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

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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

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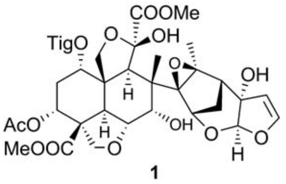
Highlights

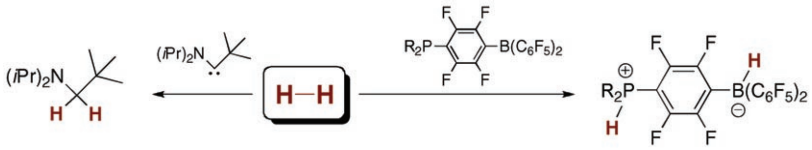
Natural Product Synthesis



1

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

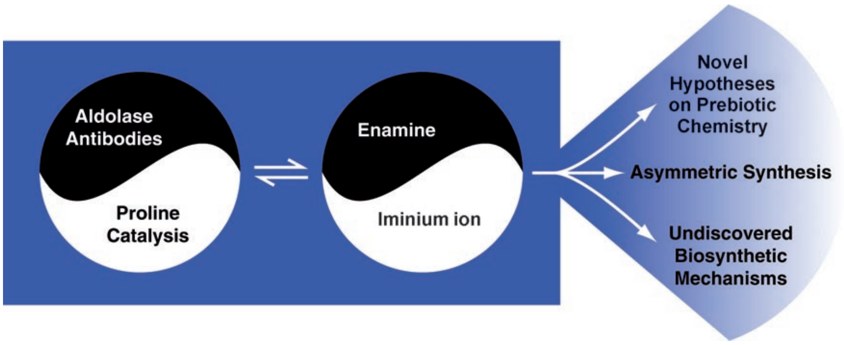
H_2 Activation



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; $R = Me_3C_6H_2$).

Essays

Organocatalysis



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 catalytic 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.

Minireviews

Diversity-Oriented Synthesis

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.

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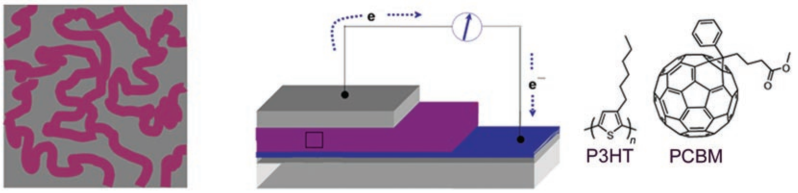
Reviews

Organic Photovoltaics



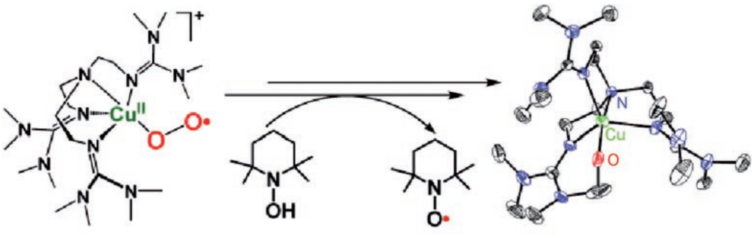
Energy from the sun: Polymer–fullerene (P3HT–PCBM) solar cells have attracted a great deal of attention recently as a result of reports of devices with efficiencies approaching 5 %. The current state-of-the-art in the field is critically examined with a focus on the lessons learned on the electronic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

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.

Copper Superoxo Complexes



1 2

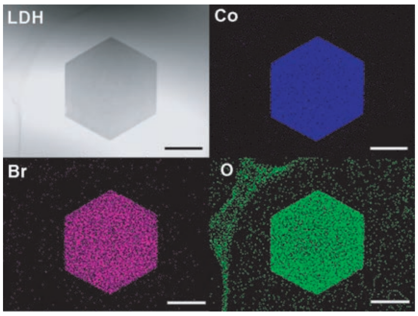
Donor makes the difference: The mononuclear η^1-superoxo copper(II) complex **1** undergoes dioxygen activation with the addition of hydrogen-atom donors. Net O_2-derived O-atom insertion into the *N*-methyl group of the ligand leads to formation of a copper(II)-alkoxide product **2**. The cupric superoxo species **1** itself is not capable of the observed hydroxylation reaction.

Phase Transitions

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

Topochemical Synthesis of Monometallic (Co^{2+}–Co^{3+}) Layered Double Hydroxide and Its Exfoliation into Positively Charged $Co(OH)_2$ Nanosheets

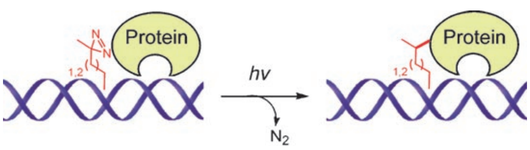
From platelets to sheets: A topochemical phase conversion employing bromine in acetonitrile transforms β-$Co(OH)_2$ into monometallic Co^{2+}–Co^{3+} layered double hydroxide (LDH) with a Co^{2+}/Co^{3+} ratio of 2:1 (see the elemental maps of Co, Br, and O in a Br^--intercalated Co^{2+}–Co^{3+} LDH platelet). Further treatment allows exfoliation of Co^{2+}–Co^{3+} LDH into positively charged $Co(OH)_2$ nanosheets. Scale bars: 2 μm.



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

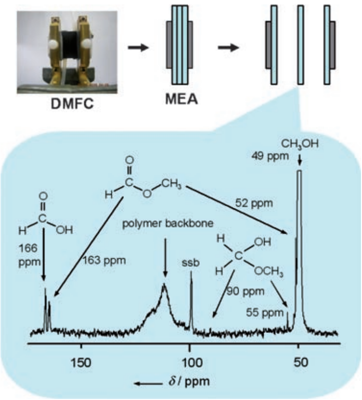


Small modification, large effect: Diazirine can be installed quickly and simply in the major or minor groove of DNA for efficient photo-cross-linking to proteins (see picture). This method should be suitable for mapping out protein–DNA interactions, in particular those that may be sensitive to steric hindrance.

Fuel Cells

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

Methanol Behavior in Direct Methanol Fuel Cells



Methanol crossover and reaction intermediates are studied in a direct methanol fuel cell (DMFC) by means of ^2D and ^{13}C 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).

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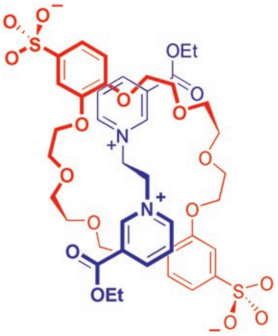
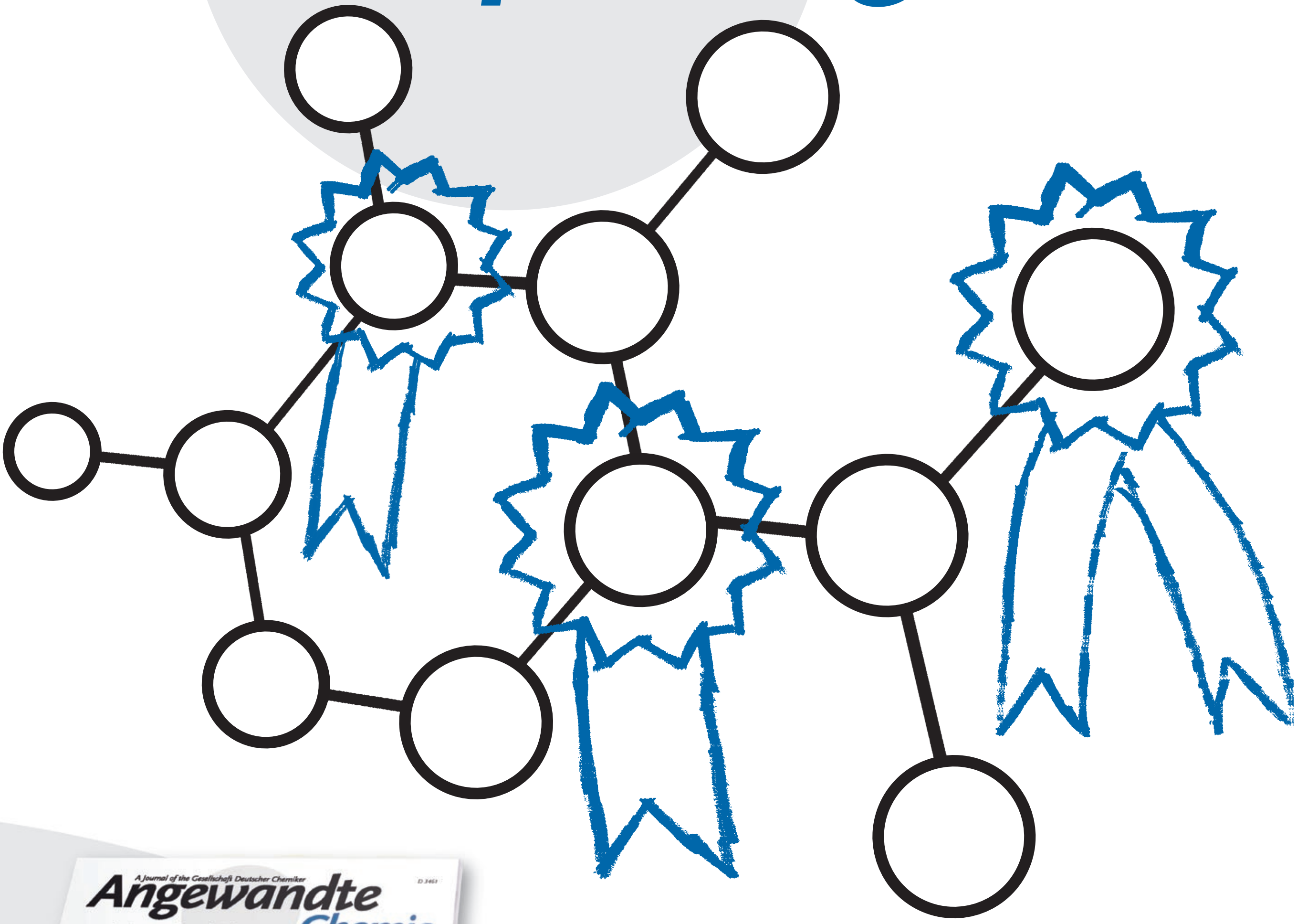
[2]Pseudorotaxanes

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

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).

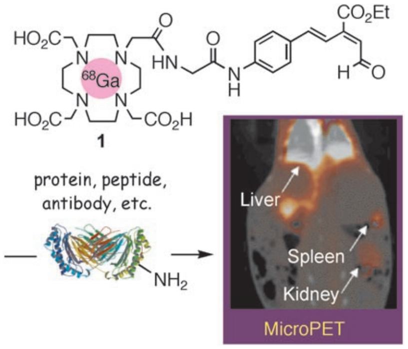




Molecular Imaging

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 6π-Azaelectrocyclization: Visualization of Sialic Acid Dependent Circulatory Residence of Glycoproteins

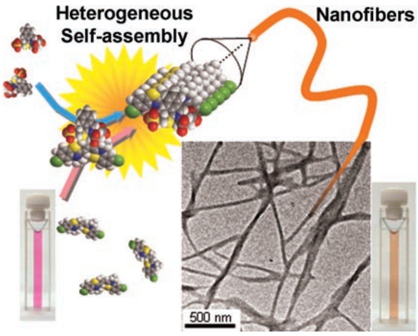


On target: Lysine residues in picomole samples of a peptide, proteins, and a monoclonal antibody were rapidly and selectively labeled by a dota-based probe (**1**, see scheme). Positron emission tomography imaging of [^{68}Ga]dota-labeled orosomucoid and asialoorosomucoid for the first time visualized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

Molecular 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

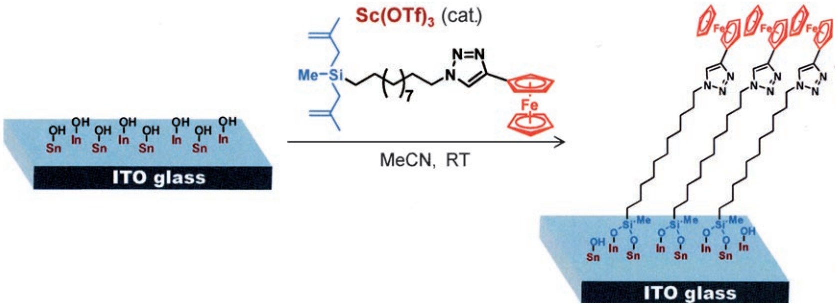


A pretty pair: Self-assembly has been used to amplify and translate the structural information of amino acids into spectroscopic and morphological information (see scheme). It combines in situ premodification of various amino acids and their specific association with a cyanine dye. Conversion of the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

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

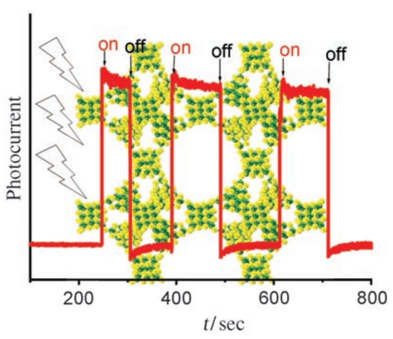


Surface paradise: Facile catalytic post-grafting of the surface of glass or indium tin oxide (ITO, see picture) with a variety of functional groups has been achieved. Methallylsilanes serve as the grafting reagent and the surfaces show remarkable chemical stability.

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



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.

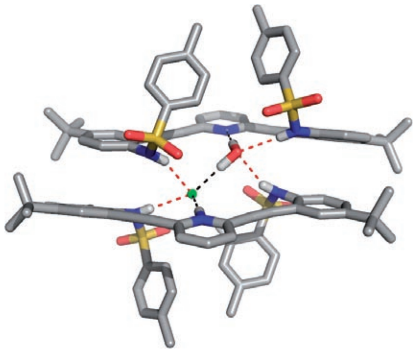
Contents

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

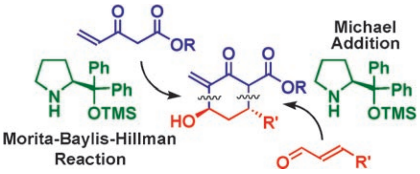
Mix and match: A new series of receptors reveals an unusual propensity to form 2+2 hydrogen-bonded dimers with water or hydrogen halides. Remarkably, water and hydrogen chloride impart nearly identical structural features to the dimers. In fact, in one case (see picture, Cl green, O red, N blue, S yellow),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

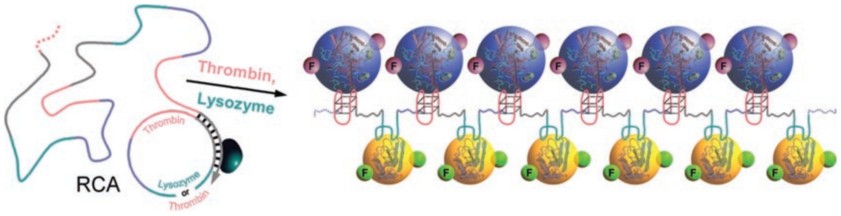


Simply complex: An organocatalytic tandem Michael/Morita–Baylis–Hillman reaction has been developed in which secondary amine catalysts allow for a very selective, scalable synthesis of highly substituted optically active cyclohexanones (see scheme, TMS = trimethylsilyl). Mechanistic studies indicate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

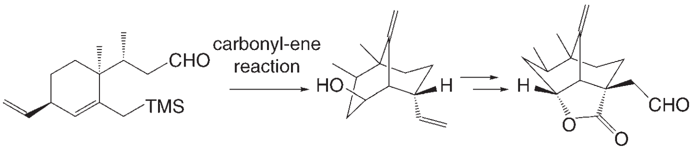


The biomachinery of rolling-circle amplification relying on protein–aptamer interactions on DNA scaffolds was used to create one-dimensional DNA–protein/DNA–protein–nanoparticle hierarchical assemblies. These conjugates can serve as further templates for the immobilization of gold nanoparticles.

Natural Product Synthesis

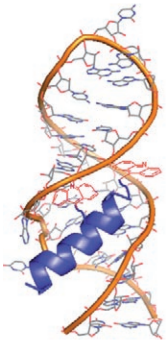
K. Takahashi, M. Watanabe,
T. Honda* ________ **131–133**

Highly Efficient Stereocontrolled Total Synthesis of (+)-Upial



(+)-Upial

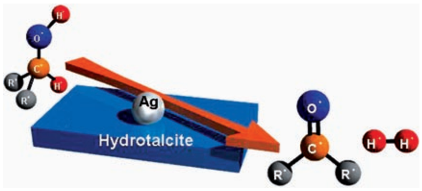
Dual benefit: (+)-Upial, isolated from the sponge *Dysidea fragilis* (Kaneohe Bay, Hawaii), as a nonisoprenoid sesquiterpene aldehyde lactone, was efficiently synthesized. The key step involved an intramolecular carbonyl–ene reaction, in which the stereocontrolled construction of a bicyclo[3.3.1]nonane ring with five asymmetric carbon centers and the facile introduction of the *exo*-methylene unit were achieved in a single step (see scheme).



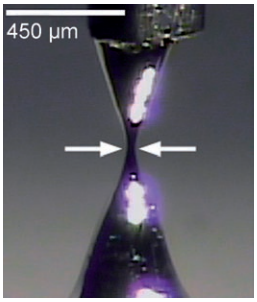
Hold on tight: Amphiphilic α-helical peptides that contain acridine moieties were synthesized, and their binding affinities toward hairpin RNA targets were evaluated. The dramatic increase in binding affinities (40-fold for RRE, 170-fold for TAR) demonstrates that conjugation of intercalators that operate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

Amphiphilic Peptides

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.

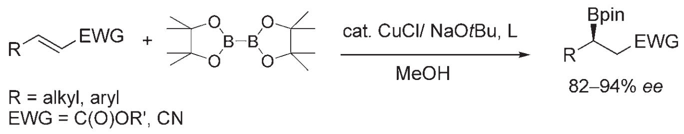


Heterogeneous Catalysis



A great GaIn: Micrometer-sized conformal 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



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

VIP

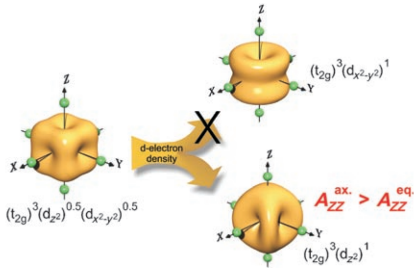
Contents

EPR Spectroscopy

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

Superhyperfine Interaction in $[MnF_6]^{3-}$

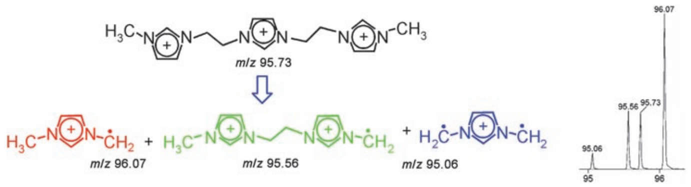
Resolved at last: A conventional spectrometer afforded the first EPR spectrum of a manganese(III) complex, namely $[MnF_6]^{3-}$, featuring clearly resoved superhyperfine interactions. It is shown how the nature of the Jahn–Teller distortion and the concomitant electronic structure (see picture) can 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

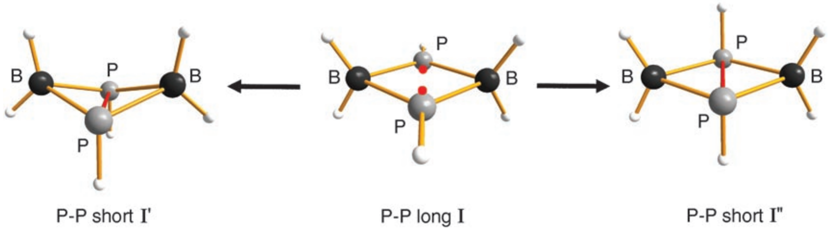


A window of opportunity: New types of gaseous multiply charged (di-)radicals based on ionic liquids have been prepared by ESI MS/MS techniques by using imidazolium ion sites to act as “handles”. Dissociation of gaseous $(CH_2)_n$-bridged triimidazolium ions leads to groups of multiply charged (di-)radicals contained within a narrow window of one m/z unit (see spectrum).

Bond-Stretch Isomers

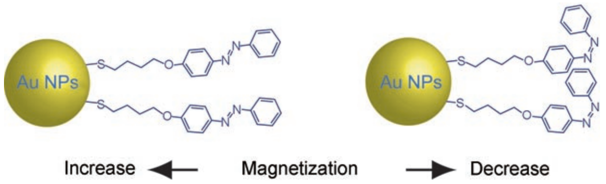
V. Gandon, J.-B. Bourg, F. S. Tham,
W. W. Schoeller,* G. Bertrand* **155 – 159**

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



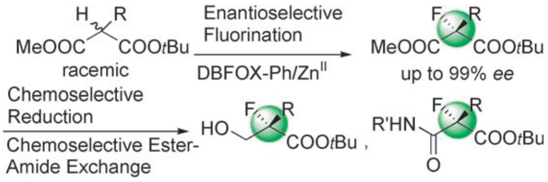
Really (di)radical: Calculations show that parent 2,4-diborata-1,3-diphosphoniocyclobutane-1,3-diyl **I** has a negligible singlet–triplet energy gap (1.2 kcal mol^{-1}) and would be a perfect diradical that could undergo both disrotatory and conrotatory ring closures to give bicyclo[1.1.0]butane derivatives **I**′ and **I**″. The synthesis of a type **I**′ derivative is presented.

Photomagnetic Effects



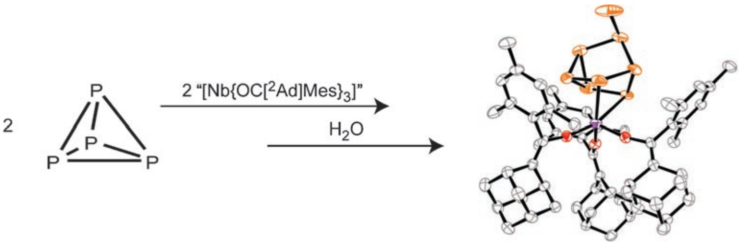
Out of nowhere: Significant photoinduced changes in ferromagnetism have been observed at the interfaces between gold nanoparticles (Au NPs) and azobenzene-derivatized thiols. These photomagnetic effects could be attributed to photoinduced changes in d-charge losses resulting from the photoisomerization of the azo ligands (see picture), which are accompanied by the inversion of surface dipoles to the opposite sign.

Asymmetric Synthesis



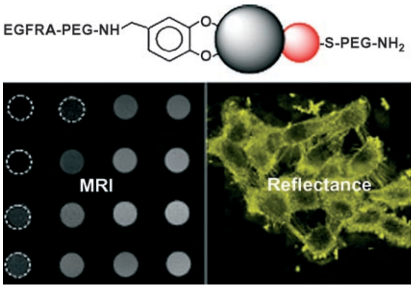
At the leading edge: Chiral fluoromalonates can be prepared with very high stereocontrol by enantioselective fluorination of racemic malonates and using a $Zn(OAc)_2$/DBFOX–Ph catalyst (see scheme), thus providing an efficient alternative route to conventional microbial desymmetrization for the preparation of fluorinated chiral building blocks. Several pharmaceutically attractive compounds were prepared by using this method.

P_4 Activation



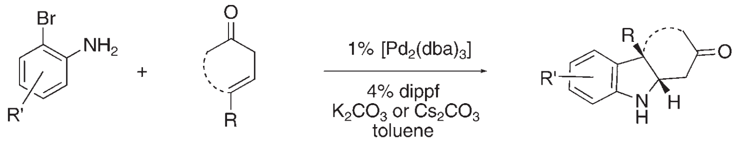
Eight's company: Disproportionation of $[NbI(OC[^2Ad]Mes)_3(thf)]$ in the presence of P_4 results in reductive coupling of two molecules of P_4. The resulting complex, which features a niobium phosphinidene moiety, can subsequently be hydrolyzed (see picture; P orange, Nb blue, O red; ^{2}Ad = 2-adamantylidene; Mes = 2,4,6-$Me_3C_6H_2$).

Multifunctional Nanoprobes



Heavy lifting: Dumbbell-shaped Au–Fe_3O_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 Au–Fe_3O_4 nanoparticles are promising as a new type of multifunctional probe for diagnostic and therapeutic applications.

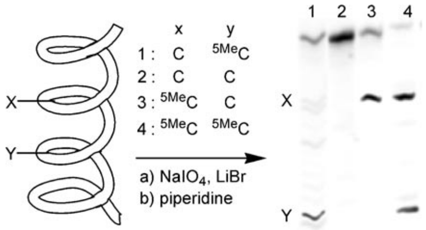
Tricyclic Indolines



Indolines in short order: A catalyst system which allows for efficient γ-arylation of β,γ-unsaturated ketones is described (see scheme; dippf=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.

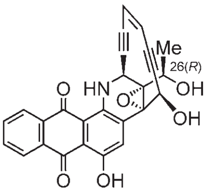
Epigenetic Sequencing

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 promotor to be determined under in vitro conditions.



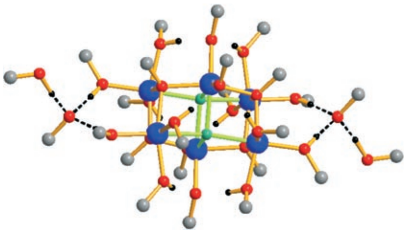
Natural Product Synthesis

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.



1: uncialamycin

Magnesium Alkoxide Fluoride

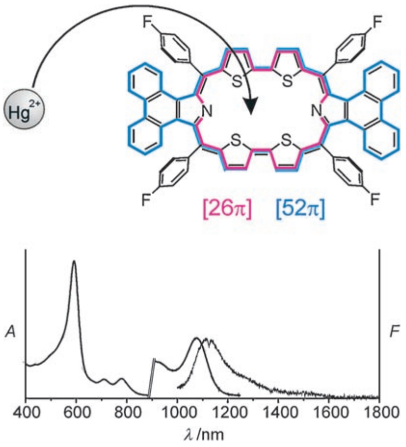


Partial fluorolysis of magnesium alkoxide with HF leads to an unexpected crystalline magnesium alkoxide fluoride intermediate. The hexanuclear, cationic dicubane unit is bridged by unusual μ_4-F atoms and hydrogen-bonded to two methoxide anions, resulting in a triple-ionic structure (see picture, F green, Mg blue, O red, C gray, H black).

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

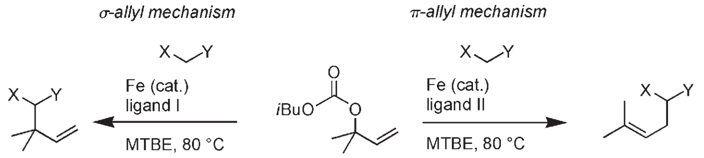


Sending signals: The first core-modified, expanded porphyrin with polyaromatic units fused to the pyrrole rings absorbs far into the near-infrared and shows fluorescence that stretches into the second optical window of telecommunication. Doping a polyurethane membrane with the dye yields Hg^{2+}-responsive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

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

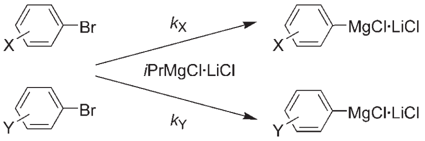


Iron at the crossroads: A remarkable mechanistic dichotomy in iron-catalyzed allylic substition increases not only the scope of regioselective allylic alkylation but could also herald the development of asymmetric allylic substitution (see Scheme, MTBE = methyl *tert*-butyl ether). Depending on the ligand used, either a σ- or a π-allyl mechanism is observed.

Grignard Reagents

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

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

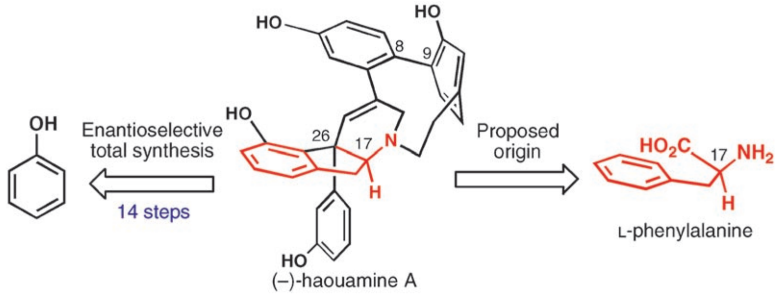


Against expectation: How can the site of Br–Mg exchange in multiply brominated compounds be predicted? Competition experiments with different substituents X and Y (see scheme; X, Y = H, F, Cl, Br, CF_3, CO_2tBu, CN) reveal a counterintuitive order of substituent effects. The aim of the study is to enable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

Natural Products

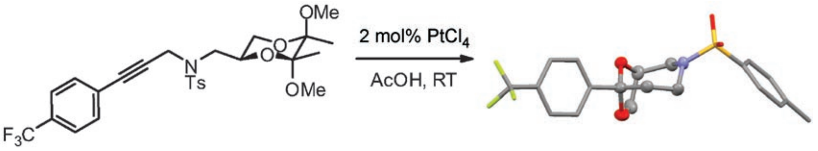
N. Z. Burns, P. S. Baran* ——— 205 – 208

On the Origin of the Haouamine Alkaloids



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

Contents



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).

The issues for December 2007 appeared online on the following dates
Issue 45: November 8. · Issue 46: November 16. · Issue 47: November 23. · Issue 48: December 5.

Service