanchez-Gaytan, W. Cui, Y. Kim,
M. A. Mendez-Polanco, T. V. Duncan,
M. Fryd, B. B. Wayland,
S.-J. Park* ______________ **9235 – 9238**

Interfacial Assembly of Nanoparticles in Discrete Block-Copolymer Aggregates



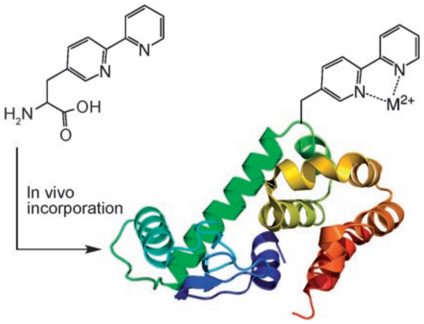
In the nanosphere: The cooperative self-assembly of CdSe/ZnS nanoparticles and an amphiphilic block copolymer leads to unique spherical assemblies. In these assemblies, the nanoparticles (green circles) are located at the interface between an outer polymer shell and an inner polymer core (see picture).

Nonnatural Amino Acids

J. Xie, W. Liu, P. G. Schultz* **9239 – 9242**

A Genetically Encoded Bidentate, Metal-Binding Amino Acid

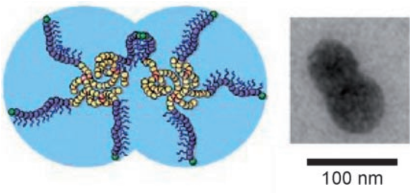
A two-ring binder: To facilitate the design of metalloproteins, the bidentate, metal-binding amino acid bipyridylalanine (BpyAla) was genetically encoded in *E. coli* in response to the amber nonsense codon with high fidelity and yield. The incorporation of BpyAla requires a BpyAla-specific aminoacyl-tRNA synthetase, which was evolved in a stepwise fashion. The structural basis of selective recognition of BpyAla by this synthetase was also determined.



Polymer Nanostructures

T. He, D. J. Adams, M. F. Butler
C. T. Yeoh, A. I. Cooper,*
S. P. Rannard* __________ **9243 – 9247**

Direct Synthesis of Anisotropic Polymer Nanoparticles

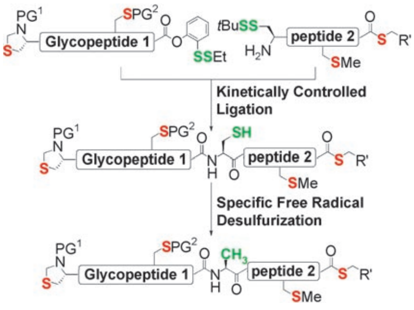


No (self-)assembly required: Both spherical and anisotropic "dumbbell" polymer nanoparticles with targeted shapes in the <100-nm size range were prepared by direct synthesis not relying on self-assembly. Atom-transfer polymerization techniques at high concentrations produce both spherical and dumbbell-like nanoparticles directly from simple vinyl monomers on a multigram scale.

Radical Reactions

Q. Wan, S. J. Danishefsky* ______ **9248 – 9252**

Free-Radical-Based, Specific Desulfurization of Cysteine: A Powerful Advance in the Synthesis of Polypeptides and Glycopolypeptides

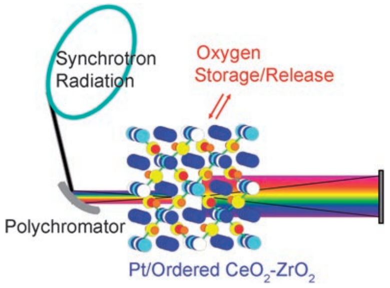


Being specific: The specific conversion of Cys (seleno-Cys) into Ala by a free-radical-mediated reduction can be achieved in an aqueous medium under mild conditions (see scheme, PG = protecting group). The conversion can be achieved in the presence of all 20 natural amino acids as well as a range of functional groups. This native chemical ligation followed by the Cys into Ala conversion will enable the synthesis of complex peptides and glycopeptides.

Heterogeneous Catalysis

T. Yamamoto, A. Suzuki, Y. Nagai, T. Tanabe, F. Dong, Y. Inada, M. Nomura, M. Tada, Y. Iwasawa* ______ **9253 – 9256**

Origin and Dynamics of Oxygen Storage/Release in a Pt/Ordered CeO_2–ZrO_2 Catalyst Studied by Time-Resolved XAFS Analysis

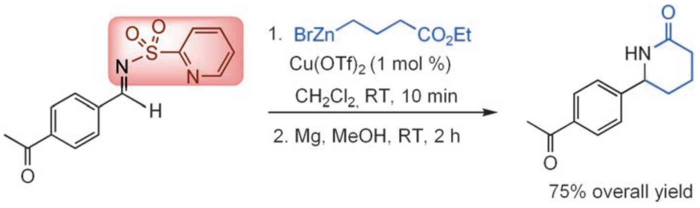


Electronic and structural dynamics of an industrially relevant Pt/CeO_2–ZrO_2 catalyst with an ordered arrangement of Ce and Zr ions during oxygen storage/release processes at 573–773 K were studied in real time by time-resolved energy-dispersive XAFS at the Zr K edge and Ce L_3 edge (see experimental setup). On the basis of these results, the roles of Ce and Zr ions in the function of the mixed-oxide catalyst were elucidated.

Addition Reactions

J. Esquivias, R. Gómez Arrayás,* J. C. Carretero* ______ **9257 – 9260**

Alkylation of Aryl *N*-(2-Pyridylsulfonyl)-aldimines with Organozinc Halides: Conciliation of Reactivity and Chemoselectivity



The best of both worlds: With a coordinating 2-pyridylsulfonyl group as the N-activating group, aromatic aldimines show unprecedented high reactivity towards the direct addition of alkyl zinc bromide reagents in the presence of catalytic amounts of $Cu(OTf)_2$. The reaction combines high reactivity with wide functional-group compatibility to provide ready access to functionalized benzylamines and derivatives (see example). Tf = trifluoromethanesulfonyl.

Heterocycle Synthesis

A. López-Pérez, R. Robles-Machín, J. Adrio, J. C. Carretero* ______ **9261 – 9264**

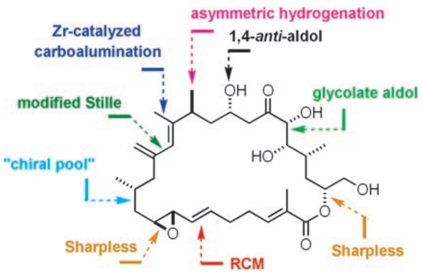
Oligopyrrole Synthesis by 1,3-Dipolar Cycloaddition of Azomethine Ylides with Bissulfonyl Ethylenes

One by one or two by two: In a general approach to the iterative construction of oligopyrroles, the cycloaddition of azomethine ylides derived from pyrrolyl α-iminoesters with 1,2-bis(phenylsulfonyl)ethylene is followed by the elimination of the sulfonyl groups in situ under basic conditions. This strategy is amenable to the introduction of one or two pyrrole units in each iterative cycle.

Natural Product Synthesis

A. Fürstner,* L. C. Bouchez, J.-A. Funel, V. Liepins, F.-H. Porée, R. Gilmour, F. Beaufils, D. Laurich, M. Tamiya ______ **9265–9270**

Total Syntheses of Amphidinolide H and G



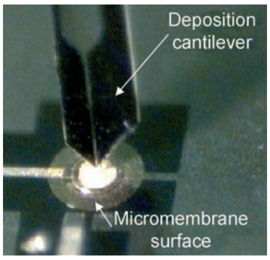
Eureka! The first conquest of the exceptionally potent cytotoxic agent amphidinolide H, which exhibits activity in the picomolar range against human epidermoid cancer cells, was long overdue. The successful route critically hinges upon the scrupulous optimization of the fragment-coupling events (see picture; RCM = ring-closing metathesis) and on the careful adjustment of the peripheral protecting-group pattern.

Biosensors

C. Ayela,* F. Vandevelde, D. Lagrange, K. Haupt,* L. Nicu ______ **9271–9274**

Combining Resonant Piezoelectric Micromembranes with Molecularly Imprinted Polymers

Layered chips: The experimental proof of concept of the combination of resonant microelectromechanical systems with molecularly imprinted polymers (MIPs) has been shown for the first time. The use of micromembrane gravimetric sensors carrying piezoelectric thin films, the surfaces of which are coated with MIPs by using a cantilever-based deposition tool (see image), is reported. The multiplexed format of the chips shows the potential of the system for the specific, label-free, reliable detection of target molecules.

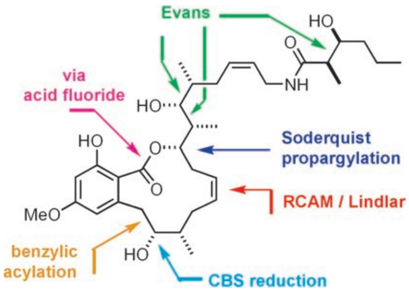


Natural Product Synthesis

A. Fürstner,* M. Bindl, L. Jean ______ **9275–9278**

Concise Total Synthesis of Cruentaren A

Converging on the target: The highly cytotoxic F-ATPase inhibitor cruentaren A constitutes an interesting lead in the quest for innovative chemotherapeutic agents for the treatment of various diseases, including cancer. Its synthesis was achieved in an overall yield of 3% by an expeditious convergent route involving a ring-closing alkyne metathesis reaction (RCAM) for the formation of the macrocyclic ring (see picture).

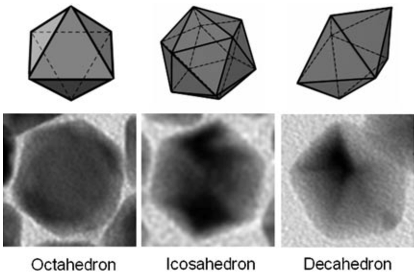


Shape-Controlled Nanoparticles

B. Lim, Y. Xiong, Y. Xia* ______ **9279–9282**

A Water-Based Synthesis of Octahedral, Decahedral, and Icosahedral Pd Nanocrystals

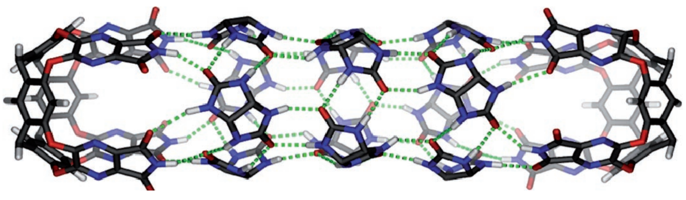
Shapes from water: Pd nanocrystals with controllable shapes are synthesized by reducing a Pd salt with citric acid in aqueous solution. Citric acid favors the formation of octahedra, icosahedra, or decahedra (see picture) owing to its strong binding to the {111} facets of Pd. Shape control of these nanocrystals is readily accomplished by adjusting the amounts of Na_2PdCl_4 precursor and citric acid added to the reaction mixture.



Extended Capsules

D. Ajami, J. Rebek, Jr.* ______ 9283 – 9286

Longer Guests Drive the Reversible Assembly of Hyperextended Capsules

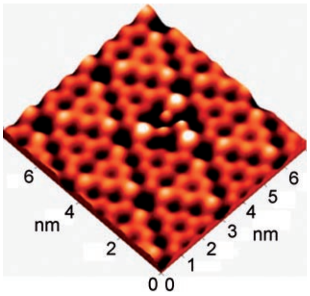


Hyperextension: A hydrogen-bonded, dimeric capsule can be expanded with four, eight, or twelve glycoluril spacers (see picture) that increase the cavity's volume by up to 530 Å^3 and its length by up to 21 Å. The extended assemblies are chiral and encapsulate a variety of normal alkanes. The expanded capsules suggest that increasingly complex capsules may emerge from other spacers with hydrogen-bonding capabilities and curved surfaces.

Silicon Surface Chemistry

Y. Makoudi, M. Arab, F. Palmino,
E. Duverger, C. Ramseyer, F. Picaud,
F. Chérioux* ______ 9287 – 9290

A Stable Room-Temperature Molecular Assembly of Zwitterionic Organic Dipoles Guided by a Si(111)-7×7 Template Effect



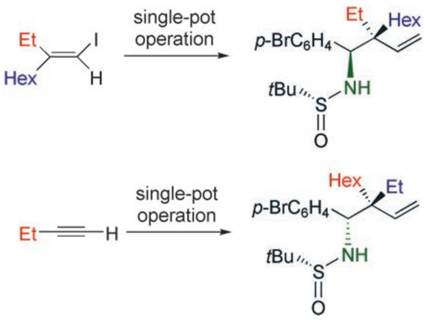
Chiral assemblies of achiral molecules: High-resolution STM images of zwitterionic organic dipoles deposited on Si(111)-7×7 show a chiral molecular assembly on this surface (see picture). Density functional calculations demonstrate that a sulfonato group can act as an electrostatic shield that protects the π skeleton of organic molecules from the dangling bonds of semiconductor surfaces, which is a major advance in the deposition of π-conjugated molecules.

Asymmetric Synthesis

G. Kolodney, G. Sklute, S. Perrone,
P. Knochel, I. Marek* ______ 9291 – 9294

Diastereodivergent Synthesis of Enantiomerically Pure Homoallylic Amine Derivatives Containing Quaternary Carbon Stereocenters

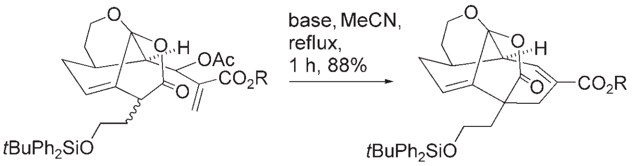
Freedom of choice: Both enantiomers of free homoallylic amines with two stereogenic centers (including a quaternary center) can be prepared at will from vinyl copper intermediates derived from either a vinyl iodide or an alkyne (see examples; the sulfinyl group is cleaved readily under mild acidic conditions). In this one-pot strategy, zinc homologation of the vinyl copper species is followed by treatment with a sulfinylimine derivative.



Synthetic Methods

B. Prabhudas, D. L. J. Clive* 9295 – 9297

All-Carbon Intramolecular Conjugate Displacement Reactions: An Effective Route to Carbocycles

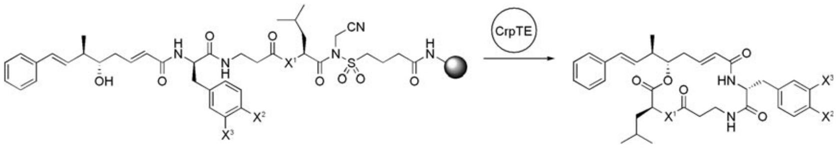


Working together: Synergy between Michael addition and S$_N$2′ displacement allows stabilized carbanions or the nucleophilic carbon atoms of enamines to undergo intramolecular addition to an α,β-unsaturated ester unit bearing an allylic leaving group to generate unsaturated carbocycles (see scheme). The starting esters are available by a selenium-based alternative to the classical Baylis–Hillman reaction, and complex structures can be assembled.

Solid-Phase Methods

W. Seufert, Z. Q. Beck,
D. H. Sherman* ______ **9298 – 9300**

Enzymatic Release and Macrolactonization of Cryptophycins from a Safety-Catch Solid Support

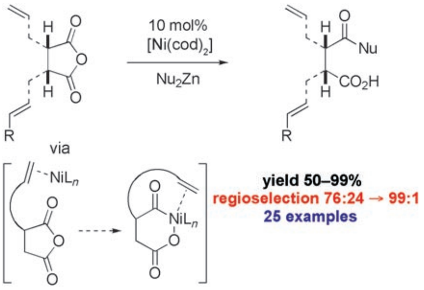


Thioesters need not apply: Cryptophycin thioesterase (CrpTE) cleaves and macrolactonizes linear cryptophycin substrates bound to activated safety-catch PEGA resin. This novel enzymatic solid-phase approach was used to further investigate the tolerance of CrpTE for structural variations of substrates.

Regioselective Cross-Coupling

R. L. Rogers, J. L. Moore,
T. Rovis* ______ **9301 – 9304**

Alkene-Directed Regioselective Nickel-Catalyzed Cross-Coupling of Cyclic Anhydrides with Diorganozinc Reagents



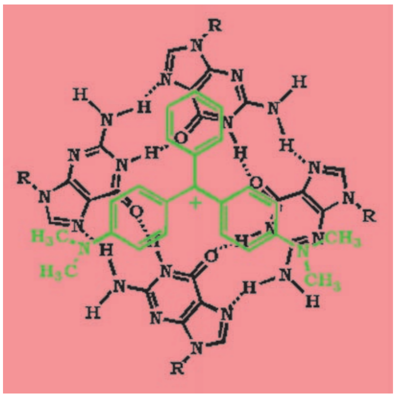
The -enes have it! A resident alkene directs a nickel-catalyzed cross-coupling of cyclic anhydrides with diorganozinc reagents. Relative directing effects parallel the stability of nickel–alkene complexes, with less-hindered terminal olefins dominating over internal olefins.

Dye Binding

A. C. Bhasikuttan,* J. Mohanty,
H. Pal ______ **9305 – 9307**

Interaction of Malachite Green with Guanine-Rich Single-Stranded DNA: Preferential Binding to a G-Quadruplex

Bound to be better: The formation of a strong complex between the chromophoric dye malachite green (MG, in green) and the G-quadruplex structure (represented in black) of the guanine-rich single-strand oligomer sequence d(G$_2$T)$_{13}$G results in a 100-fold enhancement of the fluorescence yield of MG. The existence of an intra- or interstrand G-quadruplex structure depends on the oligomer concentration and the ionic strength of the solution.

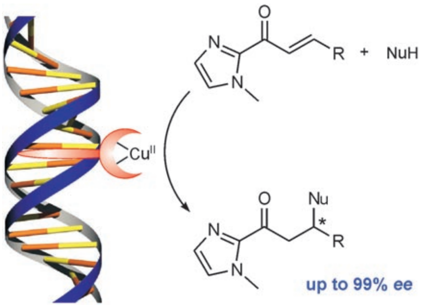


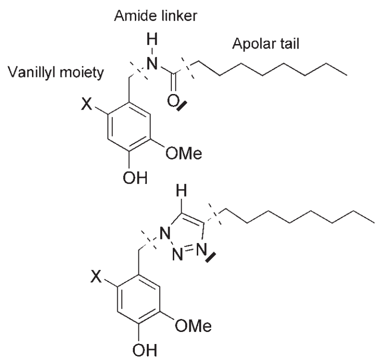
Asymmetric Catalysis

D. Coquière, B. L. Feringa,
G. Roelfes* ______ **9308 – 9311**

DNA-Based Catalytic Enantioselective Michael Reactions in Water

High, but not dry: A highly enantioselective Michael reaction in water has been developed by using a simple DNA-based catalyst. Enantioselectivities of up to 99% *ee* could be obtained by using nitromethane and dimethyl malonate as the nucleophiles and α,β-unsaturated 2-acylimidazoles as the Michael acceptors. The reactions can be performed on a preparative scale and the catalyst can be recycled.





Fooling nature: The replacement of amide and alkene groups in a biological setting with the 1,2,3-triazole group led to the discovery of compounds with a unique vanilloid/cannabinoid mixed profile. For example, the natural amides (see picture, above) and their triazole mimics (below) exhibit similar agonistic (X = H) or antagonistic (X = I) activity towards the TRPV1 receptor; however, only the triazole derivatives also show cannabinomimetic activity.

Drug Design

G. Appendino,* S. Bacchiega, A. Minassi, M. G. Cascio, L. De Petrocellis, V. Di Marzo* ———— **9312 – 9315**

The 1,2,3-Triazole Ring as a Peptido- and Olefinomimetic Element: Discovery of Click Vanilloids and Cannabinoids

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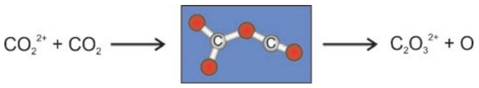


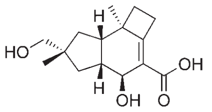
100 years after the prediction of the existence of C_2O_3 by Berthelot, doubly charged $C_2O_3^{2+}$ has been identified as a product in the reaction of CO_2^{2+} with CO_2 (see scheme). The occurrence of this reaction for such a small dication indicates that bond-forming processes might play a much larger role in reactions of dications than has been anticipated to date.

Dications

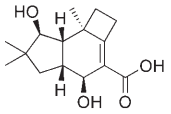
J. Roithová, C. L. Ricketts, D. Schröder,* S. D. Price ———— **9316 – 9319**

Bond Formation with Maintenance of Twofold Charge: Generation of $C_2O_3^{2+}$ in the Reaction of CO_2^{2+} with CO_2

Fresh pasture for the [2+2+2] cycloaddition: The two sesquiterpenoids pasteurestin A and B, which exhibit strong and selective antibacterial activity against *Pasteurella haemolytica*, have been prepared in a synthesis relying on a [2+2+2] Vollhardt enediyne cycloaddition. The previously unknown absolute and relative configurations were established, and the biological profile was specified more precisely.



pasteurestin A



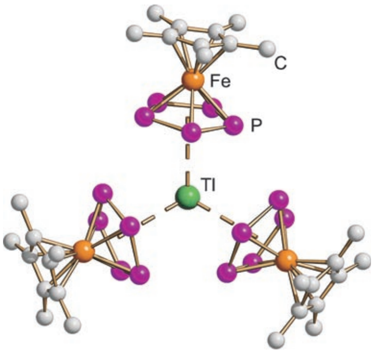
pasteurestin B

Natural Product Synthesis

M. Kögl, L. Brecker, R. Warrass, J. Mulzer* ———— **9320 – 9322**

Total Synthesis and Configurational Assignment of Pasteurestin A and B

Pentaphosphaferrocene coordinates as a π ligand to the large monocation Tl$^+$. In addition, one of the phosphorus atoms of each *cyclo*-P_5 moiety coordinates to a neighboring Tl$^+$ ion to give a one-dimensional polymer. Even at low temperatures, fast rotation of the P_5 rings is observed in solution and in the solid state.



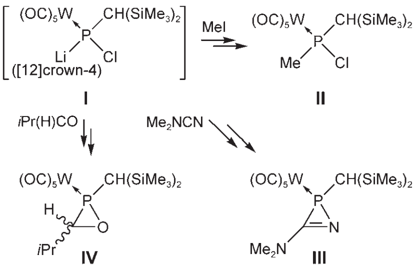
Coordination Polymers

S. Welsch, L. J. Gregoriades, M. Sierka, M. Zabel, A. V. Virovets, M. Scheer* ———— **9323 – 9326**

Unusual Coordination Behavior of P_n-Ligand Complexes with Tl$^+$

Contents

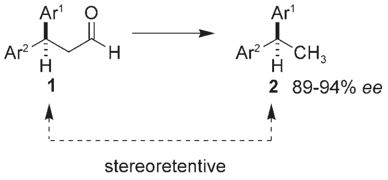
Phosphinidenoid Complexes



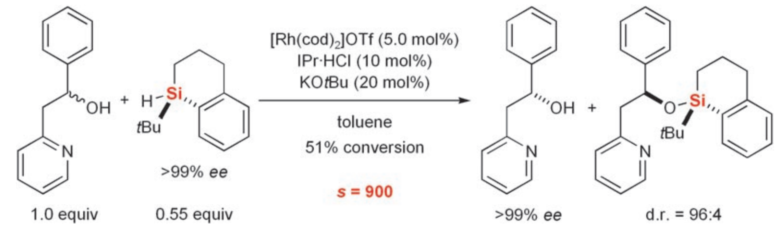
Caught in the trap: Two different routes to the thermally unstable phosphinidenoid complex **I** are described, and chemical evidence for this novel intermediate is provided through selective reactions. For example, methyl iodide, dimethylcyanamide, or butyraldehyde furnished complexes **II**, **III**, and **IV** (see scheme) under very mild conditions.

Asymmetric Catalysis

Cut it out! Convenient procedures have been delineated for the synthesis of optically active, functionalized 1,1-diarylethanes by decarbonylation of β,β-diarylpropionaldehydes. The process can be conducted as a one-pot 1,4-addition/decarbonylation sequence. Aldehydes are used as removable steering groups in this new strategy for the preparation of optically active building blocks.

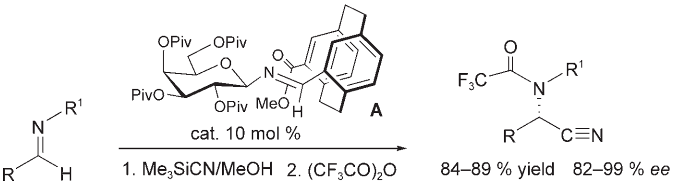


Kinetic Resolution



Slick silicon: A low-molecular-weight silane ($C_{13}H_{20}Si$, 204.38 $g\,mol^{-1}$) with silicon-centered chirality is capable of discriminating enantiomeric rhodium–substrate complexes in dehydrogenative Si–O coupling reactions with outstanding selectivity factors (see scheme, s = selectivity factor).

Organocatalysis



Self-activation: *N*-Glycosyl imines **A** of planar chiral [2.2]paracyclophane carbaldehydes act as efficient enantioselective organocatalysts for the Strecker synthesis of α-amino nitriles, although they do not contain a hydrogen-bond donor or a Brønsted acid function. They activate themselves by deprotononation of hydrogen cyanide and catalyze the formation of both aliphatic and aromatic amino nitriles with high enantioselctivity.

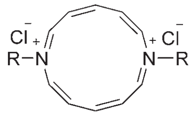
Supporting information is available on the WWW (see article for access details).

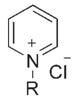
A video clip is available as Supporting Information on the WWW (see article for access details).

Service

Corrigendum

The authors of this Communication wish to alter the proposed structure of annulene **1**, a system that had previously been reported by Yamaguchi et al.[1] After one of the authors (F.M.M.) had originally inspected the then available analytical data (^{1}H and ^{13}C NMR spectra, elemental analysis, and ESI-MS data), he affirmed that they were (and still are) consistent with the annulene system. In particular, parent mass spectral signals at *m*/*z* 531.44353, 587.50648, and 643.56867 for the $R = C_{12}H_{25}$, $C_{14}H_{29}$, and $C_{16}H_{33}$ derivatives, respectively, all correspond to the mass of [**1**$-Cl^-$]$^+$. Recently, however, Prof. M. Cristl suggested[2] that the pyridinium salt **2** would be an alternative and more likely possibility. There exists an intriguing ambiguity in this case because **1** and **2** have indistinguishable NMR spectra and elemental analyses and because our [**1**$-2\,Cl^-$]$^{2+}$ base peak and the [**2**$-Cl^-$]$^+$ parent peak happen to have identical masses. We are now able to differentiate the two structures through weak ^{13}C-containing MS signals. These signals have a shift one mass unit higher than the all-^{12}C signal (consistent with [**2**$-Cl^-$]$^+$) as opposed to 0.5 units higher (consistent with [**1**$-2\,Cl^-$]$^{2+}$). In view of these new data, our peaks at $m/z > 500$ must, we surmise, arise from dimers of **2** in the gas phase. Fortunately, the altered identity of the compound in no way affects our high-level calculations on the annulene structure. Moreover, our conclusion based on the NMR data, namely, that the terminal methyl groups of the chains loop within a micelle so as to contact the micelle surface, remains valid, although the micelles are now more classical in nature than we had previously envisioned.





$R = C_{12}H_{25}$, $C_{14}H_{29}$, and $C_{16}H_{33}$

1

2

[12]Annulene Gemini Surfactants: Structure and Self-Assembly

L. Shi, D. Lundberg, D. G. Musaev, F. M. Menger* ———— **5889–5891**

Angew. Chem. Int. Ed. **2007**, *46*

DOI 10.1002/anie.200702140

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[1] I. Yamaguchi, Y. Gobara, M. Sato, *Org. Lett.* **2006**, *8*, 4279.

[2] M. Christl, private communication.

Corrigendum

Metal-Free Catalytic Hydrogenation

P. A. Chase, G. C. Welch, T. Jurca,
D. W. Stephan* ____________ **8050–8053**

Angew. Chem. Int. Ed. **2007**, *46*

DOI 10.1002/anie.200702908

In their Communication the authors stated that “non-transition-metal catalysts for hydrogenation reactions are all but unknown.” However, it should be noted that non-transition-metal systems have been shown to effect hydrogenation under more forcing conditions. For example, DeWitt, Ramp, and Trapasso demonstrated hydrogenation with $i\mathrm{Pr}_3\mathrm{B}$ under 67 atm (1000 psi) H_2 at 220 °C.[1] Similarly, Haenel and co-workers[2] among others[3] showed hydrogenation of coal under almost 148 atm (15 MPa) H_2 and at 280–350 °C using BI_3 or alkyl boranes. As well, superacid systems have also been shown to effect hydrogenation of alkenes at H_2 pressures of at least 35 atm.[4]

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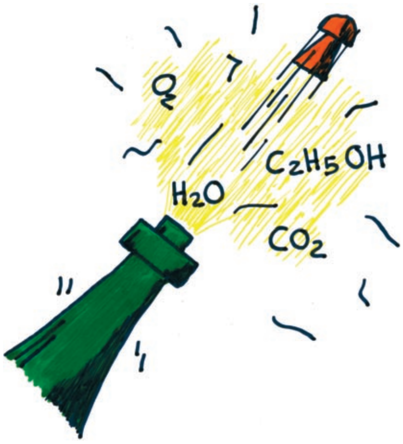
[1] a) E. J. DeWitt, F. L. Ramp, L. E. Trapasso, *J. Am. Chem. Soc.* **1961**, *83*, 4672 – 4672; b) F. L. Ramp, E. J. DeWitt, L. E. Trapasso, *Org. Chem.* **1962**, *27*, 4368 – 4372.

[2] a) E. Osthaus, M. W. Haenel in *Coal Science and Technology*, *Vol. 11*, Elsevier, Amsterdam, **1987**, pp. 765 – 768 (Proc. 1987 Intern. Conf. Coal Sci., Eds.: J. A. Moulijn, K. A. Nater, H. A. G. Chermin); b) M. Yalpani, R. Köster, M. W. Haenel, *Erdoel Kohle Erdgas Petrochem.* **1990**, *43*, 344 – 347; c) M. W. Haenel, J. Narangerel, U.-B. Richter, A. Rufinska, *Angew. Chem.* **2006**, *118*, 1077 – 1082; *Angew. Chem. Int. Ed.* **2006**, *45*, 1061 – 1066; d) M. W. Haenel, J. Narangerel, U.-B. Richter, A. Rufinska, *Prep. Pap. Am. Chem. Soc. Div. Fuel Chem.* **2006**, *51*, 741 – 742.

[3] a) M. Yalpani, T. Lunow, R. Köster, *Chem. Ber.* **1989**, *122*, 687 – 693; b) M. Yalpani, R. Köster, *Chem. Ber.* **1990**, *123*, 719 – 724.

[4] a) M. Siskin, *J. Am. Chem. Soc.* **1974**, *96*, 3641; b) J. Wristers, *J. Am. Chem. Soc.* **1975**, *97*, 4312.



The editorial staff and the publishers thank all readers, authors, referees, and advertisers for their interest and support over the past year and wish them all a happy new year.