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:

*T. Robert, J. Velder, H.-G. Schmalz**
Enantioselective Copper-Catalyzed 1,4-Addition of Grignard Reagents to Cyclohexenone Using Taddol-Derived Phosphine–Phosphite Ligands and 2-Methyl-THF as a Solvent

*A. D. Shaller, W. Wang, H. Gan, A. D. Q. Li**
Tunable Molecular Assembly Codes Direct Reaction Pathways

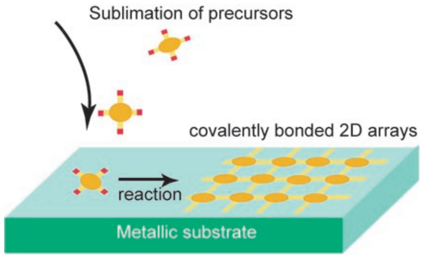
D. Staack, A. Fridman, A. Gutsol, Y. Gogotsi, G. Friedman**
Nanoscale Corona Discharge in Liquids Enabling Nanosecond Optical Emission Spectroscopy

*C. Hawner, K. Li, V. Cirriez, A. Alexakis**
Copper-Catalyzed Asymmetric Conjugate Addition of Aryl Aluminum Reagents to Trisubstituted Enones: Construction of Aryl-Substituted Quaternary Centers

Books

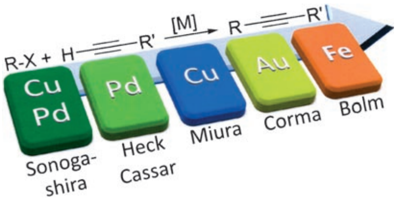
Highlights

Beyond supramolecular self-assembly: On-surface covalent coupling of organic precursors is a powerful method to obtain 1D or 2D robust molecular arrays on a substrate (see picture) that have numerous potential applications in nanotechnology. Significant advances have recently been made in this field including imine formation, dehydration of boronic acids, esterification, as well as radical and carbene coupling reactions.



Surface Chemistry

On-Surface Covalent Coupling in Ultrahigh Vacuum



Commoners displacing the nobility? The scope of the Sonogashira coupling is widening with the discovery of new catalytic systems based on a variety of metals (see picture). In particular, cheap common metals are finding a place in transformations that were previously controlled by noble metals. The developments are examined, and the advantages and disadvantages of the various catalytic systems are discussed.

C–C Coupling

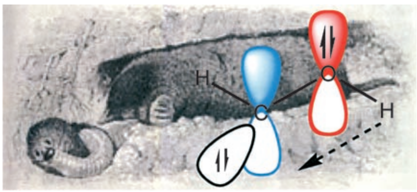
Catalysts for the Sonogashira Coupling—The Crownless Again Shall Be King

Tunnel Effect

G. Bucher* ________ **6957 – 6958**

Hydroxycarbene: Watching a Molecular Mole at Work

Finding a pico-mole: like a mole, hydroxycarbene prefers to tunnel through barriers. Generated from glyoxylic acid by pyrolysis, H–C–OH rearranges to formaldehyde within two hours even in solid argon at $T = 10$ K. This behavior is best rationalized by quantum mechanical tunneling.

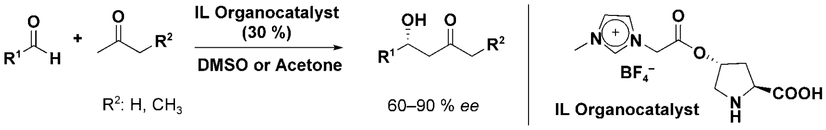


Minireviews

Ionic Liquids

P. Domínguez de María* ___ **6960 – 6968**

“Nonsolvent” Applications of Ionic Liquids in Biotransformations and Organocatalysis



More than mere solvents: Room-temperature ionic liquids (RTILs) are generally regarded as promising neoteric solvents for bio- and organocatalytic reactions. This Minireview highlights other applications of RTILs and shows that the potential of these compounds extends well beyond their use as versatile solvents (see example in scheme). Many of the concepts examined can be implemented readily in other areas of chemistry. DMSO = dimethyl sulfoxide.

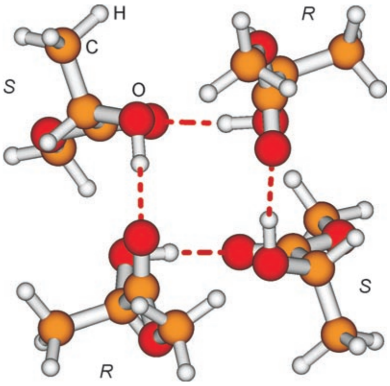
Reviews

Chirality

A. Zehnacker,*
M. A. Suhm* ________ **6970 – 6992**

Chirality Recognition between Neutral Molecules in the Gas Phase

Relative handedness matters: Chirality recognition phenomena may be classified according to the lifetime of the chiral configurations of the interacting partners, leading to differentiation between chirality discrimination, chirality induction, and chirality synchronization processes. These phenomena are studied in vacuum isolation at low temperature, using rotational, vibrational, electronic, and photoionization spectroscopy.



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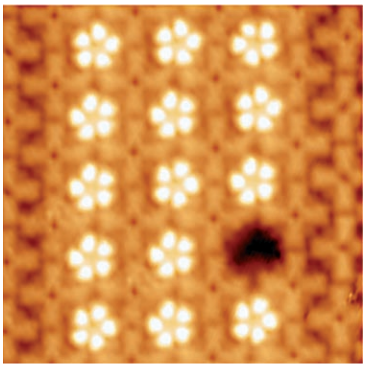
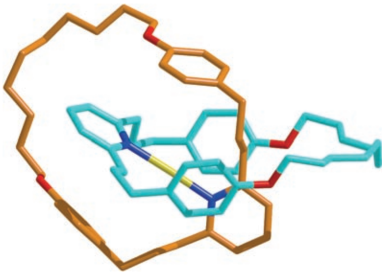
Communications



Reading between the lines: Three types of weakly bonded networks are observed when octachlorozinc phthalocyanine molecules are adsorbed onto Ag(111). Insertion of a corannulene guest into these phases to give either stable lines or chessboard structures can be observed by scanning tunneling microscopy (see picture). Corannulene molecules can be removed from the bicomponent packing at 4.6 K, which leads to artificial patterning of the surface.

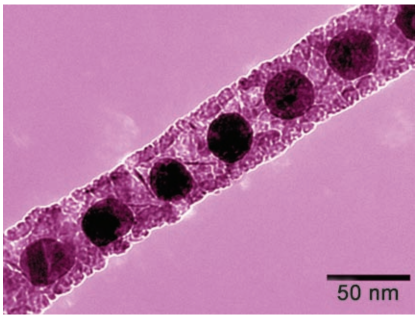
Supramolecular Chemistry



Gold member: The last of the simple metal coordination geometries (linear) joins the family of metal–ligand arrangements that have been used to template the formation of mechanical bonds. Both catenanes and rotaxanes are assembled about a gold(I) template. The picture shows the molecular structure of the gold(I) catenate, viewed parallel to its N–Au–N bond.

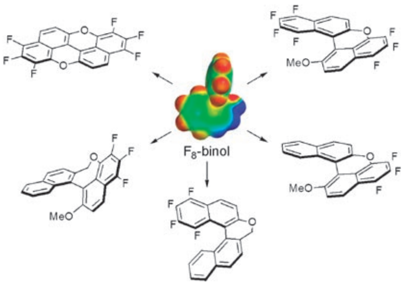
Gold(I)-Template Synthesis

Pt@$CoAl_2O_4$ inorganic nanopeapods (see picture) consisting of well-defined Pt nanoparticle chains embedded in $CoAl_2O_4$ are synthesized by the pulsed electrodeposition of Co/Pt multilayered nanowires into an anodic aluminum oxide (AAO) membrane and a subsequent high-temperature solid-state reaction between Co/Pt nanowires and AAO. The pulse durations for Pt and Co depositions control the size and separation of Pt nanoparticles.

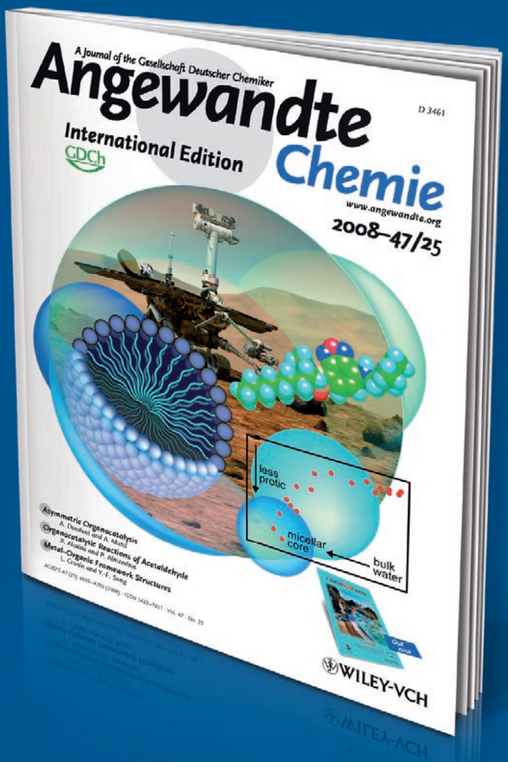


Nanoparticle Chains

Partially fluorinated binol scaffolds (see picture) offer a versatile entry into helically chiral materials. The different fluorine substitution patterns in these molecules lead to substantial changes in their crystal packing arrangements, which should facilitate the discovery and development of novel materials for applications ranging from semiconductor synthesis to catalysis.



Fluoroaromatics



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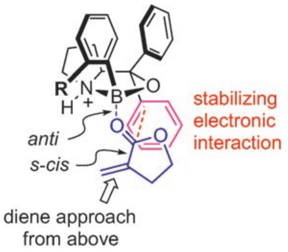

All *cis*-tems go! The first detailed computational investigations into the title reaction validate Corey's two pre-transition-state models and reveal a third Lewis acid coordination mode (see picture), which operates for esters having *s-cis* $C{=}C{-}C{=}O$ groups. The new pre-transition-state model explains the unexpected enantioselectivity witnessed for several Diels–Alder reactions and does not involve a C−H···O hydrogen bond.

Cycloaddition

M. N. Paddon-Row,* L. C. H. Kwan,
A. C. Willis,
M. S. Sherburn* **7013 – 7017**

Enantioselective Oxazaborolidinium-Catalyzed Diels–Alder Reactions without CH····O Hydrogen Bonding

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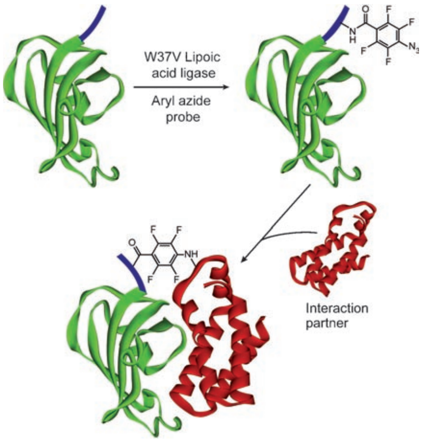

Labeled and linked: The small-molecule binding site of *Escherichia coli* lipoic acid ligase was re-engineered to accept a fluorinated aryl azide probe in place of lipoic acid. Labeling with this mutant is highly specific for LAP fusion proteins. In cell lysate, FK506 binding protein was labeled and rapamycin-dependent photo-cross-linking to its interaction partner was demonstrated.

Enzyme Engineering

H. Baruah, S. Puthenveetil, Y.-A. Choi,
S. Shah, A. Y. Ting* **7018 – 7021**

An Engineered Aryl Azide Ligase for Site-Specific Mapping of Protein–Protein Interactions through Photo-Cross-Linking

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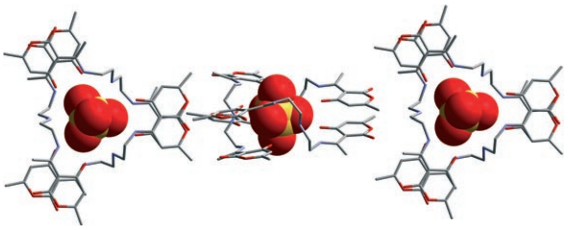

One ring to rule them out: Preorganization of simple polyamine podands in the presence of nitrate or sulfate affords a new kind of C_3-symmetrical supramolecular ring. Although not rigid, the ring's cavity is stabilized by a network of noncovalent interactions and displays an amazing level of selectivity for these two anions in a number of competitive anion/solvent environments.

Supramolecular complexes

K. Užarević, I. Đilović,
D. Matković-Čalogović, D. Šišak,
M. Cindrić* **7022 – 7025**

Anion-Directed Self-Assembly of Flexible Ligands into Anion-Specific and Highly Symmetrical Organic Solids

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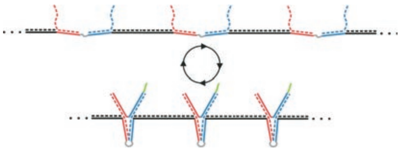


Machine tool: A molecular machine built from DNA utilizes the cooperative actions of many molecular tweezers units to achieve larger-scale movements. The device is able to contract to 75 % of its fully extended length (see picture), is driven by a set of two "fuel" strands, and can be cycled.

Molecular Devices

D. Lubrich,* J. Lin, J. Yan **7026 – 7028**

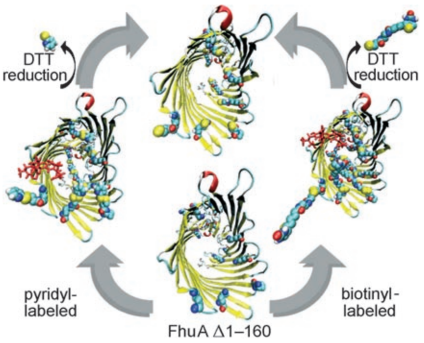
A Contractile DNA Machine

Contents

Protein Modifications

O. Onaca, P. Sarkar, D. Roccatano,
T. Friedrich, B. Hauer, M. Grzelakowski,
A. Güven, M. Fioroni,
U. Schwaneberg* ———— **7029 – 7031**

Functionalized Nanocompartments (Synthosomes) with a Reduction-Triggered Release System

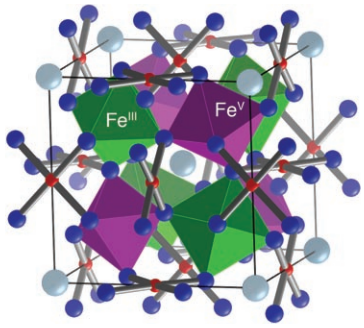


An open and shut case: The developed synthosomes are a subclass of polymersomes with a block-copolymer membrane and a modified embedded transmembrane channel protein (FhuA Δ1–160; see top view of model), which acts as a selective gate. The first reduction-triggered and sterically controlled release system for transmembrane control of the chemical fluxes has been developed by chemically labeling lysine residues in the channel of FhuA Δ1–160.

Magnetic Materials

I. Yamada,* K. Takata, N. Hayashi,
S. Shinohara, M. Azuma, S. Mori,
S. Muranaka, Y. Shimakawa,
M. Takano ———— **7032 – 7035**

A Perovskite Containing Quadrivalent Iron as a Charge-Disproportionated Ferrimagnet



Ferri interesting: $\mathrm{CaCu^{II}_3Fe^{IV}_4O_{12}}$, prepared at 15 GPa and 1300 K, undergoes a charge disproportionation ($2\,\mathrm{Fe^{IV}} \rightarrow \mathrm{Fe^{III}} + \mathrm{Fe^{V}}$) and electrical, magnetic, and structural changes at 210 K. The $\mathrm{Fe^{III}O_6}$ and $\mathrm{Fe^{V}O_6}$ octahedra are ordered in a rock-salt manner (see picture; Ca gray, O blue, Cu red), and the low-temperature phase has the ferrimagnetic structure $\mathrm{Cu^{II}}(S=1/2,\downarrow)_3\mathrm{Fe^{III}}(S=5/2,\uparrow)_2\mathrm{Fe^{V}}(S=3/2,\uparrow)_2$.

Programmed Nanopores

D. C. Danila, L. T. Banner, E. J. Karimova,
L. Tsurkan, X. Wang,
E. Pinkhassik* ———— **7036 – 7039**

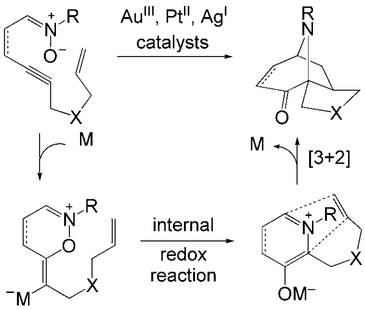
Directed Assembly of Sub-Nanometer Thin Organic Materials with Programmed-Size Nanopores

Nanocolander: Sub-nanometer thin organic materials with uniform imprinted pores are formed by controlled polymerization within temporary self-assembled scaffolds. Pores are measured by a colored size-probe retention assay. A nanocapsule with no pores retains yellow, red, and blue probes and is colored brown; 0.8 nm pores lead to release of yellow probes, while capsules with 1.3 nm pores only retain blue probes.

Gold Catalysis

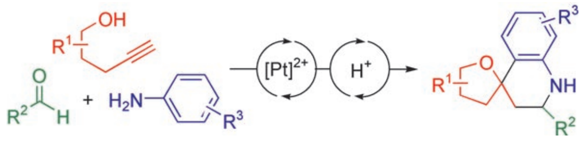
H.-S. Yeom, J.-E. Lee,
S. Shin* ———— **7040 – 7043**

Gold-Catalyzed Waste-Free Generation and Reaction of Azomethine Ylides: Internal Redox/Dipolar Cycloaddition Cascade



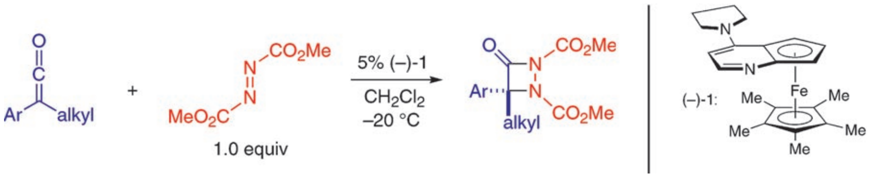
High-octane synthesis: Azomethine ylides can be generated from an internal redox reaction of a nitrone-tethered alkyne under electrophilic metal catalysis (see scheme; M = metal). This novel and atom-economical generation of an azomethine ylide does not involve potentially explosive diazo derivatives. The azomethine ylide can participate in a dipolar cycloaddition cascade to provide an azabicyclo[3.2.1]octane.

Multicomponent Reactions



Three's company: Functionalized spirocyclic quinoline derivatives are easily synthesized in a one-pot three-component coupling process involving the reaction of alkynol, aldehyde, and aniline derivatives (see scheme). The process is carried out in the presence of catalytic amounts of a platinum(II) complex and a protic acid.

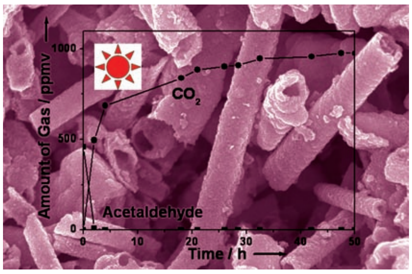
Asymmetric Catalysis



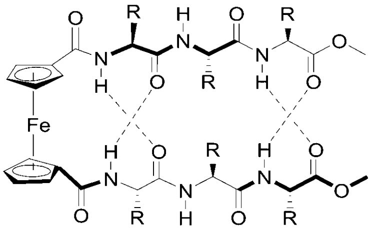
Get ready for take off: A planar-chiral derivative of 4-pyrrolidinopyridine (**1**) mediates the title transformation (see scheme) in a convergent manner with good enantioselectivity, thus giving the first catalytic asymmetric synthesis of aza-β-lactams.

Tungsten Photocatalysts

Shine a light! High-purity tungstic acid hydrate nanotubes and nanoporous-walled WO_3 nanotubes (see picture) were synthesized. The platinum-loaded WO_3 nanotubes show a photocatalytic activity in the degradation of acetaldehyde about three and eight times greater than that of commercial WO_3 particles and nitrogen-doped TiO_2, respectively.



Peptide Chemistry



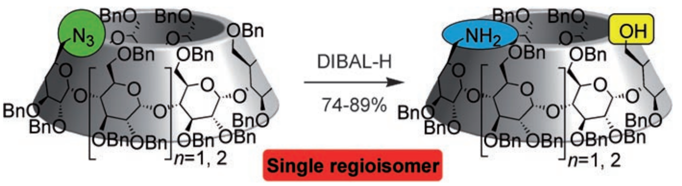
Crease crossing peptide embossing: The first tripeptide ferrocene foldamers to adopt an extended β-sheet-like structure in solution and solid state are presented. The flexibility of peptide substituents in 1,*n*′-ferrocene-bispeptide conjugates was thought to prevent the formation of extended β-sheet foldamers. The results suggest that ferrocene is a valuable scaffold for extended β-sheets.

Contents

Asymmetric Cyclodextrins

S. Guieu, M. Sollogoub* ___ **7060 – 7063**

Regiospecific Tandem Azide-Reduction/Deprotection To Afford Versatile Amino Alcohol-Functionalized α- and β-Cyclodextrins

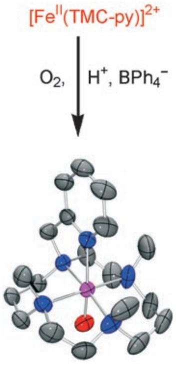


Cyclic conundrum: Deciphering the cyclic directionality of cyclodextrins allows the precise regiospecific synthesis of functionalized cyclodextrins with diametrically opposed amino and hydroxy groups (see scheme; DIBAL-H = diisobutylaluminum hydride, Bn = benzyl) through a tandem azide-reduction/debenzylation mechanism. A remarkable feature of this process is the long-distance discrimination between two equidistant benzyl groups on β-cyclodextrin.

Dioxygen Activation

A. Thibon, J. England, M. Martinho,
V. G. Young, Jr., J. R. Frisch, R. Guillot,
J.-J. Girerd, E. Münck,* L. Que, Jr.,*
F. Banse* ___ **7064 – 7067**

Proton- and Reductant-Assisted Dioxygen Activation by a Nonheme Iron(II) Complex to Form an Oxoiron(IV) Intermediate



With a little help from some friends: With the aid of $HClO_4$ as proton and BPh_4^- as electron source, the Fe complex of a pentadentate pyridyl-appended cyclam ligand can activate dioxygen to yield the corresponding oxoiron(IV) complex (see scheme; TMC-py = 1-(2′-pyridylmethyl)-4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecane; C gray, Fe magenta, N blue, O red). This transformation is proposed to occur via a hydroperoxoiron(III) intermediate.

Cycloadditions

X. Qi, J. M. Ready* ___ **7068 – 7070**

Synthesis of Cyclopentenones from Cyclopropanes and Silyl Ynol Ethers

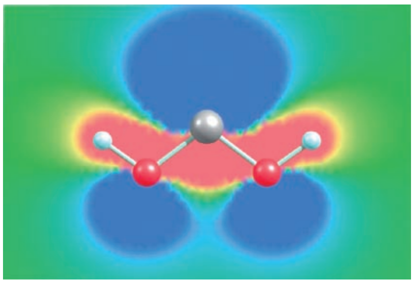
Exploiting an opening: Lewis acid promoted ring-opening of donor–acceptor cyclopropanes generates a 1,3-zwitterion; cycloaddition with a silyl ynol ether leads to a general synthesis of cyclopentenones (see scheme). Substitution is tolerated on the ynol and on all positions of the cyclopropane to give tri-, tetra-, and pentasubstituted cyclopentenones in high yield.

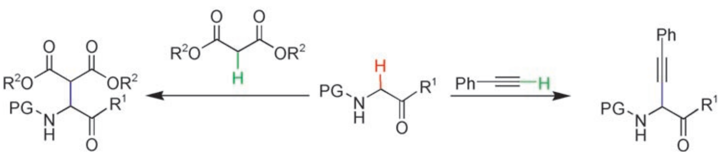
Reactive Intermediates

P. R. Schreiner,*
H. P. Reisenauer ___ **7071 – 7074**

Spectroscopic Identification of Dihydroxycarbene

Out and about: CO_2 extrusion from simple α-keto carboxylic acids can be used to prepare hitherto unknown hydroxycarbenes. High-vacuum flash pyrolysis of oxalic acid or its monomethyl ester enabled the preparation and characterization of dihydroxy- (**1**) and hydroxymethoxycarbene, respectively, both of which are stabilized through π-type out-of-plane and in-plane σ conjugation (the HOMO of *s-trans,s-trans*-**1** is shown).





Come on glycine: Two different types of glycine derivatives are α-functionalized using cross-dehydrogenative-coupling (CDC) reactions. The method allows the efficient attachment of a malonate or aromatic alkyne group on the α-position of the glycine derivatives under very mild conditions.

Synthetic Methods

L. Zhao, C.-J. Li* **7075 – 7078**

Functionalizing Glycine Derivatives by Direct C–C Bond Formation

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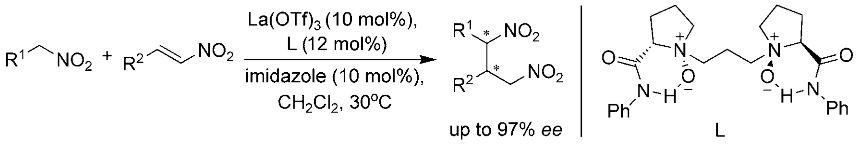

It all adds up: A chiral La(OTf)$_3$/*N*,*N*′-dioxide complex has been developed for the asymmetric direct Michael addition of nitroalkanes to nitroalkenes. This reaction afford 1,3-dinitro compounds with two stereocenters in good yields with high diastereo- and enantioselectivity (up to d.r. 93:3, 97% *ee*; see scheme, Tf = trifluoromethanesulfonyl) under mild conditions.

Asymmetric Catalysis

X. Yang, X. Zhou, L. Lin, L. Chang, X. Liu, X. Feng* **7079 – 7081**

Highly Enantioselective Direct Michael Addition of Nitroalkanes to Nitroolefins Catalyzed by La(OTf)$_3$/*N*,*N*′-Dioxide Complexes

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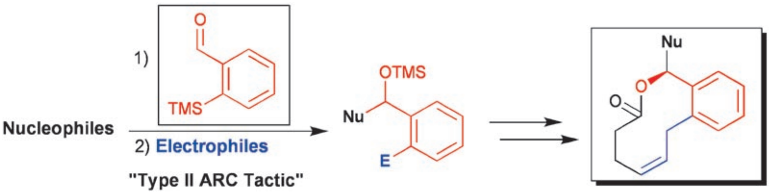
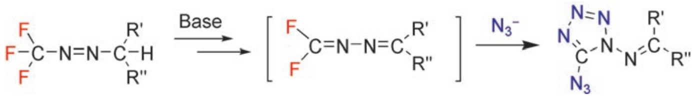


ARC de triomphe: *Ortho*-TMS benzaldehyde permits efficient multicomponent union of a variety of nucleophiles and electrophiles, including the first example of a Pd-mediated ARC Type II process. A "proof-of-concept" synthetic sequence was designed and implemented for construction of a focused library of "natural product-like" compounds (see scheme). ARC: anion relay chemistry.

Synthetic Methods

A. B. Smith, III,* W.-S. Kim, W. M. Wuest **7082 – 7086**

Ortho-TMS Benzaldehyde: An Effective Linchpin for Type II Anion Relay Chemistry (ARC)



N&Ns: The C–F bond of trifluoromethylazoalkanes, in the presence of a hydrogen at the α carbon, is activated under basic conditions to form a difluoromethylene intermediate with a conjugated double bond, which is transformed in good yield to the corresponding 5-azido-(1-dialkylimino)tetrazole by reaction with NaN$_3$.

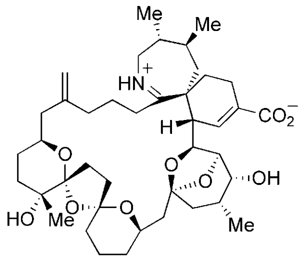
Synthetic Methods

T. Abe, G.-H. Tao, Y.-H. Joo, Y. Huang, B. Twamley, J. M. Shreeve* **7087 – 7090**

Activation of the C–F Bond: Transformation of CF$_3$N=N- into 5-Azidotetrazoles

---

A familiar ring: A ruthenium-catalyzed cycloisomerization of an enyne, synthesized by an *exo*-selective Diels–Alder reaction with an α-methylene lactone as the dienophile, proved to be highly effective for the construction of the 27-membered carbocycle of pinnatoxin A. The total synthesis was completed upon the formation of the seven-membered cyclic imine by self-catalyzed dehydration.


pinnatoxin A

Natural Product Synthesis

S. Nakamura,* F. Kikuchi, S. Hashimoto* **7091 – 7094**

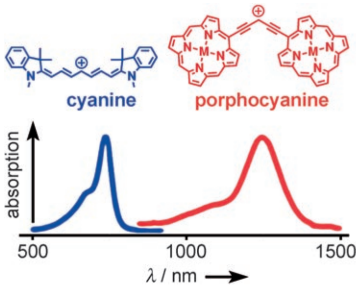
Total Synthesis of Pinnatoxin A

Nonlinear Optics

K. J. Thorley, J. M. Hales, H. L. Anderson,*
J. W. Perry* ______ **7095 – 7098**

Porphyrin Dimer Carbocations with Strong Near Infrared Absorption and Third-Order Optical Nonlinearity

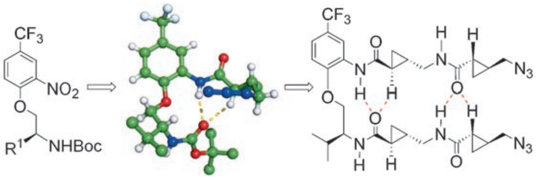
Colored carbocations beyond the visible! A porphyrin dimer carbocation is synthesized with effective delocalization over 18 conjugated bonds. Placing a carbocation at the center of a conjugated porphyrin dimer shifts its absorption into the infrared and results in strong ultrafast nonlinear optical behavior.



Foldamers

C. R. Jones, M. K. N. Qureshi,
F. R. Truscott, S.-T. D. Hsu, A. J. Morrison,
M. D. Smith* ______ **7099 – 7102**

A Nonpeptidic Reverse Turn that Promotes Parallel Sheet Structure Stabilized by C–H⋯O Hydrogen Bonds in a Cyclopropane γ-Peptide

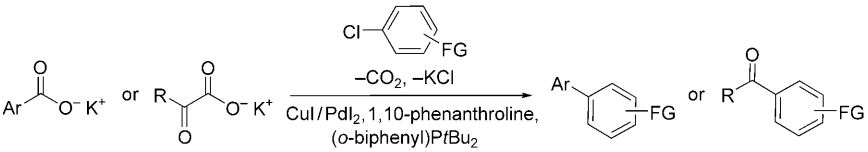


A twist of fate: Parallel-turn linkers comprising an amino acid derived alcohol conjoined with an aromatic amide through a flexible linkage adopt reverse-turn conformations. Cyclopropane tetra- and hexapeptide analogues form a C–H⋯O hydrogen-bond-stabilized parallel-sheet conformation (see scheme). NMR studies confirm the presence of hydrogen bonds in these structures.

Synthetic Methods

L. J. Gooßen,* B. Zimmermann,
T. Knauber ______ **7103 – 7106**

Palladium/Copper-Catalyzed Decarboxylative Cross-Coupling of Aryl Chlorides with Potassium Carboxylates



Even non-activated aryl chlorides undergo decarboxylative cross-coupling reactions in the presence of a catalyst system generated in situ from CuI, 1,10-phenanthroline, PdI_2, and di(*tert*-butyl)biphenylphosphane. The new catalyst is useful for both the synthesis of biaryl compounds from aromatic carboxylates and the synthesis of aryl ketones from salts of α-ketocarboxylic acids (see scheme; FG = functional group; R = aryl, alkyl).

Activation of Alkanes

F. Parrino, A. Ramakrishnan,
H. Kisch* ______ **7107 – 7109**

Semiconductor-Photocatalyzed Sulfoxidation of Alkanes

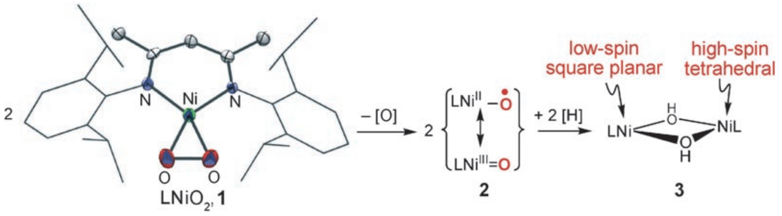
$$\text{R-H} + SO_2 + 1/2\, O_2 \xrightarrow[TiO_2]{\text{Vis}} RSO_3H$$

The C–H activation of alkanes with visible light is possible with a semiconductor as the photocatalyst. Upon irradiation, a mixture of titanium dioxide, sulfur dioxide, and oxygen can be used to convert alkanes into the corresponding sulfonic acids (see scheme).

Superoxonickel Complexes

S. Yao, E. Bill, C. Milsmann, K. Wieghardt, M. Driess* ——— **7110 – 7113**

A "Side-on" Superoxonickel Complex $[LNi(O_2)]$ with a Square-Planar Tetracoordinate Nickel(II) Center and Its Conversion into $[LNi(\mu\text{-}OH)_2NiL]$

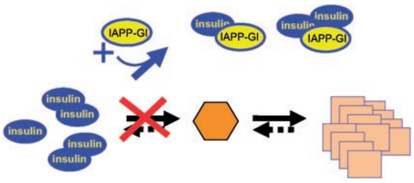


Radically mild: The first room-temperature isolable, structurally characterized superoxonickel(II) complex **1** with a square-planar tetracoordinate Ni^{II} center is capable of gentle oxygen-transfer reactions to form the proposed intermediate **2**, which acts as a hydrogen scavenger and dimerizes to homovalent complex **3** with both square-planar (low-spin) and tetrahedral (high-spin) Ni^{II} centers. $L = CH\{C(Me)(2,6\text{-}iPr_2C_6H_3N\}_2$.

Inhibition of Protein Aggregation

A. Velkova, M. Tatarek-Nossol, E. Andreetto, A. Kapurniotu* ——— **7114 – 7118**

Exploiting Cross-Amyloid Interactions to Inhibit Protein Aggregation but not Function: Nanomolar Affinity Inhibition of Insulin Aggregation by an IAPP Mimic



Potential aggregate preventer: The designed peptide IAPP-GI inhibits the non-native aggregation of insulin without affecting its function. As the peptide also blocks aggregation of key amyloid peptides that occur in Alzheimer's disease and type II diabetes, it is a promising drug candidate.

RNA Detection

T. N. Grossmann, L. Röglin, O. Seitz* ——— **7119 – 7122**

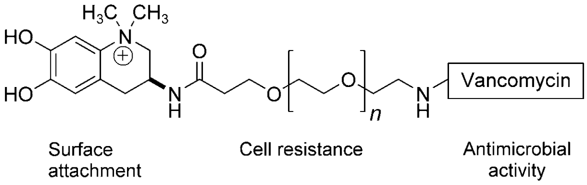
Target-Catalyzed Transfer Reactions for the Amplified Detection of RNA

Strong signals: The RNA-catalyzed transfer of a biotin reporter was used to preamplify a signal that was detected in an enzyme-based readout, thereby increasing its sensitivity. The advantages of combining the covalent attachment of biotin and preamplification were demonstrated by the detection of 500 attomol HIV RNA. The flexibility requirements of DNA- and RNA-catalyzed transfer reactions were tested.

Functional Surfaces

J.-Y. Wach, S. Bonazzi, K. Gademann* ——— **7123 – 7126**

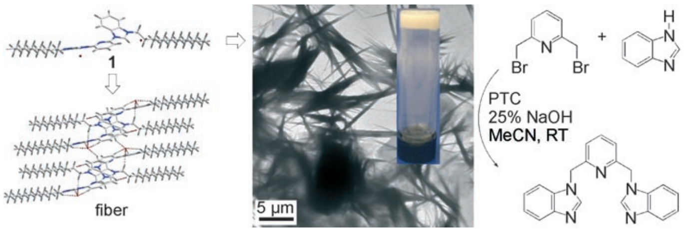
Antimicrobial Surfaces through Natural Product Hybrids



The power of two! A natural product hybrid (see structure) composed of a siderophore and an antibiotic separated by a poly(ethylene glycol) linker enables the preparation of antimicrobial and cell-resistant surfaces by a simple dip-and-rinse procedure. The anachelin siderophore (left) binds strongly to TiO_2 surfaces, and vancomycin is responsible for antibiotic activity.

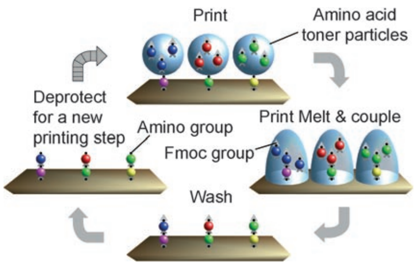
Contents

Phase Transfer Catalysis



Simply structured benzimidazolium salts efficiently gelate a variety of polar organic solvents. π-Stacking, hydrogen bonding, and van der Waals interactions are responsible for the self-assembly process. A packing model is deduced from the single crystal structure of gelator **1**. Fiber aggregates of benzimidazolium salts in acetonitrile are efficient phase-transfer catalysts (PTCs) for N-alkylation.

Biotechnology



Special delivery: The "freezing" of activated amino acid derivatives within solid particles enables a laser printer to deliver these "postal packages" to defined locations on a solid support with high resolution. Subsequent parallel coupling is initiated simply by melting a whole layer of 20 different amino acid particles (see schematic representation; Fmoc = 9-fluorenylmethoxycarbonyl).

Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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