



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:

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

P. Berrouard, A. Najari, A. Pron, D. Gendron, P.-O. Morin, J.-R. Pouliot, J. Veilleux, M. Leclerc*
Synthesis of 5-Alkyl[3,4-c]thienopyrrole-4,6-dione-Based Polymers through Direct Heteroarylation

J. Zeng, C. Zhu, J. Tao, M. Jin, H. Zhang, Z.-Y. Li, Y. Zhu, Y. Xia*
Controlling the Nucleation and Growth of Silver on Palladium Nanocubes by Manipulating the Reaction Kinetics

C. A. DeForest, K. S. Anseth*
Photoreversible Patterning of Biomolecules within Click-Based Hydrogels

H. Chinen, K. Mawatari, Y. Pihosh, K. Morikawa, Y. Kazoe, T. Tsukahara, T. Kitamori*
Enhancement of Proton Mobility in Extended Nanospace Channels

S. Handa, L. M. Slaughter*
Enantioselective Alkynylbenzaldehyde Cyclizations Catalyzed By Chiral Gold(I) Acyclic Diaminocarbene Complexes That Contain Weak Au–Arene Interactions



*“My favorite reaction is the Robinson synthesis of tropinone.
I am waiting for the day when someone will discover the 30-hour day ...”*
This and more about Michael Willis can be found on page 1304.

Author Profile

Michael Willis _____ 1304



T. Maschmeyer



J. Bremner



J. Gooding



M. Stenzel



M. Brimble



R. Payne

News

2011 Royal Australian Chemical Institute National Award Winners — 1305–1306

Porous Polymers

Michael S. Silverstein, Neil R. Cameron, Marc A. Hillmyer

reviewed by A. Cooper _____ 1307

Heterocycles in Natural Product Synthesis

Krishna C. Majumdar, Shital K. Chattopadhyay

reviewed by S. A. Snyder _____ 1307

Books

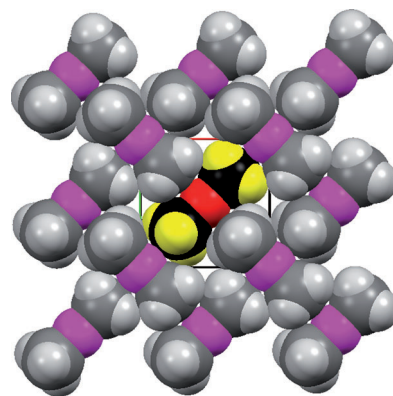
Highlights

Organometallic Structures

W. Clegg* ————— 1310–1311

Main-Group Metal–Alkyls: Simple Formulae but Complex Structural Chemistry

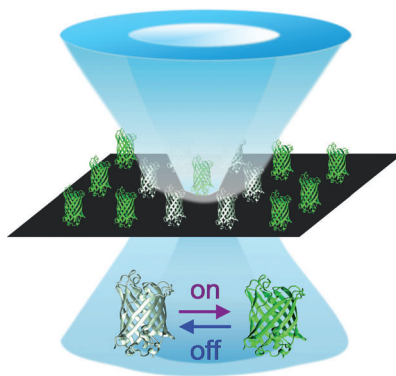
Subtle differences: By using a combination of advanced crystallographic techniques and complementary computational approaches to assess the relative energies and conformational preferences, Me_2Zn has been shown to form two different crystal structures. At temperatures above 180 K the methyl groups are staggered, whereas below 180 K the methyl groups are eclipsed. In contrast, the two ethyl groups in Et_2Zn are shown to be mutually *cis*.



Biotechnology

G. U. Nienhaus* ————— 1312–1314

A Fatigue-Resistant Photoswitchable Fluorescent Protein for Optical Nanoscopy



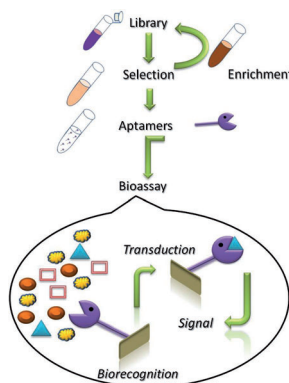
Like the battery bunny: The novel photo-switchable fluorescent protein rsEGFP can be cycled between its fluorescent and nonfluorescent states more than a thousand times and is, therefore, a superb marker for high-resolution RESOLFT imaging (RESOLFT = reversible saturable optical fluorescence transition) and data storage applications.

Reviews

Artificial Aptamers

M. Mascini,* I. Palchetti,
S. Tombelli ————— 1316–1332

Nucleic Acid and Peptide Aptamers: Fundamentals and Bioanalytical Aspects



Antibody alternatives: This Review covers the peculiarities of the two major classes of affinity molecules produced by evolutionary approaches: nucleic acid aptamers and combinatorial non-immunoglobulin proteins (termed here, for convenience, simply peptide aptamers). The applications of these molecules in the bioanalytical field are discussed.

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individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Communications

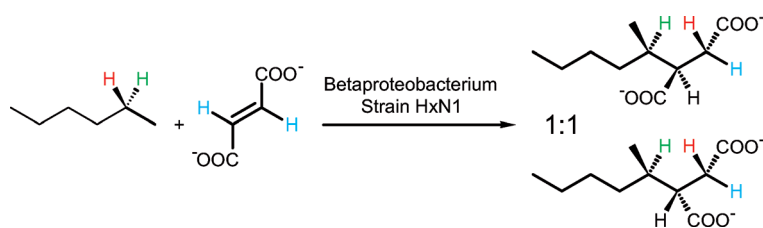
Alkane Activation

R. Jarling, M. Sadeghi, M. Drozdowska, S. Lahme, W. Buckel, R. Rabus, F. Widdel, B. T. Golding,* H. Wilkes* — 1334–1338

Stereochemical Investigations Reveal the Mechanism of the Bacterial Activation of *n*-Alkanes without Oxygen



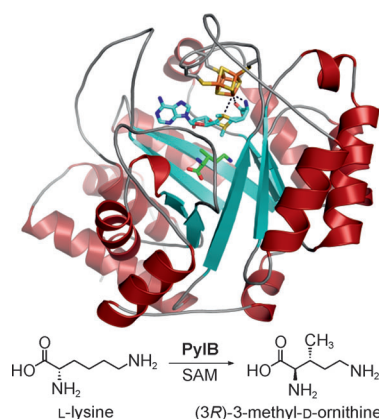
Frontispiece



Anaerobic growth of the bacterium strain HxN1 with *n*-hexane gives nearly equal amounts of (2*R*,1'*R*)- and (2*S*,1'*R*)-(1-methylpentyl)succinate, which are formed by the radical addition of the hydrocarbon to fumarate (see scheme). The highly

selective attack on the pro-*S* hydrogen atom at C2 of *n*-hexane is associated with inversion of the configuration at C2 during binding to fumarate and exhibits isotopic discrimination against a C–²H bond.

Made by the barrel load: The biosynthetic pathway of the recently discovered 22nd amino acid, pyrrolysine, starts with an isomerization of lysine to methylornithine, catalyzed by PylB. The X-ray crystal structure of PylB is determined (see picture) and shows it has a TIM barrel fold. The sealed central cavity contains a [4Fe-4S] cluster, *S*-adenosylmethionine (SAM), and methylornithine, whose 2*R*,3*R* configuration could be confirmed. The data suggest a fragmentation–recombination mechanism via a glycy radical intermediate.



Pyrrolysine Biosynthesis

F. Quitterer, A. List, W. Eisenreich, A. Bacher, M. Groll* — 1339–1342

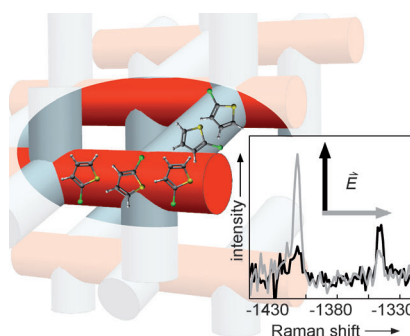
Crystal Structure of Methylornithine Synthase (PylB): Insights into the Pyrrolysine Biosynthesis



Front Cover



Pore relations: Reagent molecules form head-to-tail chains in the pores of ZSM-5 zeolite particles in the presence or absence of acidic sites, according to multiplex coherent anti-Stokes Raman scattering spectromicroscopy (mCARS). The molecular ordering in the pores makes it possible to characterize the crystallographic subunits of individual ZSM-5 particles with (sub)micrometer spatial resolution in three dimensions.



Zeolite Imaging

K. F. Domke,* J. P. R. Day, G. Rago, T. A. Riemer, M. H. F. Kox, B. M. Weckhuysen, M. Bonn — 1343–1347

Host–Guest Geometry in Pores of Zeolite ZSM-5 Spatially Resolved with Multiplex CARS Spectromicroscopy



Inside Cover

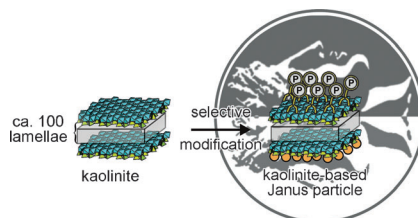


Kaolinite-Based Janus Particles

D. Hirsemann, S. Shylesh, R. A. De Souza,
B. Diar-Bakerly, B. Biersack, D. N. Mueller,
M. Martin, R. Schobert,
J. Breu* 1348–1352



Large-Scale, Low-Cost Fabrication of
Janus-Type Emulsifiers by Selective
Decoration of Natural Kaolinite Platelets



Kaolinite platelets have inherent Janus character owing to a polar crystal structure. This character is, however, ineffective without selective modification of the two hydrophilic external basal surfaces. Amplification of the difference in the chemical nature of the surfaces is achieved by cation exchange on one side and by covalent grafting on the other. After adjustment of the surface tension, kaolinite is an effective emulsifier.



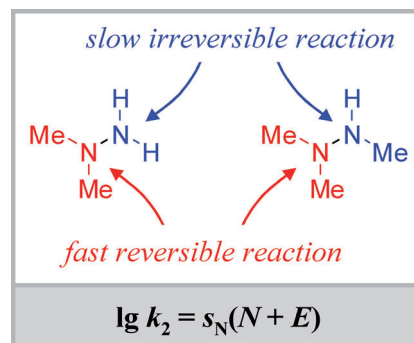
Ambident Reactivity

T. A. Nigst, J. Ammer,
H. Mayr* 1353–1356



Ambident Reactivities of
Methylhydrazines

Kinetics versus thermodynamics: Methyl groups increase the nucleophilic reactivity of the substituted position of hydrazines and reduce the nucleophilicity of the adjacent nitrogen center. As a result, the tertiary nitrogen atom of 1,1-dimethylhydrazine is 3000 times more reactive than the NH_2 group, but under thermodynamic control substitution of an NH_2 proton occurs (see picture).

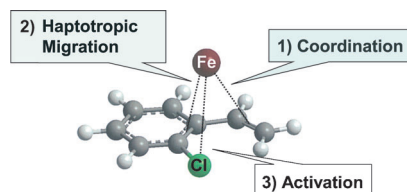


Iron Catalysis

S. Gülaç,
A. Jacobi von Wangelin* 1357–1361



Chlorostyrenes in Iron-Catalyzed Biaryl
Coupling Reactions



An effective protocol for iron-catalyzed biaryl syntheses by coupling chlorostyrenes with aryl Grignard reagents requires only mild reaction conditions and tolerates various functional groups. The underlying activation of deactivated aryl chlorides proceeds through a rate-determining coordination of the catalyst to the vinyl substituent and subsequent haptotropic migration along the conjugated π system to the site of C–Cl bond cleavage.

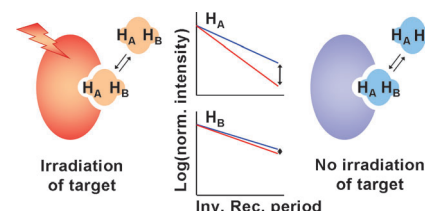
Drug Design

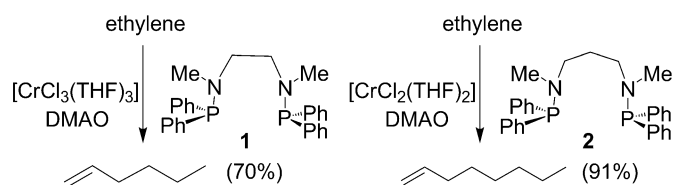
Y. Mizukoshi, A. Abe, T. Takizawa,
H. Hanzawa, Y. Fukunishi, I. Shimada,*
H. Takahashi* 1362–1365



An Accurate Pharmacophore Mapping
Method by NMR Spectroscopy

Irradiation makes the difference: The relaxation-rate differences of individual ligand protons (H_A , H_B) between the experiment with (see picture, red) and that without (blue) saturation of the protons of the protein target reflect the proximity to the protein surface. Thus, the binding portions of ligand molecules could be identified using this “difference of inversion recovery rate with and without target irradiation” (DIRECTION) method.





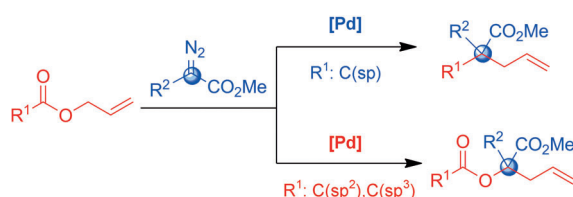
Small change, big difference: The introduction of an additional CH_2 group into the bridge of ligands with two P/N units leads to a different selectivity of the corresponding chromium-based catalysts. Whereas **1** produces an ethylene trimeri-

zation system, **2** provides an unprecedented ethylene tetramerization system that produces 1-octene with high purity and little or no polymer side products (see scheme; DMAO = Me_3Al -depleted methylaluminoxane).

Ethylene Tetramerization

Y. Shaikh, K. Albahily, M. Sutcliffe,
V. Fomitcheva, S. Gambarotta,*
I. Korobkov, R. Duchateau* . **1366–1369**

A Highly Selective Ethylene
Tetramerization Catalyst



Take two: α -Diazocarbonyl compounds display a diverse pattern of reactivity upon palladium-catalyzed reaction with esters. Esters bearing an alkynyl group on the carbonyl carbon atom lead to two different C–C bonds at the same carbon atom in a

single operation through decarboxylation and migratory insertion, whereas aromatic and benzylic acid derivatives afford aromatic and benzylic esters bearing an O-substituted quaternary carbon center.

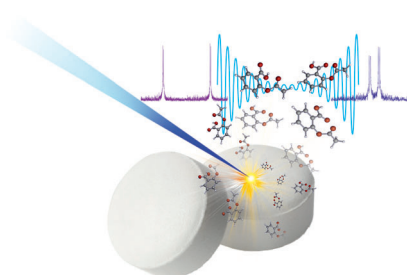
Palladium Catalysis

Z. S. Chen, X. H. Duan, P. X. Zhou, S. Ali,
J. Y. Luo, Y. M. Liang* — **1370–1374**

Palladium-Catalyzed Divergent Reactions of α -Diazocarbonyl Compounds with Allylic Esters: Construction of Quaternary Carbon Centers



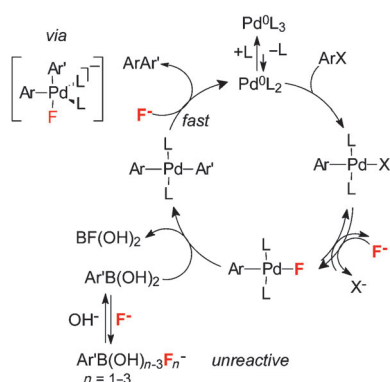
Accurate structural information: The first high-resolution study of isolated gas-phase acetyl salicylic acid (aspirin) is reported. Solid aspirin was vaporized by laser ablation, expanded in a supersonic jet, and characterized by Fourier transform microwave spectroscopy (see picture). Two different neutral structures have been identified from the analysis of the rotational spectrum.



Gas-Phase Conformations

C. Cabezas, J. L. Alonso,* J. C. López,
S. Mata — **1375–1378**

Unveiling the Shape of Aspirin in the Gas Phase



Fluoride ions play three roles in the Suzuki–Miyaura reaction. They favor the reaction by formation of *trans*- $[\text{ArPdF}(\text{PPh}_3)_2]$, which reacts with $\text{Ar}'\text{B}(\text{OH})_2$ in an unprecedented rate-determining transmetalation, and by promoting the reductive elimination from the *trans*- $[\text{ArPdAr}'(\text{PPh}_3)_2]$ intermediate. Conversely, F^- disfavors the reaction by formation of unreactive anionic $\text{Ar}'\text{B}(\text{OH})_{n-3}\text{F}_n^-$ ($n = 1–3$), leading to two antagonistic effects of F^- in the transmetalation.

Suzuki–Miyaura Reactions

C. Amatore,* A. Jutand,*
G. Le Duc — **1379–1382**

The Triple Role of Fluoride Ions in Palladium-Catalyzed Suzuki–Miyaura Reactions: Unprecedented Transmetalation from $[\text{ArPdFL}_2]$ Complexes

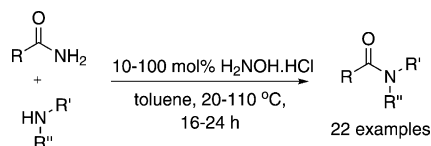


Catalytic Transamidation

C. L. Allen,* B. N. Atkinson,
J. M. J. Williams 1383–1386



Transamidation of Primary Amides with Amines Using Hydroxylamine Hydrochloride as an Inorganic Catalyst



Metal-free catalysis: A method for the transamidation of primary amides with primary or secondary amines provides access to secondary and tertiary amides, by utilizing catalytic quantities of hydroxylamine hydrochloride to activate the chemically robust primary amide group (see scheme). A mechanism of primary amide activation through a hydrogen-bonding complex is proposed.

Biomass Conversion

Y.-T. Cheng, J. Jae, J. Shi, W. Fan,
G. W. Huber* 1387–1390



Production of Renewable Aromatic Compounds by Catalytic Fast Pyrolysis of Lignocellulosic Biomass with Bifunctional Ga/ZSM-5 Catalysts



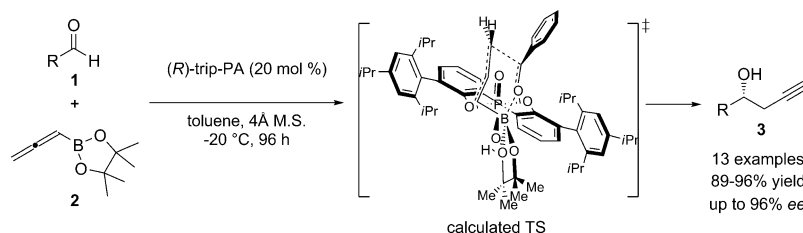
Burn, baby, burn! A new bifunctional catalyst (Ga/ZSM-5) displays increased selectivity for the production of aromatic compounds during the catalytic fast pyrolysis of biomass. With this Ga-promoted ZSM-5 catalyst, olefins such as ethylene and propylene, which are produced as intermediates, are more efficiently converted into aromatic compounds, especially benzene. Ga/ZSM-5 also promotes decarbonylation and olefin-aromatization reactions.

Asymmetric Propargylation

P. Jain, H. Wang, K. N. Houk,*
J. C. Antilla* 1391–1394



Brønsted Acid Catalyzed Asymmetric Propargylation of Aldehydes



Which gets activated? A versatile and highly enantioselective chiral Brønsted acid catalyzed method for the propargylation of aldehydes is described to provide a range of chiral homopropargylic alco-

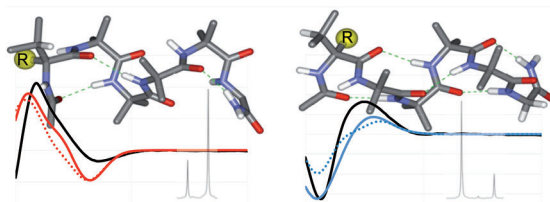
hols. Computational studies support the belief that the chiral phosphoric acid activates the allenyl boronic acid pinacol ester reagent rather than the aldehyde.

Helical Peptides

R. A. Brown, T. Marcelli, M. De Poli,
J. Solà, J. Clayden* 1395–1399

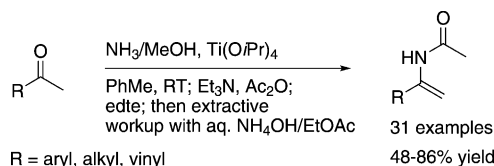


Induction of Unexpected Left-Handed Helicity by an N-Terminal L-Amino Acid in an Otherwise Achiral Peptide Chain



Peptide helices containing L-amino acids are typically right-handed. Exceptions are peptide helices containing the achiral amino acids 2-aminoisobutyric acid and glycine with a single chiral amino acid at the N terminus. These helices are left-

handed when the N-terminal residue is a common tertiary proteinogenic amino acid, such as L-valine (see picture, left), but right-handed when the N-terminal residue is the quaternary amino acid L- α -methylvaline (right).



- 1 step
- no redox
- safe reagents (no NH_2OH , no oxime)
- room temperature
- simple extractive workup
- edte renders Ti alkoxide water soluble

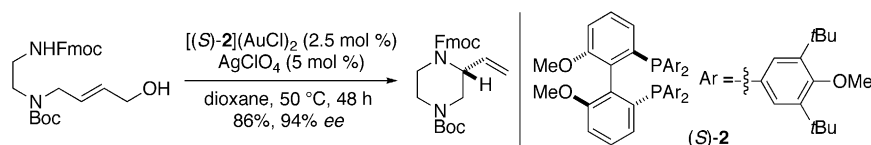
A one-step conversion of ketones into *N*-acetyl enamides was developed. The process employs safe and inexpensive reagents, proceeds under mild conditions, and tolerates diverse functional

groups. The addition of edte (*N,N,N',N'*-tetrakis(2-hydroxyethyl)ethylenediamine) prior to workup enables water solubilization of Ti alkoxides and allows a simple extractive workup.

Enamide Synthesis

J. T. Reeves,* Z. Tan, Z. S. Han, G. Li, Y. Zhang, Y. Xu, D. C. Reeves, N. C. Gonnella, S. Ma, H. Lee, B. Z. Lu, C. H. Senanayake — 1400–1404

Direct Titanium-Mediated Conversion of Ketones into Enamides with Ammonia and Acetic Anhydride



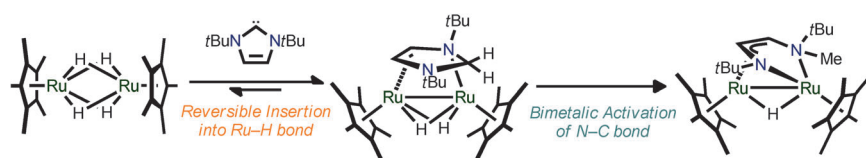
Aliphatic nitrogen heterocycles—either five- or six-membered—are formed in high yield and with up to 94% ee when a

1:2 mixture of [(*S*)-2](AuCl)₂ and AgClO₄ is used as the catalyst for the title reaction.

Allylic Amination

P. Mukherjee, R. A. Widenhoefer* — 1405–1407

Gold(I)-Catalyzed Enantioselective Intramolecular Dehydrative Amination of Allylic Alcohols with Carbamates



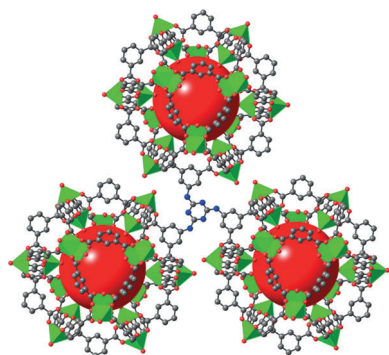
Reversible insertion of NHC: 1,3-Di-*tert*-butylimidazol-2-ylidene was inserted into a ruthenium-hydride bond of [Cp*₂Ru(μ-H)₂Ru(Cp*)₂] to form a 4-imidazoline complex that underwent a dynamic process, namely 1,3-migratory pendulum motion

of the 4-imidazoline ligand (see scheme). Bimetallic-system-assisted N-C bond cleavage of the imidazoline ligand proceeded to generate a pseudo-diazaruthenacycle.

NHC Ligands

A. Kaiho, H. Suzuki* — 1408–1411

Reversible Insertion of 1,3-Di-*tert*-butylimidazol-2-ylidene into a Ru-H Bond and Bimetallic Activation of a N-C Bond of Imidazoline



Open and friendly: The smallest member of the *rht*-type metal-organic frameworks (MOFs, see picture) constructed by a hexacarboxylate ligand with a nitrogen-rich imino triazine backbone shows a significantly enhanced gas binding affinity relative to all other isorecticular *rht*-type MOFs. The high adsorption capacity and remarkable selectivity of CO₂ are attributed to the high density of open metal and Lewis basic sites in the framework.

Metal-Organic Frameworks

B. Li, Z. Zhang, Y. Li, K. Yao, Y. Zhu, Z. Deng, F. Yang, X. Zhou, G. Li, H. Wu, N. Nijem, Y. J. Chabal, Z. Lai, Y. Han, Z. Shi,* S. Feng, J. Li* — 1412–1415

Enhanced Binding Affinity, Remarkable Selectivity, and High Capacity of CO₂ by Dual Functionalization of a *rht*-Type Metal-Organic Framework

Stability of DNA

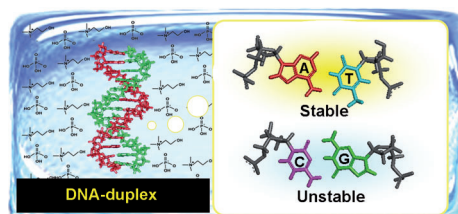
H. Tateishi-Karimata,
N. Sugimoto* — 1416–1419



A–T Base Pairs are More Stable Than G–C
Base Pairs in a Hydrated Ionic Liquid



Back Cover



A green solvent: Quantitative thermodynamic analyses shows that A–T base pairs are more stable than G–C base pairs in the hydrated ionic-liquid choline dihydrogen-

phosphate because of specific interactions between DNA bases and choline ions.

Microcapsules

T. S. Shim, S.-H. Kim, C.-J. Heo,
H. C. Jeon, S.-M. Yang* — 1420–1423

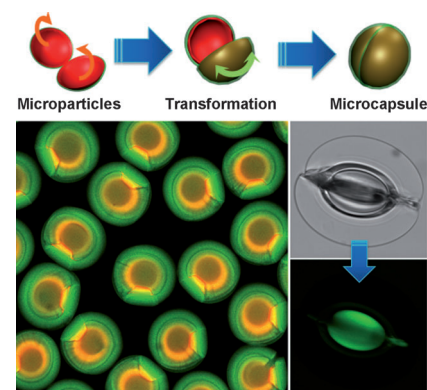


Controlled Origami Folding of Hydrogel
Bilayers with Sustained Reversibility for
Robust Microcarriers



Inside Back Cover

Soft origami structures: Planar bilayer microparticles consisting of active and passive layers show a structural transformation to microcapsules because of an anisotropic volume expansion (see picture). The soft hydrogel materials used for both layers facilitate the reversible transformation and complete closure of the compartment, which enables in situ encapsulation and triggered release of micro- to nanoscopic active ingredients.

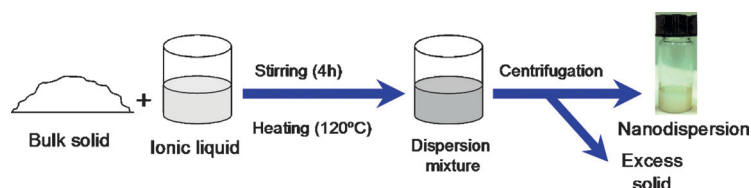


Nanoparticles

B. Rodríguez-Cabo, E. Rodil,
H. Rodríguez, A. Soto,
A. Arce* — 1424–1427



Direct Preparation of Sulfide
Semiconductor Nanoparticles from the
Corresponding Bulk Powders in an Ionic
Liquid



Just add liquid and stir: Dispersions of metal sulfide nanoparticles (CdS, ZnS, PbS, and MnS) can be prepared directly by mixing the corresponding bulk solid with an appropriate ionic liquid, without fur-

ther additives or solvents (see scheme). The selection of the ionic liquid is critical for the viability of this nanoparticle preparation method.

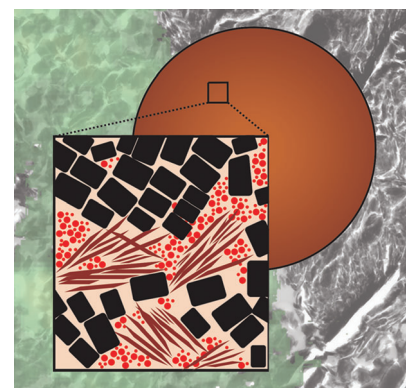
Fluid Catalytic Cracking

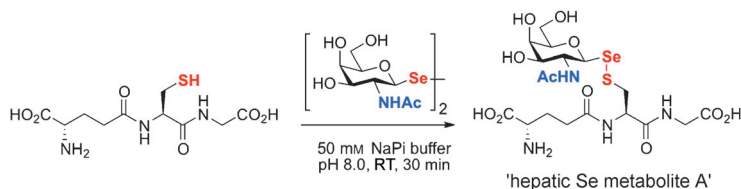
M. A. Karreman, I. L. C. Buurmans,
J. W. Geus, A. V. Agronskaia,
J. Ruiz-Martínez, H. C. Gerritsen,
B. M. Weckhuysen* — 1428–1431



Integrated Laser and Electron Microscopy
Correlates Structure of Fluid Catalytic
Cracking Particles to Brønsted Acidity

Cracking the crackers: Integrated laser and electron microscopy was applied to study individual fluid catalytic cracking catalyst particles (see picture) deactivated according to an industrially relevant protocol. New insights have been obtained by correlating Brønsted acidity changes, visualized using fluorescence microscopy, with structural transformations in the zeolite and matrix components, as observed with electron microscopy.





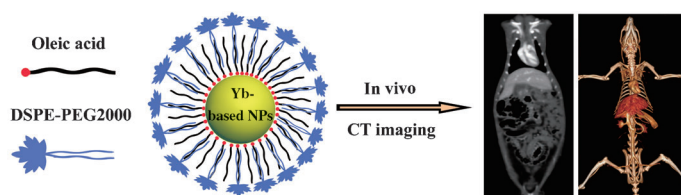
Introducing selenium: The synthesis and full characterization of human hepatic Se metabolite A has been accomplished by using a robust, efficient, and Cys-specific selenenylation protocol (see scheme;

NaPi = sodium phosphate). The selenenylsulfide linkage is sufficiently stable to allow quantification of Se-containing glycoconjugates in biological fluids by using atomic detection methods.

Metabolites

O. Boutureira, G. J. L. Bernardes, M. Fernández-González, D. C. Anthony, B. G. Davis* — 1432 – 1436

Selenenylsulfide-Linked Homogeneous Glycopeptides and Glycoproteins: Synthesis of Human "Hepatic Se Metabolite A"



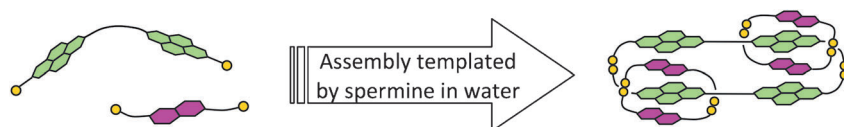
Enlightening particles: A contrast agent for in vivo X-ray computed tomography (CT) imaging is composed of an Yb-based nanoparticle (NP) that is stabilized with oleic acid and modified with the biocom-

patible polymer DSPE-PEG 2000 (see picture). The contrast agent exhibits long circulation time in vivo and low toxicity and is also much more effective than a clinical iodinated agent.

Imaging Agents

Y. L. Liu, K. L. Ai, J. H. Liu, Q. H. Yuan, Y. Y. He, L. H. Lu* — 1437 – 1442

A High-Performance Ytterbium-Based Nanoparticulate Contrast Agent for In Vivo X-Ray Computed Tomography Imaging



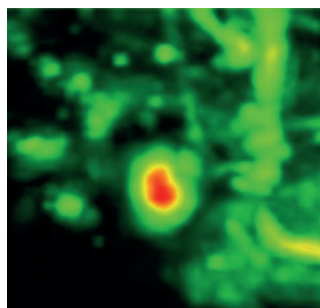
Three rings: The self-assembly of a water-soluble [3]catenane from a library composed of two linear building blocks, both terminated by cysteine components, is promoted either by a high salt concentration or by the presence of spermine.

The spermine-templated synthesis of the [3]catenane shows that such structures can exhibit strong binding interactions with a biologically relevant target in water under near-physiological conditions.

Catenanes

F. B. L. Cougnon, N. A. Jenkins, G. D. Pantoş,* J. K. M. Sanders* — 1443 – 1447

Templated Dynamic Synthesis of a [3]Catenane



Skin-deep: The combination of a near-infrared fluorescent protein (iRFP) and deep-tissue photoacoustic tomography clearly demonstrates the superiority of iRFP over other genetically encoded probes. Impressive resolution (280 μ m lateral and 75 μ m axial) was obtained at a depth of 4 mm in a live animal, and volumetric images of a tumor were produced (see image), thus allowing the spatially resolved monitoring of its development.

Imaging Agents

G. S. Filonov, A. Krumholz, J. Xia, J. Yao, L. V. Wang,* V. V. Verkhusha* — 1448 – 1451

Deep-Tissue Photoacoustic Tomography of a Genetically Encoded Near-Infrared Fluorescent Probe

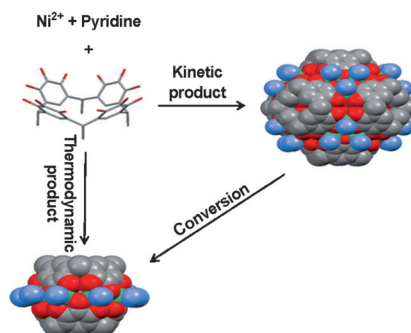


Molecular Capsules

H. Kumari, A. V. Mossine, S. R. Kline,
C. L. Dennis, D. A. Fowler, S. J. Teat,
C. L. Barnes, C. A. Deakyne,*
J. L. Atwood* ————— 1452 – 1454



Controlling the Self-Assembly of Metal-Seamed Organic Nanocapsules



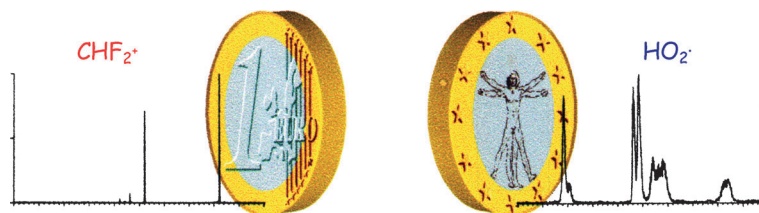
Thermodynamic versus kinetic control:

Small-angle neutron scattering (SANS) and single-crystal X-ray diffraction data have been used to elucidate the effect of temperature, solvent, and metal identity on the formation of dimeric or hexameric metal-seamed pyrogallol[4]arene capsules. Higher temperatures, methanol solution, and the use of nickel metal favor dimer formation (see scheme).

C–H Activation

G. de Petris,* G. Angelini, O. Ursini,
M. Rosi, A. Troiani ————— 1455 – 1458

Linking Ion and Neutral Chemistry in C–H Bond Electrophilic Activation: Generation and Detection of HO₂[•] Reactive Radicals in the Gas Phase



The flip side: Both the charged and uncharged products formed by C–H bond electrophilic activation have been experimentally detected in the gas phase. The

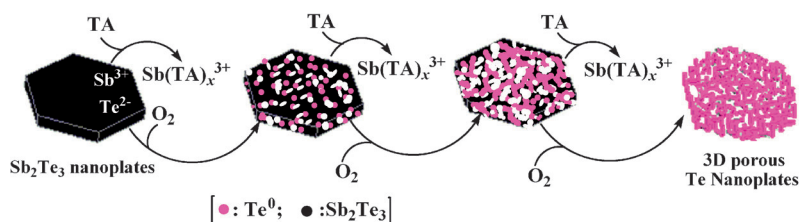
HO₂[•] radical is formed by a process involving the prototypical oxygen-centered radical cation O₂^{•+} and the methane derivative CH₂F₂.

Mesoporous Materials

H. Zhang, H. Wang, Y. Xu, S. Zhuo, Y. Yu,
B. Zhang* ————— 1459 – 1463



Conversion of Sb₂Te₃ Hexagonal Nanoplates into Three-Dimensional Porous Single-Crystal-Like Network-Structured Te Plates Using Oxygen and Tartaric Acid



Pore genius: Sb₂Te₃ hexagonal nanoplates can be transformed into 3D porous network-structured Te plates by the dissolution of Sb³⁺ ions induced by tartaric acid (TA), the O₂-assisted oxidation of Te²⁻ ions to Te⁰, and a subsequent Ostwald

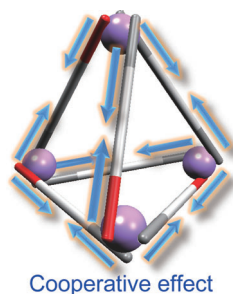
ripening process (see picture). These Te plates can be adopted as templates for the synthesis of 3D porous nanowire-based (or nanotube-based) metal and metal telluride nanoplates.

Stereochemistry

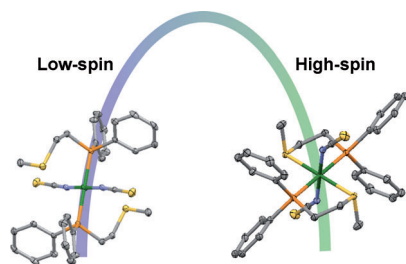
N. Ousaka, J. K. Clegg,
J. R. Nitschke* ————— 1464 – 1468



Nonlinear Enhancement of Chiroptical Response through Subcomponent Substitution in M₄L₆ Cages



One for all, all for one: A self-assembled M₄L₆ cage, incorporating small amounts of enantiopure subcomponents at the peripheries, forms predominantly with a one-handed twist at all metal centers. Strong stereochemical coupling between metal centers in the cage amplifies energy differences between the ΔΔΔΔ and ΛΛΛΛ diastereomers as compared to analogous mononuclear metal complexes (see picture; red and gray bars denote chiral and achiral subcomponents, respectively).



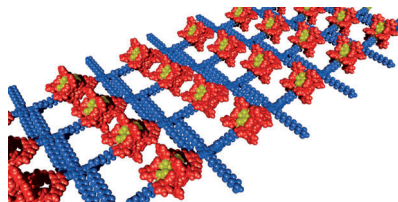
Freeze-frame: Octahedral and square-planar structural isomers, representing the two “end states” in a hemilabile ligand bond-breaking isomerization reaction, have been characterized in solution by spectroscopic methods and in the solid state by X-ray crystallography (see picture: Ni green, C gray, P orange, N blue, S yellow).

Coordination Chemistry

C. W. Machan, A. M. Lifschitz, C. L. Stern, A. A. Sarjeant, C. A. Mirkin* **1469–1472**

Crystallographic Snapshots of the Bond-Breaking Isomerization Reactions Involving Nickel(II) Complexes with Hemilabile Ligands

Networking: A bisporphyrin compound possessing an electron-deficient guest moiety assembles in a head-to-tail manner to form polymeric aggregates. Diffusion-ordered NMR spectroscopy and viscosity measurements of the aggregates confirmed the formation of sizable supramolecular polymers. Widely spread nanonetworks (see picture) are formed in solid state.

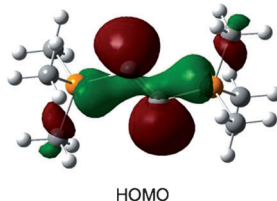
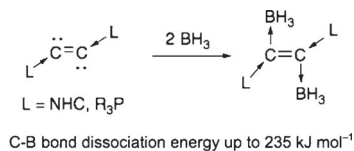


Supramolecular Polymers

T. Haino,* A. Watanabe, T. Hirao, T. Ikeda **1473–1476**

Supramolecular Polymerization Triggered by Molecular Recognition between Bisporphyrin and Trinitrofluorenone

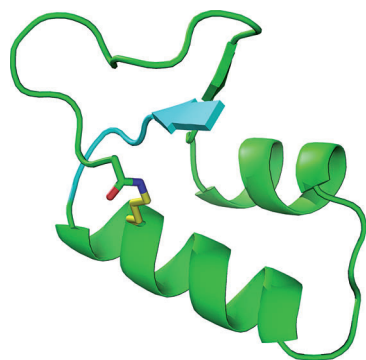
New C-based ligands? Inspired by recent work on main group allotropes, a theoretical examination of Lewis base (NHC, phosphine) stabilized dicarbon has been carried out. The results indicate that the phosphine and NHC adducts of C_2 have significantly different electronic structures and that both types of molecules should be powerful, bifunctional carbon-based ligands.



Dicarbon

J. L. Dutton,* D. J. D. Wilson* **1477–1480**

Lewis Base Stabilized Dicarbon: Predictions from Theory



Lassoed at the other end: Original synthetic and structure determination methods were used to make a protein molecule with an unprecedented linear-loop polypeptide chain topology, and to characterize its X-ray structure.

Protein Topology

K. Mandal, B. L. Pentelute, D. Bang, Z. P. Gates, V. Y. Torbeev, S. B. H. Kent* **1481–1486**

Design, Total Chemical Synthesis, and X-Ray Structure of a Protein Having a Novel Linear-Loop Polypeptide Chain Topology



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Antagonistic Functions for One-Pot
Tandem Reactions

N. R. Shiju,* A. H. Alberts,
S. Khalid, D. R. Brown,
G. Rothenberg* _____ 9615–9619

Angew. Chem. Int. Ed. **2011**, 50

DOI: 10.1002/anie.201101449

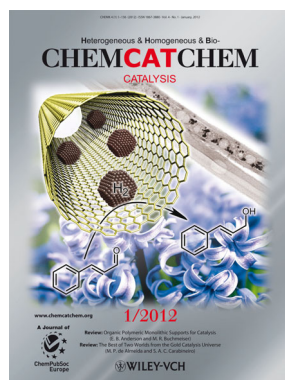
In this Communication, extra citations are added to reference [4] as follows:

[4] x) A. Kuschel, M. Drescher, T. Kuschel, S. Polarz, *Chem. Mater.* **2010**, 22, 1472; y) S. Shylesh, A. Wagener, A. Seifert, S. Ernst, W. R. Thiel, *Angew. Chem.* **2010**, 122, 188; *Angew. Chem. Int. Ed.* **2010**, 49, 184.

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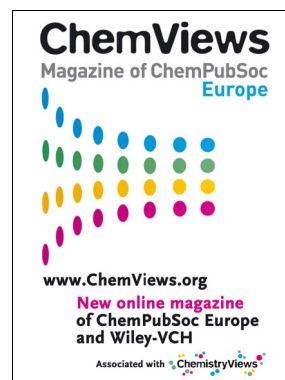
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