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:

*B. Merner, L. Dawe, G. Bodwell**
1,1,8,8-Tetramethyl[8](2,11)teropyrenophane: Half of an Aromatic Belt and a Segment of an (8,8) Single-Walled Carbon Nanotube

*B. Liu, H. Wang, H. Xie, B. Zeng, J. Chen, J. Tao, T. B. Wen, Z. Cao, H. Xia**
Osmapyridine and Osmapyridinium from a Formal [4+2] Cycloaddition Reaction

*J. Alonso-Gómez, P. Rivera-Fuentes, N. Harada, N. Berova, F. Diederich**
An Enantiomerically Pure Alleno-Acetylenic Macrocycle: Synthesis and Rationalization of Its Outstanding Chiroptical Response

*P. García-García, M. Fernández-Rodríguez, E. Aguilar**
Gold-Catalyzed Cycloaromatization of 2,4-Dien-6-yne Carboxylic Acids: Synthesis of 2,3-Disubstituted Phenols and Unsymmetrical Bi- and Terphenyls

*H. Jiang, P. Elsner, K. L. Jensen, A. Falcicchio, V. Marcos, K. A. Jørgensen**
Achieving Molecular Complexity by Organocatalytic One-Pot Strategies: A Fast Entry for the DeNovo Synthesis of Sphingoids, Amino Sugars, and Polyhydroxylated α-Amino Acids

*T. Kucharski, Z. Huang, Q.-Z. Yang, Y. Tian, N. Rubin, C. Concepcion, R. Boulatov**
Kinetics of Thiol/Disulfide Exchange Correlates Weakly with the Restoring Force in the Disulfide Moiety

Author Profile

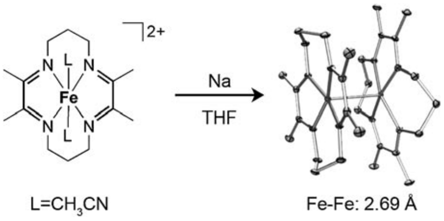
"The biggest challenge facing scientists is finding technology for green energy. If I could have dinner with three famous scientists from history, they would be Bohr, Einstein, and Heisenberg. …"
This and more about Joost N. H. Reek can be found on page 5074.

Books

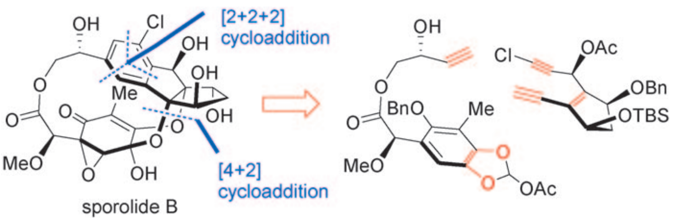
Highlights

Metal–Metal Interactions

Full metal bonding: The reduction of a six-coordinate, mononuclear Werner-type iron(II) complex (see scheme) resulted in the isolation of a compound with an extraordinarily rare, unsupported Fe–Fe bond having an experimental Fe–Fe distance of 2.6869(6) Å and a calculated bond order of 0.5.



Natural Products

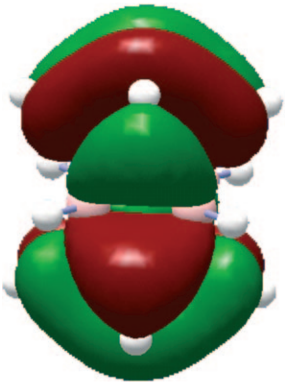


Closing rings: A recent total synthesis of sporolide B by the Nicolaou group is highlighted by two advantageous cycloadditions. Firstly, a regioselective [2+2+2] cycloaddition of highly elaborate substrates assembles the halogenated aromatic ring and subsequently an *ortho*-quinone [4+2] cyclization closes stereoselectively the dioxane-containing macrocycle. These approaches should be considered in complex target syntheses.

Minireviews

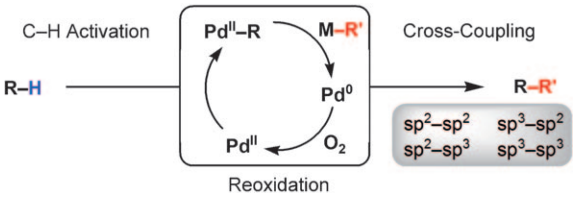
Boron Radicals

To "B" or not to "B": The unusual bonding of boron in organoboranes or oligoboron clusters is not only apparent in diamagnetic molecules but also in paramagnetic systems, including mixed-valent species and oligoborane/carborane cluster radicals. The picture shows the singly occupied molecular orbital of the radical ion $[C_4B_8R_4H_8]^{\bullet-}$, determined by DFT calculations.



Reviews

Synthetic Methods



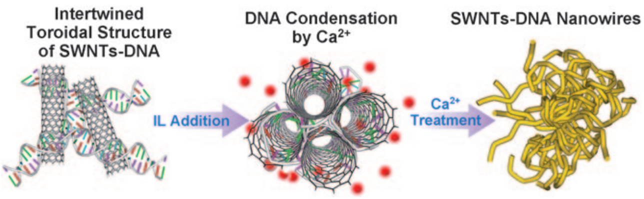
Pick your Pd partners: A number of catalytic systems have been developed for palladium-catalyzed C–H activation/C–C bond formation. Recent studies concerning the palladium(II)-catalyzed coupling of C–H bonds with organometallic reagents through a Pd^{II}/Pd^0 catalytic cycle are discussed (see scheme), and the versatility and practicality of this new mode of catalysis are presented. Unaddressed questions and the potential for development in the field are also addressed.

For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Wiley-VCH, 111 River Street, Hoboken, NJ 07030. Annual subscription price for institutions: US$ 7225/6568 (valid for print and electronic / print or electronic delivery); for 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.

Nanofiber Networks

C. K. Lee, S. R. Shin, J. Y. Mun, S.-S. Han, I. So, J.-H. Jeon, T. M. Kang, S. I. Kim, P. G. Whitten, G. G. Wallace, G. M. Spinks,* S. J. Kim* **5116 – 5120**

Tough Supersoft Sponge Fibers with Tunable Stiffness from a DNA Self-Assembly Technique

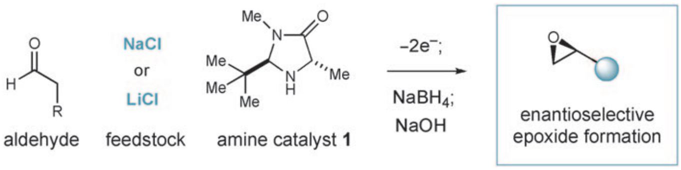


Tough and soft: Highly porous, spongelike materials self-assemble by calcium ion condensation of DNA-wrapped carbon nanotubes (SWNTs–DNA; see picture, IL = ionic liquid). The toughness, modulus, and swellability of the electrically conductive sponges can be tuned by controlling the density and strength of interfiber junctions. The sponges have compliances similar to the softest natural tissue, while robust interfiber junctions give high toughness.

Organocatalysis

M. Amatore, T. D. Beeson, S. P. Brown, D. W. C. MacMillan* **5121 – 5124**

Enantioselective Linchpin Catalysis by SOMO Catalysis: An Approach to the Asymmetric α-Chlorination of Aldehydes and Terminal Epoxide Formation

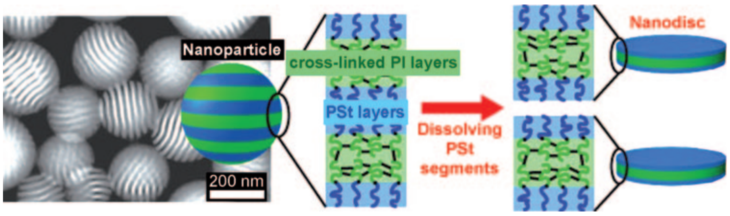


Time for SOme MOre: For the first time SOMO (singly occupied molecular orbital) activation has been exploited to allow a new approach to the α-chlorination of aldehydes. This transformation can be readily implemented as part of a linchpin catalysis approach to the enantioselective production of terminal epoxides.

Polymer Nanostructures

T. Higuchi,* A. Tajima, K. Motoyoshi, H. Yabu,* M. Shimomura **5125 – 5128**

Suprapolymer Structures from Nanostructured Polymer Particles



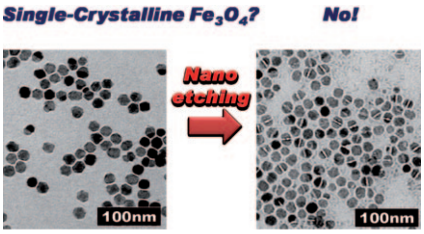
Divide and conquer: Polymer nanoparticles with phase-separation structures prepared with block copolymers and homopolymer blends were used to fabricate unique suprapolymer structures by cross-linking one polymer moiety and dissolving the other (see scheme; PI = polyisoprene, PSt = polystyrene).

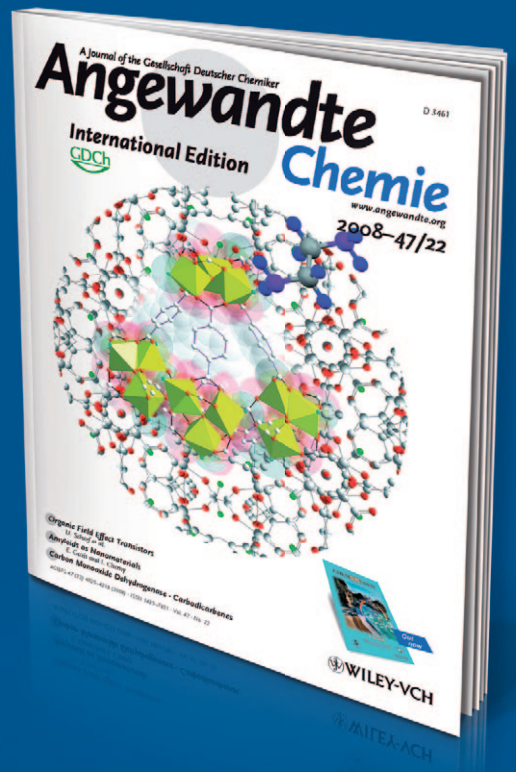
Nanoparticle Crystallinity

H. Kim, M. Lee, Y. Kim, J. Huh, H. Kim, M. Kim, T. Kim, V. N. Phan, Y.-B. Lee, G.-R. Yi, S. Haam, K. Lee* **5129 – 5133**

Quantitative Assessment of Nanoparticle Single Crystallinity: Palladium-Catalyzed Splitting of Polycrystalline Metal Oxide Nanoparticles

Crystal gazing: A simple Pd-catalyzed site-specific nanoetching method was developed to visualize the polycrystalline nature of Fe_3O_4 (see picture), Fe_2O_3, $MnFe_2O_4$, $CoFe_2O_4$, and MnO nanoparticle systems. The technique relies on the very fast etching speed of the grain interface within bi- or polycrystalline nanocrystals.




A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
International Edition
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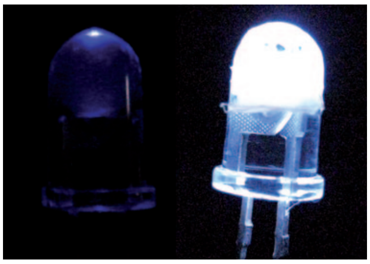
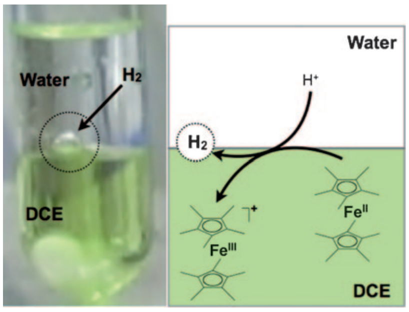
2008–47/22
WILEY-VCH

DNA Nanofibers



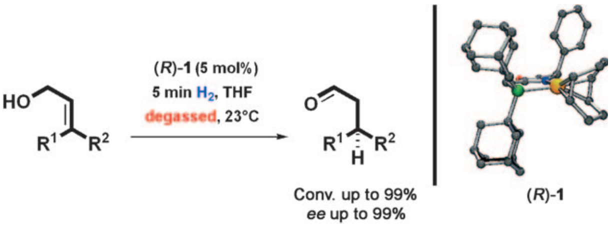
A DNA spin-off: Electrospinning of DNA complexes gives nanofibers with a highly ordered morphology that allows homogeneous distribution of encapsulated multiple chromophores. The emission color can be controlled by suitable choice of the donor–acceptor pair and the doping ratio. Pure white-light emission from nanofibers is demonstrated (see picture).

Hydrogen Evolution



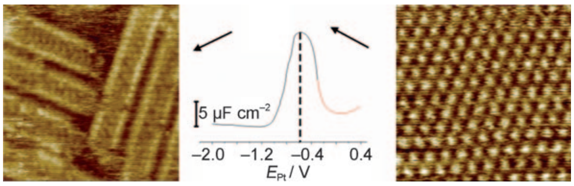
Blowing bubbles: Hydrogen evolution by proton reduction with $[(C_5Me_5)_2Fe]$ occurs at a soft interface between water and 1,2-dichloroethane (DCE). The reaction proceeds by proton transfer assisted by $[(C_5Me_5)_2Fe]$ across the water–DCE interface with subsequent proton reduction in DCE. The interface essentially acts as a proton pump, allowing hydrogen evolution by directly using the aqueous proton.

Asymmetric Catalysis



Nothing to sm(Ir)k at: Under appropriate reaction conditions, iridium hydride catalysts promote the isomerization of primary allylic alcohols. The best catalysts, like (*R*)-**1** (P green, O red, N blue, Ir yellow), deliver the desired chiral aldehydes with excellent enantioselectivity and good yields. Mechanistic hypotheses have been developed on the basis of preliminary investigations.

Ionic Liquids



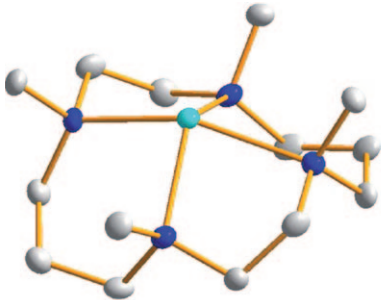
Ring any bells? The differential capacitance curve of Au(100) in neat $[BMI]BF_4$ (BMI = 1-butyl-3-methylimidazolium) ionic liquid has a bell-shaped feature (see picture). The adsorption of BMI^+ shows a disorder–order transition and depends on the structure of the surface. Ordered adsorption in a micelle-like structure stabilizes the underlying Au surface.

Germanium Cations (1)

F. Cheng, A. L. Hector, W. Levason,
G. Reid,* M. Webster,
W. Zhang ——— **5152 – 5154**

Germanium(II) Dications Stabilized by Azamacrocycles and Crown Ethers

A crown for germanium: Neutral aza- and oxamacrocycles enable stabilization of halide-free germanium(II) dications (see structure, Ge teal, N blue, C gray). The resulting structures show a marked dependence upon the denticity, donor type, and ring size of the macrocycle.

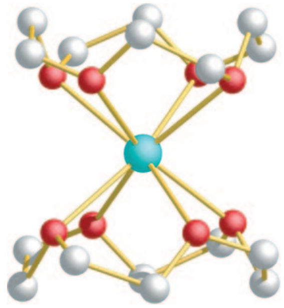


Germanium Cations (2)

P. A. Rupar, R. Bandyopadhyay,
B. F. T. Cooper, M. R. Stinchcombe,
P. J. Ragogna, C. L. B. Macdonald,*
K. M. Baines* ——— **5155 – 5158**

Cationic Crown Ether Complexes of Germanium(II)

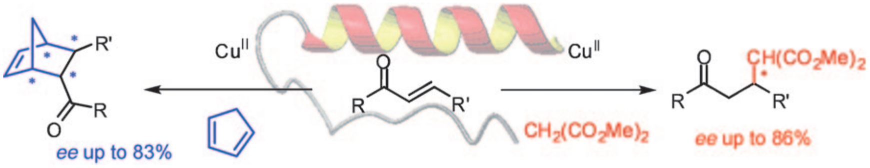
Fit for a king: Cationic complexes of Ge^{II} can be prepared by using crown ethers to stabilize and protect the germanium center. Three different crown ethers were employed: [12]crown-4 (see structure, Ge teal, O red, C gray), [15]crown-5, and [18]crown-6. The structures of the cationic complexes depend on the cavity size of the crown ether and on the substituent on germanium.



Enzyme Design

D. Coquière, J. Bos, J. Beld,
G. Roelfes* ——— **5159 – 5162**

Enantioselective Artificial Metalloenzymes Based on a Bovine Pancreatic Polypeptide Scaffold



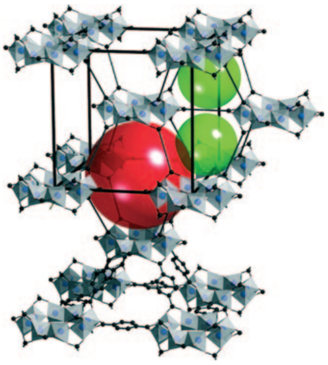
Site creation: Enantioselective artificial metalloenzymes have been created by grafting a new active site onto bovine pancreatic polypeptide through the introduction of an amino acid capable of coordinating a copper(II) ion. This hybrid catalyst gave good enantioselectivities in the Diels–Alder and Michael addition reactions in water (see scheme) and displayed a very high substrate selectivity.

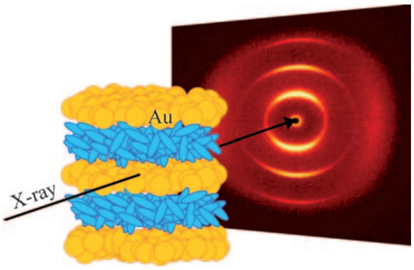
Metal–Organic Frameworks

T. Ahnfeldt, N. Guillou, D. Gunzelmann,
I. Margiolaki, T. Loiseau, G. Férey,
J. Senker, N. Stock* ——— **5163 – 5166**

$[Al_4(OH)_2(OCH_3)_4(H_2N\text{-}bdc)_3]\cdot x\,H_2O$: A 12-Connected Porous Metal–Organic Framework with an Unprecedented Aluminum-Containing Brick

Al together now! A new stable aluminum aminoterephthalate system contains octameric building blocks that are connected by organic linkers to form a 12-connected net (see picture). The structure adopts a cubic centered packing motive in which octameric units replace individual atoms, thus forming distorted octahedral (red sphere) and tetrahedral cages (green spheres) with effective accessible diameters of 1 and 0.45 nm, respectively.



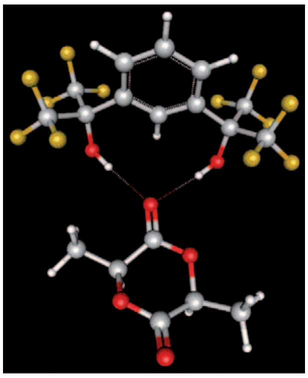


Spontaneous formation of smectic and columnar structures was observed when spherical gold nanoparticles were functionalized with mesogenic thiols (see layered structure and X-ray pattern of a sample in smectic phase). The particle ordering is stimulated by softening of the interparticle potential and flexibility for deformation of the grafting layer.

Nanomaterials

M. Wojcik, W. Lewandowski, J. Matraszek, J. Mieczkowski, J. Borysiuk, D. Pociecha,* E. Gorecka ———— **5167 – 5169**

Liquid-Crystalline Phases Made of Gold Nanoparticles



Recognize this! A hydrogen-bonding motif based on hexafluorinated alcohol derivatives (see picture; O red, F yellow) activates electrophilic substrates. The catalytic activity of the hydrogen-bonded systems was demonstrated for the ring-opening polymerization of a variety of strained heterocycles. Narrowly dispersed polymers with predictable molecular weights were obtained with end-group fidelity.

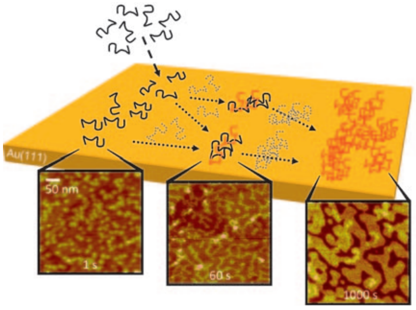
Organocatalysis

O. Coulembier, D. P. Sanders, A. Nelson, A. N. Hollenbeck, H. W. Horn, J. E. Rice, M. Fujiwara, P. Dubois, J. L. Hedrick* ———— **5170 – 5173**

Hydrogen-Bonding Catalysts Based on Fluorinated Alcohol Derivatives for Living Polymerization

---

Go for the gold! The structural evolution of peptide binding and assembly on a Au(111) surface is dynamic and involves surface diffusion and multiple stages of molecular thin-film topology development (see schematic depiction and corresponding AFM images). The new fundamental observations may form the basis of peptide-based novel hybrid molecular technologies of the future.



Peptide Adsorption and Assembly

C. R. So, C. Tamerler, M. Sarikaya* ———— **5174 – 5177**

Adsorption, Diffusion, and Self-Assembly of an Engineered Gold-Binding Peptide on Au(111) Investigated by Atomic Force Microscopy

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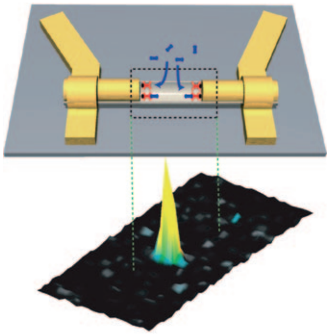


Click to fill the gap: The in situ modular fabrication of molecular transport junctions in nanogaps generated by on-wire lithography is achieved by using click chemistry (see picture). The formation of molecular junctions proceeds in high yields and can be used to test different molecules; the triazole group also maintains conjugation in the molecular wires. Raman spectroscopy is used to characterize the molecular assembly processes.

Molecular Electronics

X. Chen, A. B. Braunschweig, M. J. Wiester, S. Yeganeh, M. A. Ratner,* C. A. Mirkin* ———— **5178 – 5181**

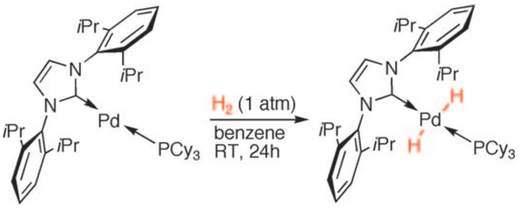
Spectroscopic Tracking of Molecular Transport Junctions Generated by Using Click Chemistry

Contents

Homogeneous Catalysis

S. Fantasia, J. D. Egbert, V. Jurčík,
C. S. J. Cazin, H. Jacobsen, L. Cavallo,
D. M. Heinekey,*
S. P. Nolan* ______________ **5182 – 5186**

Activation of Hydrogen by Palladium(0): Formation of the Mononuclear Dihydride Complex *trans*-[Pd(H)$_2$(IPr)(PCy$_3$)]

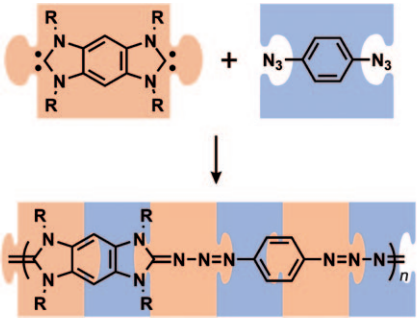


An even split: In sharp contrast with the general behavior of Pd^0 complexes, [Pd(IPr)(PCy$_3$)] is able to activate the H–H bond. The resulting *trans*-[Pd(H)$_2$(IPr)(PCy$_3$)] is the first isolated mononuclear dihydride palladium compound. Its formation is supported by multinuclear NMR spectroscopy, density functional calculations, and X-ray diffraction studies. The stability and reactivity of this new species are examined.

Polymers

D. J. Coady, D. M. Khramov,
B. C. Norris, A. G. Tennyson,
C. W. Bielawski* ___________ **5187 – 5190**

Adapting N-Heterocyclic Carbene/Azide Coupling Chemistry for Polymer Synthesis: Enabling Access to Aromatic Polytriazenes



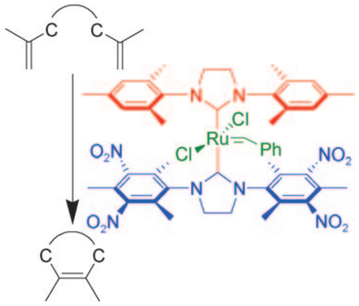
A click by any other name: Coupling bis(N-heterocyclic carbene)s with bis(azide)s afforded a novel class of conjugated polytriazenes. These polymers were rendered electrically conductive upon doping, and fluorene-containing variants exhibited luminescence. This adaptation of N-heterocyclic carbene (NHC)/azide coupling chemistry to polymer synthesis reveals the potential of NHCs as building blocks for accessing polymers having useful electronic properties.

Homogeneous Catalysis

T. Vorfalt, S. Leuthäußer,
H. Plenio* ________________ **5191 – 5194**

An [(NHC)(NHC$_{EWG}$)RuCl$_2$(CHPh)] Complex for the Efficient Formation of Sterically Hindered Olefins by Ring-Closing Metathesis

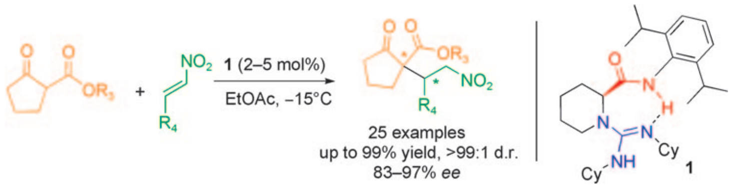
NHC with EWGs for RCM: Ruthenium complexes with two N-heterocyclic carbenes (NHCs), one of them substituted with electron-withdrawing groups (EWGs), are highly efficient (pre)catalysts for the synthesis of tetrasubstituted olefins and trisubstituted olefins by ring-closing metathesis reactions (RCM, see scheme).



Organocatalysis

Z. P. Yu, X. H. Liu, L. Zhou, L. L. Lin,
X. M. Feng* ______________ **5195 – 5198**

Bifunctional Guanidine via an Amino Amide Skeleton for Asymmetric Michael Reactions of β-Ketoesters with Nitroolefins: A Concise Synthesis of Bicyclic β-Amino Acids

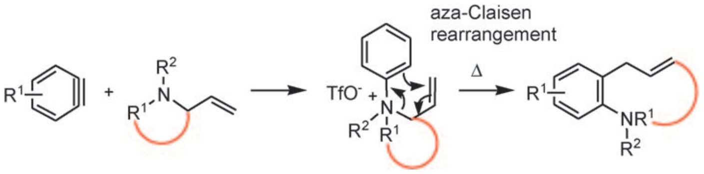


Two activations are better than one: The chiral bifunctional guanidine **1**, which features an amino amide backbone, catalyzes the asymmetric Michael addition of a range of substrates and gives products with excellent stereoselectivities. The method also allows the efficient synthesis of optically pure β-amino acid esters. Both the guanidine group and the NH proton of the amide were important for the dual activation.

Rearrangement

A. A. Cant, G. H. V. Bertrand, J. L. Henderson, L. Roberts, M. F. Greaney* ———— **5199 – 5202**

The Benzyne Aza-Claisen Reaction

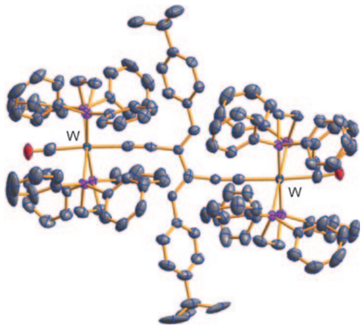


Adding an aryne to a tertiary allylamine affords *o*-allylaniline products of an aza-Claisen rearrangement. The aryne simultaneously provides the π component for the rearrangement and the quaternization event that lowers the activation energy for the sigmatropic shift. The reaction was applied to the synthesis of medium-ring benzannulated amines (see scheme).

Metallacumulenes

S. N. Semenov, O. Blacque, T. Fox, K. Venkatesan, H. Berke* ———— **5203 – 5206**

Self-Coupling of a 4-H-Butatrienylidene Tungsten Complex

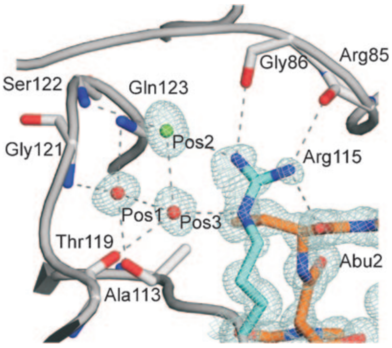


Tungsten tryst: A 4-H-butatrienylidene complex of tungsten was successfully isolated and structurally characterized. It undergoes a unique self-coupling, which leads to a dimer (see picture; P pink, O red) with a cross-conjugated π system and with electrochemically and magnetically active metal centers.

Structural Biology

C. M. Stegmann, D. Seeliger, G. M. Sheldrick, B. L. de Groot, M. C. Wahl* ———— **5207 – 5210**

The Thermodynamic Influence of Trapped Water Molecules on a Protein–Ligand Interaction

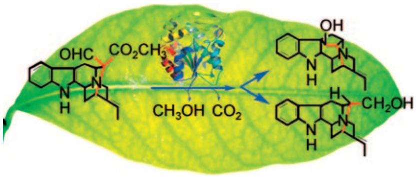


Water molecules doing time: Atomic-resolution crystal structures of the PPIase domain of cyclophilin G, alone and in complex with cyclosporin A, and together with MD simulations and calorimetry, reveal how trapped water molecules influence the thermodynamic profile of a protein–ligand interaction.

Indole Alkaloids

L. Yang, M. Hill, M. Wang, S. Panjikar, J. Stöckigt* ———— **5211 – 5213**

Structural Basis and Enzymatic Mechanism of the Biosynthesis of C_9- from C_{10}-Monoterpenoid Indole Alkaloids



Cutting carbons: The three-dimensional structure of polyneuridine aldehyde esterase (PNAE) gives insight into the enzymatic mechanism of the biosynthesis of C_9- from C_{10}-monoterpenoid indole alkaloids (see scheme). PNAE is a very substrate-specific serine esterase. It harbors the catalytic triad S87-D216-H244, and is a new member of the α/β-fold hydrolase superfamily. Its novel function leads to the diversification of alkaloid structures.

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