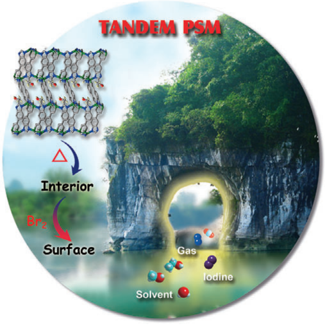
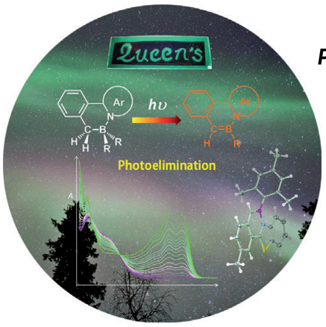
Supramolecular catalysts …

… relying on cooperation between Mg ions and a chelating complex (represented by carp in the picture) were developed by K. Ishihara and co-workers in their Communication on page 4549 ff. The enantioselective 1,4-hydrophosphinylation of α,β-unsaturated esters with diaryl phosphine oxides and 1,2-hydrophosphonylation of α,β-unsaturated ketones with dialkyl phosphites was achieved using chiral 3:2 complexes of (*R*)-(H_8-)BINOLate/Mg^{II} ions.

Metal–Organic Frameworks

Postsynthetic modification (PSM) of a new metal–organic framework, both at the surface and inside the channels, is described by M. H. Zeng, M. Kurmoo, and co-workers in their Communication on page 4538 ff.



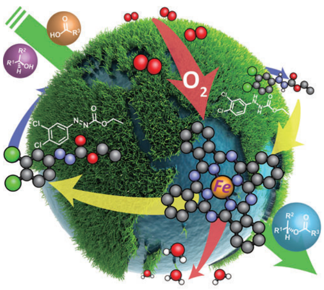


Photoelimination

Highly fluorescent azaborines can be prepared through photoelimination of B,N-heterocyclic compounds in solution and in the solid state, as demonstrated by S. Wang et al. in their Communication on page 4544 ff.

Iron Catalysis

In their Communication on page 4613 ff., T. Taniguchi and co-workers report Mitsunobu reactions using catalytic amounts of iron phthalocyanine and recyclable ethyl 2-arylhydrazinecarboxylates in the presence of air.



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Service

Author Profile

"My favorite food is Indian or Thai.
I like refereeing because sometimes the manuscripts are surprisingly good ..."
This and more about Burkhard König can be found on page 4520.

News

D. G. Blackmond

R. H. Friend

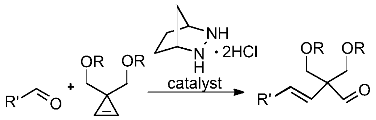
H. Topsøe

B. D. Freeman

Books

Highlights

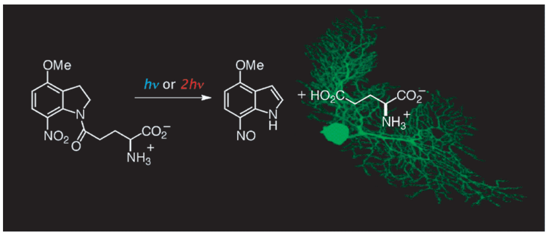
Synthetic Methods



The heat is on: A new [3+2] cycloaddition/cycloreversion strategy allows for catalytic and thermally allowed carbonyl–olefin metathesis (see scheme). This strategy opens opportunities for new developments in the field of carbonyl–olefin metathesis, which traditionally relied on stoichiometric amounts of transition-metal reagents or photochemical promotion.

Reviews

Two-Photon Probes

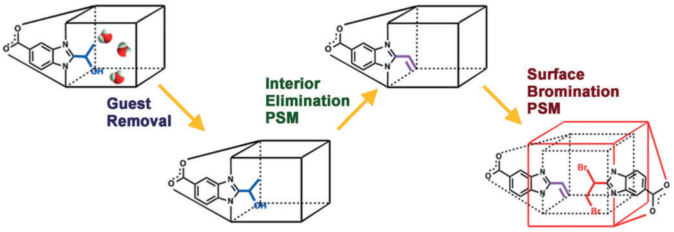


A leading light: Molecular systems that can be remotely controlled by light are gaining increasing importance in cell biology and neurosciences because of the spatial and temporal precision that is achievable with laser microscopy. Two-photon excitation has significant advantages over one-photon approaches deep in biological tissues, but the design of "smart" probes compatible with cell physiology is challenging.

Communications

Metal–Organic Frameworks

Frontispiece



Inside and outside: Two consecutive postsynthetic modifications, first an elimination reaction in the channels and then bromination at the surface, were realized in a new hybrid metal–organic framework. The dramatic effects of the different groups in the channels and at the surface were studied using gas sorption and the loading/release of solvent and iodine.

For the USA and Canada:
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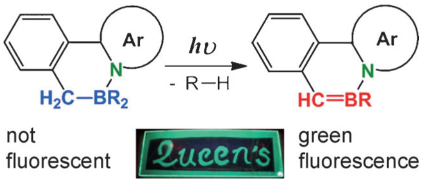
Photochemistry

J. S. Lu, S. B. Ko, N. R. Walters, Y. Kang, F. Sauriol, S. Wang* ______ **4544 – 4548**

Formation of Azaborines by Photoelimination of B,N-Heterocyclic Compounds

Inside Back Cover



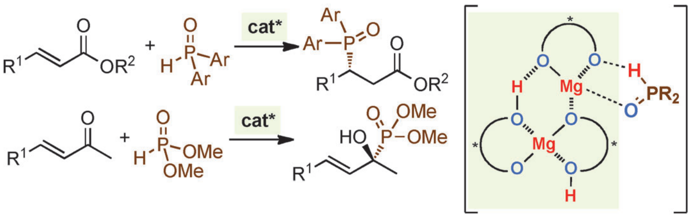
Highly fluorescent π-conjugated polycyclic azaborines can be prepared from B,N-heterocyclic compounds with a BR_2-CH_2 unit through the elimination of an R-H molecule (see scheme). These clean photoelimination reactions occur both in solution and in polymers doped with the precursors.

Asymmetric Catalysis

M. Hatano, T. Horibe, K. Ishihara* ______ **4549 – 4553**

Chiral Magnesium(II) Binaphtholates as Cooperative Brønsted/Lewis Acid–Base Catalysts for the Highly Enantioselective Addition of Phosphorus Nucleophiles to α,β-Unsaturated Esters and Ketones

Front Cover

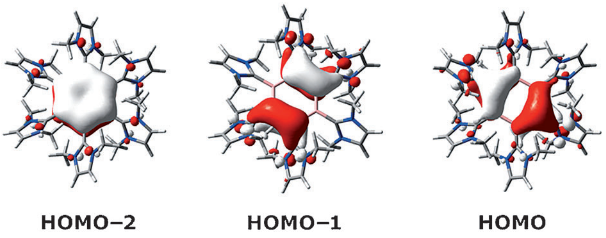


A little cooperation goes a long way: The cooperative Brønsted/Lewis acid–base supramolecular catalysts formed in situ from simple chiral magnesium(II) binaphtholate aqua complexes promoted the highly enantioselective 1,4-hydrophosphinylation of α,β-unsaturated esters with diaryl phosphine oxides and 1,2-hydrophosphonylation of α,β-unsaturated ketones with dialkyl phosphites (see scheme).

Computational Chemistry

T. B. Tai,* M. T. Nguyen* ______ **4554 – 4557**

Boron–Boron Multiple Bond in $[B(NHC)]_2$: Towards Stable and Aromatic $[B(NHC)]_n$ Rings

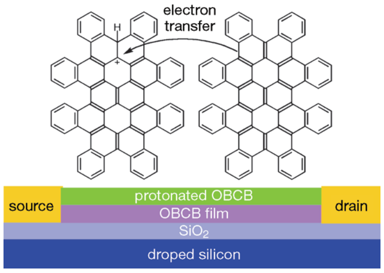


Chained up: The π conjugation along B-C-N chains and a shift into a deep valence area of σ molecular orbitals (HOMO−6) are the reasons for the high stability of the dimer $[B(NHC)]_2$ (NHC = N-heterocyclic carbene). The cyclic compounds $[B(NHC)]_n$ (see selected MOs for $n=6$) exhibit structural and aromatic features similar to the corresponding hydrocarbons $(CH)_n$.

Materials Chemistry

S. Xiao, S. J. Kang, Y. Zhong, S. Zhang, A. M. Scott, A. Moscatelli, N. J. Turro, M. L. Steigerwald, H. Li,* C. Nuckolls* ______ **4558 – 4562**

Controlled Doping in Thin-Film Transistors of Large Contorted Aromatic Compounds



Bigger and better: The new thin-film organic material octabenzcircumbiphenyl (OBCB; see scheme) forms an active layer in a field effect transistor, which can be switched simultaneously with two different inputs, that is, electrical bias and protonation.

Sharp and
refreshing
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Chemie
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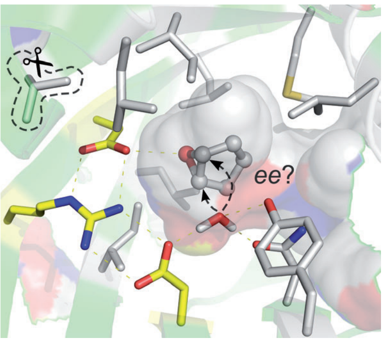

Cluster model: Large active-site models (see figure) are used to investigate the selectivity of limonene epoxide hydrolase, both the wild type and mutants optimized through directed evolution. Good agreement is found between theory and the experimental data, thus demonstrating that the quantum chemical cluster approach can be a powerful tool in the field of asymmetric biocatalysis.

Biocatalysis

M. E. S. Lind, F. Himo* —— **4563 – 4567**

Quantum Chemistry as a Tool in Asymmetric Biocatalysis: Limonene Epoxide Hydrolase Test Case

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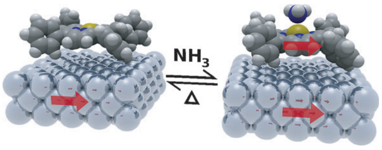


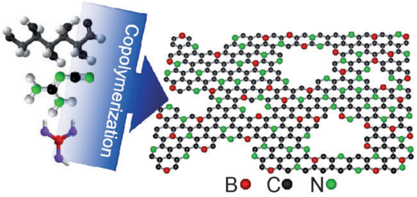
Amazing ammonia: The molecular spin state of Ni^{II} porphyrin, supported on a ferromagnetic Co surface, can be reversibly switched between spin-off ($S=0$) and spin-on ($S=1$) states upon coordination and decoordination of the gaseous ligand NH_3, respectively (see picture). This finding clearly indicates the possible use of the system as a single-molecule-based magnetochemical sensor and in spintronics.

Magnetochemistry

C. Wäckerlin, K. Tarafder, J. Girovsky, J. Nowakowski, T. Hählen, A. Shchyrba, D. Siewert, A. Kleibert, F. Nolting, P. M. Oppeneer, T. A. Jung,* N. Ballav* —— **4568 – 4571**

Ammonia Coordination Introducing a Magnetic Moment in an On-Surface Low-Spin Porphyrin

---



A simple but powerful chemical process—the copolymerization of biomass (glucose) and boric acid as templated by dicyandiamide (see picture)—was used to fabricate high-quality doped graphene monoliths with through-plane nanopores. The holey graphene monoliths had a high surface area and showed excellent performance as metal-free carbocatalysts for selective oxidation.

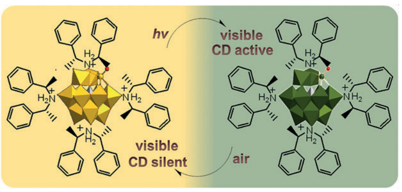
Carbocatalysis

X. H. Li,* M. Antonietti —— **4572 – 4576**

Polycondensation of Boron- and Nitrogen-Codoped Holey Graphene Monoliths from Molecules: Carbocatalysts for Selective Oxidation

---

Managing the blues: Chiral heteropoly blues of achiral polyoxometalate clusters were created through an intermolecular interaction with a chiral organic compound. Controllable chiroptical switching of the cluster complexes was possible through reversible photochromism of the polyoxometalates (see picture).



Polyoxometalates

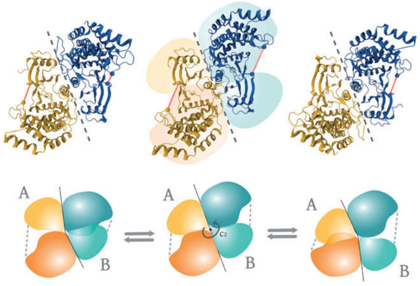
Y. Wang, H. Li, C. Wu, Y. Yang, L. Shi, L. Wu* —— **4577 – 4581**

Chiral Heteropoly Blues and Controllable Switching of Achiral Polyoxometalate Clusters

Protein Dynamics

M. Sahún-Roncero, B. Rubio-Ruiz,
G. Saladino, A. Conejo-García,
A. Espinosa, A. Velázquez-Campoy,
F. L. Gervasio, A. Entrena,
R. Hurtado-Guerrero* ______ **4582 – 4586**

The Mechanism of Allosteric Coupling in Choline Kinase α1 Revealed by the Action of a Rationally Designed Inhibitor

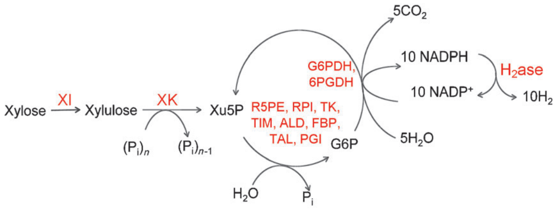


Applying a CHOK hold: Combined experimental and computational studies of the binding mode of a rationally designed inhibitor of the dimeric choline kinase α1 (CHOKα1) explain the molecular mechanism of negative cooperativity (see scheme) and how the monomers are connected. The results give insight into how the symmetry of the dimer can be partially conserved despite a lack of conservation in the static crystal structures.

Biocatalysis

J. S. Martín del Campo, J. Rollin,
S. Myung, Y. Chun, S. Chandrayan,
R. Patiño, M. WW Adams,
Y.-H. P. Zhang* ____________ **4587 – 4590**

High-Yield Production of Dihydrogen from Xylose by Using a Synthetic Enzyme Cascade in a Cell-Free System



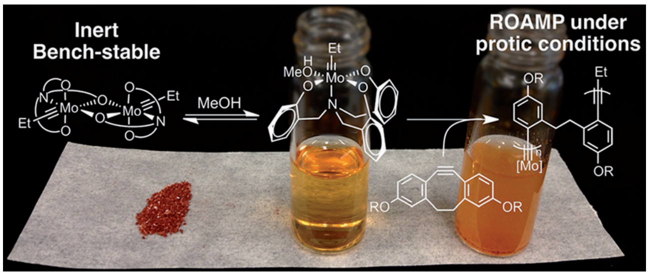
Let enzymes work: H_2 was produced from xylose and water in one reactor containing 13 enzymes (red). By using a novel polyphosphate xylulokinase (XK), xylose was converted into H_2 and CO_2 with approaching 100% of the theoretical yield. The findings suggest that cell-free biosystems could produce H_2 from biomass xylose at low cost. Xu5P = xylulose 5-phosphate, G6P = glucose 6-phosphate.

Alkyne Metathesis

D. W. Paley, D. F. Sedbrook, J. Decatur,
F. R. Fischer, M. L. Steigerwald,
C. Nuckolls* ____________ **4591 – 4594**

Alcohol-Promoted Ring-Opening Alkyne Metathesis Polymerization

Inside Cover



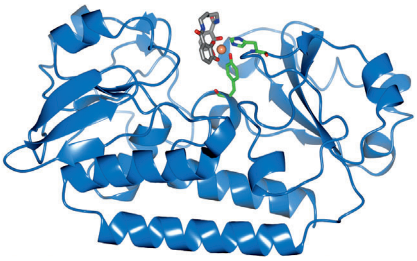
Alcohol is the answer! An inactive, air-stable, dimeric molybdenum alkylidyne complex is activated toward ring-opening alkyne metathesis polymerization (ROAMP) by the addition of methanol. The ROAMP is compatible with water and phenol-containing substrates and with the in situ photochemical generation of alkyne monomers from cyclopropenones.

Siderophores

D. J. Raines, O. V. Moroz, K. S. Wilson,
A.-K. Duhme-Klair* ________ **4595 – 4598**

Interactions of a Periplasmic Binding Protein with a Tetradentate Siderophore Mimic

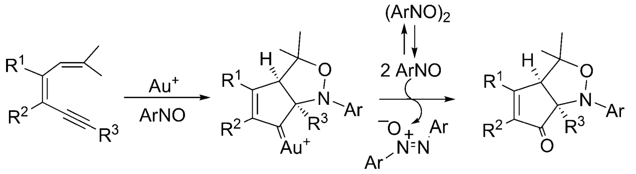
Iron-bound structure: The ferric complex of a tetradentate siderophore mimic was synthesized and co-crystallized with the periplasmic binding protein CeuE of *Campylobacter jejuni*. In addition to electrostatic and hydrogen-bonding interactions between the binding pocket and the substrate, the structure showed direct coordination of two amino acid side chains to the Fe^{III} center (orange, see figure).



Synthetic Methods

C. H. Chen, Y. C. Tsai,
R.-S. Liu* ———— **4599 – 4603**

Gold-Catalyzed Cyclization/Oxidative [3+2] Cycloadditions of 1,5-Enynes with Nitrosobenzenes without Additional Oxidants

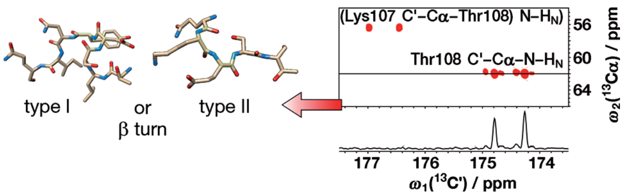


Golden control: The title reaction (see scheme) proceeds with high stereocontrol to generate the heterocyclic products in good yield. Experiments to probe the mechanism were performed.

NMR Spectroscopy

J. Stanek, S. Saxena, L. Geist, R. Konrat,*
W. Koźmiński* ———— **4604 – 4606**

Probing Local Backbone Geometries in Intrinsically Disordered Proteins by Cross-Correlated NMR Relaxation

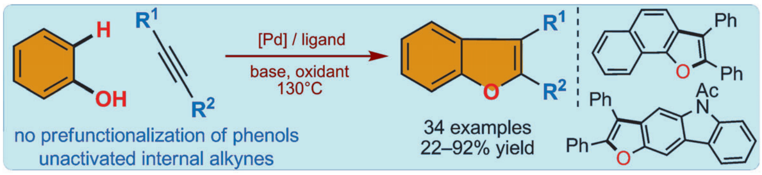


An ultra-high-resolution NMR experiment for the measurement of intraresidue $^{1}H(i)$–$^{15}N(i)$–$^{13}C'(i)$ dipolar–chemical shift anisotropy relaxation interference is employed to extract information about local backbone geometries in intrinsically disordered proteins. The study of tumor suppressor BASP1 revealed a population shift of β-turn geometries at low pH conditions and a compaction of the BASP1 structural ensemble.

Synthetic Methods

M. R. Kuram, M. Bhanuchandra,
A. K. Sahoo* ———— **4607 – 4612**

Direct Access to Benzo[*b*]furans through Palladium-Catalyzed Oxidative Annulation of Phenols and Unactivated Internal Alkynes

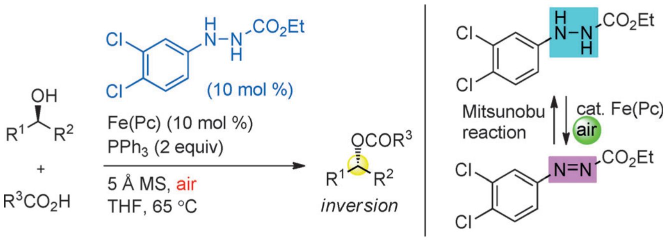


2,3-Disubstituted benzo[*b*]furans are prepared in one step from commercially available phenols and readily accessible unactivated internal alkynes (see scheme). This Pd-catalyzed oxidative annulation has a broad substrate scope and allows access to a wide range of benzo[*b*]furans.

Synthetic Methods

D. Hirose, T. Taniguchi,*
H. Ishibashi ———— **4613 – 4617**

Recyclable Mitsunobu Reagents: Catalytic Mitsunobu Reactions with an Iron Catalyst and Atmospheric Oxygen



Aerobic recycling: A catalytic amount of a hydrazine reagent is sufficient to promote Mitsunobu reactions in the presence of triphenylphosphine, an iron catalyst, and air. The active form of the catalyst, an azo species, can be readily generated by iron-catalyzed aerobic oxidation. MS = molecular sieves, Pc = phthalocyanine.

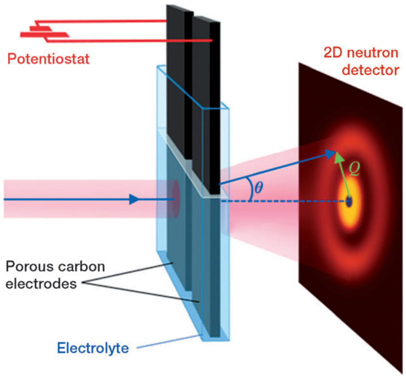
Back Cover

Carbon Materials

S. Boukhalfa, L. He, Y. B. Melnichenko, G. Yushin* ______ 4618 – 4622

Small-Angle Neutron Scattering for In Situ Probing of Ion Adsorption Inside Micropores

Confined ions: The high penetrating power and sensitivity of neutron scattering to isotope substitution are harnessed to observe changes in the ion concentration in a porous carbon material as a function of the applied potential and the pore size. Depending on the solvent properties and the solvent–pore-wall interactions, either enhanced or reduced ion electroadsorption may take place.

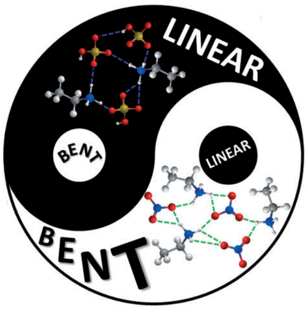


Hydrogen Bonds

R. Hayes, S. Imberti, G. G. Warr, R. Atkin* ______ 4623 – 4627

The Nature of Hydrogen Bonding in Protic Ionic Liquids

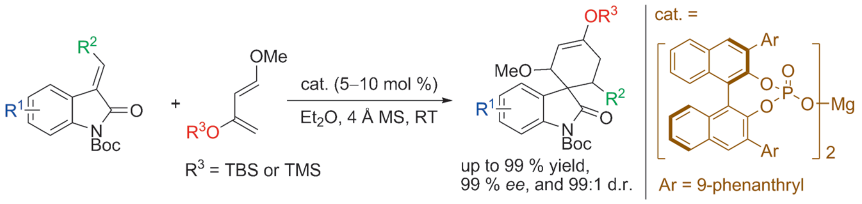
The size, direction, strength, and distribution of hydrogen bonds in several protic ionic liquids (PILs) has been elucidated using neutron diffraction and computer simulation. There is significant variation in PIL hydrogen bond interactions ranging from short and linear to long and bi-/trifurcated. The nature of the PIL's hydrogen bonds reflects its macroscopic properties.



Asymmetric Catalysis

G. Li, T. Liang, L. Wojtas, J. C. Antilla* ______ 4628 – 4632

An Asymmetric Diels–Alder Reaction Catalyzed by Chiral Phosphate Magnesium Complexes: Highly Enantioselective Synthesis of Chiral Spirooxindoles



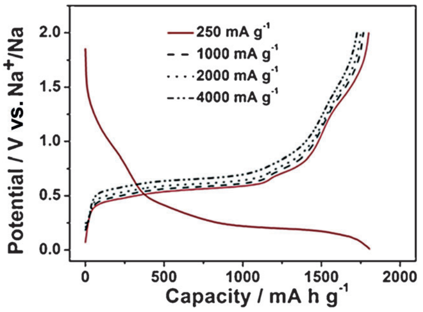
Mild Magic: A mild, enantioselective Diels–Alder reaction, catalyzed by a chiral magnesium phosphate species, has been developed for the synthesis of various chiral spirooxindoles. Molecular sieves were found to have a considerable effect when used as additives in this reaction.

Anode Materials

J. Qian, X. Wu, Y. Cao, X. Ai, H. Yang* ______ 4633 – 4636

High Capacity and Rate Capability of Amorphous Phosphorus for Sodium Ion Batteries

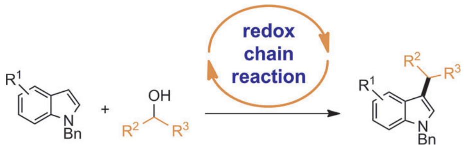
Turning on your P/C: An amorphous phosphorus/carbon (a-P/C) composite was synthesized using simple mechanical ball milling of red phosphorus and conductive carbon powders. This material gave an extraordinarily high sodium ion storage capacity of 1764 mA h g^{-1} (see graph) with a very high rate capability, showing great promise as a high capacity and high rate anode material for sodium ion batteries.



Synthetic Methods

X. Han, J. Wu* ———— **4637 – 4640**

Redox Chain Reaction—Indole and Pyrrole Alkylation with Unactivated Secondary Alcohols



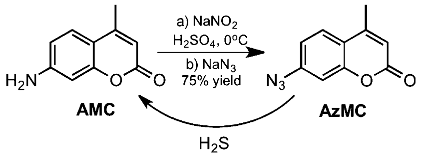
Secondary role: Indole and pyrrole derivatives are alkylated with unactivated secondary aliphatic alcohols by a Brønsted acid-catalyzed redox chain reaction mechanism. Broad functional-group tolerance has been demonstrated and preliminary studies suggest that 1,4-reduction of a putative indolyl carbocation is the dominant mechanistic pathway.

Fluorescent Probes

M. K. Thorson, T. Majtan, J. P. Kraus, A. M. Barrios* ———— **4641 – 4644**

Identification of Cystathionine β-Synthase Inhibitors Using a Hydrogen Sulfide Selective Probe

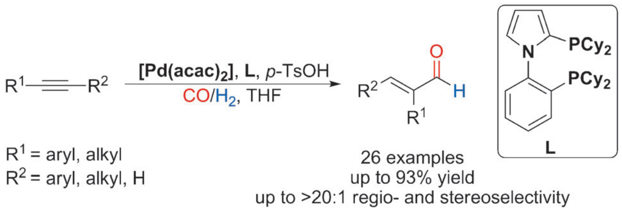
Buzzing with activity: A hydrogen sulfide selective fluorogenic probe, 7-azido-4-methylcoumarin (AzMC), serves as a highly sensitive assay for cystathionine β-synthase activity, and is suitable for the high-throughput discovery of novel enzyme inhibitors.



Hydroformylation

X. Fang, M. Zhang, R. Jackstell, M. Beller* ———— **4645 – 4649**

Selective Palladium-Catalyzed Hydroformylation of Alkynes to α,β-Unsaturated Aldehydes

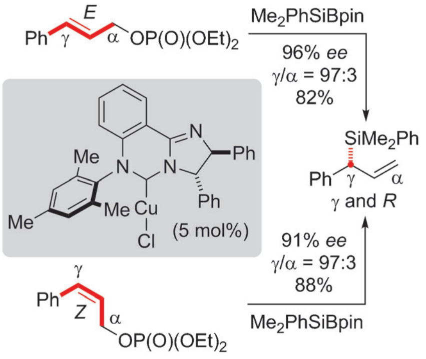


Atom-efficient: A selective palladium catalyst system is used for the hydroformylation of alkynes (see picture). In this syngas reaction, various alkynes were smoothly transformed to synthetically interesting α,β-unsaturated aldehydes in good yields with high regio- and stereoselectivity.

Allylic Substitution

L. B. Delvos, D. J. Vyas, M. Oestreich* ———— **4650 – 4653**

Asymmetric Synthesis of α-Chiral Allylic Silanes by Enantioconvergent γ-Selective Copper(I)-Catalyzed Allylic Silylation

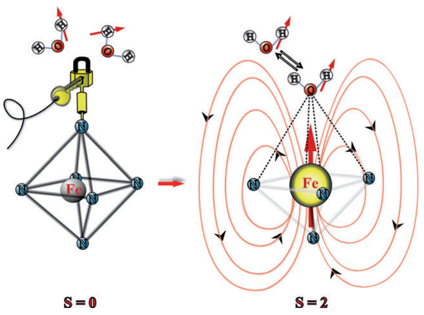


Gamma way: Regio- and enantioselective allylic substitution with a silicon nucleophile generated by copper(I)-catalyzed Si–B bond activation provides direct access to α-chiral allylic silanes from linear acceptors. The enantioconvergent catalysis employing McQuade's six-membered N-heterocyclic-carbene–copper(I) catalyst is applicable to aryl- and alkyl-substituted allylic phosphates (see scheme).

Magnetogenic Probes

F. Touti, P. Maurin,
J. Hasserodt* ______ **4654 – 4658**

Magnetogenesis under Physiological Conditions with Probes that Report on (Bio-)Chemical Stimuli

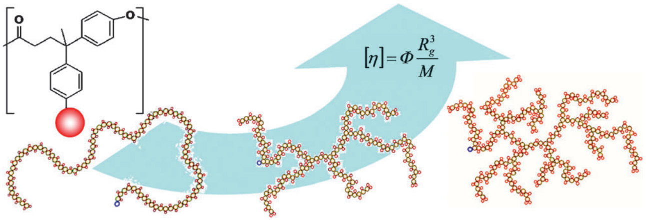


Switched on: A molecular concept allows the generation of magnetism in an aqueous sample under the influence of a freshly added (bio-)chemical analyte. The analyte (a chemical reagent or enzyme) triggers the conversion of the probe, a diamagnetic chelate compound, into a paramagnetic compound (see scheme). The two probes prepared are easily accessible iron(II) chelates, and are operative at physiological conditions and/or in serum.

Segmental Density of Polymers

A. Lederer,* W. Burchard, A. Khalyavina,
P. Lindner, R. Schweins ______ **4659 – 4663**

Is the Universal Law Valid for Branched Polymers?



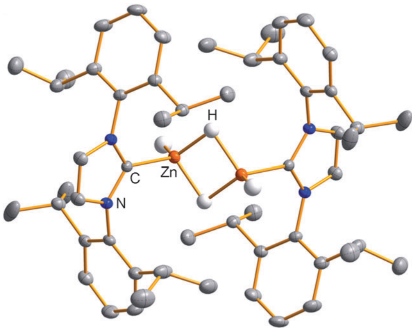
A matter of phis: The size of macromolecules is determined by the "universal calibration" based on the Flory–Fox equation (see scheme). The effect of the segmental density of real branched systems on this equation is investigated. To study this effect, accurately prepared polymers with discrete molecular properties were characterized in detail and precisely evaluated.

Zinc Hydride

A. Rit, T. P. Spaniol, L. Maron,*
J. Okuda* ______ **4664 – 4667**

Molecular Zinc Dihydride Stabilized by N-Heterocyclic Carbenes

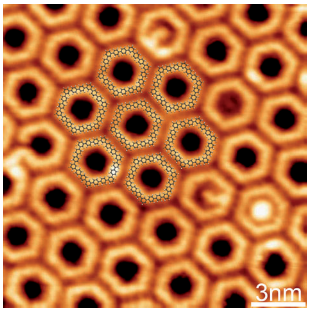
Solubility problems solved: The first examples of discrete soluble zinc dihydride adducts with NHC ligands reacted with CO_2 to produce formate species and efficiently catalyzed the dehydrocoupling of silanes with methanol. These compounds were characterized both in solution and in the solid state (see picture).



Nanotrough Arrays

Q. T. Fan, C. C. Wang, Y. Han, J. F. Zhu,*
W. Hieringer, J. Kuttner, G. Hilt,
J. M. Gottfried* ______ **4668 – 4672**

Surface-Assisted Organic Synthesis of Hyperbenzene Nanotroughs

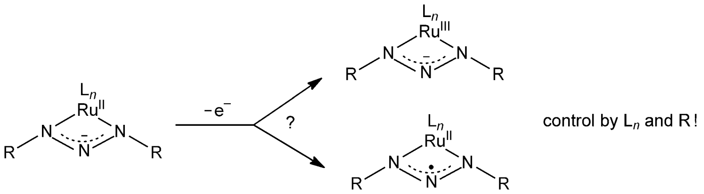


A hexagonal macrocycle consisting of 18 phenylene units (hyperbenzene) was synthesized on a Cu(111) surface in ultrahigh vacuum by Ullmann coupling of six 4,4″-dibromo-*m*-terphenyl molecules. The large diameter of 21.3 Å and the ability to assemble in arrays makes hyperbenzene an interesting candidate for a nanotrough that could enclose metallic, semiconducting, or molecular quantum dots.

Redox-Active Ligands

F. Ehret, M. Bubrin, S. Záliš, W. Kaim* —— **4673 – 4675**

Discovering More Non-Innocence: Triazenido versus Triazenyl Radical Ligand Function, and a Comment on $[NO_2]^n$ as a "Suspect" Ligand

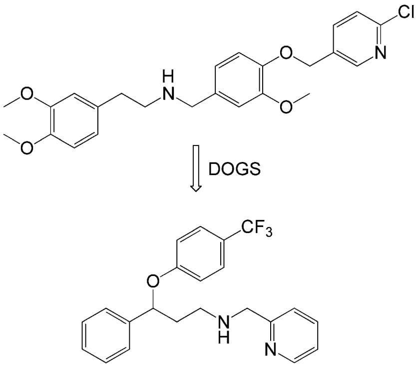


The unusual suspects: Depending on co-ligands L_n and the effects of substituents (R), the well-known triazenides $[N(NR)_2]^-$ may act as EPR detectable coordinated triazenyl ligands, $[N(NR)_2]^{\bullet}$ (see scheme). They are thus new non-innocent ligands and are related to the hitherto unused non-innocent nitrogen dioxide ligand, $[NO_2]^{\bullet}$.

Computer-Based Drug Design

B. Spänkuch, S. Keppner, L. Lange, T. Rodrigues, H. Zettl, C. P. Koch, M. Reutlinger, M. Hartenfeller, P. Schneider, G. Schneider* **4676 – 4681**

Drugs by Numbers: Reaction-Driven De Novo Design of Potent and Selective Anticancer Leads

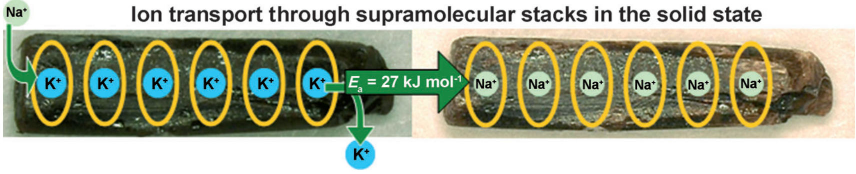


A potent and selective inhibitor of the anticancer target Polo-like kinase 1 was found by computer-based molecular design. This type II kinase inhibitor was synthesized as suggested by the design software DOGS and exhibited significant antiproliferative effects against HeLa cells without affecting nontransformed cells. The study provides a proof-of-concept for reaction-based de novo design as a leading tool for drug discovery.

Ion Channels

C. D. Assouma, A. Crochet, Y. Chérémond, B. Giese, K. M. Fromm* —— **4682 – 4685**

Kinetics of Ion Transport through Supramolecular Channels in Single Crystals

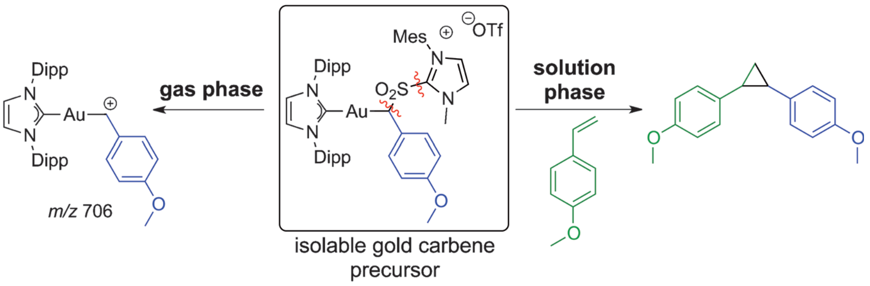


Single-crystal to single-crystal transformations are possible by ion-exchange and transport reactions through supramolecular channels that are composed of crown ether molecules and use trihalide ions as scaffolds. Kinetic measurements of ion transport at different temperatures provide activation energy data and show that a very fast exchange of K^+ ions with Na^+ ions occurs.

Gold Catalysis

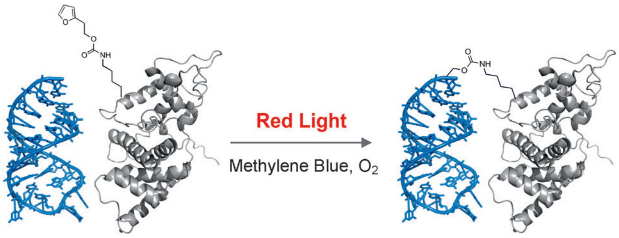
D. H. Ringger, P. Chen* —— **4686 – 4689**

Rational Design of a Gold Carbene Precursor Complex for a Catalytic Cyclopropanation Reaction



Bridging gas- and solution-phase chemistry: A gold(I) carbene precursor complex has been developed and investigated for catalytic cyclopropanation. Formation of the carbene intermediate was first probed by mass spectrometry, followed by cyclopropanation of *p*-methoxystyrene in solution. The imidazolylidene leaving group serves as a base generated in situ that is necessary in the putative catalytic cycle.

Protein–RNA Interactions



Well red: A protein-RNA crosslinker has been genetically encoded that can be controlled with red light (see scheme), thus offering high penetration depths in biological materials. This should enable the discovery and mapping of transient protein–RNA interactions and enable the design of peptide- and protein-based drugs for RNA-targeted photodynamic therapy.

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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