



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. Amaya, H. Sakane, T. Hirao*

A Concave-Bound CpFe Complex of Sumanene as a Dished-Up Metal in a π -Bowl

A. M. Brizard, M. C. Stuart, K. J. van Bommel, A. Friggeri, M. R. de Jong, J. H. van Esch*

Nanostructures by Orthogonal Self-Assembly of Hydrogelators and Surfactants

H.-C. Chiu,* Y.-W. Lin, Y.-F. Huang, C.-K. Chuang, C.-S. Chern
Polymer Vesicles Containing Small Vesicles within Interior Aqueous Compartments and pH-Responsive Transmembrane Channels

M. J. Hangauer, C. R. Bertozzi*

A FRET-Based Fluorogenic Phosphine for Live-Cell Imaging with the Staudinger Ligation

A. Baumgartner, K. Sattler, J. Thun, J. Breu*

A Novel Route to Microporous Materials: Oxidative Pillaring of Micas

M. Kirchmann, K. Eichele, F. M. Schappacher, R. Pöttgen, L. Wesemann*

Octahedral Coordination Compounds of the Ni, Pd, Pt Triad

News

Organic Chemistry:

C.-H. Wong Honored _____ 30

Materials Science:

Prize for N. Martín _____ 30

Biochemistry:

F. H. Arnold Awarded _____ 30

Books

Sensory-Directed Flavor Analysis

Ray Marsili

reviewed by K. Breme, X. Fernandez,
U. J. Meierhenrich _____ 31

The Way of Synthesis

Tomáš Hudlický, Josephine W. Reed

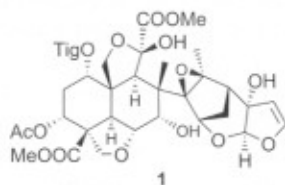
reviewed by U. Rinner, J. Mulzer _____ 32

Highlights

Natural Product Synthesis

J. Jauch* _____ 34–37

Total Synthesis of Azadirachtin—Finally Completed After 22 Years

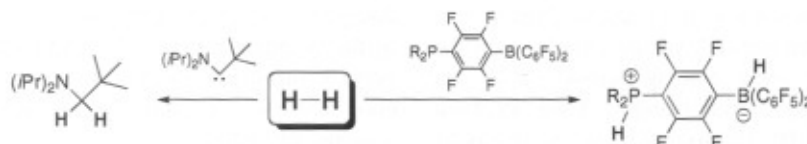


Patience pays off: 22 years ago Ley and co-workers started their project on the synthesis of azadirachtin (**1**)—a project which they recently completed successfully with the first total synthesis of this complex natural product. This milestone of natural product synthesis is acknowledged in this Highlight. Tig = tigloyl = (*E*)-2-methyl-2-butenoyl

H₂ Activation

A. L. Kenward, W. E. Piers* _____ 38–41

Heterolytic H₂ Activation by Nonmetals



Nice cleavage: Two new strategies for the transition-metal-free activation of σ bonds are presented, namely, Bertrand's activation of dihydrogen by carbenes (see

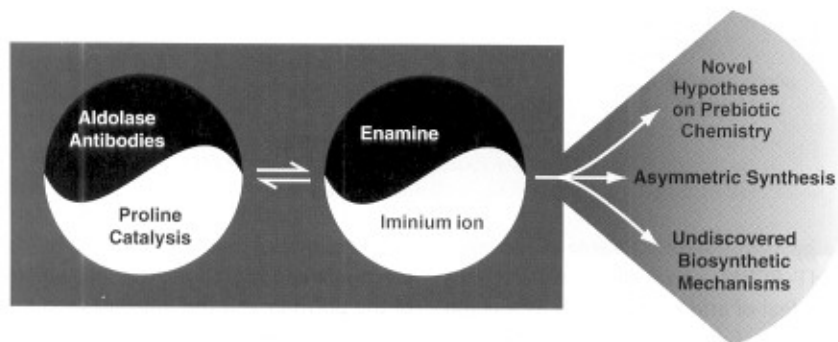
picture, left) and Stephan's "frustrated" Lewis acid/base pairs (right; $R = \text{Me}_3\text{C}_6\text{H}_2$).

Essays

Organocatalysis

C. F. Barbas III* ————— 42–47

Organocatalysis Lost: Modern Chemistry, Ancient Chemistry, and an Unseen Biosynthetic Apparatus



One enigma leads in three directions: The Hajos–Wiechert reaction presented an enigma that went unsolved for three decades. With the unravelling of this enigma, organocatalysis plays a major role in the development of efficient cata-

lytic asymmetric methodologies. The mechanisms of organocatalysis also shed light on the origin of homochirality essential for life and provide clues to yet-to-be-discovered biosynthetic mechanisms at work in living organisms today.

Variety is the spice of life: A new strategy for the synthesis of small molecules that involves three phases is discussed: the building of chiral components, their intermolecular coupling, and intramolecular cyclization of strategically placed functional groups. This build/couple/pair strategy efficiently yields stereochemically and skeletally diverse small molecules and is a promising path in the discovery of effective probes and drugs.



Minireviews

Diversity-Oriented Synthesis

T. E. Nielsen, S. L. Schreiber* — 48–56

Towards the Optimal Screening Collection: A Synthesis Strategy

For the USA and Canada:
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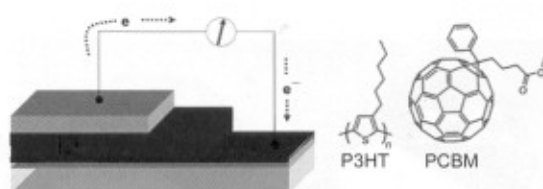
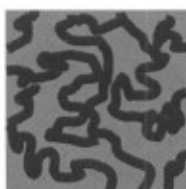
electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Reviews

Organic Photovoltaics

B. C. Thompson, J. M. J. Fréchet* 58–77

Polymer–Fullerene Composite Solar Cells



Energy from the sun: Polymer–fullerene (P3HT–PCBM) solar cells have attracted a great deal of attention recently as a result of reports of devices with efficiencies approaching 5%. The current state-of-the-art in the field is critically examined with a

focus on the lessons learned on the electronic and morphological interactions of the polymer and the fullerene, and the areas where improvements still need to be made for the optimization of such devices.

Communications

Quasiracemic Materials

K. A. Wheeler,* R. C. Grove, R. E. Davis, W. S. Kassel 78–81

Rediscovering Pasteur's Quasiracemates

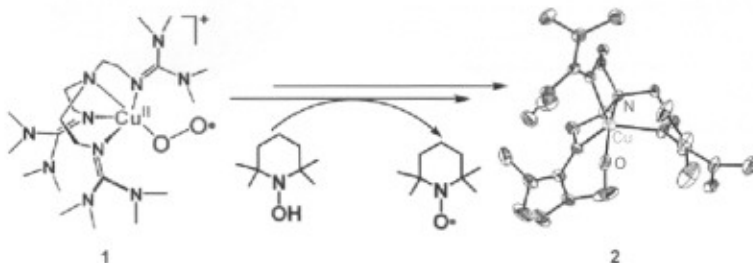
A fresh Pasteur: Reconstruction of Pasteur's 1853 account of peculiar three-component crystals has confirmed the identities of the two crystalline phases as ammonium (+)-bitartrate (central crystal) and a quasiracemate of ammonium (+)-bitartrate/(–)-bimalate (adjoining crystal laths). The quasiracemate contains approximately inversion-related molecular assemblies in which each bitartrate and bimalate component forms a homomeric catemeric motif.



VIP Copper Superoxo Complexes

D. Maiti, D.-H. Lee, K. Gaoutchenova, C. Würtele, M. C. Holthausen, A. A. Narducci Sarjeant, J. Sundermeyer, S. Schindler, K. D. Karlin* 82–85

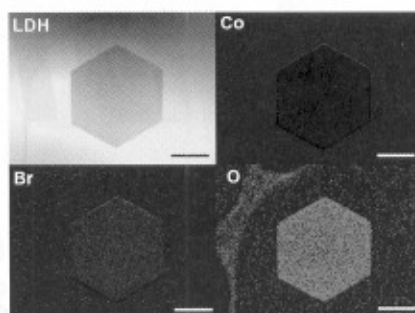
Reactions of a Copper(II) Superoxo Complex Lead to C–H and O–H Substrate Oxygenation: Modeling Copper-Monooxygenase C–H Hydroxylation



Donor makes the difference: The mononuclear η^1 -superoxo copper(II) complex 1 undergoes dioxygen activation with the addition of hydrogen-atom donors. Net O_2 -derived O-atom insertion into the N-

methyl group of the ligand leads to formation of a copper(II)-alkoxide product 2. The cupric superoxo species 1 itself is not capable of the observed hydroxylation reaction.

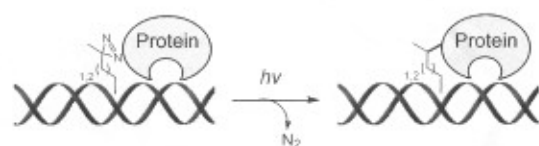
From platelets to sheets: A topochemical phase conversion employing bromine in acetonitrile transforms β -Co(OH)₂ into monometallic Co²⁺-Co³⁺ layered double hydroxide (LDH) with a Co²⁺/Co³⁺ ratio of 2:1 (see the elemental maps of Co, Br, and O in a Br⁻-intercalated Co²⁺-Co³⁺ LDH platelet). Further treatment allows exfoliation of Co²⁺-Co³⁺ LDH into positively charged Co(OH)₂ nanosheets. Scale bars: 2 μ m.



Phase Transitions

R. Ma,* K. Takada, K. Fukuda, N. Iyi,
Y. Bando, T. Sasaki — 86–89

Topochemical Synthesis of Monometallic (Co²⁺-Co³⁺) Layered Double Hydroxide and Its Exfoliation into Positively Charged Co(OH)₂ Nanosheets



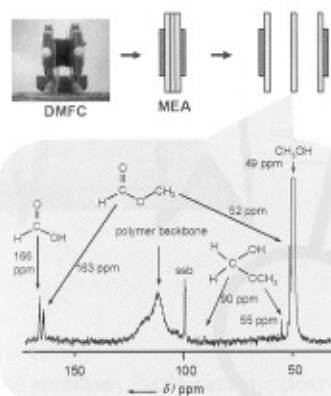
Small modification, large effect: Diazirine can be installed quickly and simply in the major or minor groove of DNA for efficient photo-cross-linking to proteins

(see picture). This method should be suitable for mapping out protein-DNA interactions, in particular those that may be sensitive to steric hindrance.

Protein-DNA Interactions

U. K. Shigdel, J. Zhang, C. He* — 90–93

Diazirine-Based DNA Photo-Cross-Linking Probes for the Study of Protein-DNA Interactions



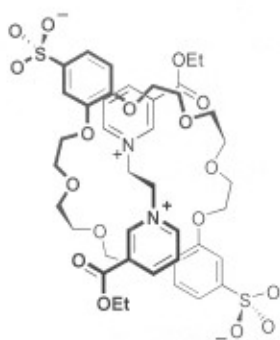
Methanol crossover and reaction intermediates are studied in a direct methanol fuel cell (DMFC) by means of ²D and ¹³C MAS NMR spectroscopy. A membrane electrode assembly (MEA) composed of three polymer electrolyte membrane (PEM) layers is used in the DMFC, and the middle PEM film is extracted to perform the NMR measurements (see image).

Fuel Cells

Y. Paik, S.-S. Kim, O. H. Han* — 94–96

Methanol Behavior in Direct Methanol Fuel Cells

Anionic wheels for cationic axles: Significant electrostatic ion-ion interactions dramatically increase the stability of interpenetrated molecules. In highly polar solvents, formation of [2]pseudorotaxanes is observed, in which crown ether wheels (see picture, red) having anionic sulfonate groups counter the pyridinium cations of the axle (blue).

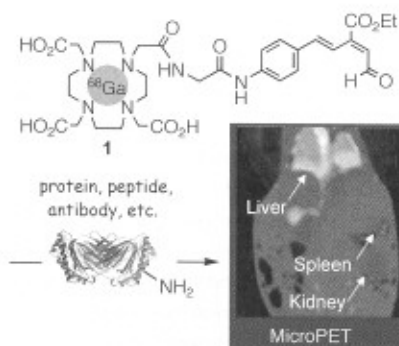


[2]Pseudorotaxanes

D. J. Hoffart, J. Tiburcio,* A. de la Torre,
L. K. Knight, S. J. Loeb* — 97–101

Cooperative Ion-Ion Interactions in the Formation of Interpenetrated Molecules

On target: Lysine residues in picomole samples of a peptide, proteins, and a monoclonal antibody were rapidly and selectively labeled by a dota-based probe (**1**, see scheme). Positron emission tomography imaging of [^{68}Ga]dota-labeled orosomucoid and asialoorosomucoid for the first time visualized a difference in the clearance process of glycoproteins in the presence or absence of the sialic acid residue.



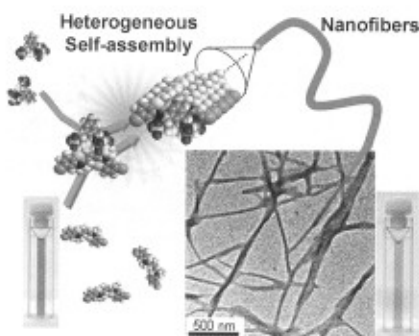
Molecular Imaging



K. Tanaka, T. Masuyama, K. Hasegawa, T. Tahara, H. Mizuma, Y. Wada, Y. Watanabe, K. Fukase* — 102–105

A Submicrogram-Scale Protocol for Biomolecule-Based PET Imaging by Rapid 6 π -Azoelectrocyclization: Visualization of Sialic Acid Dependent Circulatory Residence of Glycoproteins

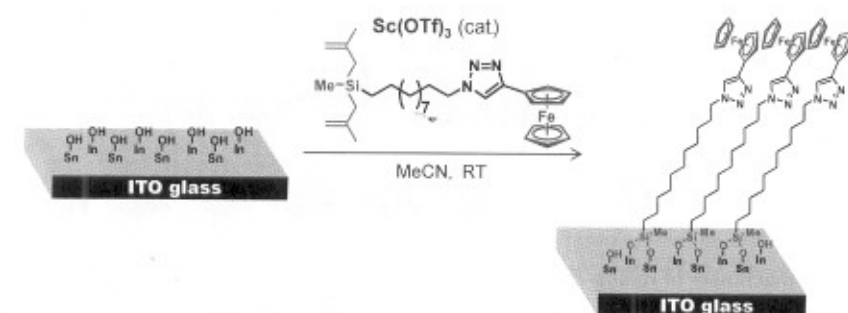
A pretty pair: Self-assembly has been used to amplify and translate the structural information of amino acids into spectroscopic and morphological information (see scheme). It combines in situ premodification of various amino acids and their specific association with a cyanine dye. Conversion of the amino acids into their isoindole derivatives enhances the intermolecular interactions of the amino acid/dye pair to spontaneously form nanostructures.



Molecular Assembly

T. Shiraki, M.-a. Morikawa, N. Kimizuka* — 106–108

Amplification of Molecular Information through Self-Assembly: Nanofibers Formed from Amino Acids and Cyanine Dyes by Extended Molecular Pairing



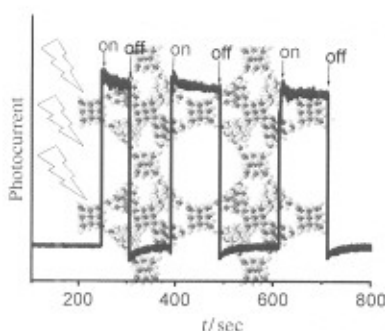
Surface Modification

Y.-R. Yeon, Y. J. Park, J.-S. Lee, J.-W. Park, S.-G. Kang, C.-H. Jun* — 109–112

Sc(OTf)₃-Mediated Silylation of Hydroxy Functional Groups on a Solid Surface: A Catalytic Grafting Method Operating at Room Temperature

Surface paradise: Facile catalytic post-grafting of the surface of glass or indium tin oxide (ITO, see picture) with a variety of functional groups has been achieved.

Methylsilanes serve as the grafting reagent and the surfaces show remarkable chemical stability.



Light switch: A photoelectric chalcogenide with a (3,4)-connected open-framework structure based on large Cd–S–SAr clusters with boracite-type topology has been synthesized. Its structure (depicted: Cd green, S yellow; Ar omitted) and optical properties have been characterized. The superlattice reproducibly generates a transient photocurrent on excitation by visible light (see picture). SAr = 3-methylbenzenethiolate.

Metal Chalcogenide Frameworks

Q. Zhang, Y. Liu, X. Bu, T. Wu, P. Feng* — 113–116

A Rare (3,4)-Connected Chalcogenide Superlattice and Its Photoelectric Effect

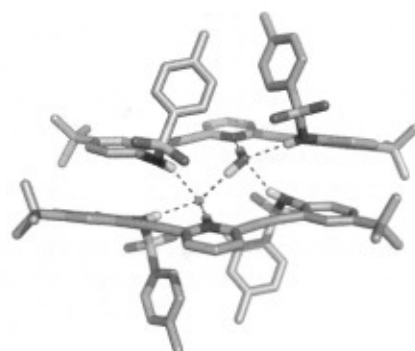
Self-Assembled Dimers

O. B. Berryman, C. A. Johnson II,
L. N. Zakharov, M. M. Haley,*
D. W. Johnson* 117–120



Water and Hydrogen Halides Serve the Same Structural Role in a Series of 2+2 Hydrogen-Bonded Dimers Based on 2,6-Bis(2-anilinoethynyl)pyridine Sulfonamide Receptors

Mix and match: A new series of receptors reveals an unusual propensity to form 2+2 hydrogen-bonded dimers with water or hydrogen halides. Remarkably, water and hydrogen chloride impart nearly identical structural features to the dimers. In fact, in one case (see picture, Cl green, O red, N blue, S yellow), one water molecule and one chloride ion work in concert to form a hydrogen-bonded dimer stitched together with seven hydrogen bonds.

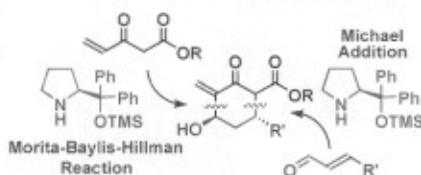


Organocatalytic Tandem Reaction

S. Cabrera, J. Alemán, P. Bolze,
S. Bertelsen, K. A. Jørgensen* 121–125



An Unexpected Organocatalytic Asymmetric Tandem Michael/Morita–Baylis–Hillman Reaction

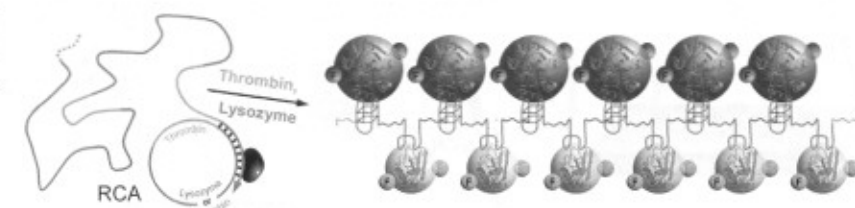


Simply complex: An organocatalytic tandem Michael/Morita–Baylis–Hillman reaction has been developed in which secondary amine catalysts allow for a very selective, scalable synthesis of highly substituted optically active cyclohexanones (see scheme, TMS = trimethylsilyl). Mechanistic studies indicate an active role of the secondary amine catalyst in the Morita–Baylis–Hillman reaction.

Nanostructures

Z. Cheglakov, Y. Weizmann,
A. B. Braunschweig, O. I. Wilner,
I. Willner* 126–130

Increasing the Complexity of Periodic Protein Nanostructures by the Rolling-Circle-Amplified Synthesis of Aptamers



The biomachinery of rolling-circle amplification relying on protein–aptamer interactions on DNA scaffolds was used to create one-dimensional DNA–protein/

DNA–protein–nanoparticle hierarchical assemblies. These conjugates can serve as further templates for the immobilization of gold nanoparticles.

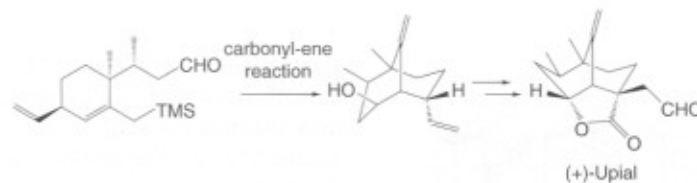


Natural Product Synthesis

K. Takahashi, M. Watanabe,
T. Honda* 131–133

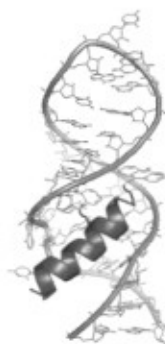


Highly Efficient Stereocontrolled Total Synthesis of (+)-Upial



Dual benefit: (+)-Upial, isolated from the sponge *Dysidea fragilis* (Kaneohe Bay, Hawaii), as a nonisoprenoid sesquiterpene aldehyde lactone, was efficiently synthesized. The key step involved an intramolecular carbonyl–ene reaction, in

which the stereocontrolled construction of a bicyclo[3.3.1]nonane ring with five asymmetric carbon centers and the facile introduction of the *exo*-methylene unit were achieved in a single step (see scheme).



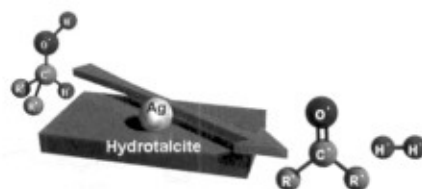
Hold on tight: Amphiphilic α -helical peptides that contain acridine moieties were synthesized, and their binding affinities toward hairpin RNA targets were evaluated. The dramatic increase in binding affinities (40-fold for RRE, 170-fold for TAR) demonstrates that conjugation of intercalators that operate by different binding modes (ionic or hydrogen bonding) leads to one of the most tightly binding pharmacophores against RNA targets.

Amphiphilic Peptides

Y. Lee, S. Hyun, H. J. Kim,
J. Yu* 134–137

Amphiphilic Helical Peptides Containing Two Acridine Moieties Display Picomolar Affinity toward HIV-1 RRE and TAR

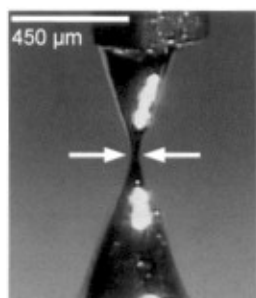
Additive free: Hydrotalcite-supported silver nanoparticles act as a highly efficient heterogeneous catalyst for the dehydrogenation of diverse alcohols (see picture) in the absence of any acceptors such as molecular oxygen, hydrogen peroxide, or unsaturated organic compounds. The solid Ag catalyst was readily reusable without any loss of activity and selectivity.



Heterogeneous Catalysis

T. Mitsudome, Y. Mikami, H. Funai,
T. Mizugaki, K. Jitsukawa,
K. Kaneda* 138–141

Oxidant-Free Alcohol Dehydrogenation Using a Reusable Hydrotalcite-Supported Silver Nanoparticle Catalyst

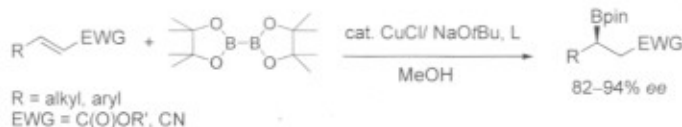


A great GaIn: Micrometer-sized conformational electrodes formed from the title compound are shown to be ideal for measuring the electrical properties of self-assembled monolayers. The image shows the bifurcation of the EGaIn between a metal needle and an Ag surface (not shown) at the point indicated by the two white arrows. The portion above the arrows will form the EGaIn electrode.

Self-Assembled Monolayers

R. C. Chiechi, E. A. Weiss, M. D. Dickey,
G. M. Whitesides* 142–144

Eutectic Gallium–Indium (EGaIn): A Moldable Liquid Metal for Electrical Characterization of Self-Assembled Monolayers



Asymmetric β -boration of acyclic α,β -unsaturated carbonyl compounds provides ready access to enantioenriched functionalized organoboron compounds. A range of acyclic unsaturated esters and

nitriles reacted with high enantioselectivity and good yields at room temperature using a copper catalyst and planar chiral diphosphine ligands (L).

Asymmetric Catalysis

J.-E. Lee, J. Yun* 145–147

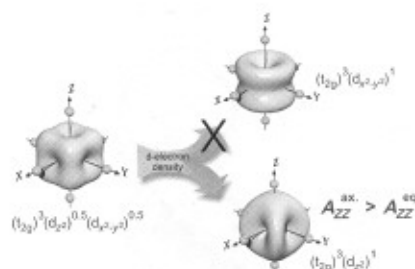
Catalytic Asymmetric Boration of Acyclic α,β -Unsaturated Esters and Nitriles

EPR Spectroscopy

Q. Scheifele, T. Birk, J. Bendix,*
P. L. W. Tregenna-Piggott,*
H. Weihe* 148–150

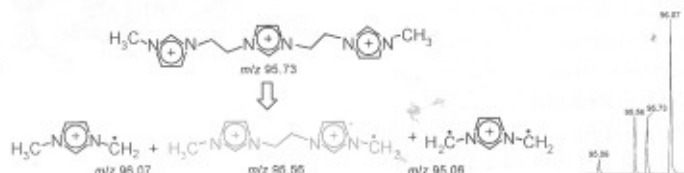
Superhyperfine Interaction in $[\text{MnF}_6]^{3-}$

Resolved at last: A conventional spectrometer afforded the first EPR spectrum of a manganese(III) complex, namely $[\text{MnF}_6]^{3-}$, featuring clearly resolved superhyperfine interactions. It is shown how the nature of the Jahn–Teller distortion and the concomitant electronic structure (see picture) can be deduced from a single EPR spectrum and how the electronic structure of the central ion is reflected in the superhyperfine interaction with the surrounding ligands.



Gas-Phase Chemistry

F. M. Nachtigall, Y. E. Corilo, C. C. Cassol,
G. Ebeling, N. H. Morgon, J. Dupont,*
M. N. Eberlin* 151–154



Multiply Charged (Di-)Radicals

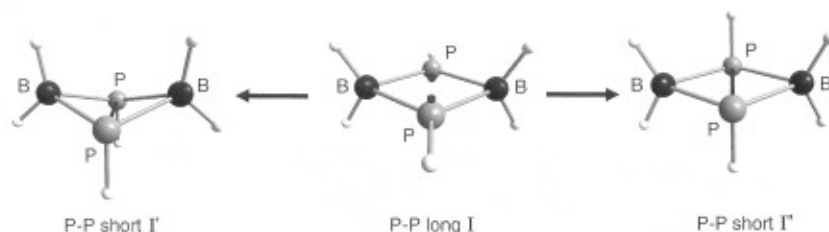
A window of opportunity: New types of gaseous multiply charged (di-)radicals based on ionic liquids have been prepared by ESI MS/MS techniques by using imidazolium ion sites to act as “handles”.

Dissociation of gaseous $(\text{CH}_2)_n$ -bridged triimidazolium ions leads to groups of multiply charged (di-)radicals contained within a narrow window of one m/z unit (see spectrum).

Bond-Stretch Isomers

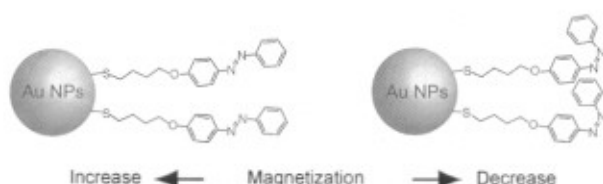
V. Gandon, J.-B. Bourg, F. S. Tham,
W. W. Schoeller,* G. Bertrand* 155–159

The Existence of Two Short-Bond Isomers for Bicyclo[1.1.0]butane Derivatives Based on Boron and Phosphorus



Really (di)radical: Calculations show that parent 2,4-diborata-1,3-diphosphoniocyclobutane-1,3-diyl I has a negligible singlet–triplet energy gap ($1.2 \text{ kcal mol}^{-1}$) and would be a perfect diradical that could

undergo both disrotatory and conrotatory ring closures to give bicyclo[1.1.0]butane derivatives I' and I''. The synthesis of a type I' derivative is presented.



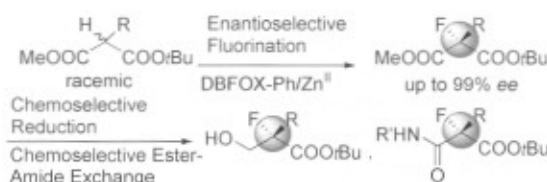
Out of nowhere: Significant photoinduced changes in ferromagnetism have been observed at the interfaces between gold nanoparticles (Au NPs) and azobenzene-derivatized thiols. These photomagnetic effects could be attributed to photoin-

duced changes in d-charge losses resulting from the photoisomerization of the azo ligands (see picture), which are accompanied by the inversion of surface dipoles to the opposite sign.

Photomagnetic Effects

M. Suda, N. Kameyama, M. Suzuki,
N. Kawamura, Y. Einaga* — 160–163

Reversible Phototuning of
Ferromagnetism at Au–S Interfaces at
Room Temperature



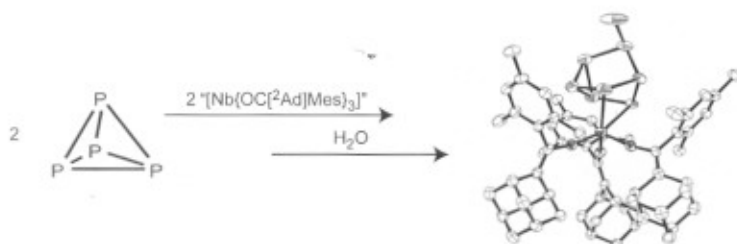
At the leading edge: Chiral fluoromalonates can be prepared with very high stereocontrol by enantioselective fluorination of racemic malonates and using a $\text{Zn}(\text{OAc})_2/\text{DBFOX-Ph}$ catalyst (see scheme), thus providing an efficient

alternative route to conventional microbial desymmetrization for the preparation of fluorinated chiral building blocks. Several pharmaceutically attractive compounds were prepared by using this method.

Asymmetric Synthesis

D. S. Reddy, N. Shibata,* J. Nagai,
S. Nakamura, T. Toru,*
S. Kanemasa — 164–168

Desymmetrization-like Catalytic
Enantioselective Fluorination of
Malonates and Its Application to
Pharmaceutically Attractive Molecules



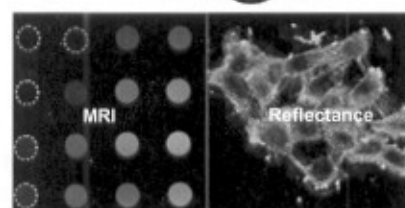
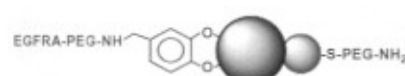
Eight's company: Disproportionation of $[\text{Nb}(\text{OC}(\text{Ad})\text{Mes})_3(\text{thf})]$ in the presence of P_4 results in reductive coupling of two molecules of P_4 . The resulting complex, which features a niobium phosphinidene

moiety, can subsequently be hydrolyzed (see picture; P orange, Nb blue, O red; ^2Ad = 2-adamantylidene; Mes = 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$).

P_4 Activation

B. M. Cossairt,
C. C. Cummins* — 169–172

A Reactive Niobium Phosphinidene P_8
Cluster Obtained by Reductive Coupling
of White Phosphorus



Heavy lifting: Dumbbell-shaped $\text{Au-Fe}_3\text{O}_4$ nanoparticles are made biocompatible and suitable for attachment to A431 cells. The particles are magnetically and optically active and are useful for simultaneous magnetic and optical detection (see picture). The $\text{Au-Fe}_3\text{O}_4$ nanoparticles are promising as a new type of multifunctional probe for diagnostic and therapeutic applications.

Multifunctional Nanoprobes

C. Xu, J. Xie, D. Ho, C. Wang, N. Kohler,
E. G. Walsh, J. R. Morgan, Y. E. Chin,
S. Sun* — 173–176

$\text{Au-Fe}_3\text{O}_4$ Dumbbell Nanoparticles as
Dual-Functional Probes

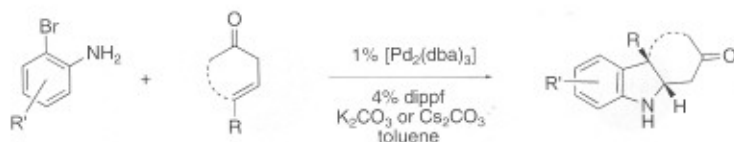


Tricyclic Indolines

A. M. Hyde, S. L. Buchwald* — 177–180



Palladium-Catalyzed γ -Arylation of β,γ -Unsaturated Ketones: Application to a One-Pot Synthesis of Tricyclic Indolines



Indolines in short order: A catalyst system which allows for efficient γ -arylation of β,γ -unsaturated ketones is described (see scheme; dipfp = 1,1'-bis(diisopropylphosphanyl)ferrocene, dba = *trans,trans*-

dibenzylideneacetone). This method can be applied to a one-pot, two-step synthesis of polycyclic indolines from simple starting materials.

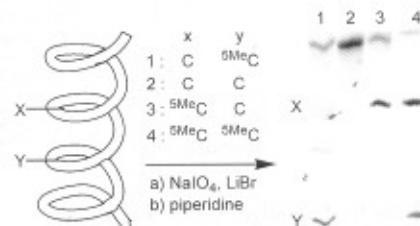
Epigenetic Sequencing

S. Bareyt, T. Carell* — 181–184



Selective Detection of 5-Methylcytosine Sites in DNA

A distinguished result: 5-Methylcytosine can be distinguished from all other nucleobases in DNA by selective conversion of the C5–C6 double bond into a bromohydrine followed by piperidine-induced strand cleavage at the reaction site (see picture). This procedure allows the methylation status of the p16 promoter to be determined under *in vitro* conditions.



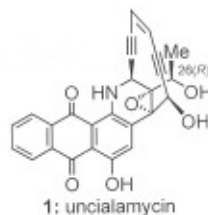
Natural Product Synthesis

K. C. Nicolaou*, J. S. Chen, H. Zhang, A. Montero — 185–189



Asymmetric Synthesis and Biological Properties of Uncialamycin and 26-*epi*-Uncialamycin

The highly potent DNA-cleaving molecule uncialamycin (1) was prepared in an asymmetric total synthesis featuring an enantioselective Noyori reduction. Compound 1 and its C26 epimer exhibit impressive broad-spectrum antibacterial properties and highly potent antitumor activities against a variety of cell lines.



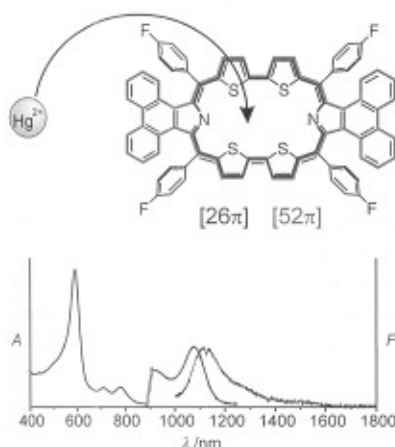
Magnesium Alkoxide Fluoride

A. Dimitrov, S. Wuttke, S. Troyanov, E. Kemnitz* — 190–192

$\text{Mg}_6\text{F}_2(\text{OMe})_{10}(\text{MeOH})_{14}$ —An Alkoxide Fluoride of an Alkaline Earth Metal



Partial fluorolysis of magnesium alkoxide with HF leads to an unexpected crystalline magnesium alkoxide fluoride intermediate. The hexanuclear, cationic dicubane unit is bridged by unusual $\mu_4\text{-F}$ atoms and hydrogen-bonded to two methoxide anions, resulting in a triple-ionic structure (see picture, F green, Mg blue, O red, C gray, H black).



Sending signals: The first core-modified, expanded porphyrin with polyaromatic units fused to the pyrrole rings absorbs far into the near-infrared and shows fluorescence that stretches into the second optical window of telecommunication. Doping a polyurethane membrane with the dye yields Hg^{2+} -responsive optical test strips.

Expanded Porphyrins

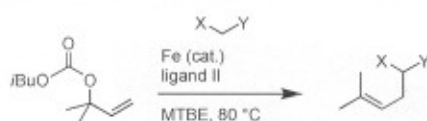
D. Wu, A. B. Descalzo, F. Weik, F. Emmerling, Z. Shen,* X.-Z. You,* K. Rurack* 193–197

A Core-Modified Rubyrin with *meso*-Aryl Substituents and Phenanthrene-Fused Pyrrole Rings: A Highly Conjugated Near-Infrared Dye and Hg^{2+} Probe

σ -allyl mechanism



π -allyl mechanism



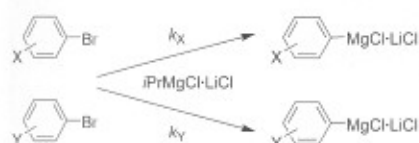
Iron at the crossroads: A remarkable mechanistic dichotomy in iron-catalyzed allylic substitution increases not only the scope of regioselective allylic alkylation but could also herald the development of

asymmetric allylic substitution (see Scheme, MTBE = methyl *tert*-butyl ether). Depending on the ligand used, either a σ - or a π -allyl mechanism is observed.

Allylic Substitution

B. Plietker,* A. Dieskau, K. Möws, A. Jatsch 198–201

Ligand-Dependent Mechanistic Dichotomy in Iron-Catalyzed Allylic Substitutions: σ -Allyl versus π -Allyl Mechanism

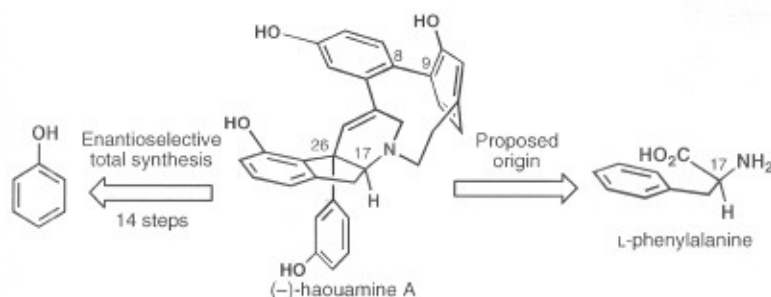


Against expectation: How can the site of Br–Mg exchange in multiply brominated compounds be predicted? Competition experiments with different substituents X and Y (see scheme; X, Y = H, F, Cl, Br, CF_3 , CO_2tBu , CN) reveal a counterintuitive order of substituent effects. The aim of the study is to enable the selectivity of halogen–magnesium exchange reactions of polyfunctional compounds to be predicted.

Grignard Reagents

L. Shi, Y. Chu, P. Knochel, H. Mayr* 202–204

Relative Rates of Bromine–Magnesium Exchange Reactions in Substituted Bromobenzene Derivatives



Not what it seemed: Careful reinvestigation of the classic Chichibabin pyridine synthesis has provided evidence against a spontaneous tetramerization pathway in the biosynthesis of the haouamine alka-

loids. A simple enantioselective synthesis of haouamine A has illuminated its absolute configuration and points towards a phenylalanine-based biosynthesis.

Natural Products

N. Z. Burns, P. S. Baran* 205–208

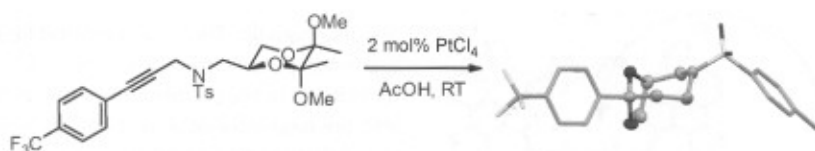
On the Origin of the Haouamine Alkaloids

Domino Sequence

A. Diéguez-Vázquez, C. C. Tzschucke,
W. Y. Lam, S. V. Ley* 209–212



PtCl₄-Catalyzed Domino Synthesis of
Fused Bicyclic Acetals



At sixes and sevens: The synthesis of [4.2.1]- and [3.2.1]-fused bicyclic acetals by an intramolecular double alkoxylation of alkyne diols is reported. The course of the reaction depends on the substitution of the triple bond. Terminal alkynes give the

[3.2.1]bicyclic product by a 6-*exo* pathway, whereas aryl alkynes undergo almost exclusively a 7-*endo* cyclization to give the [4.2.1]bicycles (see scheme, Ts = toluene-4-sulfonyl).



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).

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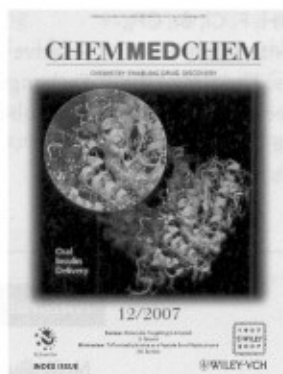
Spotlights *Angewandte's*

Sister Journals 24–25

Keywords 214

Authors 215

Preview 217



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