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:

*X. Zhang, T. J. Emge, K. C. Hultzsch**
A Chiral Phenoxyamine Magnesium Catalyst for the Enantioselective Hydroamination/Cyclization of Aminoalkenes and Intermolecular Hydroamination of Vinyl Arenes

M. A. Newton, M. Di Michiel, A. Kubacka, A. Iglesias-Juez, M. Fernández-García
Observing Oxygen Storage and Release at Work under Cycling Redox Conditions: Synergies between Noble Metal and Oxide Promoter

Editorial

“Good things speak for themselves ...

Author Profile

*“The greatest scientific advance of the last decade can only be recognized after another 50 years.
The biggest challenge facing scientists is storage of energy ...”*
This and more about Herbert Mayr can be found on page 34.

News

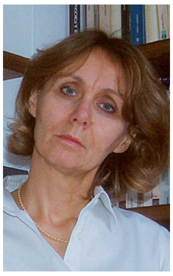
H.-J. Böhm

T. Geelhaar

P. Schwille

C. Moberg

L. F. Nazar



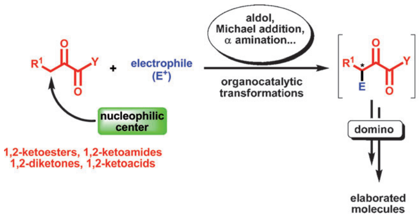
R. Sessoli

Books

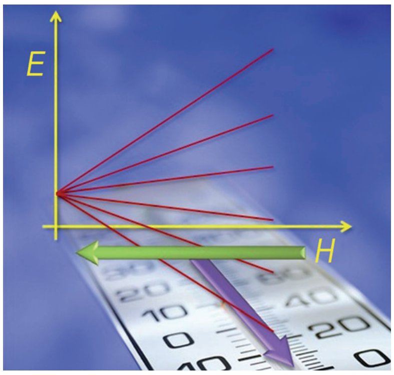
Highlights

Organocatalysis

Organocatalysis likes them too! 1,2-dicarbonyl compounds possess high synthetic potential because of their adjacent multiple reactive centers. Recent contributions indicate that these reactive species, with an appropriate activation mode, may also act as efficient pronucleophiles in asymmetric organocatalyzed sequential or domino transformations including C–C or C–N bond formation (see scheme).



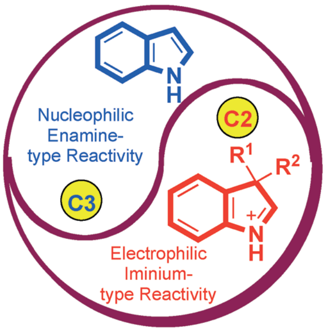
Molecular Magnetism



Fridge magnets: Molecular magnetism appears to be able to provide an alternative route for low-temperature refrigeration by providing molecules with large spin and weak magnetic anisotropy that display a large magnetocaloric effect.

Indole Chemistry

Think electrophilic: While the classical π-excessive indole is well-known for its electrophilic substitutions at position C3, recent advances in asymmetric catalysis resulted in a surge in utilizing the less discussed electrophilic properties of iminium-type intermediates (see picture) in complex annulations of indoles. Advances in Au^{I} catalysis also allow an umpolung of the classical indole C3 reactivity.



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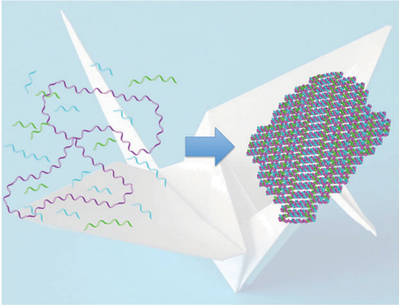
Essays

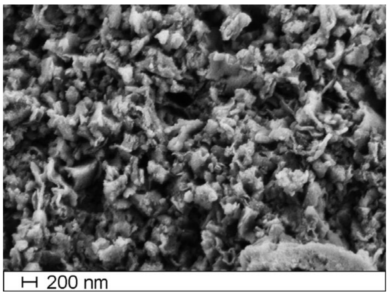
Onkel Fritz: In his lecture at the Centennial Celebration of The Fritz Haber Institute, Fritz Stern reflects on the strengths and flaws of the Institute's founder. Can we judge a person without considering the historical and cultural context? In a sense, Haber's life encompassing triumph and tragedy is a reflection of his country at that time.

Minireviews



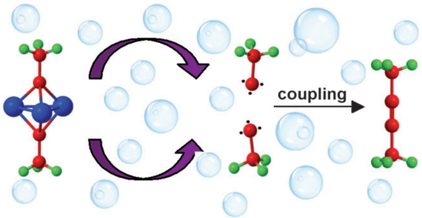
Know when to fold 'em: As in the ancient art of paper folding, where a single sheet of paper is modeled into beautiful shapes, DNA origami technology allows nanoscale-addressable objects to be created from one single strand of DNA (see picture).

Reviews



Multipurpose catalyst: Graphitic carbon nitride (g-C_3N_4; see SEM image) is an effective (photo)catalyst for a whole series of reactions. This Review describes the synthesis of g-C_3N_4, how the band positions and bandgaps can be varied by copolymerization and doping and how changes in the solid-state structure can improve heterogeneous organocatalyst effectiveness.

Communications

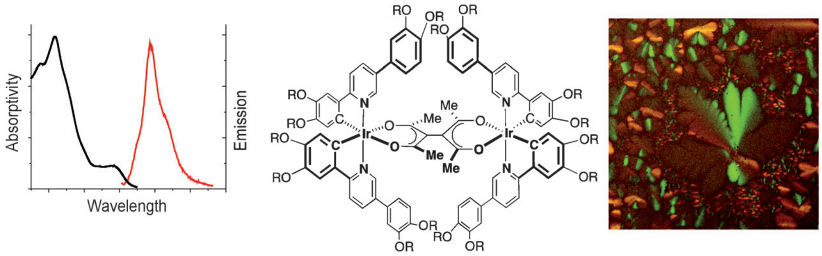


They do exist! Free carbyne radicals can be prepared at room temperature in an aqueous solution by the decomposition of mono- or trinuclear metal (M) complexes containing alkylidyne ligands (see scheme; red C, blue M, green H). The generated radicals then react to form a variety of organic compounds by chain-lengthening reactions in solution. They also exhibit hydrogen, oxygen, or carbon abstraction from solvent, reactant, or product molecules.

Luminescent Metallomesogens

A. M. Prokhorov, A. Santoro, J. A. G. Williams, D. W. Bruce* — **95 – 98**

Phosphorescent Mesomorphic Dyads Based on Tetraacetylethane Complexes of Iridium(III)



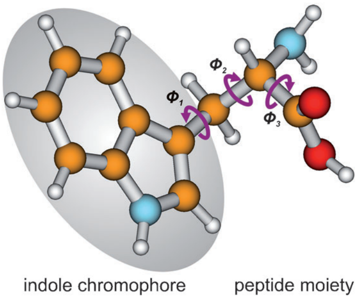
A good combination: Dimeric iridium(III) luminophores with tetraacetylethane bridges led to liquid-crystalline materials with very high photoluminescence quantum yields (see picture). The same design principle allowed for the preparation of heteronuclear iridium(III)–platinum(II) dyads, which were also luminescent.

Amino Acid Conformers

I-R. Lee, A. Gahlmann, A. H. Zewail* — **99 – 102**

Structural Dynamics of Free Amino Acids in Diffraction

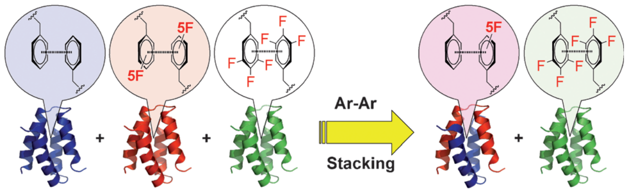
The amino acid tryptophan exhibits complex structural changes both in the ground state, owing to multiple conformations, and upon excitation, because of the involvement of nonradiative pathways. The first report of structural dynamics using combined ultrafast electron diffraction and laser desorption methods is presented.



Aromatic Stacking

C. J. Pace, H. Zheng, R. Mylvaganam, D. Kim, J. Gao* — **103 – 107**

Stacked Fluoroaromatics as Supramolecular Synthons for Programming Protein Dimerization Specificity

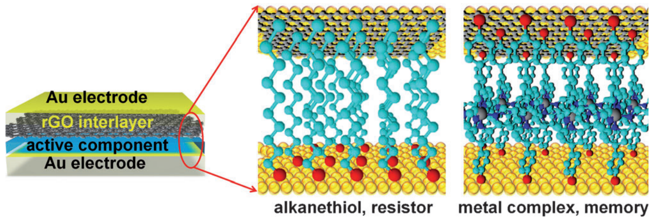


Aromatic "bonding": Although known to exist in proteins, aromatic stacking interactions and the energetic factors important for it are not well understood. A systematic investigation of aromatic stacking interactions in a protein model system using a series of fluorinated phenylalanine analogues illustrates the importance of dipole–dipole and dipole–induced-dipole coupling to the stability and self-sorting properties of aromatic stacking pairs.

Molecular Electronics

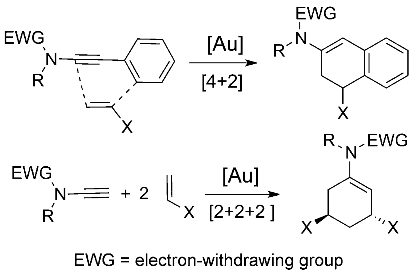
S. Seo, M. Min, J. Lee, T. Lee, S.-Y. Choi, H. Lee* — **108 – 112**

Solution-Processed Reduced Graphene Oxide Films as Electronic Contacts for Molecular Monolayer Junctions

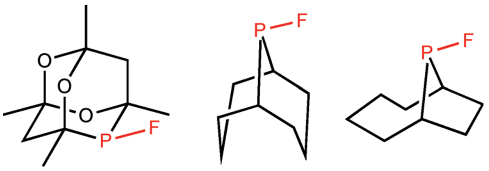


Reduction to the essential: A highly conductive and soft carbon interlayer of reduced graphene oxide (rGO) prevents the formation of a filamentary current path, achieving both high yield and true molecular effects in monolayer-based molecular devices. Junctions of the rGO interlayer contacts with molecular monolayers elucidate the molecularly resolved electronic properties of molecular resistors and nonvolatile memories.

As good as gold: Gold-catalyzed intermolecular [4+2] cycloadditions of 2-arylynamides with alkenes and gold-catalyzed [2+2+2] cycloadditions of terminal ynamides with enol ethers have been developed (see scheme). The [4+2] cycloaddition is compatible with a range of alkenes and arylynamides and the [2+2+2] cycloaddition can also accommodate a variety of different arylynamide and enol ether substrates.

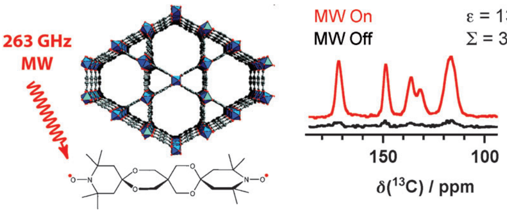


Synthetic Methods



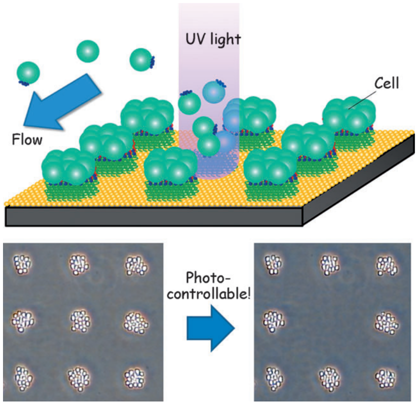
Ligand maps lead to treasure! The activity of complexes of fluorophosphines (R_2PF) in catalytic hydroformylation and hydrocyanation is predicted from a ligand map. However, the instability of R_2PF to disproportionation is well-documented. Examples of R_2PF ligands (see scheme) are described that are stabilized to such an extent that they can be used in catalysis and are shown to be highly effective.

Fluorophosphines



A matter of minutes: Dynamic nuclear polarization (DNP) is applied to enhance the signal of solid-state NMR spectra of metal–organic framework (MOF) materials. The signal enhancement enables the acquisition of high-quality 1D ^{13}C solid-state NMR spectra, 2D ^{1}H–^{13}C dipolar HETCOR and 1D ^{15}N solid-state NMR spectra with natural isotopic abundance in experiment times on the order of minutes. MW = microwaves.

NMR Spectroscopy of MOFs



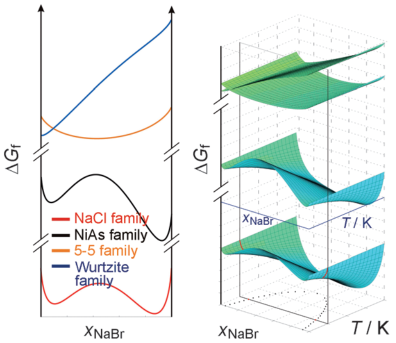
Cells in the spotlight: A substrate was coated with a poly(ethylene glycol) (PEG) segment bound to a lipid through a linker that was cleaved by UV irradiation to leave a PEG-coated area. Irradiation of an arbitrary pattern easily and rapidly yielded a high-contrast cell pattern. Only the targeted cells on the cell pattern were selectively detached without cell damage on a microfluidic device (see picture).

Cell Patterning

Metastable Phase Diagrams

M. Jansen,* I. V. Pentin,
J. C. Schön ______ 132 – 135

A Universal Representation of the States of Chemical Matter Including Metastable Configurations in Phase Diagrams



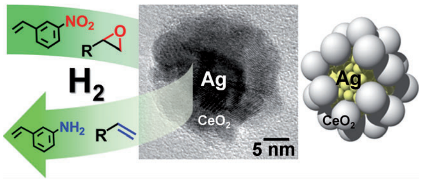
Metastable matter: Traditional equilibrium phase diagrams show thermodynamic ground states of matter and thus fail to reflect the real world of chemical materials which to a large degree consists of metastable compounds. Inclusion of metastable compounds in "extended" phase diagrams is shown by determining all modifications that are locally ergodic on the relevant time and temperature scales and computing their Gibbs enthalpies (see picture).

Heterogeneous Catalysis

T. Mitsudome, Y. Mikami, M. Matoba,
T. Mizugaki, K. Jitsukawa,
K. Kaneda* ______ 136 – 139

Design of a Silver–Cerium Dioxide Core–Shell Nanocomposite Catalyst for Chemoselective Reduction Reactions

Back Cover



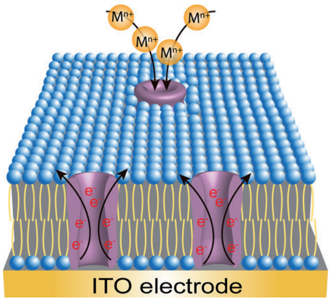
Shelling out: A core–shell nanocomposite comprising an Ag nanoparticle core and a CeO_2 nanoparticle shell catalyzes the chemoselective reduction of both nitrostyrenes and epoxides while retaining the C=C bonds (see picture). Reactions with the core–shell structures show greater chemoselectivity than conventional oxide-supported metal nanoparticles.

Biological Membranes

L.-X. Qin, Y. Li, D.-W. Li, C. Jing,
B.-Q. Chen, W. Ma, A. Heyman,
O. Shoseyov, I. Willner, H. Tian,
Y.-T. Long* ______ 140 – 144

Electrodeposition of Single-Metal Nanoparticles on Stable Protein 1 Membranes: Application of Plasmonic Sensing by Single Nanoparticles

Inside Back Cover



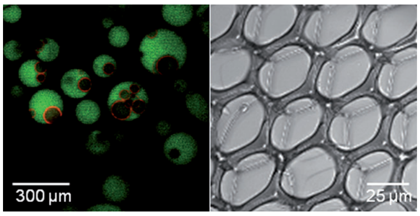
Light in the dark: Metal nanoparticles ($M = Ag^0$, Au^0, or Cu^0) were electrodeposited onto ion-channel pores of a stable protein 1 membrane (see picture). The metal nanoparticles were implemented for detection of antigen–antibody binding events at the single-particle level using dark field microscopy and plasmon resonance Rayleigh scattering.

Interfacial Assembly

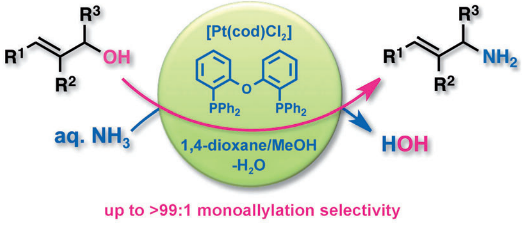
C. Miesch, I. Kosif, E. Lee, J.-K. Kim,
T. P. Russell,* R. C. Hayward,*
T. Emrick* ______ 145 – 149

Nanoparticle-Stabilized Double Emulsions and Compressed Droplets

Stable double emulsions, both oil-in-water-in-oil and water-in-oil-in-water, stabilized by two types of nanoparticles residing at the o/w interfaces (see picture; red: CdSe quantum dots) were prepared in a simple fashion by shaking, and with narrow size distributions by microcapillary flow focusing. These double-emulsion droplets proved stable against coalescence throughout solvent evaporation, allowing for formation of nanoparticle foams and hexagonally arrayed structures.



Synthetic Methods

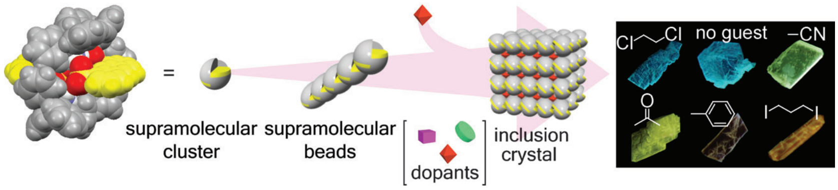


Direct amination of unactivated allylic alcohols with aqueous ammonia was catalyzed by a Pt/phosphine complex to give the corresponding allylamines along with water as the sole by-product. Under optimized reaction conditions, primary allylamines were obtained as major products with excellent monoallylation selectivity. cod = 1,5-cyclooctadiene.

K. Das, R. Shibuya, Y. Nakahara,
N. Germain, T. Ohshima,*
K. Mashima* ______ **150–154**

Platinum-Catalyzed Direct Amination of Allylic Alcohols with Aqueous Ammonia: Selective Synthesis of Primary Allylamines

Luminescent Inclusion Crystals



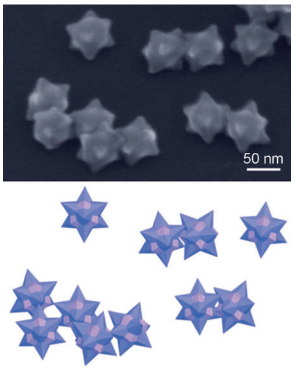
Luminescent jewels: Unusually shaped fluorescent supramolecular clusters assemble into one-dimensional π-stacked supramolecular beads to eventually crystallize with a wide range of solvent molecules (see picture). The included solvent molecules modulate the fluorescence colors of the inclusion crystals from blue to orange-yellow as is known for the colors of gemstones.

T. Hinoue, M. Miyata, I. Hisaki,
N. Tohnai* ______ **155–158**

Guest-Responsive Fluorescence of Inclusion Crystals with π-Stacked Supramolecular Beads

Bimetallic Nanocrystals

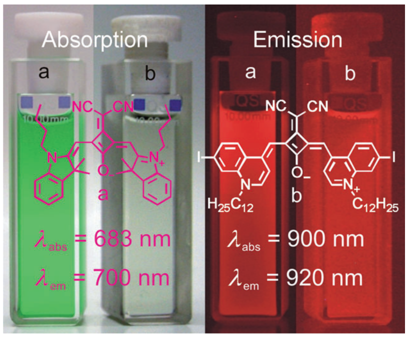
The many faces of noble metals: Through the simultaneous reduction of Au and Pd ions in the presence of octahedral Au nanocrystal (NC) seeds, hexoctahedron-like convex Au@Pd core–shell NCs, enclosed predominantly by high-index {12 5 3} facets, were synthesized under aqueous room-temperature conditions (see picture). The convex Au@Pd NCs showed much higher electrocatalytic properties toward ethanol oxidation than other types of Au@Pd NCs.



D. Kim, Y. W. Lee, S. B. Lee,*
S. W. Han* ______ **159–163**

Convex Polyhedral Au@Pd Core–Shell Nanocrystals with High-Index Facets

Near-Infrared Fluorophores



A lucky chance: An unexpected halogen effect afforded novel squaraine-based bright near-infrared (NIR) fluorophores with nearly total transparency in the visible region and bright emission in the NIR region beyond 900 nm (see picture).

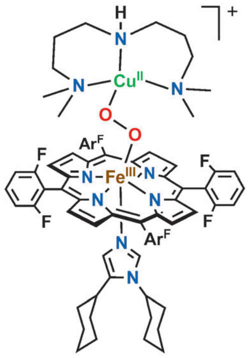
U. Mayerhöffer, B. Fimmel,
F. Würthner* ______ **164–167**

Bright Near-Infrared Fluorophores Based on Squaraines by Unexpected Halogen Effects

Heme–Peroxo–Copper Adducts

M. T. Kieber-Emmons, M. F. Qayyum,
Y. Li, Z. Halime, K. O. Hodgson,
B. Hedman, K. D. Karlin,*
E. I. Solomon* **168 – 172**

Spectroscopic Elucidation of a New Heme/Copper Dioxygen Structure Type: Implications for O···O Bond Rupture in Cytochrome c Oxidase



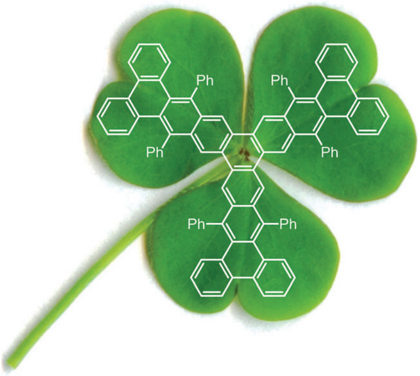
All's well that ends well: The geometric and electronic structure of the first end-on heme–peroxo–copper adduct (see picture) was elucidated using UV/Vis, resonance Raman, and X-ray absorption spectroscopy and is supported by DFT calculations. Coordination of the axial base is correlated to a spin-state change, leading to enhanced biomimetic reactivity, and gives insight into O—O bond cleavage by cytochrome c oxidase.

Arynes

J. M. Alonso, A. E. Díaz-Álvarez, A. Criado,
D. Pérez, D. Peña,* E. Guitián **173 – 177**

[16]Cloverphene: a Clover-Shaped *cata*-Condensed Nanographene with Sixteen Fused Benzene Rings

Living in clover: Sequential [4+2] and [2+2+2] aryne cycloadditions allow the isolation of cloverlike and archlike nanographenes (see picture). This approach led to the synthesis of the largest *cata*-condensed aromatic hydrocarbon that has been obtained to date, a system formed by 16 fused benzene rings (22 benzene rings in total) and 102 sp^2 carbon atoms.

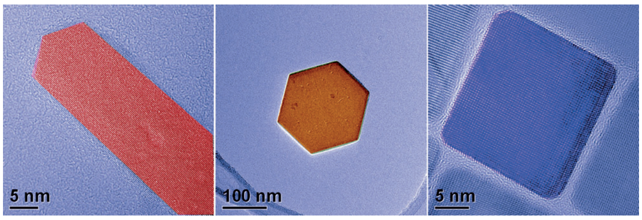


Inside Cover

Architecture Effects

X. M. Zhou, J. Y. Lan, G. Liu,* K. Deng,
Y. L. Yang, G. J. Nie, J. G. Yu,*
L. J. Zhi* **178 – 182**

Facet-Mediated Photodegradation of Organic Dye over Hematite Architectures by Visible Light

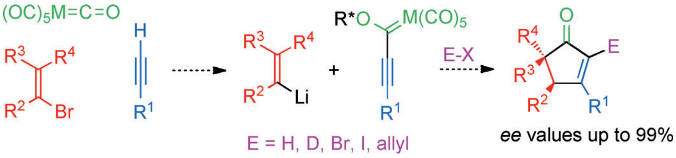


Photodegradation of rhodamine B in the presence of H_2O_2 by visible light over α-Fe_2O_3 architectures has been investigated (see picture; left to right: 1D nanorods, 2D nanoplates, 3D nanocubes). A link between the exposed facets of α-Fe_2O_3 architectures and their photoreactivity is established, following {110} > {012} ≫ {001}.

Synthetic Methods

J. Barluenga,* A. Álvarez-Fernández,
Á. L. Suárez-Sobrino,
M. Tomás **183 – 186**

Regio- and Stereoselective Synthesis of Cyclopentenones: Intermolecular Pseudo-Pauson–Khand Cyclization

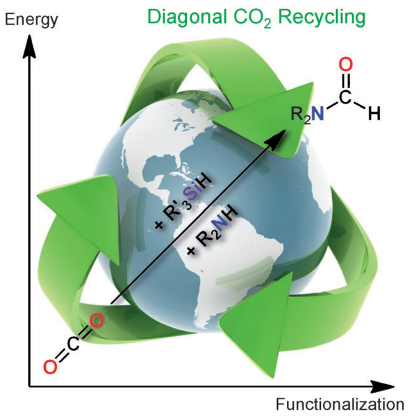


Doing the two step: A very simple two-step access to polysubstituted cyclopentenones from terminal alkynes, $[M(CO)_6]$, and bromoalkenes is described. This protocol is an alternative to the intermolecular Pauson–Khand reaction, and can be used with a variety of bromoalkenes. Moreover, the final quenching allows the installation of reactive electrophiles (E). The enantiopure product cyclopentenones can be synthesized with an all-carbon-substituted quaternary stereocenter.

CO$_2$ Recycling

C. Das Neves Gomes, O. Jacquet,
C. Villiers, P. Thuéry, M. Ephritikhine,
T. Cantat* **187 – 190**

A Diagonal Approach to Chemical Recycling of Carbon Dioxide: Organocatalytic Transformation for the Reductive Functionalization of CO$_2$



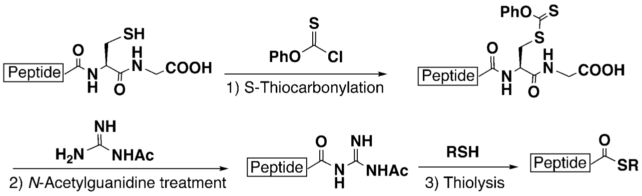
Lateral thinking: A diagonal approach to CO$_2$ recycling has been explored for the formation of both functionalized and energetic chemicals featuring a reduced carbon center. The strategy relies on the tandem use of a functionalization reagent and a reductant that can be independently modified to access a wide spectrum of chemicals from CO$_2$. It is exemplified with an organocatalytic process to convert CO$_2$ into formamides (see picture).

Front Cover

Peptide Synthesis

R. Okamoto,* K. Morooka,
Y. Kajihara* **191 – 196**

A Synthetic Approach to a Peptide α-Thioester from an Unprotected Peptide through Cleavage and Activation of a Specific Peptide Bond by *N*-Acetylguanidine

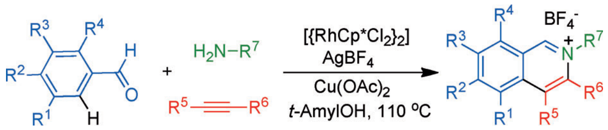


A different route to peptide α-thioesters through a new peptide-bond-cleavage method at a cysteine residue by S-thiocarbonylation and subsequent treatment with *N*-acetylguanidine is described (see scheme). The resultant peptidyl-*N*-acetylguanidine can be converted into the corresponding peptide α-thioester and is also usable as an alternative to a peptide α-thioester. This method allows efficient kinetically controlled ligation in the presence of thiols.

C–H Activation

J. Jayakumar, K. Parthasarathy,
C.-H. Cheng* **197 – 200**

One-Pot Synthesis of Isoquinolinium Salts by Rhodium-Catalyzed C–H Bond Activation: Application to the Total Synthesis of Oxychelerythrine

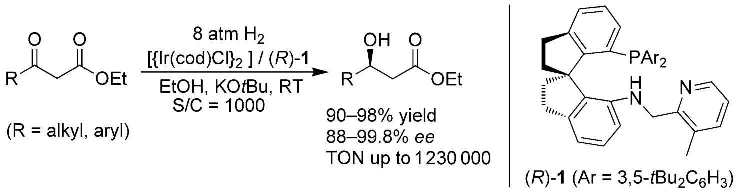


It's worth its salt: The title reaction leads to the synthesis of highly substituted isoquinolinium salts (see scheme; Cp* = Me_5C_5). The reaction proceeds through a C–H activation and a subsequent annulation in the presence of a rhodium catalyst. The reaction mechanism is discussed as well as its application to the synthesis of the natural product oxychelerythrine.

Synthetic Methods

J.-H. Xie,* X.-Y. Liu, X.-H. Yang, J.-B. Xie,
L.-X. Wang, Q.-L. Zhou* **201 – 203**

Chiral Iridium Catalysts Bearing Spiro Pyridine-Aminophosphine Ligands Enable Highly Efficient Asymmetric Hydrogenation of β-Aryl β-Ketoesters

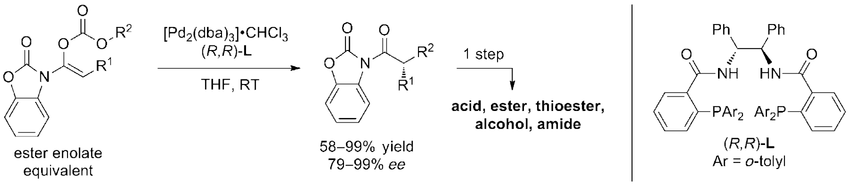


Tons of TONs: Chiral iridium catalysts bearing ligand **1** are highly efficient for the asymmetric hydrogenation of β-substituted β-ketoesters. The product β-hydroxyesters are delivered in high yield with excellent enantioselectivities and high turnover numbers (TONs). cod = 1,5-cyclooctadiene.

Ester Enolate Alkylations

B. M. Trost,* D. J. Michaelis, J. Charpentier, J. Xu ———— 204 – 208

Palladium-Catalyzed Allylic Alkylation of Carboxylic Acid Derivatives: *N*-Acyloxazolinones as Ester Enolate Equivalents



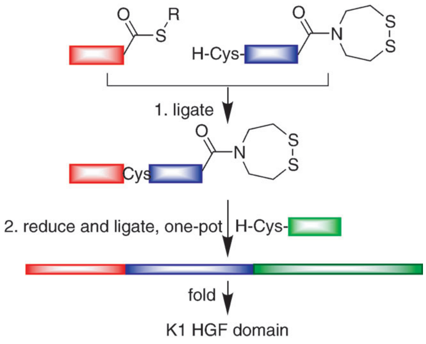
Triple A: A general asymmetric allylic alkylation of ester enolate equivalents at the carboxylic acid oxidation state is reported. *N*-Acylbenzoxazolinone-derived enol carbonates were synthesized and employed in the palladium-catalyzed alkylation reaction. The imide products were readily converted into a series of carboxylic acid derivatives without loss of enantiopurity.

Chemical Protein Synthesis

N. Ollivier, J. Vicogne, A. Vallin, H. Drobecq, R. Desmet, O. El Mahdi, B. Leclercq, G. Goormachtigh, V. Fafeur, O. Melnyk* ———— 209 – 213

A One-Pot Three-Segment Ligation Strategy for Protein Chemical Synthesis

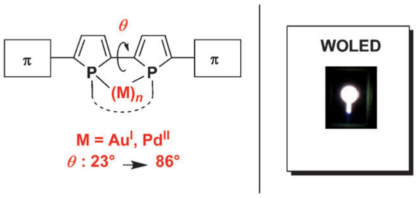
Three in one: Native chemical ligation (NCL) and bis(2-sulfanylethyl)amido (SEA) ligation allow the one-pot assembly of three peptide segments in the N-to-C direction. The SEA group (see picture, blue) is switched off by intramolecular disulfide bond formation during NCL. Then, a phosphine switches it on to trigger the second SEA ligation step. The K1 domain of the hepatocyte growth factor was synthesized and found to be biologically active.



Phosphorous Heterocycles

H. Chen, W. Delaunay, L. J. Yu, D. Joly, Z. Y. Wang, J. Li, Z. S. Wang, C. Lescop, D. Tondelier, B. Geffroy, Z. Duan,* M. Hissler,* F. Mathey,* R. Réau* ———— 214 – 217

2,2′-Biphospholes: Building Blocks for Tuning the HOMO–LUMO Gap of π-Systems Using Covalent Bonding and Metal Coordination

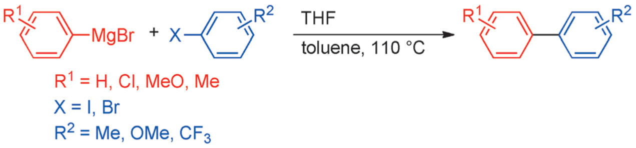


A new angle: The insertion of a 2,2′-biphosphole subunit into π-conjugated systems offers a new way to control the HOMO–LUMO gap. Tuning of the dihedral angle (*θ*) between the two phosphorous heterocycles, either by metal coordination or covalent bonding through the P substitution can lead to control of the band gap. These new π-conjugated systems can be used as emitting materials in white organic light-emitting devices (WOLEDs).

Radical Reactions

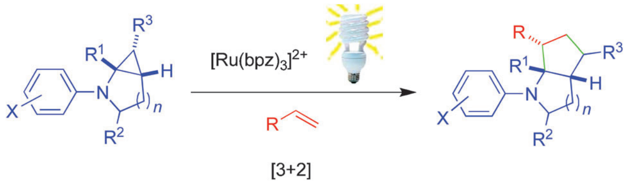
E. Shirakawa,* Y. Hayashi, K. Itoh, R. Watabe, N. Uchiyama, W. Konagaya, S. Masui, T. Hayashi* ———— 218 – 221

Cross-Coupling of Aryl Grignard Reagents with Aryl Iodides and Bromides through $S_{RN}1$ Pathway



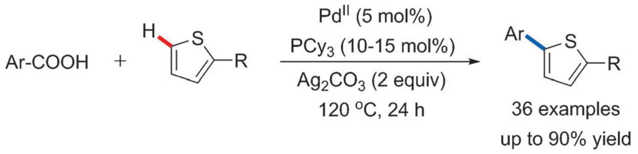
Game, SET, and match: Aryl Grignard reagents undergo coupling with aryl halides when toluene is used as a solvent in combination with a small amount of tetrahydrofuran (see scheme). The reaction proceeds through an $S_{RN}1$ mechanism, and does not require any transition metal catalysts.

Visible-Light Photocatalysis



It's the power of light! A visible-light-mediated intermolecular [3+2] cycloaddition of mono- and bicyclic cyclopropylamines with olefins catalyzed by $[Ru(bpz)_3](PF_6)_2\cdot 2\,H_2O$ has been developed to furnish aminocyclopentane derivatives in good yields (see scheme, bpz = 2,2′-bipyrazine). Saturated 5,5- and 6,5-fused heterocycles are obtained in synthetically useful yields and diastereoselectivity.

Homogeneous Catalysis

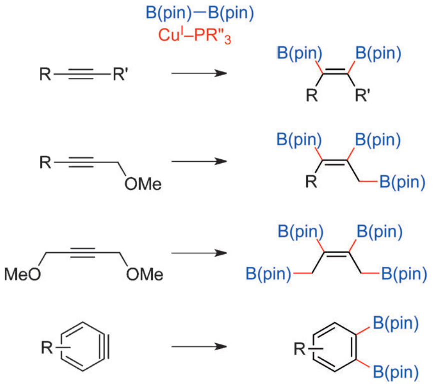


An efficient method involving a Pd/PCy_3 catalyst in combination with a stoichiometric amount of Ag_2CO_3 has been established for the decarboxylative C–H bond arylation of thiophenes to give 2-arylthiophenes (see scheme; Cy = cyclohexyl). Electron-rich, electron-deficient, and heterocyclic benzoic acids can be used as the arylating reagent and a broad range of substituents on the thiophene are tolerated.

Nitrogen Oxides

A good catch: N-Heterocyclic carbenes (NHCs) form stable adducts with nitrous oxide (N_2O) under mild reaction conditions. The adducts display unique reactivity as evidenced by an alkylation reaction which leads to a rupture of the N–N bond.

Borylation

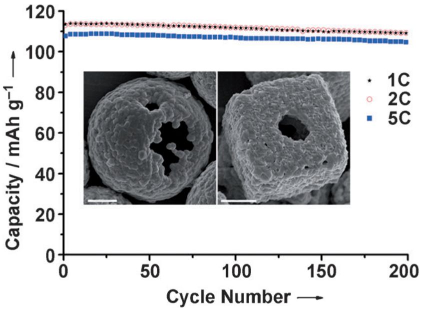


One, two, three, four: A copper(I)–phosphine complex catalyzes the diborylation of alkynes and arynes, and the tri- or tetraborylation of propargyl ethers (see scheme; pin = pinacolato). In the latter cases, the C–O bond(s) as well as the C≡C bond are borylated in one pot. Furthermore, a diborylation product serves as an intermediate in the efficient synthesis of *ortho*-terphenyls with pharmacological activity.

Nanotechnology

L. Zhou, D. Y. Zhao,
X. W. Lou* ________ 239–241

$LiNi_{0.5}Mn_{1.5}O_4$ Hollow Structures as High-Performance Cathodes for Lithium-Ion Batteries

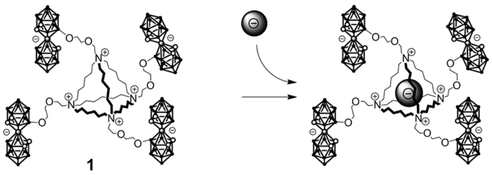


Built to last: Uniform $LiNi_{0.5}Mn_{1.5}O_4$ hollow microspheres and microcubes (see picture; scale bars: 1 μm) with nanosized building blocks have been synthesized by a facile impregnation method followed by a simple solid-state reaction. The resultant $LiNi_{0.5}Mn_{1.5}O_4$ hollow structures deliver a discharge capacity of about 120 mA h g^{-1} over prolonged cycling and exhibit excellent rate capability.

Supramolecular Interactions

A. Ursu, F. P. Schmidtchen* __ 242–246

Selective Host–Guest Binding of Anions without Auxiliary Hydrogen Bonds: Entropy as an Aid to Design



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Entropy matters! In contrast to classic host–guest design, which employs dedicated enthalpic interactions of the binding partners, the novel electroneutral host **1** binds its anionic guests by virtue of an overwhelmingly positive entropy of association. The prime driving force is guest desolvation. Despite the total omission of hydrogen bonding, host **1** is one of the best electroneutral receptors known for binding anions in polar solution.

DOI: 10.1002/anie.201108448

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 1962, *Angewandte Chemie International Edition* appeared 12 times per year but already published both Communications and Reviews across all areas of chemistry. The first issue of 1962 contains original contributions by some of today's best-known names who had already made enormous contributions to their fields.

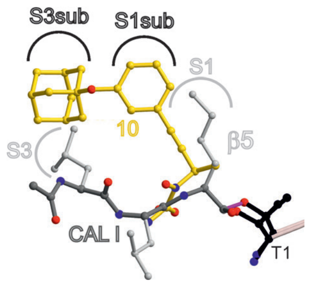
The Ugi reaction is often the first that springs to mind if we are asked to name a multicomponent reaction today. This reaction was pioneered more than 50 years ago and in a Review, Ivar Ugi discussed his latest results in the one-stage synthesis of organic nitrogen compounds. The reactions, which started with two to five different components, proceed by the α-addition of immonium ions and anions to isonitriles, accompanied by secondary reactions.

Another highly exploited reaction in modern organic chemistry is the 1,3-dipolar cycloaddition. This reaction was already being explored 50 years ago and the Communications section contains three contributions by Rolf Huisgen on the cycloaddition reaction of syndones with alkynes and alkenes, and 1,3-dipolar additions with nitrile ylides.

The name of Georg Wittig (Nobel Prize in Chemistry 1979) is synonymous with organophosphorus chemistry, and he reported the synthesis of penta-aryl derivatives of Group 5 elements in a Communication that contained only 12 lines of text. This procedure was an improvement on the synthesis of phosphorane derivatives that could not be extended to the arsenic series.

"A highly refractive red oil" was the product from the reaction of solid $BaCS_3$ with ice-cold 10 % hydrochloric acid that was reported by Gerhard Gattow and Bernt Krebs. Characterization of this product by using the techniques available at the time, including cryoscopic molecular weight determination, IR spectroscopy, and decomposition analysis, showed it to be trithiocarbonic acid H_2CS_3.

Read more in Issue 1/1962

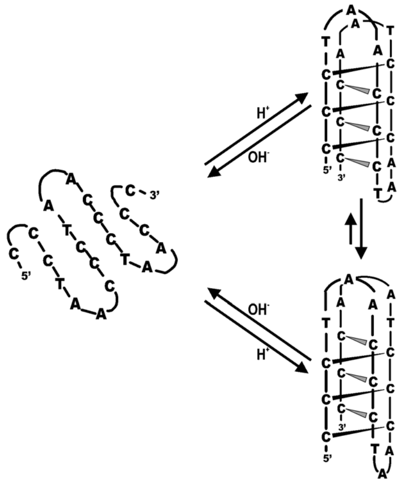


Inhibitors with a new mechanism of action are needed for 20S proteasome (CP) inhibition owing to the ineffectiveness of current market drugs against some types of solid tumors. A novel class of nonpeptidic CP inhibitors has been developed, which display reversible and noncovalent binding. The structure-based design of these highly active and site-specific inhibitors revealed unexplored binding subpockets.

20S Proteasome Inhibitors

N. Gallastegui, P. Beck, M. Arciniega,
R. Huber, S. Hillebrand,
M. Groll* ______ **247 – 249**

Hydroxyureas as Noncovalent Proteasome Inhibitors



Get the zipper right: Time-resolved NMR spectroscopy measurements reveal kinetic partitioning for pH-induced DNA i-motif formation (see scheme). The data characterize the folding pathway of i-motifs and provide a biophysical based description of pH-dependent folding processes as utilized in live-cell pH sensors.

DNA Folding

A. L. Lieblein, J. Buck, K. Schlepckow,
B. Fürtig, H. Schwalbe* ______ **250 – 253**

Time-Resolved NMR Spectroscopic Studies of DNA i-Motif Folding Reveal Kinetic Partitioning

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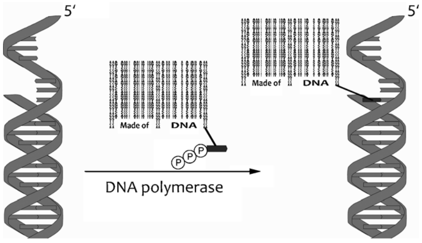
Designer labels: DNA polymerases are able to incorporate oligodeoxynucleotide-(ODN)-modified nucleotides that are 40-times bigger than the natural substrate. The result is bio-barcoded DNA (see scheme). Incorporation of an ODN-modified nucleotide can be detected in solution and on solid support by hybridization of a fluorescent-dye-labeled DNA strand complementary to the ODN.

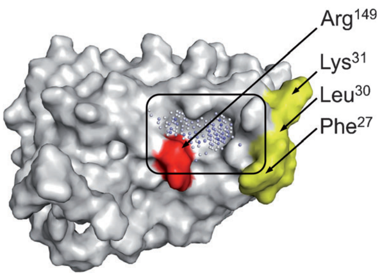


DNA Modification

A. Baccaro, A.-L. Steck,
A. Marx* ______ **254 – 257**

Barcoded Nucleotides

Interfering with interferon: A low-molecular-weight inhibitor has been discovered that blocks the interaction between interferon-α (IFN-α) and its receptor (see picture for a model of the interfaces). The resulting lead compound significantly reduces IFN-α production in vitro. NMR and SPR experiments confirm the direct interaction of the inhibitor with IFN-α.



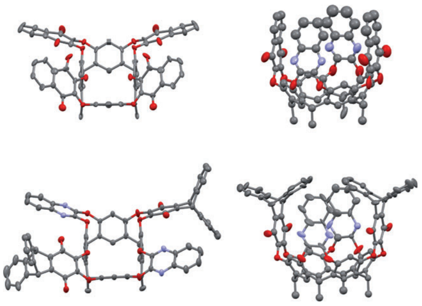
Computer-Assisted Drug Screening

T. Geppert, S. Bauer, J. A. Hiss, E. Conrad,
M. Reutlinger, P. Schneider, M. Weisel,
B. Pfeiffer, K.-H. Altmann, Z. Waibler,
G. Schneider* ______ **258 – 261**

Immunosuppressive Small Molecule Discovered by Structure-Based Virtual Screening for Inhibitors of Protein–Protein Interactions

Redox-Active Cavitands

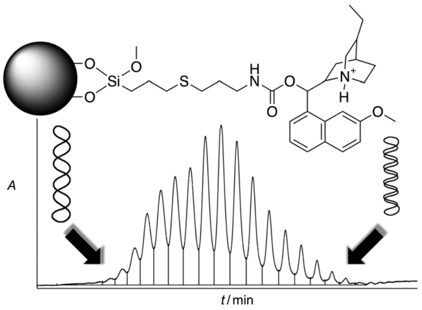
Catch it if you can! Redox-active resorcin[4]arene cavitands with quinone walls can be reversibly reduced to the hydroquinone form, influencing their host–guest complexation strength. Specifically, a top-covered triptycenequinone cavitand forms kinetically stable complexes with cycloalkanes; this complexation is weaker in the reduced hydroquinone form.



VIP

Plasmid DNA Topoisomers

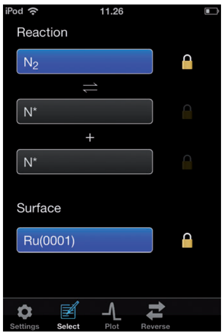
Recognizing pDNA supercoils: Differently supercoiled species of the same plasmid DNA can be separated by topology-selective chromatography. Two-dimensional HPLC proved that the supercoiling changes during fermentation. Thus, a new quality criterium might help to optimize the effectivity of future genetic drugs and vaccines.



And Finally

Web Applications

A rich source: Calculated reaction and activation energies for elementary coupling reactions occurring on metal surfaces can be found by using a web application. This tool provides access to data for reactions of molecules with up to three C, N, or O atoms on a number of different transition-metal surfaces. The underlying dataset is generated from a consistent set of DFT calculations and extrapolations based on linear scaling relations.



Reaction
N_2
⇄
N*
+
N*

Surface
Ru(0001)

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

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

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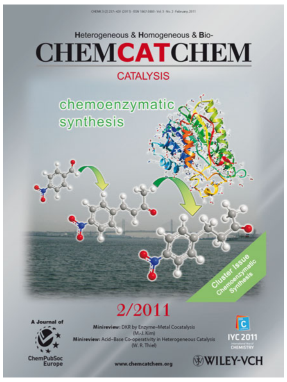
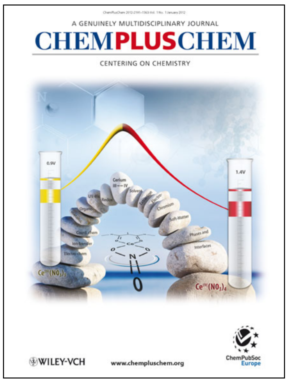


www.chemcatchem.org



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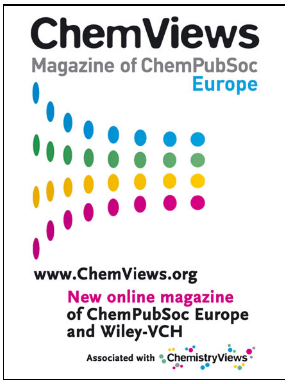

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