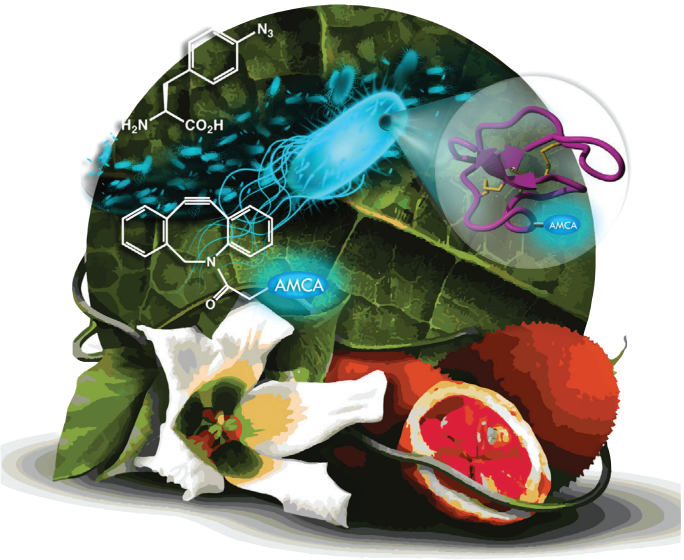
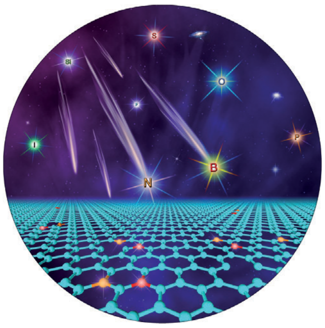
Cyclotides are natural microproteins …

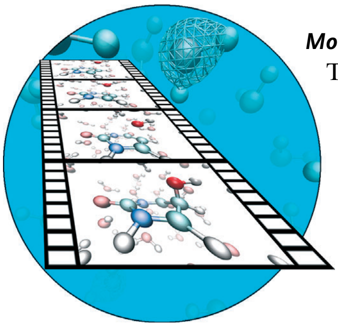


… found in plants with a head-to-tail circular Cys-knotted topology. In their Communication on page 3126 ff., J. A. Camarero et al. show the recombinant production of a fluorescently labeled cyclotide inside live bacterial cells. Grown in the presence of *p*-azidophenylalanine and a dibenzocyclooctyne derivative of the fluorescent dye aminomethylcoumarin acetate (AMCA) the peptide is labeled in vivo. Cover art: Isaac Mora.

Oxygen Reduction Reaction

B/N-doped graphene shows a synergistic effect that boosts its catalytic activity for oxygen reduction. The excellent catalytic performance of the new metal-free catalyst is comparable to that of commercial Pt/C, as explained by S. Z. Qiao et al. in their Communication on page 3110 ff.



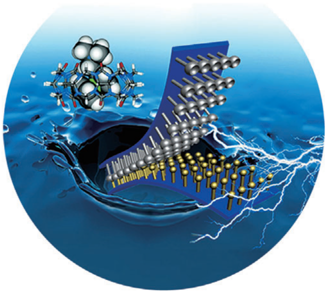


Molecular Dynamics

The Coulombic explosion of a uracil molecule, set off by an ionized water molecule, is studied by M.-A. Hervé du Penhoat, M.-F. Politis, et al. in their Communication on page 3160 ff. They used molecular dynamics methods to investigate the influence of ionizing radiation on DNA.

Supramolecular Assembly

Underwater adhesion between two surfaces was produced using the host–guest binding pair of cucurbit[7]uril and aminomethylferrocene. In their Communication on page 3140 ff., K. Kim et al. demonstrate the strength and reversibility of this supramolecular velcro.



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"In a spare hour, I chat with friends.
If I could be anyone for a day, I would be a poet …"
This and more about Zhenyang Lin can be found on page 3062.

News

S. Perrier

L. Spiccia

P. Thordarson

K. A. Stubbs

P. Rutledge

T. Maschmeyer

S. Grimme

B. Meunier

M. Brimble

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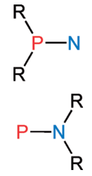
Books

Highlights

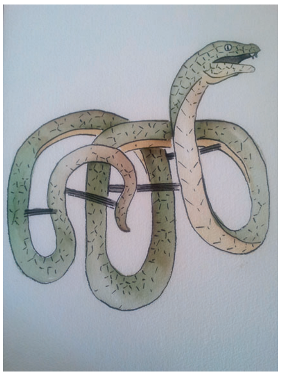
PN Chemistry

Finally isolated: The isolation of a nitridophosphane(V) was described for the first time by the research group of Bertrand. The reactivity and the possibility of stabilizing labile R_2PN/R_2NP species (see structure) are discussed.



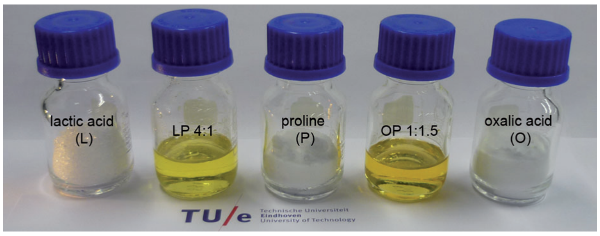
Venoms to Drugs

The black mamba snake here illustrates the structure of mambaglin-1, a pain-relieving peptide found in its venom. Thick gray lines lines represent the four disulfide bonds linking Cys1–3, 2–4, 5–6, and 7–8. The N-terminus of the 57 amino acid peptide is at the head of the snake and the C-terminus at the tail. The peptide has potential as a pharmacological probe or drug lead. Image design by David Craik and drawing by Peta Harvey, University of Queensland.



Minireviews

Green Solvents



Liquefaction: LTTMs are promising "green" media for multiple applications, including separation processes. They can be formed by mixing high-melting-point starting materials, which form a liquid as a result of hydrogen-bond interactions (see picture). Among LTTMs, deep-eutectic solvents (DESs) are presented as renewable, biodegradable, and cost-effective alternatives to conventional ionic liquids (ILs).

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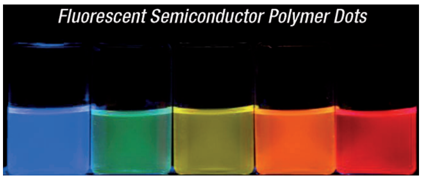
Reviews

Polymer Dots

C. Wu, D. T. Chiu* ———— **3086 – 3109**

Highly Fluorescent Semiconducting Polymer Dots for Biology and Medicine

On the dot: As a new class of fluorescent nanoparticles, semiconducting polymer dots, exhibit excellent characteristics such as extraordinary fluorescence brightness, fast emission rates, excellent photostability, nonblinking, and nontoxicity. This review summarizes recent advances of the polymer dots as nanoparticle labels for biological and medical applications (see figure).



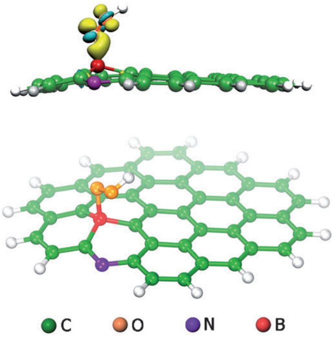
Communications

Oxygen Reduction

Y. Zheng, Y. Jiao, L. Ge, M. Jaroniec, S. Z. Qiao* ———— **3110 – 3116**

Two-Step Boron and Nitrogen Doping in Graphene for Enhanced Synergistic Catalysis

Frontispiece

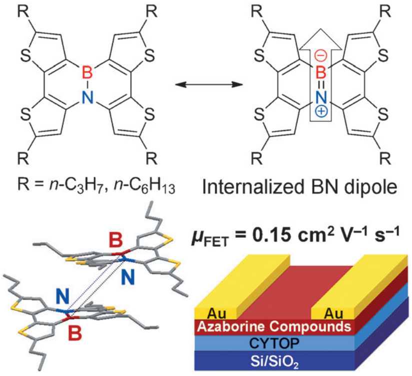


Don't be a dope: be a double dope! Graphene was doped with both boron and nitrogen at well-defined doping sites to induce a synergistic effect that boosts its catalytic activity for oxygen reduction (see structure). The excellent catalytic performance of the new metal-free catalyst is comparable to that of commercial Pt/C.

Molecular Electronics

X.-Y. Wang, H.-R. Lin, T. Lei, D.-C. Yang, F.-D. Zhuang, J.-Y. Wang,* S.-C. Yuan,* J. Pei* ———— **3117 – 3120**

Azaborine Compounds for Organic Field-Effect Transistors: Efficient Synthesis, Remarkable Stability, and BN Dipole Interactions

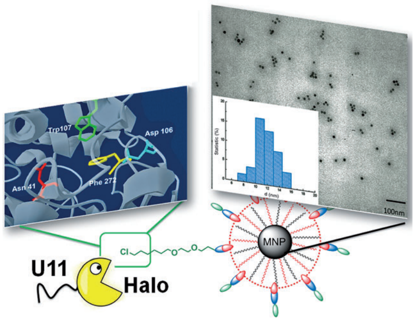


Boron–nitrogen units were incorporated into thiophene-fused polycyclic aromatic compounds. Organic field-effect transistors based on these azaborine compounds were fabricated, demonstrating a novel engineering concept of organic semiconductors and providing opportunities of a broad class of BN-containing compounds for application in future organic electronic devices (see picture; μ_{FET} = hole mobility).

Peptide Nanoconjugation

S. Mazzucchelli,* M. Colombo, P. Verderio, E. Rozek, F. Andreata, E. Galbiati, P. Tortora, F. Corsi, D. Prosperi* ———— **3121 – 3125**

Orientation-Controlled Conjugation of Haloalkane Dehalogenase Fused Homing Peptides to Multifunctional Nanoparticles for the Specific Recognition of Cancer Cells



In control: The ligand positioning and orientation on multifunctional nanoparticles (MNP) are controlled by using a versatile bimodular approach that exploits an 11 amino acid (U11) homing peptide genetically fused with a haloalkane dehalogenase (HALO) enzyme. The resultant nanoparticles have good targeting efficiency and selectivity toward broadly occurring urokinase plasminogen activator receptor positive human cancer cells.

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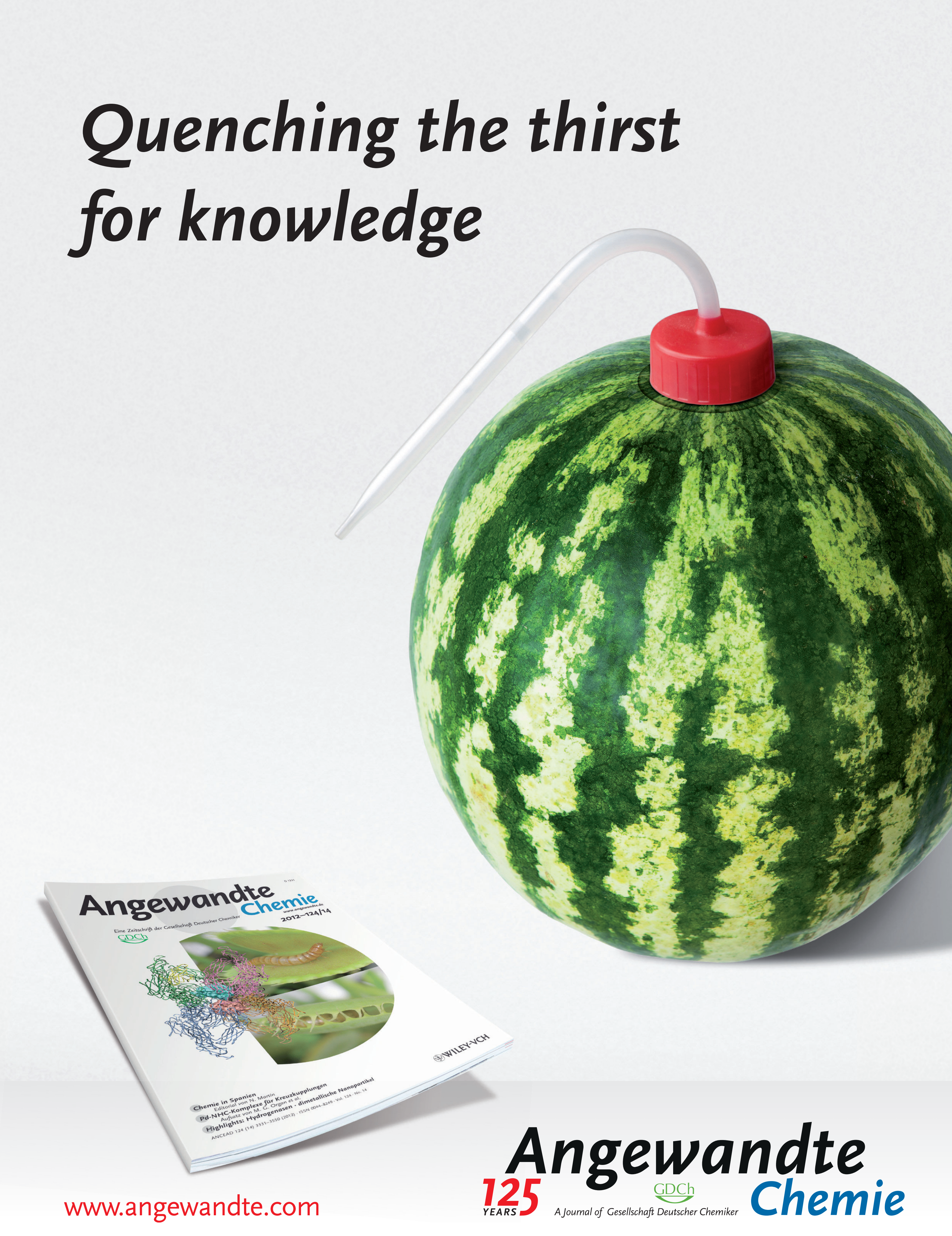
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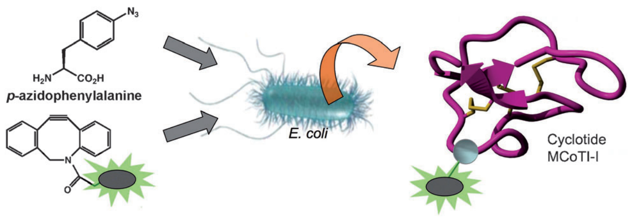
Cyclic Peptides

K. Jagadish, R. Borra, V. Lacey, S. Majumder, A. Shekhtman, L. Wang, J. A. Camarero* ———— **3126–3131**

Expression of Fluorescent Cyclotides using Protein Trans-Splicing for Easy Monitoring of Cyclotide–Protein Interactions



Going in circles: Expression of cyclotides containing non-natural amino acids (see scheme; gray sphere) inside live bacterial cells was accomplished using a highly efficient split intein in combination with nonsense codon suppressor tRNA technology. Cyclotides containing *p*-azidophenylalanine can be expressed in live bacterial cells and easily labeled using copper-free click chemistry to monitor the cyclotide–protein interactions.

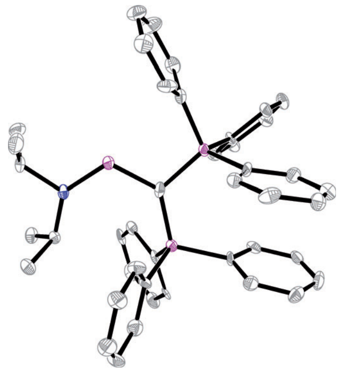
Front Cover

Phosphenium Dications

M. Q. Y. Tay, Y. Lu, R. Ganguly, D. Vidović* ———— **3132–3135**

A Carbone-Stabilized Two-Coordinate Phosphorus(III)-Centered Dication

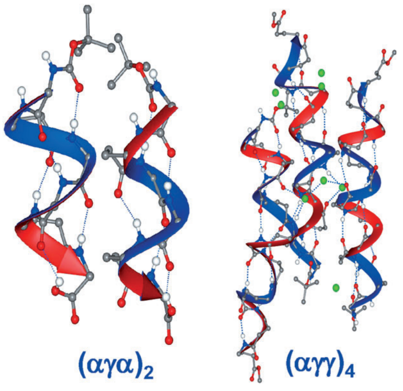
A coordinatively unsaturated dicationic phosphorus compound has been synthesized and characterized (see structure; P pink, N blue, C gray). DFT calculations revealed that the polycation should show superior Lewis acid and σ-donor properties to the corresponding bis(dimethylamino)phosphenium cations. Preliminary investigations with PMe_3 confirmed unusual reactivity patterns for the dication.



Hybrid-Peptide Helices

K. Basuroy, B. Dinesh, N. Shamala,* P. Balaram* ———— **3136–3139**

Promotion of Folding in Hybrid Peptides through Unconstrained γ Residues: Structural Characterization of Helices in $(\alpha\gamma\gamma)_n$ and $(\alpha\gamma\alpha)_n$ Sequences



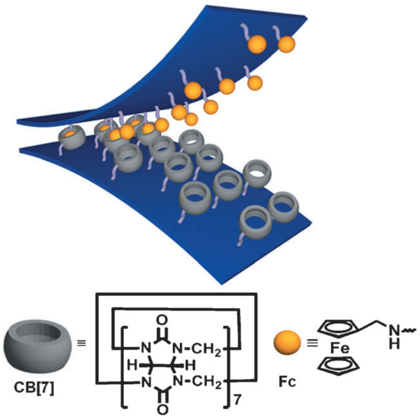
The γ-amino acid residue γ^4(R)Val promotes helical folding even in short $(\alpha\gamma\alpha)_n$ sequences. A mixed C_{12}/C_{14} helix (in which hydrogen bonds close a ring of 12 or 14 atoms) is established in a 12-residue $(\alpha\gamma\gamma)_4$ sequence (see picture, right). The 6-residue $(\alpha\gamma\alpha)_2$ sequence (left), devoid of backbone conformational constraints, folds into a C_{12}/C_{10} helix.

Supramolecular Chemistry

Y. Ahn, Y. Jang, N. Selvapalam, G. Yun,
K. Kim* **3140 – 3144**

Supramolecular Velcro for Reversible Underwater Adhesion

Back Cover



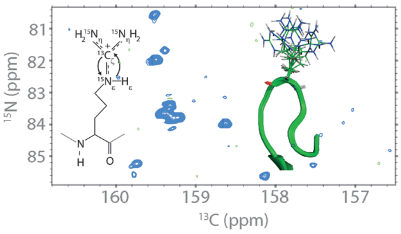
Sticky job: Excellent underwater adhesion with remarkable mechanical and chemical reversibility has been demonstrated with a supramolecular velcro using host–guest chemistry and multivalent interactions (see scheme). Silicon surfaces (blue) functionalized with cucurbit[7]uril (CB[7]) hosts and aminomethylferrocene (Fc) guests adhere under water because of their extraordinarily high affinity.

Protein NMR Spectroscopy

N. D. Werbeck, J. Kirkpatrick,
D. F. Hansen* **3145 – 3147**

Probing Arginine Side-Chains and Their Dynamics with Carbon-Detected NMR Spectroscopy: Application to the 42 kDa Human Histone Deacetylase 8 at High pH

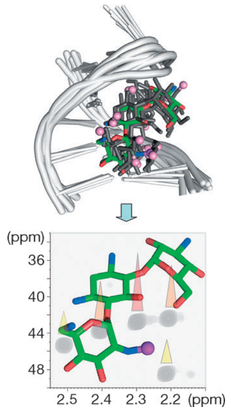
Arginine side-chains play a distinct role because of their high pK_a and perpetual positive charge. An NMR method is presented, based on carbon-detected $^{13}C_\zeta$–$^{15}N_\varepsilon$ correlation spectra, which allows probing the arginine side-chains and their dynamics at neutral-to-high pH. The methodology is demonstrated on human histone deacetylase 8.



Medicinal Chemistry

E. Jiménez-Moreno, I. Gómez-Pinto,
F. Corzana, A. G. Santana, J. Revuelta,
A. Bastida, J. Jiménez-Barbero,
C. González, J. L. Asensio* **3148 – 3151**

Chemical Interrogation of Drug/RNA Complexes: From Chemical Reactivity to Drug Design



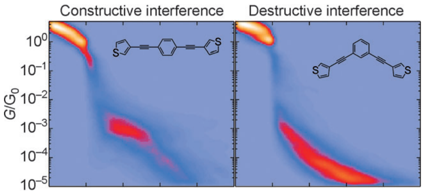
When you're in a (RNA) bind: An NMR-based method to explore the reactivity of ligand/RNA complexes can be used as source of valuable information for drug design. By combining NMR spectroscopy and a simple isotopic labeling strategy (see picture), positional chemical reactivity information can be readily extracted from complex aminoglycoside mixtures. C green, N blue, O red, Me purple.

Quantum Interference

C. R. Arroyo, S. Tarkuc, R. Frisenda,
J. S. Seldenthuis, C. H. M. Woerde,
R. Eelkema,* F. C. Grozema,*
H. S. J. van der Zant* **3152 – 3155**

Signatures of Quantum Interference Effects on Charge Transport Through a Single Benzene Ring

Molecular electronics: Charge transport through a single benzene ring is studied using the mechanically controlled break-junction technique. The low-bias conductance for a *meta*-coupled benzene ring is more than an order of magnitude smaller than that of a *para*-coupled benzene ring. This difference can be explained by a destructive quantum interference effects in the *meta*-coupled benzene (see picture).



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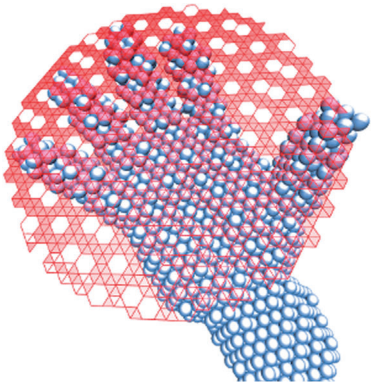
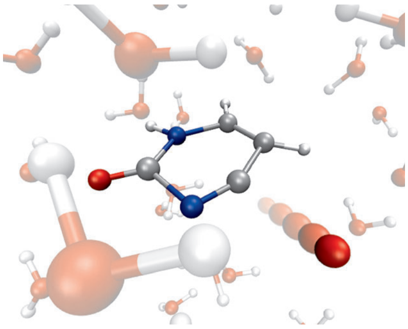


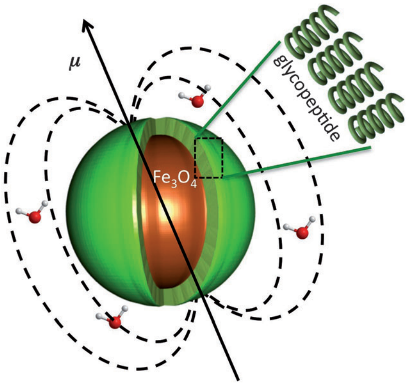
Boron synthesis, in theory: Although two-dimensional boron sheets have attracted considerable interest because of their theoretically predicted properties, synthesis of such sheets remains a challenge. The feasibility of different synthetic methods for two-dimensional boron sheets (see picture; red) was assessed using first-principles calculations, possibly paving the way towards its application in nanoelectronics.



Coulombic explosion of uracil: Ionizing radiation is used in cancer therapy to induce molecular damage in cells. Ab initio molecular dynamics were used to probe the early dissociation processes and ensuing chemical reactions following selective ionization of either uracil or the surrounding water molecules (see scheme; C gray, N blue, O red, H white).

Inside Back Cover

Sweet nanomagnets: Suspensions of glycopeptide grafted magnetic nanoparticles can be produced by *N*-carboxyanhydride ring-opening polymerization with subsequent click glycosylation. The resulting materials have a high sugar density, optimal dispersion and T_1-weighted MRI properties, and bio-recognition ability. The approach can be used to attach any type or combination of functional groups, the density of which is not limited by particle surface area.



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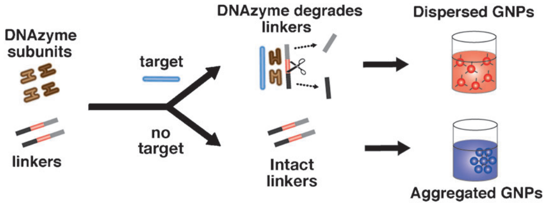
DNAzyme Biosensor

K. Zagorovsky,
W. C. W. Chan* ________ 3168 – 3171

A Plasmonic DNAzyme Strategy for Point-of-Care Genetic Detection of Infectious Pathogens



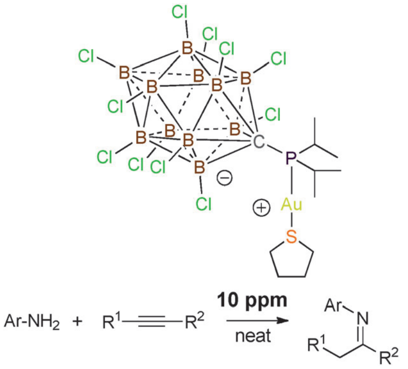
Always use detection: Signal amplification from DNAzymes (see scheme) was combined with gold nanoparticles (GNPs) to give a simple and sensitive colorimetric assay for various genetic targets. The assay has 50 pM sensitivity without the need for purification steps and can detect multiple targets in parallel. This was applied to rapidly detect gonorrhea, syphilis, malaria, and hepatitis B infections.

Carborane Ligands

V. Lavallo,* J. H. Wright, II, F. S. Tham,
S. Quinlivan ________ 3172 – 3176

Perhalogenated Carba-*closo*-dodecaborate Anions as Ligand Substituents: Applications in Gold Catalysis

Bigger and better! The single-component zwitterionic gold catalyst formed by the coordination of a phosphine ligand bearing an inert and noncoordinating carborane substituent, $CB_{11}Cl_{11}^{-}$, to an Au^{I} ion exhibited the highest reported activity for the hydroamination of alkynes with amines (see scheme). The highest turnover number observed for hydroamination with this catalyst exceeded a stunning 95 000.

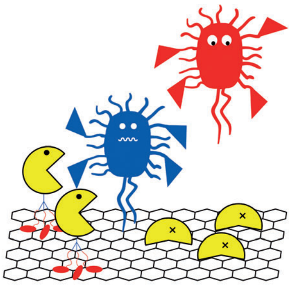


Graphene Biofunctionalization

J. A. Mann, T. Alava, H. G. Craighead,*
W. R. Dichtel* ________ 3177 – 3180

Preservation of Antibody Selectivity on Graphene by Conjugation to a Tripod Monolayer

Three is a magic number: Antibodies adsorbed on bare graphene lose their ability to recognize antigens. However, this obstacle can be overcome by the conjugation of these antibodies to self-assembled monolayers of a tripodal compound (see picture).

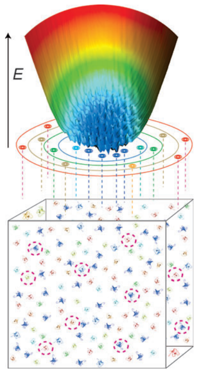


Conformational Dynamics

P. Guerry, L. Salmon, L. Mollica,
J.-L. Ortega Roldan, P. Markwick,
N. A. J. van Nuland, J. A. McCammon,
M. Blackledge* ________ 3181 – 3185

Mapping the Population of Protein Conformational Energy Sub-States from NMR Dipolar Couplings

Molecular dynamics: A general method for the statistical mechanical description of conformational energy landscapes of proteins in solution is proposed. This method combines NMR residual dipolar couplings (RDCs), sampling of conformational space using accelerated molecular dynamics simulation, and ensemble selection using model-free ensemble interpretation of RDCs (see picture).



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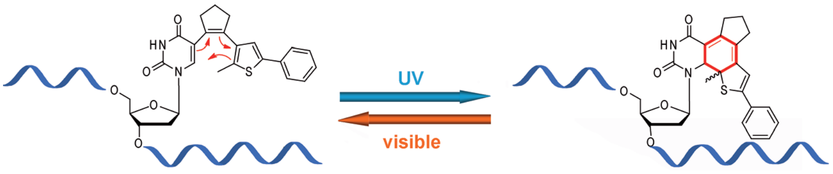
DNA Photoswitches

H. Cahová, A. Jäschke* ____ 3186 – 3190

Nucleoside-Based Diarylethene Photoswitches and Their Facile Incorporation into Photoswitchable DNA

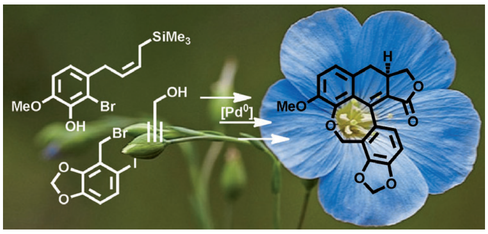


Come into the light: Pyrimidine nucleosides were found to undergo fast and reversible ring closure upon irradiation with light when covalently attached to 2-[2-methyl-5-phenylthien-3-yl]cyclopent-1-ene (see scheme). Synthesis using an aqueous-phase Suzuki–Miyaura cross-coupling allows for one-step conversion of iodo-modified oligonucleotides into fully reversible DNA photoswitches.

Total Synthesis

L. F. Tietze,* S.-C. Duefert, J. Clerc, M. Bischoff, C. Maaß, D. Stalke ____ 3191 – 3194

Total Synthesis of Linoxepin through a Palladium-Catalyzed Domino Reaction

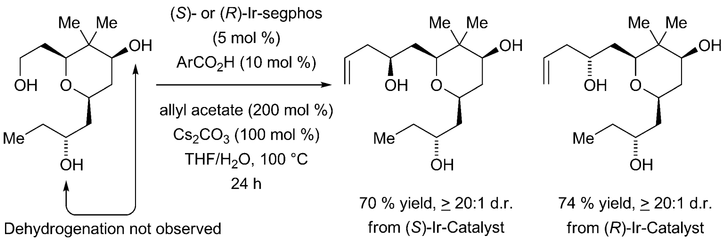


Convergent and elegant: Linoxepin (see picture), a new lignan with an unusual oxepin moiety, has been synthesized in only 10 steps. The protecting-group-free total synthesis includes a palladium-catalyzed Sonogashira reaction and a domino carbopalladation/Heck reaction of an allylsilane.

Synthetic Methods

A.-M. R. Dechert-Schmitt, D. C. Schmitt, M. J. Krische* ____ 3195 – 3198

Protecting-Group-Free Diastereoselective C–C Coupling of 1,3-Glycols and Allyl Acetate through Site-Selective Primary Alcohol Dehydrogenation



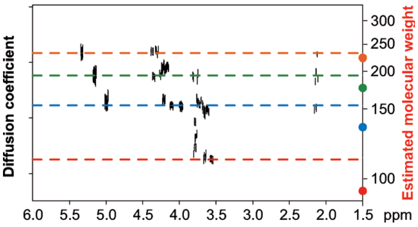
Safe from protection! A pronounced kinetic preference for primary alcohol dehydrogenation enables the site-selective iridium catalyzed C–C coupling of polyols with allyl acetate in the absence of protecting groups, premetallated reagents, chiral auxiliaries, and discrete alcohol-to-aldehyde oxidation.

Analytical Methods

R. Evans, Z. Deng, A. K. Rogerson, A. S. McLachlan, J. J. Richards, M. Nilsson, G. A. Morris* ____ 3199 – 3202

Quantitative Interpretation of Diffusion-Ordered NMR Spectra: Can We Rationalize Small Molecule Diffusion Coefficients?

Appealingly simple: A new method is described that allows the diffusion coefficient of a small molecule to be estimated given only the molecular weight and the viscosity of the solvent used. This method makes possible the quantitative interpretation of the diffusion domain of diffusion-ordered NMR spectra (see picture).



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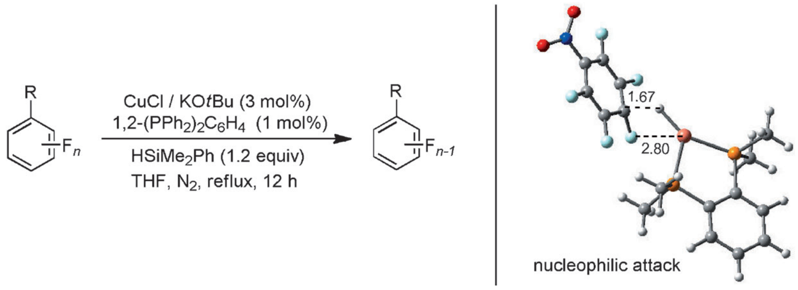
Homogeneous Catalysis

H. Lv, Y.-B. Cai, J.-L. Zhang* **3203 – 3207**

Copper-Catalyzed Hydrodefluorination of Fluoroarenes by Copper Hydride Intermediates

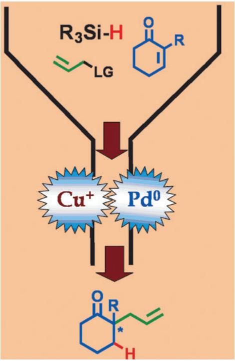


Breaking bad: Efficient copper-catalyzed C–F bond activation has been achieved by replacing fluorine with hydrogen. A copper hydride is proposed as the active intermediate, which proceeds through a nucleophilic attack on the fluorocarbon, as determined by experimental and theoretical results (see structure; C gray, H white, Cu light red, F light blue; distances in Å).

Dual Catalysis

F. Nahra, Y. Macé, D. Lambin, O. Riant* **3208 – 3212**

Copper/Palladium-Catalyzed 1,4 Reduction and Asymmetric Allylic Alkylation of α,β-Unsaturated Ketones: Enantioselective Dual Catalysis

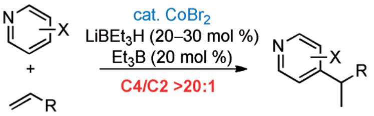


Cooperative efforts: The catalytic coupling of the two organometallic intermediates is possible through a Cu/Pd-based dual catalysis (see scheme; LG = leaving group), in which the Cu^I catalytic cycle generates catalytically the starting material for the Pd^0 catalytic cycle. Although reagents are present in stoichiometric amounts in the reaction mixture and are able to trap both active species, the desired reaction proceeds as planned.

Regioselective Catalysis

T. Andou, Y. Saga, H. Komai, S. Matsunaga,* M. Kanai* **3213 – 3216**

Cobalt-Catalyzed C4-Selective Direct Alkylation of Pyridines

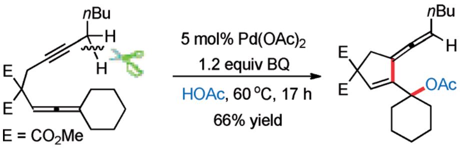


How pyridine got its tail: A new catalyst for the atom-economical C4-selective direct alkylation of pyridines is described. A combination of CoBr$_2$ and LiBEt$_3$H catalyzes the reaction of pyridines with 1-alkenes at 70 °C to give alkylation products with C4/C2 ratios of >20:1. Substrate/catalyst ratios of up to 4000, and a turnover number of 3440 were achieved.

Homogeneous Catalysis

Y. Deng, J.-E. Bäckvall* **3217 – 3221**

Palladium-Catalyzed Oxidative Acyloxylation/Carbocyclization of Allenynes



New bonds: The title reaction provides access to synthetically useful acyloxylated vinylallenes where a new C–C bond, a new C–O bond, and a new allene structure are formed. Furthermore, an aerobic version of this transformation was realized using catalytic amounts of *p*-benzoquinone (BQ) together with catalytic amounts of cobalt salophen.

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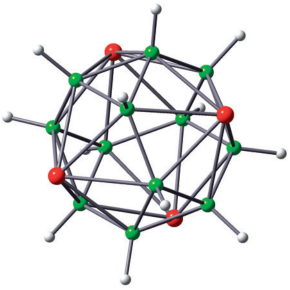
Metallaboranes

D. K. Roy, S. K. Bose, R. S. Anju,
B. Mondal, V. Ramkumar,
S. Ghosh* ______ **3222 – 3226**

Boron Beyond the Icosahedral Barrier: A 16-Vertex Metallaborane

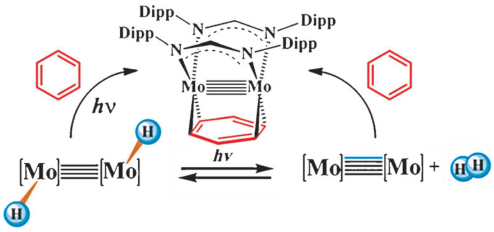


A neutral metallaborane comprising a Rh_4B_{12} polyhedron with icosioctahedron geometry with 16 vertices and 28 triangular faces was prepared (see structure; Rh: red, B: green). The cage has the shape of a 12-membered truncated tetrahedron with four capped hexagonal faces.

Metal–Metal Bonding

M. Carrasco, N. Curado, C. Maya,
R. Peloso, A. Rodríguez, E. Ruiz,
S. Alvarez,* E. Carmona* ______ **3227 – 3231**

Interconversion of Quadruply and Quintuply Bonded Molybdenum Complexes by Reductive Elimination and Oxidative Addition of Dihydrogen

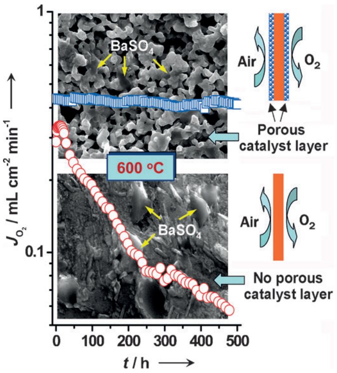


Five plus H_2 gives four: UV irradiation of a bis(amidinate) complex with a [(H)Mo≡Mo(H)] core induces reductive elimination of H_2 and formation of a known quintuply bonded Mo–Mo species (see scheme) that reacts back with H_2 to restore [(H)Mo≡Mo(H)]. UV irradiation of the bis(hydride) species in benzene and toluene gives arene complexes in which the aromatic hydrocarbon bridges the molybdenum atoms. Dipp = 2,6-diisopropylphenyl.

Gas Separation

Y. Liu, X. F. Zhu,* M. R. Li, H. Y. Liu,
Y. Cong, W. S. Yang* ______ **3232 – 3236**

Stabilization of Low-Temperature Degradation in Mixed Ionic and Electronic Conducting Perovskite Oxygen Permeation Membranes

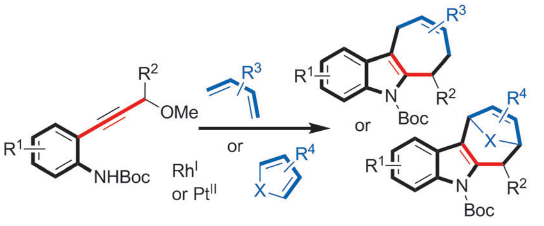


An important degradation mechanism of perovskite membranes is related to the operation-induced surface segregation of trace impurities of sulfur that appears to dramatically impact the low-temperature permeation behavior. A simple but remarkably effective method is reported that enables the low-temperature stabilization of the permeation flux in these perovskite membranes (see picture).

Heterocycles

D. Shu, W. Song, X. Li,
W. Tang* ______ **3237 – 3240**

Rhodium- and Platinum-Catalyzed [4+3] Cycloaddition with Concomitant Indole Annulation: Synthesis of Cyclohepta[*b*]indoles



Various substituted cyclohepta[*b*]indoles were prepared from propargylic ethers and dienes by a tandem indole annulation/[4+3] cycloaddition (see scheme; Boc = *tert*-butoxycarbonyl). Both acyclic and cyclic dienes participated in the [4+3] cycloaddition to afford tri- and tetracyclic products, respectively. Electron-deficient phosphine or phosphite ligands facilitated the tandem reaction.

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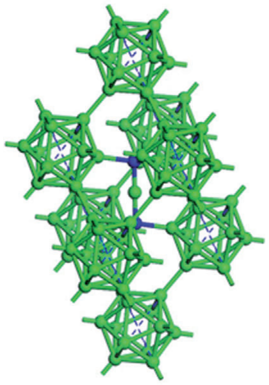
Photoelectrochemical Water Splitting

J. Liu, S. Wen, Y. Hou, F. Zuo,
G. J. O. Beran,* P. Feng* ____ 3241 – 3245

Boron Carbides as Efficient, Metal-Free, Visible-Light-Responsive Photocatalysts

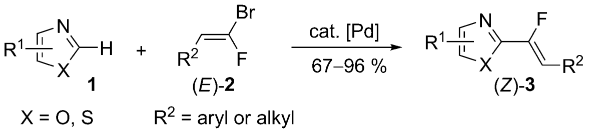
From armor plating to photocatalysis: Two photocatalysts based on boron carbides, $B_{4.3}C$ and $B_{13}C_2$, are reported. The more stable and efficient $B_{4.3}C$ exhibits H_2 evolution rates of about two orders of magnitude higher than graphitic C_3N_4, and without the need for noble metal cocatalysts. Also, both materials can act as photocathodes for photoelectrochemical water reduction under visible light irradiation.



C–H Activation

C. Schneider, D. Masi,
S. Couve-Bonnaire,* X. Pannecoucke,*
C. Hoarau* ____________ 3246 – 3249

Palladium- and Copper-Catalyzed Stereocontrolled Direct C–H Fluoroalkenylation of Heteroarenes using *gem*-Bromofluoroalkenes

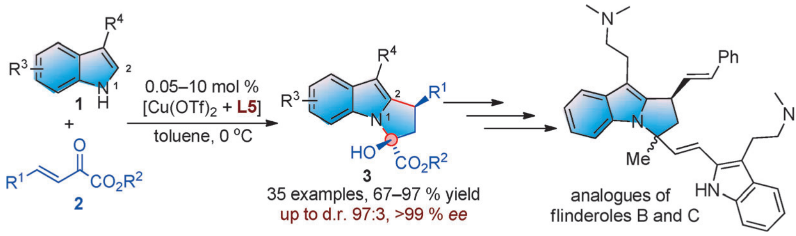


A gem of a reaction: The palladium- and copper-catalyzed base-assisted direct C–H fluoroalkenylation of heterocycles **1** with *gem*-bromofluoroalkenes (*E*)-**2** is reported. This method offers step-economical and stereocontrolled access to valuable trisubstituted heteroarylated monofluoroalkenes (*Z*)-**3**.

Indole Chemistry

H.-G. Cheng, L.-Q. Lu, T. Wang,
Q.-Q. Yang, X.-P. Liu, Y. Li, Q.-H. Deng,
J.-R. Chen,* W.-J. Xiao* ____ 3250 – 3254

Highly Enantioselective Friedel–Crafts Alkylation/*N*-Hemiacetalization Cascade Reaction with Indoles

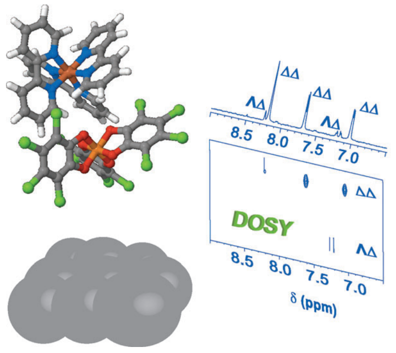


A new ring for your indole: An unprecedented copper-catalyzed enantioselective Friedel–Crafts alkylation/*N*-hemiacetalization cascade reaction with indoles and β,γ-unsaturated α-ketoesters is reported. This mild strategy provides new access to various synthetically and biologically important 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indoles in a highly enantioselective manner.

NMR Spectroscopy

M. Reddy G. N., R. Ballesteros-Garrido,
J. Lacour,* S. Caldarelli* ____ 3255 – 3258

Determination of Labile Chiral Supramolecular Ion Pairs by Chromatographic NMR Spectroscopy



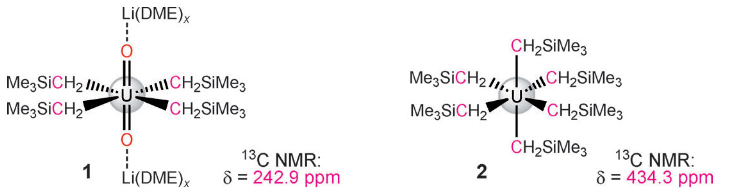
Chiral recognition: Silica-enhanced NMR diffusometry can distinguish the signals of diastereoisomeric mixtures of supramolecular ion pairs (see picture; DOSY = diffusion-ordered spectroscopy). The experiment has a shorter timescale than liquid chromatography, thus allowing an easier characterization of species that are even configurationally labile on the minutes timescale.

Uranium Chemistry

L. A. Seaman, P. Hrobárik,*
M. F. Schettini, S. Fortier, M. Kaupp,
T. W. Hayton* ________ 3259 – 3263

A Rare Uranyl(VI)–Alkyl Ate Complex [Li(DME)$_{1.5}$]$_2$[UO$_2$(CH$_2$SiMe$_3$)$_4$] and Its Comparison with a Homoleptic Uranium(VI)–Hexaalkyl

Inside Cover

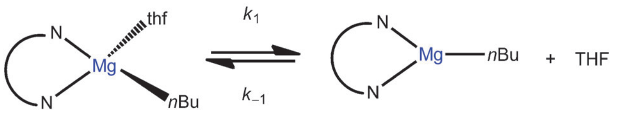


A rare tetraalkyl–uranyl "ate" complex **1** was prepared and characterized for comparison with a U^{VI}–hexaalkyl complex **2**. Both **1** and **2** feature unprecedented high-frequency methylene ^{13}C NMR shifts (see picture). That of complex **2** constitutes a new record for diamagnetic mononuclear complexes. Relativistic DFT calculations show that these extreme shifts are due to spin–orbit effects, a consequence of significant f-orbital involvement in the U–C bond.

Ligand Effects

M. H. Chisholm,* K. Choojun, A. S. Chow,
G. Fraenkel ________ 3264 – 3266

Molecular Dynamics and Ligand Exchange in Magnesium Complexes: Evidence for both Dissociative and Associative Ligand Exchange

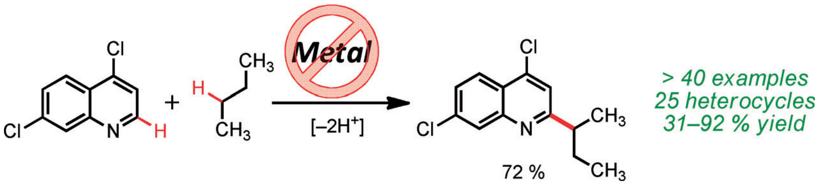


Making a swap: The titled studies provide substantial evidence for the kinetically labile Mg^{2+} ion reacting through both a dissociative (see scheme; thf = tetrahydrofuran) and an associative interchange mechanism. The findings are particularly relevant to the reactions involving [LMg*n*Bu(thf)] and *rac*-lactide in ring-opening polymerization reactions.

C-H Functionalization

A. P. Antonchick,*
L. Burgmann ________ 3267 – 3271

Direct Selective Oxidative Cross-Coupling of Simple Alkanes with Heteroarenes

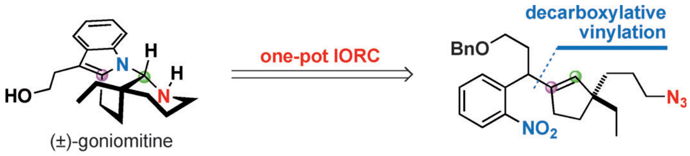


A dream reaction: An efficient and practical method for the oxidative cross-coupling of heteroaromatic compounds and simple alkanes has been developed. The desired products are smoothly and regioselectively formed under mild reaction conditions at ambient temperature in a hypervalent-iodine-mediated transformation. The method allows for preferential transformation of stronger C$_{sp^3}$–H bonds in the presence of weaker C$_{sp^3}$–H bonds under metal-free conditions.

Natural Product Synthesis

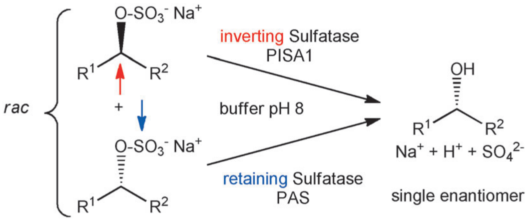
Z. Xu, Q. Wang, J. Zhu* ____ 3272 – 3276

Palladium-Catalyzed Decarboxylative Vinylation of Potassium Nitrophenyl Acetate: Application to the Total Synthesis of (±)-Goniomitine



Merge and divert: The natural product (±)-goniomitine was synthesized by a method featuring two key steps: 1) fragment coupling to a functionalized cyclopentene by a novel palladium-catalyzed decarboxylative vinylation reaction and 2) an unprecedented one-pot integrated oxidation/reduction/cyclization (IORC) process to convert the substituted cyclopentene into the tetracyclic skeleton of goniomitine with high chemo-, regio-, and diastereoselectivity.

Biotransformations



Hand in hand: The title transformation was achieved using a pair of sulfatases acting through inversion and retention of configuration on opposite substrate enantiomers. Using *Pseudomonas aeruginosa* arylsulfatase PAS with alkylsulfatase PISA1 in one-pot leads to *sec*-alcohols (80 to > 99 % conversion) with 91 to greater than 99 % *ee*.

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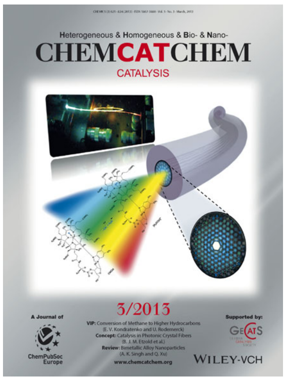

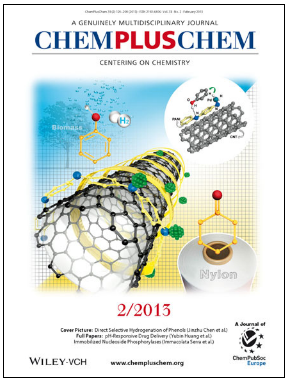

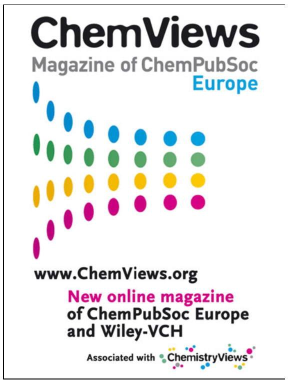

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