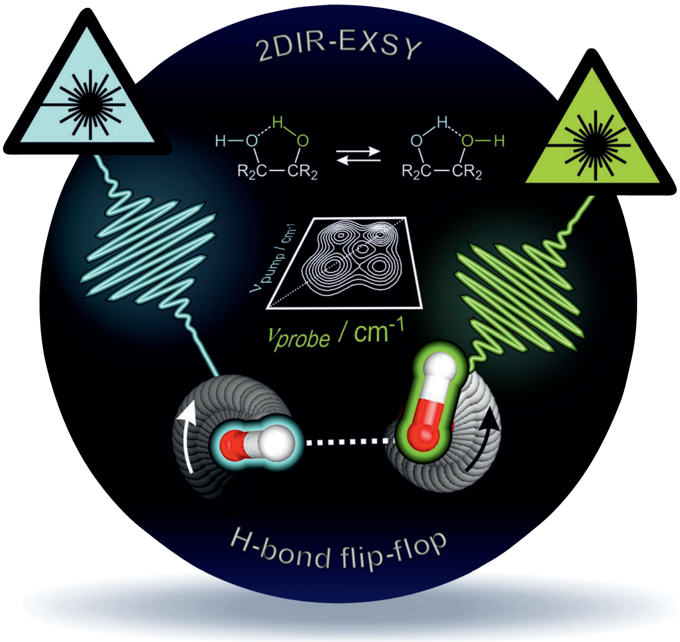
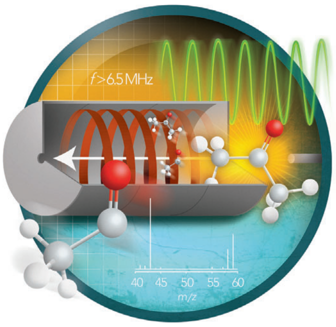
Hydrogen bonds ...

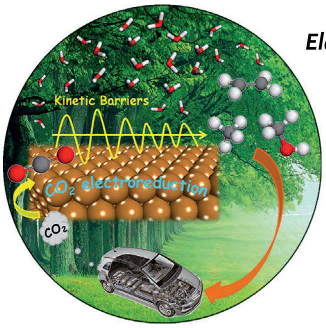


… can dynamically reverse their direction by means of an ultrafast flip-flop motion of the donor and acceptor moieties engaged in the noncovalent contact. In their Communication on page 2602 ff., P. Vöhringer and co-workers describe an application of femtosecond two-dimensional infrared exchange spectroscopy (2DIR-EXSY) in which these elementary dynamics are observed in the time domain of a simple model system, a vicinal diol.

Mass Spectrometry

In their Communication on page 2426 ff., T. Soloukі and B. Zekavat describe a new ionization technique using radio-frequency signals for the mass spectrometric analysis of volatile and semivolatile organic molecules.



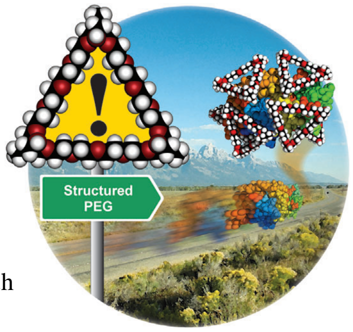


Electroreduction

CO_2 electroreduction on copper is described by M. J. Janik, A. Asthagiri, and co-workers in their Communication on page 2459 ff. DFT calculations of the activation barriers of elementary steps reveal a new path that leads to methane and ethylene.

Protein Manipulation

T. Muraoka, K. Kinbara, and co-workers report in their Communication on page 2430 ff. that a triangular PEG analogue has a lower dehydration temperature than the corresponding linear PEGs, and suppresses protein thermal aggregation with high efficiency.



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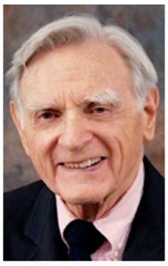
Author Profile

"My motto is 'science lies in simplicity'. I am waiting for the day when someone will discover a microscope to visualize water, ions, and gases …" This and more about Dayang Wang can be found on page 2400.

News

A. J. Bard



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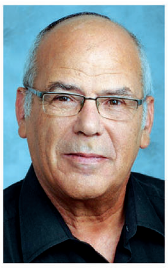

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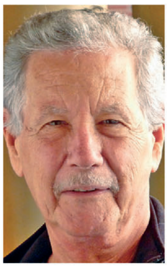


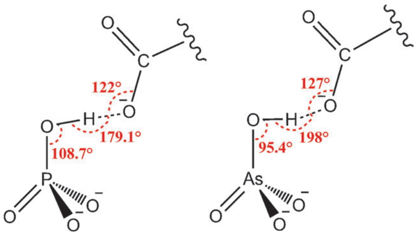
R. D. Levine

A. Ajayaghosh

Books

Highlights

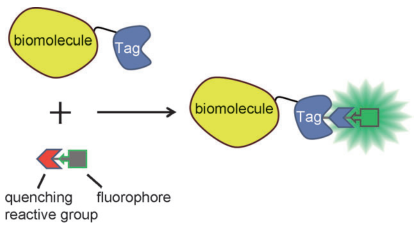
Phosphate Binding Proteins



Discriminating against arsenate: Determination of the structure of periplasmic phosphate binding proteins at very high resolution provides the basis for understanding the high discrimination of bacteria against arsenate. The results complete our insight into earlier erroneous conclusions on the ability of certain bacteria to use arsenate instead of phosphate.

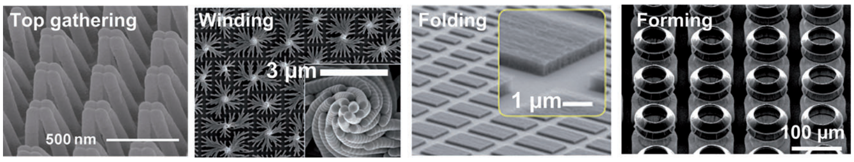
Fluorescent Labeling

A definite turn-on: Turning on fluorescence only where successful labeling is happening sounds as desirable as delivering a drug only where the drug target resides. New fluorogenic xanthene derivatives from the Bertozzi research group are getting us closer to “magic bullet” dyes (see picture).



Reviews

Nanostructures



New insights in capillary interactions between nanofilaments have led to versatile and scalable methods to build complex structures that cannot be achieved by any other processing technique. Understanding the control of this process is conducive to the development of high-performance battery and capacitor electrodes as well as photovoltaics, electrical interconnects, and other smart materials.

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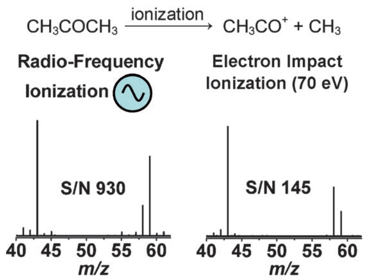
Communications

Mass Spectrometry

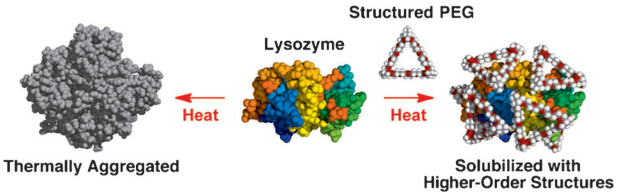
Frontispiece

A new ionization technique: A radio-frequency signal was used to ionize neutral organic molecules in the ultra-high-vacuum region of a Fourier transform ion cyclotron resonance mass spectrometer. Radio-frequency ionization (RFI) yielded signal/noise (S/N) ratios roughly six times higher than those generated by conventional 70 eV electron impact ionization (EI).



Protein Manipulation

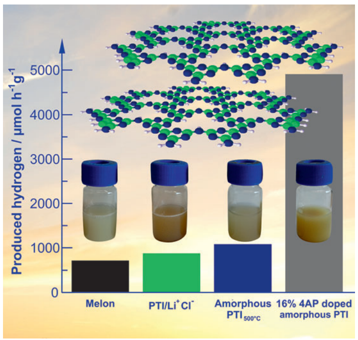
Back Cover



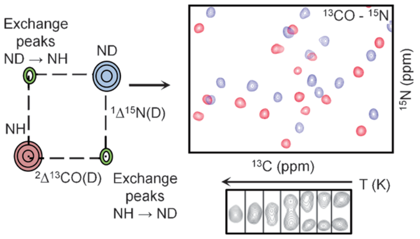
Part of the solution: A PEG with a discrete triangular structure exhibits hydrophilicity/hydrophobicity switching upon increasing temperatures, and suppresses the thermal aggregation of lysozyme to retain nearly 80% of the enzymatic activity. CD and NMR spectroscopic studies revealed that, with the structured PEG, the higher-order structures of lysozyme persist at high temperature, and the native conformation is recovered after cooling.

Photocatalysis

A new dimension: The doping of amorphous poly(triazine imide) (PTI) through ionothermal copolymerization of dicyandiamide with 4-amino-2,6-dihydroxypyrimidine (4AP) results in triazine-based carbon nitrides with increased photoactivity for water splitting compared to crystalline poly(triazine imide) (PTI/Li^+Cl^-, see picture) and melon-type carbon nitrides. This family of carbon nitride semiconductors has potential as low-cost, environmentally clean photocatalysts for solar fuel production.



Hydrogen Exchange



Kinetics and thermodynamics of amide hydrogen exchange in proteins can be investigated with two-dimensional ^{13}CO–^{15}N NMR correlation experiments (see picture). The spectra are acquired with high resolution and sensitivity. A single type of experiment on one sample serves to characterize hydrogen–deuterium fractionation factors and hydrogen-exchange rates that span three orders of magnitude.

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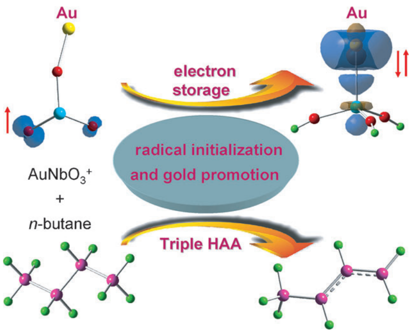
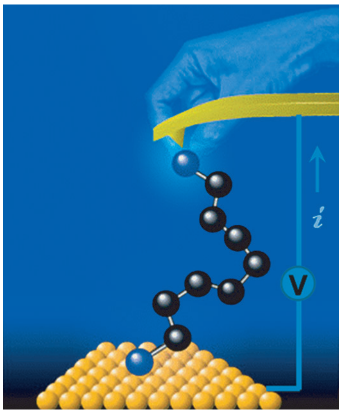


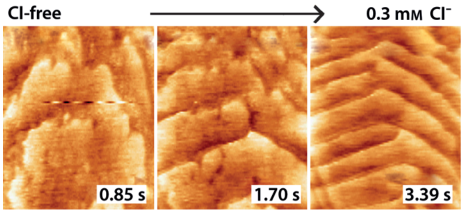
Single, double, triple: Highly selective double H atom abstraction (HAA) from ethane and triple HAA from *n*-butane by $AuNbO_3^+$ clusters have been characterized by mass spectrometry and DFT calculations. The multiple HAAs are initiated by oxygen-centered radicals and promoted by gold. The gold atoms act as electron acceptors during the triple HAAs and help to store a pair of valence electrons between Au and Nb atoms (see picture).

Gold Chemistry



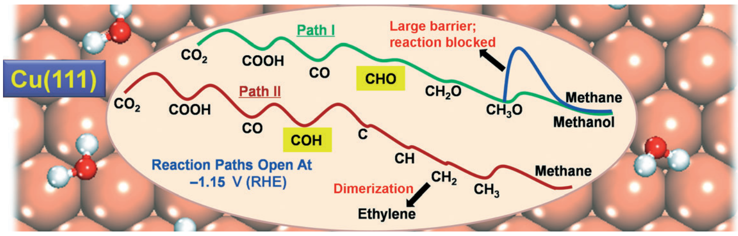
Handling the (AFM) tip: The duration of stable molecular junctions was prolonged using a tactile feedback method in which the operator can sense the force of the AFM tip on the sample surface (see picture). The movement of the tip is adjusted accordingly, maintaining a more consistent current (*i*) and voltage (V), instead of having the tip move at a constant preset speed, as in the conventional setup.

Molecular Electronics



Under the microscope: In situ, video-rate scanning-tunneling-microscopy imaging during Cu electrodeposition reveals a profound structural accelerating effect of Cl^- on the deposition process (see images). This effect could be present in systems with different metals and different additives. The structural accelerating effect is important for the fundamental understanding of electrodeposition phenomena and for applications in industry.

Electrodeposition



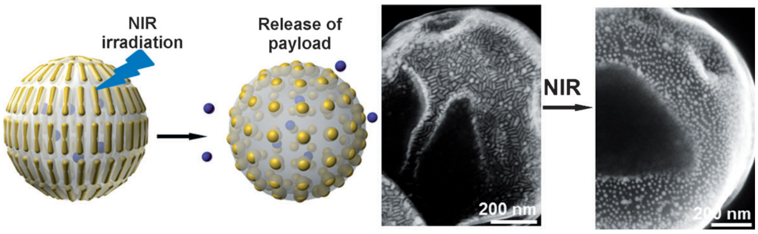
On the right path: Based on DFT calculations (incorporating the role of water solvation) of the activation barriers of elementary steps, a new path that leads to methane and ethylene for CO_2 electroreduction on Cu(111) was identified. Methane formation proceeds through reduction of CO to COH (path II, see picture), which leads to CH_x species that can produce both methane and ethylene, as observed experimentally.

Electroreduction

Giant Vesicles

J. He, Z. Wei, L. Wang, Z. Tomova, T. Babu, C. Wang, X. Han, J. T. Fourkas, Z. Nie* ______ 2463 – 2468

Hydrodynamically Driven Self-Assembly of Giant Vesicles of Metal Nanoparticles for Remote-Controlled Release



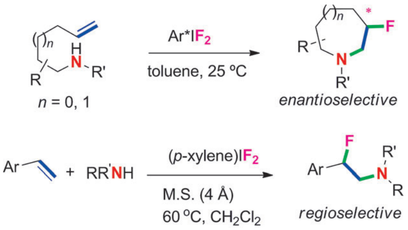
The hydrodynamics of laminar flow in a microfluidic device has been used to control the continuous self-assembly of gold nanoparticles (NPs) tethered with amphiphilic block copolymers. Spherical micelles, giant vesicles (500 nm–2.0 μm), or disk-like micelles could be formed by varying the flow rates of fluids. Such vesicles can release encapsulated hydrophilic species by using near-IR light (see picture).

Asymmetric Synthesis

W. Kong, P. Feige, T. de Haro, C. Nevado* ______ 2469 – 2473

Regio- and Enantioselective Aminofluorination of Alkenes

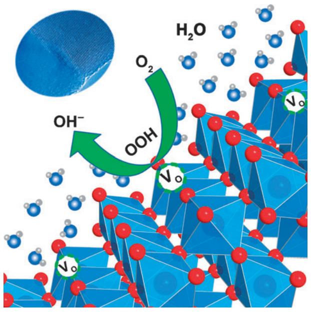
Enantio- and regioselective: The intramolecular enantioselective aminofluorination of unactivated olefins was achieved by using a chiral iodo(III) difluoride salt. A highly regioselective aminofluorination of styrenes to access 2-fluoro-2-phenylethanamines was also developed.



Heterogeneous Catalysis

F. Cheng,* T. Zhang, Y. Zhang, J. Du, X. Han, J. Chen* ______ 2474 – 2477

Enhancing Electrocatalytic Oxygen Reduction on MnO_2 with Vacancies



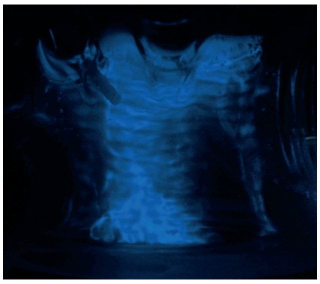
Oxygen-vacant nanocrystalline MnO_2 has been prepared by the simple process of annealing pristine oxide in Ar or O_2. Both experimental and computational studies indicate that the catalytic activity of MnO_2 towards oxygen reduction is enhanced by introducing a modest concentration of oxygen vacancies.

Sonoluminescence

A. A. Ndiaye, R. Pflieger, B. Siboulet, S. I. Nikitenko* ______ 2478 – 2481

The Origin of Isotope Effects in Sonoluminescence Spectra of Heavy and Light Water

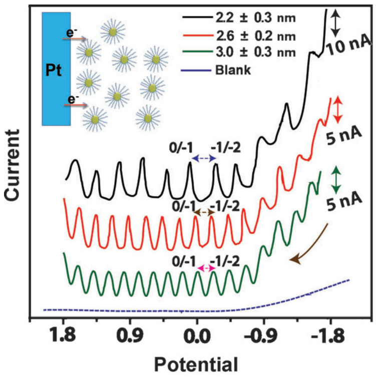
Bubble and peak: The isotope effects in the sonoluminescence spectra of light and heavy water under ultrasound indicate the formation of a non-equilibrium plasma inside the collapsing cavitation bubbles. The picture demonstrates the active cavitation zones in water at 204 kHz.



Electron Transfer

D. B. Shinde, V. K. Pillai* **2482–2485**

Electrochemical Resolution of Multiple Redox Events for Graphene Quantum Dots

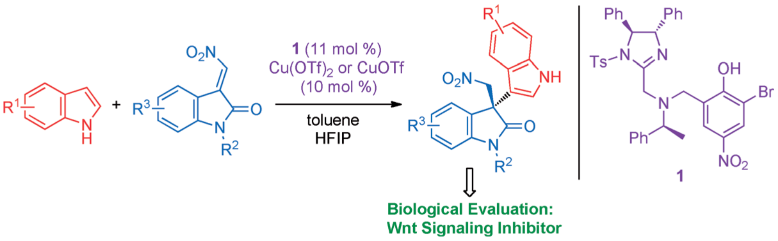


Quantum dots: A sequential, single-electron charging process of monodisperse graphene quantum dots (GQDs) encapsulated in a dodecylamine envelope, facilitating a capacitance of a few attofarads is reported. The average GQDs dimensions, as ascertained from high-resolution transmission electron microscopy and atomic force microscopy, of about 3 ± 0.3, 2.6 ± 0.2, and 2.2 ± 0.3 nm control this unprecedented behavior (see picture).

Heterocycles

T. Arai,* Y. Yamamoto, A. Awata,
K. Kamiya, M. Ishibashi,
M. A. Arai* **2486–2490**

Catalytic Asymmetric Synthesis of Mixed 3,3′-Bisindoles and Their Evaluation as Wnt Signaling Inhibitors

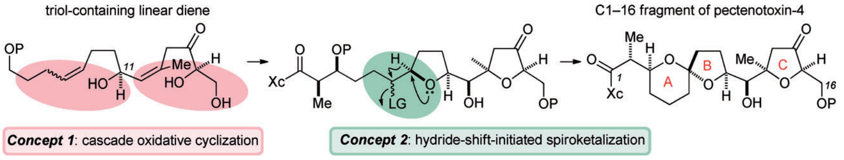


TOP class: The first efficient catalytic asymmetric coupling reaction of indoles with isatin-derived nitroalkenes was accomplished by using a complex consisting of a chiral imidazoline aminophenol ligand (**1**; see scheme) and Cu(OTf)$_2$. Biological activity of the newly formed chiral 3,3′-bisindoles was also confirmed in a Wnt signaling inhibitory assay.

Spiro Compounds

T. J. Donohoe,*
R. M. Lipiński **2491–2494**

Interplay of Cascade Oxidative Cyclization and Hydride Shifts in the Synthesis of the ABC Spiroketal Ring System of Pectenotoxin-4

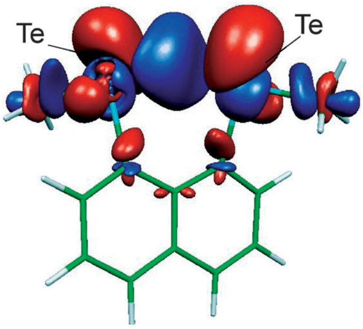


Concepts: The formation of stereochemically defined bis-THF units through a double cyclization and a hydride-shift-initiated route to spiroketals is described (see scheme; Xc = chiral auxiliary). The resulting sequence has been used in a synthesis of the C1–16 fragment of the naturally occurring antitumor agent pectenotoxin-4.

Spin–Spin Coupling

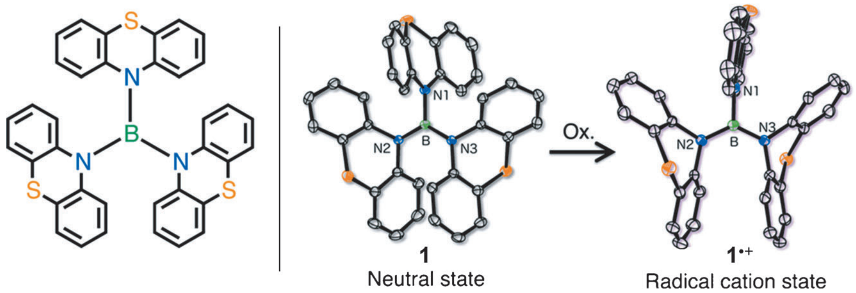
M. Bühl,* F. R. Knight, A. Křístková,
I. Malkin Ondík, O. L. Malkina,
R. A. M. Randall, A. M. Z. Slawin,
J. D. Woollins **2495–2498**

Weak Te,Te Interactions through the Looking Glass of NMR Spin–Spin Coupling



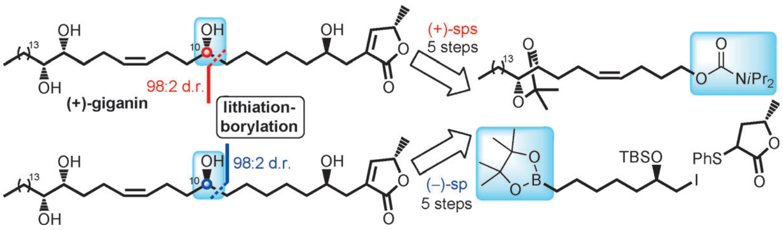
Across the bay: $J(^{125}\mathrm{Te},^{125}\mathrm{Te})$ spin–spin coupling is a highly sensitive probe into the electronic and geometric structure of 1,8-*peri*-substituted naphthalene tellurium derivatives. The coupling is related to the onset of multicenter bonding in these systems.

Redox Chemistry



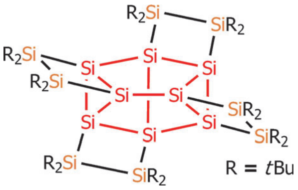
A radical comparison: The neutral (**1**) and radical cation ($\mathbf{1}^{\bullet+}$) forms of tris(*N*-phenothiazinyl)borane were prepared and their molecular structures and spectral properties investigated. The results established that $\mathbf{1}^{\bullet+}$ possessed a localized radical cation on one of the phenothiazine (PTZ) rings. The crystal structure of $\mathbf{1}^{\bullet+}$ showed elongation of the B–N bond bound to the PTZ$^{\bullet+}$ ring (B–N1: 1.53 Å).

Natural Products



The first total synthesis of (+)-giganin and its unnatural diastereoisomer (+)-C10-*epi*-giganin has been completed in a total of 13 linear steps, and 7% and 8% overall yield, respectively (see scheme; (-)-sp = (-)-sparteine, (+)-sps = (+)-sparteine surrogate). Lithiation–borylation methodology has been successfully applied in the key step, to couple together advanced intermediates with very high diastereoselectivity, thus demonstrating its power as a tool for total synthesis.

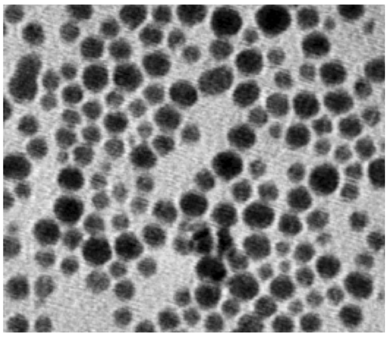
Organosilicon Chemistry



Cagey silicon: A silicon cluster, consisting of sixteen silicon atoms and composed of an octasilacuneane core (red, see picture) fused with cyclotetrasilanes (orange), was synthesized by reductive tetramerization of tetrachlorocyclotetrasilane. Analytical and theoretical studies reveal the unique structural and electronic features of this organosilicon cluster.

Solvent-Free Nanofluids

Autocondensation of organoalkoxysilanes and subsequent anion exchange produces organosiloxane supramolecular liquids which are core-free and solvent-free nanoparticle nanofluids. This hybrid supramolecular liquid, $[C_{81}H_{156}NO_3S\text{-}(SiO_{[2>x>3/2]})]_y$, exhibits (see TEM image; 200 nm width) interparticle menisci and softness (from imputed deformations) of interparticle potential.



Reaction Mechanisms

R. Dobrovetsky,
D. W. Stephan* ———— **2516 – 2519**

Catalytic Reduction of CO_2 to CO by Using Zinc(II) and In Situ Generated Carbodiphosphoranes

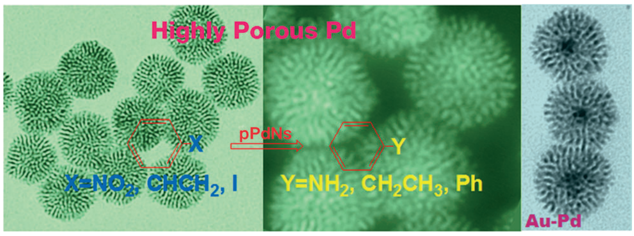
Playing it ‘CO’ol: CO_2 is catalytically reduced to CO with concurrent oxidation of phosphine to phosphineoxide by using an in situ generated catalyst derived from a carbodiphosphorane and zinc(II).

$$Et_3P + CO_2 \xrightarrow[\text{(4 mol\%)}]{CH_2I_2/ZnBr_2} Et_3P{=}O + CO$$

Nanostructures

X. Huang, Y. Li, Y. Chen, E. Zhou, Y. Xu,
H. Zhou, X. Duan,
Y. Huang* ———— **2520 – 2524**

Palladium-Based Nanostructures with Highly Porous Features and Perpendicular Pore Channels as Enhanced Organic Catalysts

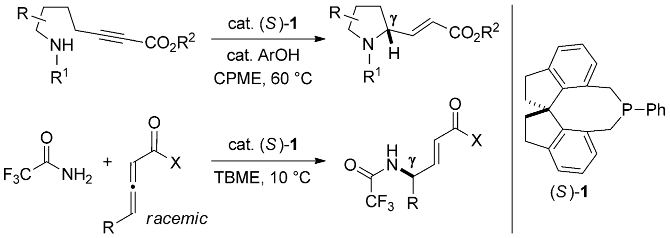


Channeling a good catalyst: Highly porous palladium nanostructures (pPdNs) with perpendicular pore channels (see picture) were prepared under mild conditions. The combination of high surface area and rich edge/corner atoms gives pPdNs better catalytic performance than known Pd catalysts for the hydrogenation of nitrobenzene and styrene and the Suzuki coupling reaction.

Enantioselective Catalysis

R. J. Lundgren, A. Wilsily, N. Marion,
C. Ma, Y. K. Chung,
G. C. Fu* ———— **2525 – 2528**

Catalytic Asymmetric C–N Bond Formation: Phosphine-Catalyzed Intra- and Intermolecular γ-Addition of Nitrogen Nucleophiles to Allenoates and Alkynoates

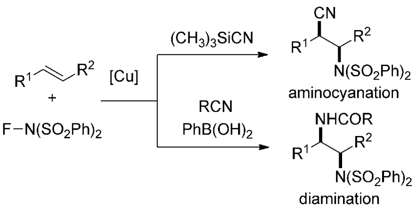


Pin the amine on the gamma: A new method has been developed for the γ-addition of nitrogen nucleophiles to γ-substituted alkynoates or allenoates through intra- and intermolecular processes that are catalyzed by spirophosphine **1** (see scheme). An asymmetric version of this reaction affords enantioenriched pyrrolidines, indolines, and γ-amino-α,β-unsaturated carbonyl compounds.

Synthetic Methods

H.-W. Zhang, Y.-W. Pu, T. Xiong,* Y. Li,*
X. Zhou, K. Sun, Q. Liu,
Q. Zhang* ———— **2529 – 2533**

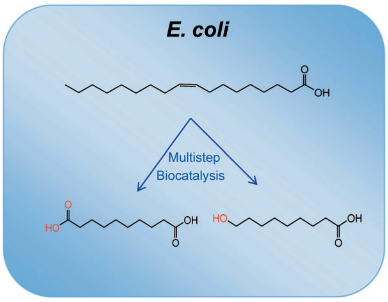
Copper-Catalyzed Intermolecular Aminocyanation and Diamination of Alkenes



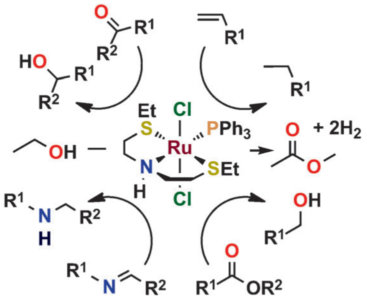
’N’ front and center: The facile construction of C–N bonds by the generation of nitrogen-centred radicals from *N*-fluorobenzenesulfonimide results in the aminative difunctionalization of alkenes. The first copper-catalyzed intermolecular aminocyanation of alkenes and diamination of styrenes were realized. Si–F and B–F interactions play a significant role in the reaction.

Enzyme Catalysis

A multistep enzyme catalysis was successfully implemented to produce long-chain α,ω-dicarboxylic and ω-hydroxycarboxylic acids from renewable fatty acids and plant oils. Sebacic acid as well as ω-hydroxynonanoic acid and ω-hydroxytridec-11-enoic acid were produced from oleic and ricinoleic acid.

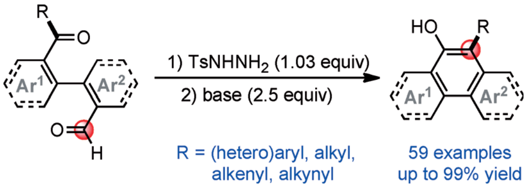


Catalytic Hydrogenation



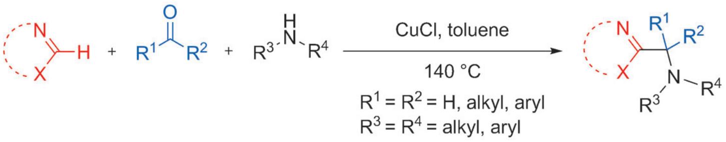
Catalyst tune-up: A readily available, air-stable amino–sulfide catalyst, $[RuCl_2(PPh_3)\{HN(C_2H_4SEt)_2\}]$, has been developed. This complex displays outstanding efficiency for the hydrogenation of a broad range of substrates with C=X bonds (esters, ketones, imines), as well as for the acceptorless dehydrogenative coupling of ethanol to ethyl acetate (see scheme).

Synthetic Methods



The different reactivity of two kinds of carbonyl groups in keto aldehyde substrates has been exploited for the synthesis of phenanthrols, naphthols, and their heteroatom-containing analogues. Key to this highly efficient and robust methodology is the catalyst-free intramolecular formal diazo carbon insertion of *N*-tosylhydrazones into keto C–C bonds (see scheme).

C-H Alkylation



Coupling the strangers: A copper-catalyzed three-component heteroarene–amine–aldehyde/ketone coupling affords a novel approach to the hitherto difficult direct secondary/tertiary C–H alkylation of azoles. This simple method allows the facile installation of diversely substituted, branched and nitrogen-containing alkyl or alkaloid side chains on the azole moiety by using readily available starting materials (see scheme).

To All(oc) involved: A palladium-catalyzed formal 5-*endo*-trig heteroannulation of enones generated in situ from amino acid derived β-keto nitriles has been realized (see scheme; Alloc = allyl carbamate). The reaction proceeds with allyl-group transfer from the carbamate protecting group to generate two new contiguous stereocenters, including one quaternary center, with high selectivity.

Heterocycles

O. K. Karjalainen, M. Nieger,
A. M. P. Koskinen* ———— **2551 – 2554**

Diastereoselective Intramolecular Allyl Transfer from Allyl Carbamate Accompanied by 5-*endo*-trig Ring Closure

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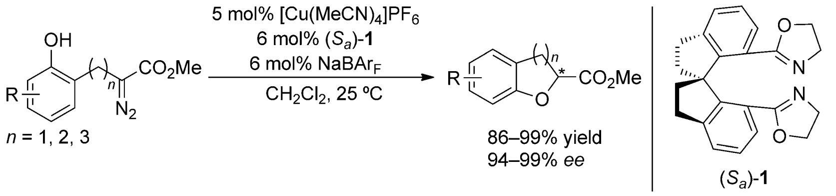

Efficient: A copper-catalyzed enantioselective intramolecular insertion of carbenoids into phenolic O—H bonds has been developed. This method can be used for the synthesis of the title compounds in high yields and excellent enantioselectivities under mild and neutral conditions (see scheme). NaBAr$_F$ = sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

Synthetic Methods

X.-G. Song, S.-F. Zhu, X.-L. Xie,
Q.-L. Zhou* ———— **2555 – 2558**

Enantioselective Copper-Catalyzed Intramolecular Phenolic O—H Bond Insertion: Synthesis of Chiral 2-Carboxy Dihydrobenzofurans, Dihydrobenzopyrans, and Tetrahydrobenzooxepines

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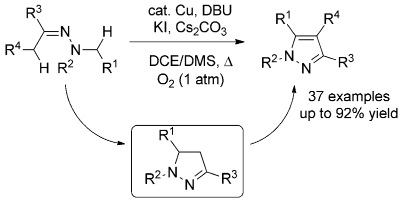

An aerobic activity: The title reaction proceeds through an oxidation/cyclization/aromatization sequence under an atmosphere of O$_2$ (see scheme; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, DCE = 1,2-dichloroethane, DMS = dimethylsulfide). This coupling reaction is the first to proceed via an iminium intermediate for a C$_{sp^3}$—H bond-functionalization process, and provides an environmentally friendly and atom-efficient access to substituted pyrazoles.

Heterocycles

G.-W. Zhang, Y. Zhao,
H.-B. Ge* ———— **2559 – 2563**

Copper-Catalyzed Aerobic Intramolecular Dehydrogenative Cyclization of N,N-Disubstituted Hydrazones through C$_{sp^3}$—H Functionalization

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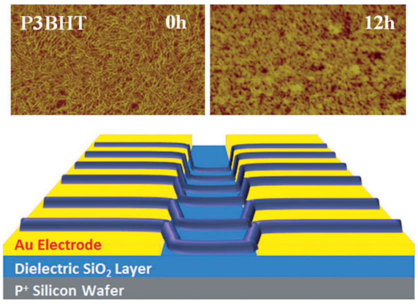
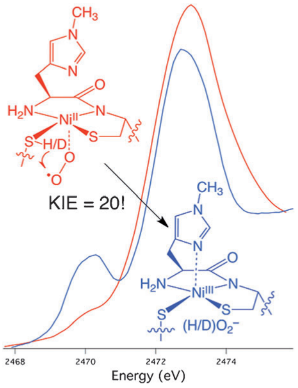


Stripes on a plane: A set of highly ordered microscopic stripes (purple; see scheme) were produced over a large area by using controlled evaporative self-assembly in a cylinder-on-Si geometry of conjugated homopolymers or all-conjugated diblock copolymer (P3BHT). The crystallinity of the as-prepared assemblies of P3BHT was greatly improved following chloroform vapor annealing, resulting in a fourfold increase in electrical conductivity.

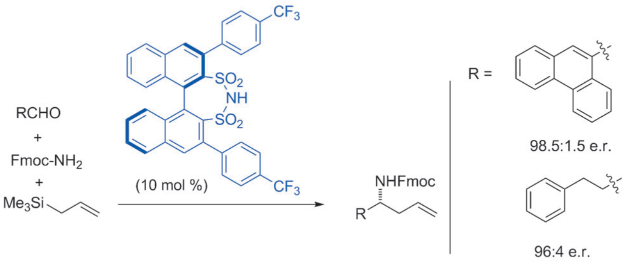
Conjugated Polymers

W. Han, M. He, M. Byun, B. Li,
Z. Lin* ———— **2564 – 2568**

Large-Scale Hierarchically Structured Conjugated Polymer Assemblies with Enhanced Electrical Conductivity



Sneaky little SOD! A metallopeptide-based mimic of nickel-containing superoxide dismutase was used to probe the mechanism of superoxide reduction by the metalloenzyme. Kinetic studies suggest a proton-coupled electron-transfer mechanism; large H/D kinetic isotope effects (KIE) are observed. XAS studies suggest the transferred H-atom is in the form of a Ni^{II}-S(H)-Cys moiety (see graph).



It takes three to make things go right: The first direct asymmetric three-component reaction of aldehydes, carbamates, and allyltrimethylsilane leading to enantioenriched homoallylic amines has been developed using a new chiral disulfonimide catalyst (see scheme). The method employs readily available, inexpensive, and nontoxic starting materials and is applicable to both aromatic and aliphatic aldehydes.

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50 Years Ago . . .

Angewandte Chemie International Edition was first published in 1962, the mother journal first in 1888. In this monthly flashback, we feature some of the articles that appeared 50 years ago. This look back can open our eyes, stimulate discussion, or even raise a smile.

In the first Review of this issue, Günther Wilke described the cyclooligomerization of butadiene using Ziegler-type catalysts, and transition-metal complexes of the resulting products. Wilke was Director of the Max Planck Institute for Coal Research from 1967–1992, and was in fact Ziegler's successor in this post.

The reaction between pentafluorosulfurchloride and amines was reported in a Communication by Bernard Cohen and Alan G. MacDiarmid. The resulting adducts were shown to decompose to produce sulfur tetrafluoride, which then reacts further with the amine. MacDiarmid shared the Nobel Prize for Chemistry in 2000 with Hideki Shirakawa and Alan J. Heeger for their work on conductive polymers. A Communication by Heeger on solar cells with a graphene oxide electron-transport layer will be published in Issue 10/2013 to coincide with our 125th Anniversary Symposium.

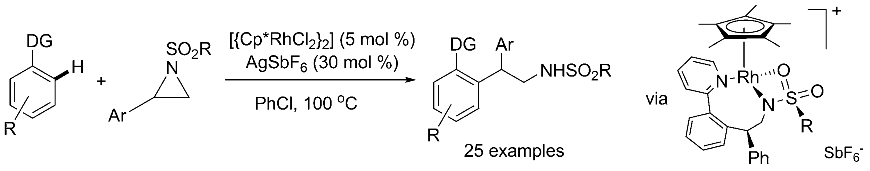
Reinhard W. Hoffmann reported how the base-catalyzed fragmentation of azobromobezene derivatives can be used to generate the *o*-bromophenyl anion, which is an intermediate in the formation of benzyne. Hoffmann's account of the changes in natural product synthesis over time was published in our Jubilee Issue 1/2013.

Read more in Issue 3/1963

C–H Activation

X. Li,* S. Yu, F. Wang, B. Wan,*
X. Yu ______ **2577 – 2580**

Rhodium(III)-Catalyzed C–C Coupling between Arenes and Aziridines by C–H Activation

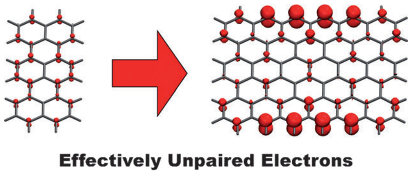


Making C–C from C–H: $[\{RhCp^*Cl_2\}_2]$/$AgSbF_6$ (Cp* = pentamethylcyclopentadienyl) can regioselectively catalyze the C–C coupling of arenes with aziridines by a C–H activation pathway. An eight-membered rhodacyclic intermediate resulting from the insertion of the Rh–C bond into the aziridine was isolated.

Graphene

F. Plasser, H. Pašalić, M. H. Gerzabek,
F. Libisch, R. Reiter, J. Burgdörfer,
T. Müller, R. Shepard,
H. Lischka* ______ **2581 – 2584**

The Multiradical Character of One- and Two-Dimensional Graphene Nanoribbons

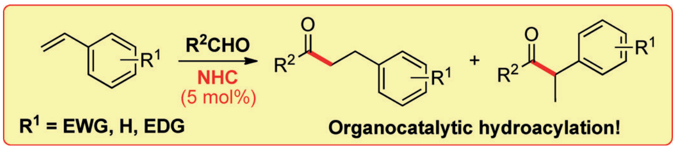


When is an acene stable? The pronounced multiradical character of graphene nanoribbons of different size and shape was investigated with high-level multireference methods. Quantitative information based on the number of effectively unpaired electrons leads to specific estimates of the chemical stability of graphene nanostructures.

Organocatalysis

M. Schedler, D.-S. Wang,
F. Glorius* ______ **2585 – 2589**

NHC-Catalyzed Hydroacylation of Styrenes

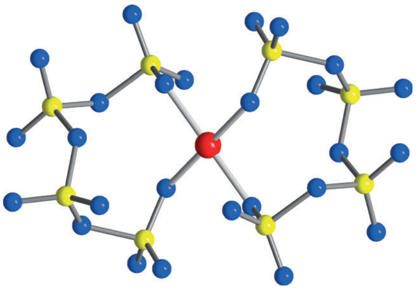


New hydroacylation catalysts: Highly electron-rich N-heterocyclic carbenes (NHCs) facilitate the intermolecular hydroacylation of unstrained olefins. This unprecedented organocatalytic coupling joins simple and abundant aldehydes and styrenes to yield valuable ketone products. EWG = electron-withdrawing group, EDG = electron-donating group.

Polysulfate Ligands

J. Bruns, T. Klüner,
M. S. Wickleder* ______ **2590 – 2592**

Bis(tetrasulfato)palladate, $[Pd(S_4O_{13})_2]^{2-}$

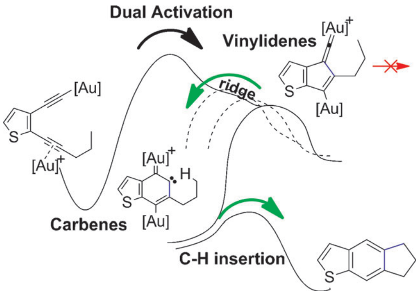


SOS: The first coordination compound containing polysulfate ligands was obtained under harsh conditions from the reaction of $K_2[PdCl_4]$ and SO_3. The compound contains a Pd^{2+} ion coordinated by two chelating tetrasulfate anions (see structure, Pd red, S yellow, O blue), which leads to a significant stabilization of the polysulfate anions compared to their uncoordinated analogues.

Dual Gold Catalysis

M. M. Hansmann,* M. Rudolph,
F. Rominger,
A. S. K. Hashmi* ______ **2593 – 2598**

Mechanistic Switch in Dual Gold Catalysis of Diynes: $C(sp^3)$–H Activation through Bifurcation—Vinylidene versus Carbene Pathways



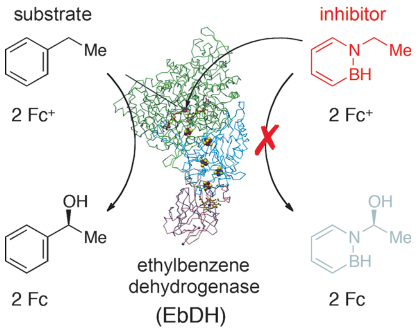
The other side of the mountain: Changing the framework of diyne systems opens up new cyclization modes for dual gold catalysis. Instead of a 5-*endo* cyclization and gold vinylidenes a 6-*endo* cyclization gives rise to gold-stabilized carbenes as key intermediates for selective C–H insertions.

Boron Mimetics

D. H. Knack, J. L. Marshall, G. P. Harlow, A. Dudzik, M. Szaleniec, S.-Y. Liu,* J. Heider* ______ **2599 – 2601**

BN/CC Isosteric Compounds as Enzyme Inhibitors: *N*- and *B*-Ethyl-1,2-azaborine Inhibit Ethylbenzene Hydroxylation as Nonconvertible Substrate Analogues

Good substrate gone bad! BN/CC isosterism of ethylbenzene leads to *N*-ethyl-1,2-azaborine and *B*-ethyl-1,2-azaborine. In contrast to ethylbenzene, which is the substrate for ethylbenzene dehydrogenase (EbDH), *N*-ethyl-1,2-azaborine (see scheme; Fc = Ferricenium tetrafluoroborate) and *B*-ethyl-1,2-azaborine are strong inhibitors of EbDH. Thus, the changes provided by BN/CC isosterism can lead to new biochemical reactivity.

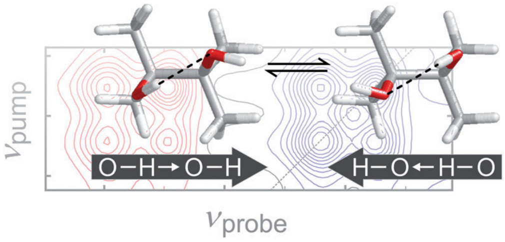


Two-Dimensional IR Spectroscopy

M. Olschewski, J. Lindner, P. Vöhringer* ______ **2602 – 2605**

A Hydrogen-Bond Flip-Flop through a Bjerrum-Type Defect

Front Cover



Back and forth: Femtosecond two-dimensional infrared exchange spectroscopy was used to study the dynamics of the reversal of an intramolecular hydrogen bond. The H-bond reversal resembles a flip-flop motion that is facilitated by two concerted disrotatory torsional isomerizations and that occurs on a time scale of about 2 ps.

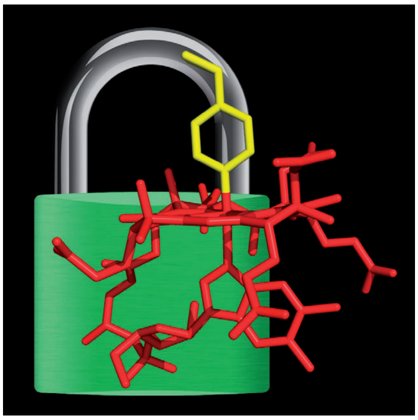
Vitamin B_{12} Antimetabolites

M. Ruetz, C. Gherasim, K. Gruber, S. Fedosov, R. Banerjee, B. Kräutler* ______ **2606 – 2610**

Access to Organometallic Arylcobaltcorrins through Radical Synthesis: 4-Ethylphenylcobalamin, a Potential “Antivitamin B_{12}”

Inside Cover

Locked B_{12}: 4-Ethylphenylcobalamin, a novel organometallic arylcobalamin, has been synthesized in a radical reaction. This vitamin B_{12} antimetabolite features a strong Co–C bond, and represents a “locked” form of vitamin B_{12} (see picture). It may be used in animal studies to induce functional vitamin B_{12} deficiency artificially to help clarify still controversial issues related to the pathophysiology of vitamin B_{12} deficiency.



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

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