



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:

J. L. Stymiest, G. Dutheuil, A. Mahmood, V. K. Aggarwal*

Lithiated Carbamates: Chiral Carbenoids for Iterative Homologation of Boranes and Boronic Esters

M. Stępień, L. Latos-Grażyński,* N. Sprutta, P. Chwalisz, L. Szterenberga

Expanded Porphyrin with a Split Personality: A Hückel Möbius Aromaticity Switch

Z. Su, Y. Xu*

Hydration of a Chiral Molecule: The Gas-Phase Study of the Propylene Oxide–(Water)₂ Ternary Cluster

A. E. Vaughn, C. L. Barnes, P. B. Duval*

A *cis* Dioxido Uranyl Complex: Fluxional Carboxylate Activation from a Reversible Polymer

L. Shi, D. Lundberg, D. G. Musaev, F. M. Menger*

[12]Annulene Gemini Compounds: Structure and Self-Assembly

M. Taoufik,* E. Le Roux, J. Thivolle-Cazat, J.-M. Basset*

Discovery of a Catalytic Reaction of Direct Transformation of Ethylene to Propylene, Catalyzed by a Tungsten Hydride Supported on Alumina WH/Al₂O₃

Nils Wiberg (1934–2007)

The Investigation of Organic Reactions and their Mechanisms

Howard Maskill

From Alchemy to Chemistry in Picture and Story

Arthur Greenberg

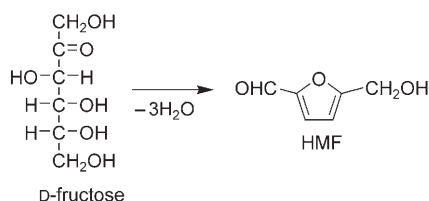
Obituary

H. Nöth, P. Paetzold _____ 5052

Books

reviewed by H. Mayr _____ 5053

reviewed by H. Hopf _____ 5054



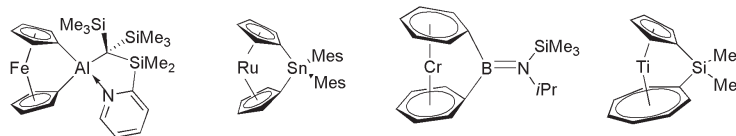
Sugar rush: The development of biorefinery technology and the use of renewable resources is gaining importance in the chemical industry. The emphasis of current research lies in the production of platform chemicals and synthesis gas (syngas) from biomass (lignocellulosic feedstock). Examples include the two-phase conversion reaction of fructose to 5-hydroxymethylfurfural (HMF; see scheme) as well as the production of syngas from glycerol using Pt-Al₂O₃.

Highlights

Biorefineries

B. Kamm* _____ 5056–5058

Production of Platform Chemicals and Synthesis Gas from Biomass



Tension you can cut without a knife: Over the past 40 years, metallocenophanes and related species have emerged as the first broad class of strained organometallic rings to be systematically developed and studied (for examples, see scheme;

Mes = 2,4,6-trimethylphenyl). This Review focuses on the synthesis, structures, and reactivities of these interesting species based on π -hydrocarbon ligands and transition-metal centers.

Reviews

Ansa Complexes

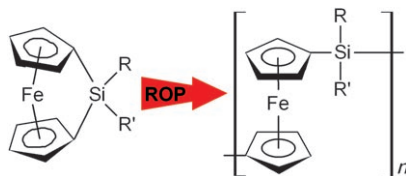
D. E. Herbert, U. F. J. Mayer, I. Manners* _____ 5060–5081

Strained Metallocenophanes and Related Organometallic Rings Containing π -Hydrocarbon Ligands and Transition-Metal Centers

Metallophenane Polymerization

V. Bellas, M. Rehahn* — 5082–5104

Polyferrocenylsilane-Based Polymer Systems

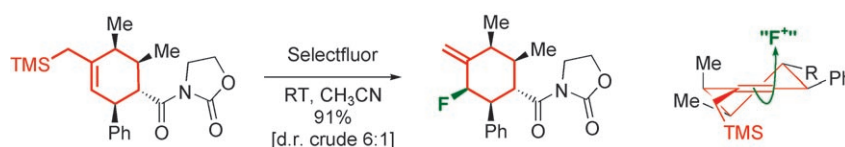


No longer in its infancy: Polyferrocenylsilane (PFS) chemistry already occupies a leading role in the field of organometallic polymers. Ring-opening polymerization (ROP) of strained ferrocenophanes (see scheme) has enabled access to a plethora of PFS-based materials with distinctive physical properties and functions. Self-assembly of PFS block copolymers and fabrication of nanostructures by various patterning techniques are also discussed.

Communications

Chiral Allylic Fluorides

Y.-h. Lam, C. Bobbio, I. R. Cooper,
V. Gouverneur* — 5106–5110



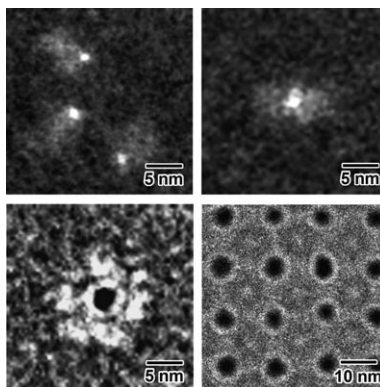
A “reverse” cycloaddition–fluorination strategy has been validated to access enantioenriched fluorinated compounds featuring up to five stereogenic centers, one of which is fluorinated. This highly

convergent process features a mild and high-yielding fluorination, for which the sense and level of stereocontrol have been probed.

Nanoparticle–Protein Assembly

M. Hu, L. Qian, R. P. Briñas, E. S. Lyman,
J. F. Hainfeld* — 5111–5114

Assembly of Nanoparticle–Protein Binding Complexes: From Monomers to Ordered Arrays



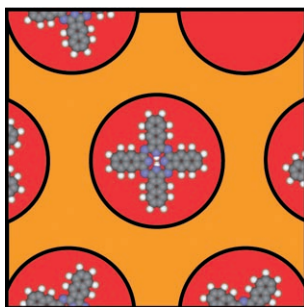
Tag it: Well-defined monomers, dimers, trimers, three-dimensional spherical shells, and two-dimensional ordered arrays of genetically engineered proteins were constructed by using functionalized gold nanoparticles. Nanoparticle size, functionality, and protein genetic motif contribute to the unique geometry, precise stoichiometry, given orientation, and high specificity of these nanoparticle–protein hybrid structures.

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\$ 5685/5168 (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.



A nanotemplate surface that functions as a regular array of traps for molecules such as naphthalocyanine (see picture) is provided by a nanomesh of hexagonal BN on Rh(111), which has now been identified as a single, complete monolayer. The 2-nm-sized pores form at regions where the layer binds strongly to the underlying metal, while the regular network of mesh wires corresponds to regions where the layer is not bonded to the substrate.

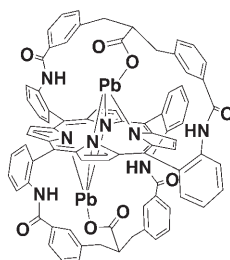
Nanostructures

S. Berner, M. Corso, R. Widmer, O. Groening, R. Laskowski, P. Blaha, K. Schwarz, A. Goriachko, H. Over, S. Gsell, M. Schreck, H. Sachdev, T. Greber, J. Osterwalder* **5115–5119**

Boron Nitride Nanomesh: Functionality from a Corrugated Monolayer



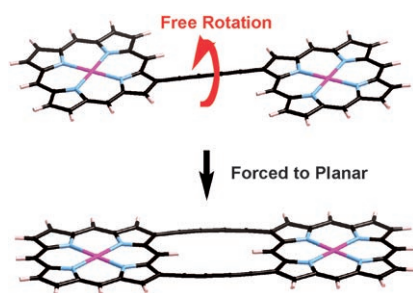
Strapped in: Insertion of Pb^{II} into a porphyrin bearing 5,15 straps with a pendant carboxylate group led to the first homobimetallic porphyrin complex of a divalent metal ion, which belongs to class III/type M in Buchler's classification of metalloporphyrins (see picture). Since the ligand also readily coordinates the isoelectronic Bi^{III} ion, it is of potential interest as a chelator for $^{212}\text{Pb}/^{212}\text{Bi}$ isotope generators.



Metalloporphyrins

Z. Halime, M. Lachkar, T. Roisnel, E. Furet, J.-F. Halet, B. Boitrel* **5120–5124**

Bismuth and Lead Hanging-Carboxylate Porphyrins: An Unexpected Homobimetallic Lead(II) Complex



Plane and simple! Doubly β -to- β 1,3-butadiyne-bridged diporphyrins have been synthesized efficiently through metal-catalyzed reactions. The double bridges enforce the two porphyrins in a perfectly planar conformation (see picture), which leads to almost a 100% increase in the two-photon absorption cross section.

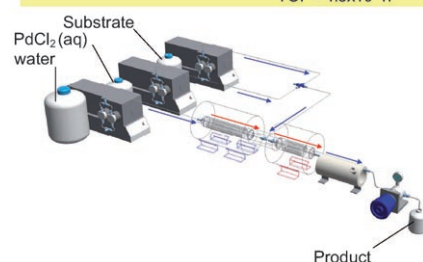
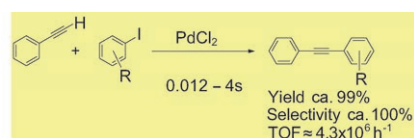
Diporphyrins

I. Hisaki, S. Hiroto, K. S. Kim, S. B. Noh, D. Kim,* H. Shinokubo,* A. Osuka* **5125–5128**

Synthesis of Doubly β -to- β 1,3-Butadiyne-Bridged Diporphyrins: Enforced Planar Structures and Large Two-Photon Absorption Cross Sections



All in a whirl: A reaction system based on “step-by-step rapid mixing and heating” with high-pressure, high-temperature water has been applied to an extremely efficient Sonogashira coupling (see picture). No organic solvents or ligands for the Pd catalyst were required. $\text{R} = \text{Me}, \text{OMe}, \text{NH}_2, \text{OH}, \text{CF}_3$.



Catalysis in Water

H. Kawanami,* K. Matsushima, M. Sato, Y. Ikushima* **5129–5132**

Rapid and Highly Selective Copper-Free Sonogashira Coupling in High-Pressure, High-Temperature Water in a Microfluidic System



Incredibly reader-friendly!



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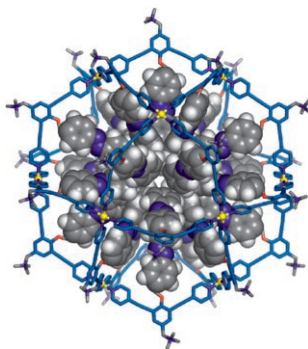
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Synergy effect: A discrete highly cationic spherical $\text{Pd}_{12}\text{L}_{24}$ complex was prepared that concentrates 24 photoresponsive azobenzene units internally (see picture; shell blue, N dark blue, Pd yellow, O red, C gray, H white; azobenzene units shown as CPK models). The concentrated azobenzenes provide a hydrophobic environment in the sphere, and the degree of hydrophobicity is reversibly changed by the isomerization of the azobenzenes.



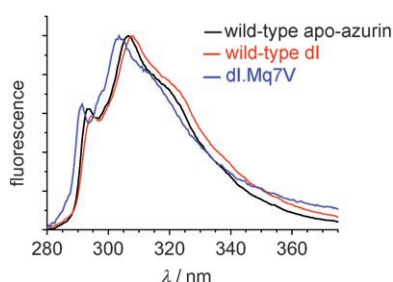
Molecular Nanoparticles

T. Murase, S. Sato,
M. Fujita* _____ 5133–5136

Switching the Interior Hydrophobicity of a Self-Assembled Spherical Complex through the Photoisomerization of Confined Azobenzene Chromophores



Kind of blue: Tryptophan residues embedded in rigid and hydrophobic protein matrices, like azurin and domain 1 of a transhydrogenase (dl), yield blue-shifted emission spectra with vibrational fine structure. These features are typical for emission from the $^1\text{L}_b$ state of indole, and not the $^1\text{L}_a$ state. Nevertheless, these proteins are found to emit from $^1\text{L}_a$, except for a mutant of domain 1 (dl.M97V), which features the most blue-shifted protein emission ever reported.



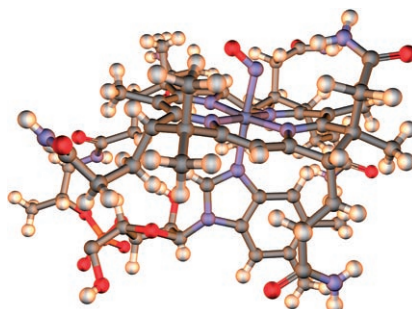
Tryptophan Fluorescence

J. Broos,* K. Tveen-Jensen, E. de Waal,
B. H. Hesp, J. B. Jackson,* G. W. Canters,
P. R. Callis _____ 5137–5139

The Emitting State of Tryptophan in Proteins with Highly Blue-Shifted Fluorescence



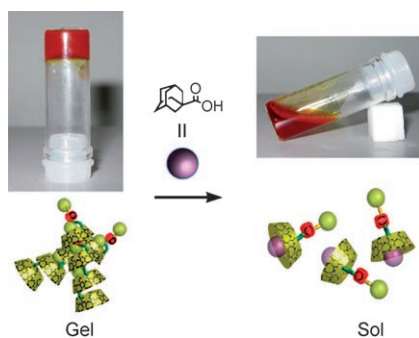
Mystery solved: The long-elusive crystal structure of nitrosylcobalamin (NOCbl) reveals that the Co–N–O angle is $117.4\text{--}121.4^\circ$; hence, NOCbl is best described as nitroxylcob(III)alamin in the solid state (see picture: Co purple, N blue, O red, P orange, C gray, H white). The length of the Co–N bond *trans* to the NO ligand is typical of those seen when strong β -axial ligands are positioned *trans* to the 5,6-dimethylbenzimidazole group.



Cobalamins

L. Hannibal, C. A. Smith, D. W. Jacobsen,
N. E. Brasch* _____ 5140–5143

Nitroxylcob(III)alamin: Synthesis and X-ray Structural Characterization



No backbone required: A supramolecular hydrogel has been synthesized from a guest-modified cyclodextrin (CD) without a polymer backbone. The β -CD forms supramolecular fibrils through host–guest interactions, and then hydrogen bonds between the CDs cross-link the fibrils to give a hydrogel. Gel-to-sol transitions can be effected by adding a competitive guest or a denaturing reagent (see example).

Supramolecular Chemistry

W. Deng, H. Yamaguchi, Y. Takashima,
A. Harada* _____ 5144–5147

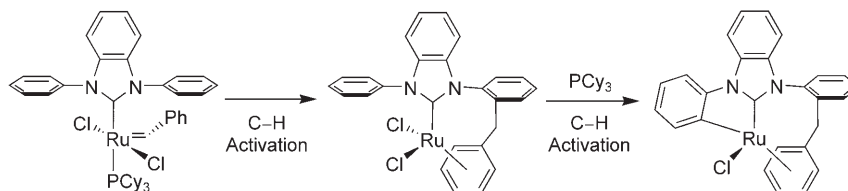
A Chemical-Responsive Supramolecular Hydrogel from Modified Cyclodextrins



C–H Activation

S. H. Hong, A. Chlenov, M. W. Day,
R. H. Grubbs* — 5148–5151

Double C–H Activation of an
N-Heterocyclic Carbene Ligand in a
Ruthenium Olefin Metathesis Catalyst



Having a breakdown: Decomposition of the olefin metathesis catalyst [(biph)(PCy₃)Cl₂Ru=C(H)Ph] (biph = *N,N'*-diphenylbenzimidazol-2-ylidene, Cy = cyclohexyl) results in benzyldiene insertion into an *ortho* C–H bond of an

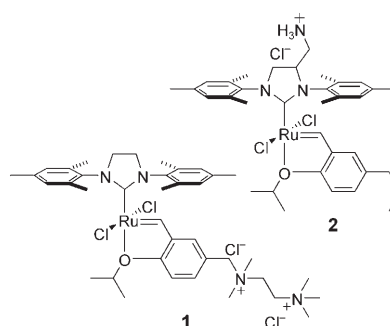
N-phenyl group of the biph ligand. The ruthenium center further inserts into another *ortho* C–H bond of the other *N*-phenyl ring to give a new Ru–C bond as a part of a five-membered metallacycle (see scheme).

Olefin-Metathesis Catalysts

J. P. Jordan, R. H. Grubbs* — 5152–5155



Small-Molecule N-Heterocyclic-Carbene-Containing Olefin-Metathesis Catalysts for Use in Water



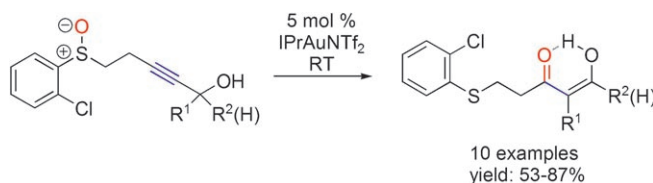
ROMPing around in water: Two well-defined, small-molecule olefin-metathesis catalysts (**1** and **2**) are introduced. While they are insufficiently stable to mediate most cross-metathesis reactions in water, these catalysts competently mediate ring-opening metathesis polymerization (ROMP) and ring-closing metathesis reactions in an aqueous environment.

Gold Carbenoids

G. Li, L. Zhang* — 5156–5159



Gold-Catalyzed Intramolecular Redox Reaction of Sulfinyl Alkynes: Efficient Generation of α -Oxo Gold Carbenoids and Application in Insertion into R–CO Bonds



Golden touch: α -Oxo Au carbenoids are efficiently generated by Au-catalyzed intramolecular redox reactions of sulfinyl alkynes. Besides cyclization to form benzo-fused sulfur-containing rings, these intermediates can participate in subse-

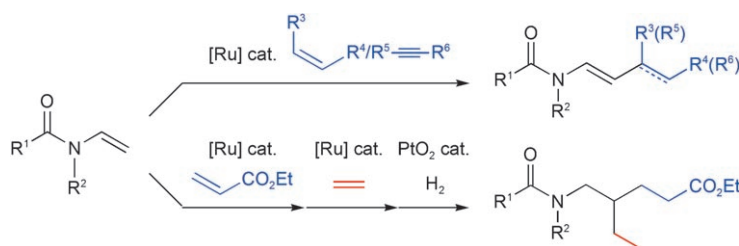
quent pinacol-type rearrangements, leading to a two-step insertion of a latent vinylcarbonylmethylene group into aldehydes or ketones (see scheme for second step).



Co-Oligomerization

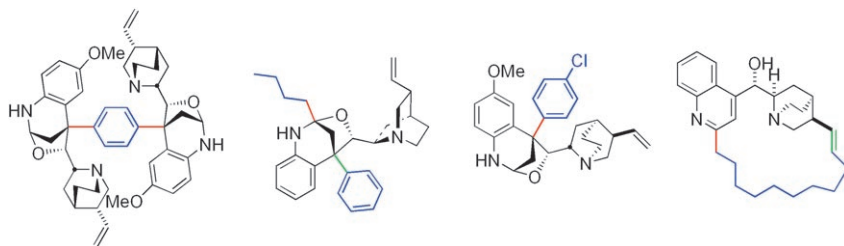
H. Tsujita, Y. Ura,* S. Matsuki, K. Wada,
T. Mitsudo, T. Kondo* — 5160–5163

Regio- and Stereoselective Synthesis of Enamides and Dienamides by Ruthenium-Catalyzed Co-Oligomerization of *N*-Vinylamides with Alkenes or Alkynes



The zero-valent ruthenium complex (η^6 -1,3,5-cyclooctatriene)bis(η^2 -dimethyl fumarate)ruthenium effectively catalyzes the highly selective codimerization of *N*-vinylamides with alkenes or alkynes and was successfully applied in the cotrim-

ization of *N*-vinylamides with ethyl acrylate and ethylene (see scheme). These reactions offer a rapid and atom-economical synthesis of biologically and synthetically important enamides and dienamides.



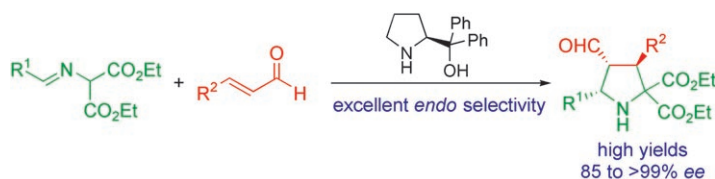
Aminal pharm: Grignard reagents undergo a surprising nucleophilic aromatic addition reaction to cinchona alkaloids to stereoselectively produce cyclic amins. Structurally diverse

alkaloid derivatives with rigid cores that bear reactive functional groups (see examples) can be readily synthesized by this simple nucleophilic alkylation protocol.

Synthetic Methods

L. Hintermann,* M. Schmitz,
U. Englert _____ **5164–5167**

Nucleophilic Addition of Organometallic Reagents to Cinchona Alkaloids: Simple Access to Diverse Architectures



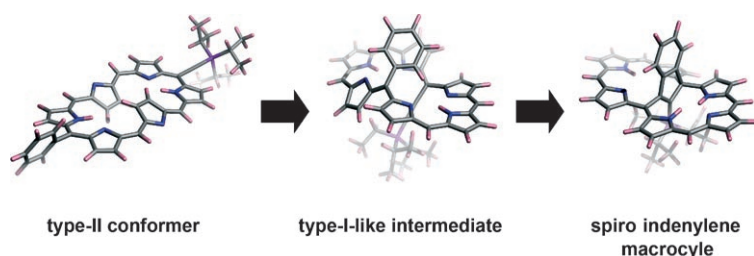
One out of a possible 16: Commercially available α,α -diphenylprolinol catalyzes the [3+2] cycloaddition of α,β -unsaturated aldehydes with azomethine ylides derived from imines to produce pyrrolidines as single regioisomers with excel-

lent diastereo- and enantioselectivities (see scheme; R^1 = aryl; R^2 = alkyl, aryl, 2-furyl). A fourth stereocenter can be introduced subsequently with complete stereoselectivity.

Asymmetric Catalysis

J. L. Vicario,* S. Reboredo, D. Badía,
L. Carrillo _____ **5168–5170**

Organocatalytic Enantioselective [3+2] Cycloaddition of Azomethine Ylides and α,β -Unsaturated Aldehydes



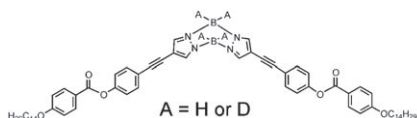
Across the great divide: Substituents located opposite one another in meso positions on a [26]hexaphyrin scaffold are forced into close contact through a dynamic conformational change. A simple aryl group and an ethynyl group in these

positions undergo a [3+2] annulation reaction either upon thermal activation or spontaneously to provide indenylene-bridged macrocycles that can serve as ligands for mixed-valence complexes (see structures).

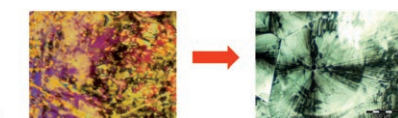
Porphyrinoids

M. Suzuki, A. Osuka* _____ **5171–5174**

Intramolecular [3+2] Annulation of 5-Aryl-, 20-Ethynyl-Substituted [26]Hexaphyrin(1.1.1.1.1.1) Triggered by Molecular Compression through a Dynamic Conformational Change



Boron coordination compounds with a roof-shaped morphology (see structure) exhibit unusual liquid-crystalline behavior with a transition (represented by the red arrow) from a nematic mesophase with



similar characteristics to those of some bent-core liquid crystals to a compact lamellar phase with a chiral organization (see microphotographs of the two phases).

Liquid Crystals

E. Cavero, D. P. Lydon, S. Uriel,
M. R. de la Fuente, J. L. Serrano,
R. Giménez* _____ **5175–5177**

Roof-Shaped Pyrazoboles as a Structural Motif for Bent-Core Liquid Crystals

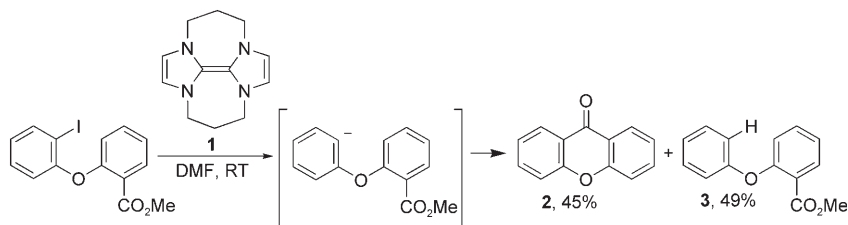


Electron Transfer

J. A. Murphy,* S. Z. Zhou, D. W. Thomson,
F. Schoenebeck, M. Mahesh, S. R. Park,
T. Tuttle,* L. E. A. Berlouis — **5178–5183**



The Generation of Aryl Anions by Double Electron Transfer to Aryl Iodides from a Neutral Ground-State Organic Super-Electron Donor



It takes two to cyclize: Aryl halides are reduced to aryl anions by double electron transfer from the neutral ground-state electron donor **1** (see scheme), as shown by the formation of a cyclic ketone (**2**). The reduced compound (**3**) is also formed.

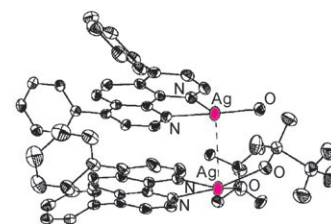
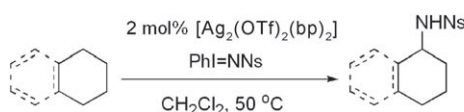
Calculations show that the loss of two electrons from **1** is both thermodynamically and kinetically viable and generates a more planar resonance-stabilized structure.

Transition-Metal Catalysis

Z. Li, D. A. Capretto, R. Rahaman,
C. He* — **5184–5186**



Silver-Catalyzed Intermolecular Amination of C–H Groups



Teamwork: The dinuclear silver complex $[\text{Ag}_2(\text{OTf})_2(\text{bp})_2]$ (OTf = trifluoromethanesulfonate, bp = bathophenanthroline) catalyzes the intermolecular amination of saturated C–H bonds by using $\text{PhI}=\text{NNs}$

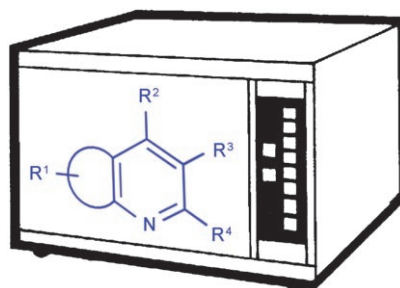
(Ns = *p*-nitrosulfonyl) as the nitrene precursor (see scheme). Preliminary investigations suggest that the dinuclear structural motif is crucial to catalytic performance.

Heterocycle Synthesis

D. D. Young, A. Deiters* — **5187–5190**



A General Approach to Chemo- and Regioselective Cyclotrimerization Reactions



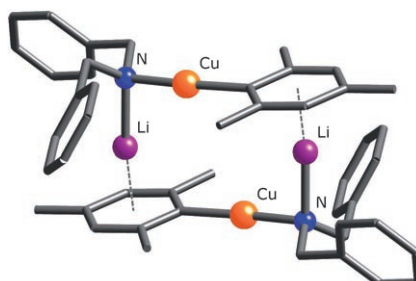
Microwave-ready heterocycles: Cobalt-catalyzed [2+2+2] cyclotrimerization of nitrile derivatives with diynes anchored to a solid support under microwave irradiation provides a universal approach to pyridine, pyridone, and iminopyridine products. The reaction is completely chemo- and regioselective, and the products are obtained in excellent yield and high purity.

Organocopper Reagents

R. P. Davies,* S. Hornauer,
P. B. Hitchcock — **5191–5194**



Structural Studies on a Lithium Organo-Amidocuprate in the Solid State and in Solution



Head-to-tail or head-to-head? A lithium amidocuprate complex has been characterized in the solid state and shown to adopt a head-to-tail conformation (see picture). 2D NMR spectroscopic studies show the presence of several structural isomers in solution, including a head-to-head isomer, resulting from Schlenk equilibrium. The presence of these isomers is postulated to have a significant influence on heterocuprate reactivity.



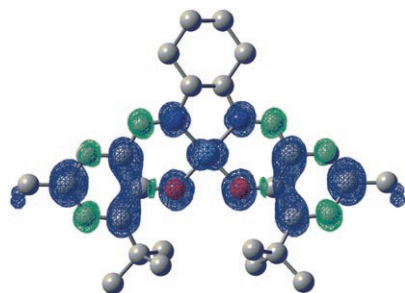
Even fused furans can be prepared by cycloisomerization of substituted allenyl ketones. The cascade reaction involves a [1,2]-migration of alkyl or aryl groups in allenyl ketones as the key step. Facile reaction in the presence of cationic com-

plexes, as well as migratory aptitude in the cycloisomerization of unsymmetrically substituted allenes, strongly supports an electrophilic mechanism for this transformation.

Furan Synthesis

A. S. Dudnik, V. Gevorgyan* 5195 – 5197

Metal-Catalyzed [1,2]-Alkyl Shift in Allenyl Ketones: Synthesis of Multisubstituted Furans

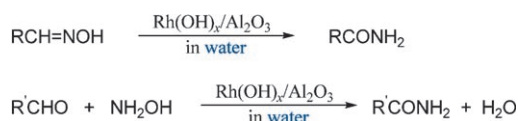


Class III delocalization? The isolation and analysis of the ligand-radical title complex has allowed description of the changes in bonding from the reduced form as well as the extent of delocalization. The intense low-energy absorption of the oxidized complex can be described as a ligand-radical transition of a highly delocalized class III mixed-valence compound.

Metal Radical Complexes

T. Storr, E. C. Wasinger, R. C. Pratt, T. D. P. Stack* 5198 – 5201

The Geometric and Electronic Structure of a One-Electron-Oxidized Nickel(II) Bis(salicylidene)diamine Complex



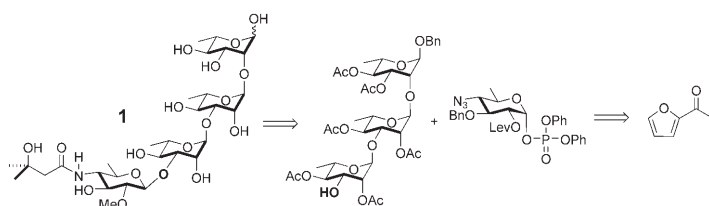
Dehydration/Rehydration in Water: Supported rhodium hydroxide ($\text{Rh(OH)}_x/\text{Al}_2\text{O}_3$) is an effective heterogeneous catalyst for the synthesis of primary amides

from aldoximes and aldehydes in water in a reaction that is entirely free of hazardous and carcinogenic organic solvents (see scheme).

Catalytic Amide Synthesis

H. Fujiwara, Y. Ogasawara, K. Yamaguchi, N. Mizuno* 5202 – 5205

A One-Pot Synthesis of Primary Amides from Aldoximes or Aldehydes in Water in the Presence of a Supported Rhodium Catalyst



Choose your poison: In the de novo asymmetric synthesis of the anthrax tetrasaccharide **1** (25 steps from acetylfuran), the absolute configurations of three L sugars and one D sugar were set by the Noyori reduction of acetylfuran with

the *S,S* and the *R,R* reagent, respectively. The configuration of the remaining carbohydrate unit was set by highly diastereoselective palladium-catalyzed glycosylation and post-glycosylation transformations.

Tetrasaccharide Synthesis

H. Guo, G. A. O'Doherty* 5206 – 5208

De Novo Asymmetric Synthesis of the Anthrax Tetrasaccharide by a Palladium-Catalyzed Glycosylation Reaction

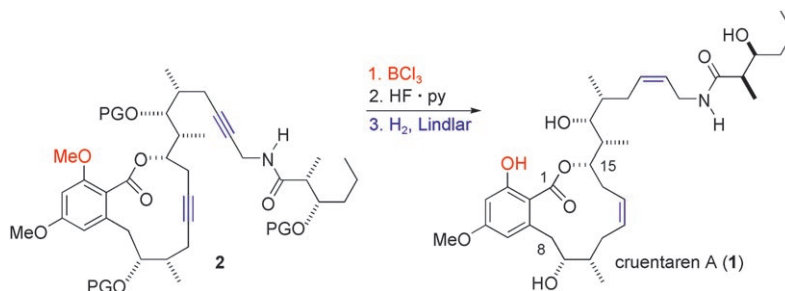


Natural Product Synthesis

V. V. Vintonyak, M. E. Maier* **5209–5211**



Total Synthesis of Cruentaren A



A triple bypass: The triple bond in the macrolactone ring of **2** served as a lock to prevent the unwanted translactonization to the δ -lactone during the formation of the side chain of the macrolide cruentar-

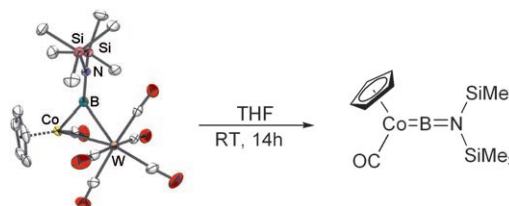
en A (**1**). Subsequent cleavage of the methyl ether and the silicon protecting groups (PG) followed by a Lindlar reduction of the two triple bonds completed the synthesis (see scheme).



Borylene Complexes

H. Braunschweig,* M. Forster, K. Radacki, F. Seeler, G. R. Whittell **5212–5214**

Stepwise Intermetal Borylene Transfer: Synthesis and Structure of Mono- and Dinuclear Cobalt–Borylene Complexes



Step by step: Stepwise transmetalation of the borylene ligand $\text{BN}(\text{SiMe}_3)_2$ from $[(\text{OC})_5\text{W}=\text{B}=\text{N}(\text{SiMe}_3)_2]$ to $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2]$ gives access to the first mono- and dinuclear cobalt borylene species and provides convincing evidence that the

intermetal borylene transfer proceeds by an associative process with a heterodimetallic intermediate (see structure) without generation of an intermediate free borylene species.

Boron Ligands

H. Braunschweig,* I. Fernández, G. Frenking,* K. Radacki, F. Seeler **5215–5218**

Synthesis and Electronic Structure of a Ferroborylene



The photochemically induced transfer of a ferroborylene yielded the first metal-bound borirene (see scheme and product structure, in which the methyl substitu-

ents are omitted). Experimental and theoretical data suggest significant π delocalization in the three-membered BC_2 ring.

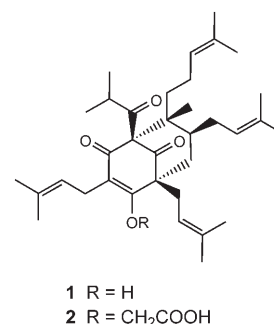
Inhibitors

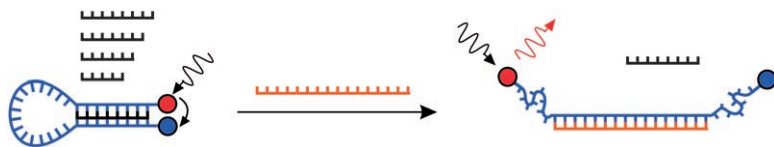
C. Gey, S. Kyrlyenko, L. Hennig, L.-H. Nguyen, A. Büttner, H. D. Pham, A. Giannis* **5219–5222**



Phloroglucinol Derivatives Guttiferone G, Aristoforin, and Hyperforin: Inhibitors of Human Sirtuins SIRT1 and SIRT2

Preventative medicine: The natural products guttiferone G and hyperforin (**1**) as well as the synthetic aristoforin (**2**) are inhibitors of human SIRT1 and SIRT2. Guttiferone G and **2** are less toxic but stronger inhibitors of cell proliferation than **1**. These compounds may be valuable tools for epigenetics and for the elucidation of the biological role of sirtuins in processes such as cancer, ageing, neurodegenerative diseases, adipositas, and diabetes.





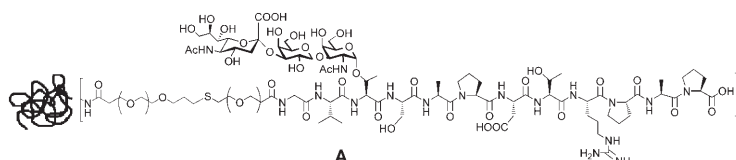
Reporting live: Triplex formation is used to construct a stem-loop probe, which is opened upon binding of the DNA target (red). The triplex molecular beacon is composed of a single DNA strand (blue), a stem-forming oligomer (black), and is

labeled with a fluorophore and a quencher (red and blue circles). This concept facilitates the introduction of further functionalities such as additional quenchers in the assembly of “superquenched” beacons.

Fluorescence Probes

T. N. Grossmann, L. Röglin,
O. Seitz* 5223 – 5225

Triplex Molecular Beacons as Modular Probes for DNA Detection



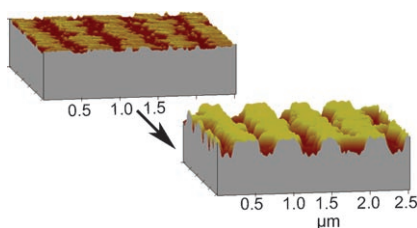
Immunologically noninterfering thioether linkages between a carrier protein (bovine serum albumin) and synthetic tumor-associated glycopeptide antigens from MUC1 (as in **A**) are important prerequisites for the development of synthetic

vaccines useful for active immunization. These thioether linkages are formed by photochemically induced addition of thiol to vinyl groups. None of the sensitive structural elements are affected.

Antitumor Vaccines

S. Wittrock, T. Becker,
H. Kunz* 5226 – 5230

Synthetic Vaccines of Tumor-Associated Glycopeptide Antigens by Immune-Compatible Thioether Linkage to Bovine Serum Albumin



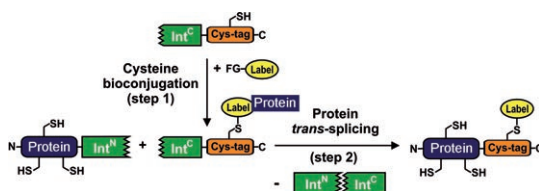
Brushing the surface: Structured polymer brushes are readily prepared by site-selective immobilization of initiators in a self-assembly process by Langmuir–Blodgett lithography with subsequent polymerization. The AFM images show a

DPPC/alkoxy amine LB film before and after surface-initiated controlled nitroxide-mediated radical polymerization. Large surface areas (several cm²) can readily be structured with this method.

Polymer Brushes

M. K. Brinks, M. Hirtz, L. Chi,* H. Fuchs,
A. Studer* 5231 – 5233

Site-Selective Surface-Initiated Polymerization by Langmuir–Blodgett Lithography



Orthogonal cysteines: The chemical modification of cysteine residues is one of the most important methods for the chemoselective bioconjugation of proteins; however, it lacks regioselectivity. By

assembling the protein from two pieces using protein *trans*-splicing, regioselectivity can be achieved. This reaction can even be performed in complex mixtures such as cell extracts.

Protein Modifications

T. Kurpiers, H. D. Mootz* 5234 – 5237

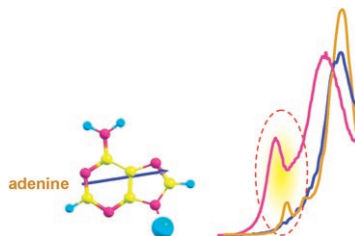
Regioselective Cysteine Bioconjugation by Appending a Labeled Cysteine Tag to a Protein by Using Protein Splicing in *trans*



Dissociative Electron Attachment

S. Denifl, P. Sulzer, D. Huber, F. Zappa,
M. Probst, T. D. Märk, P. Scheier,*
N. Injan, J. Limtrakul, R. Abouaf,
H. Dunet _____ **5238 – 5241**

Influence of Functional Groups on the
Site-Selective Dissociation of Adenine
upon Low-Energy Electron Attachment



The butterfly effect (a small change can have large repercussions): Dissociative electron attachment (DEA) was used to probe the reactivities of purine derivatives. A change of the substituent at the C6 position of adenine strongly affects the ion yield of the closed-shell dehydrogenated anion (see picture), although the hydrogen loss can be ascribed exclusively to the diametric N9 position.



Supporting information is available on the WWW
(see article for access details).



A video clip is available as Supporting Information
on the WWW (see article for access details).

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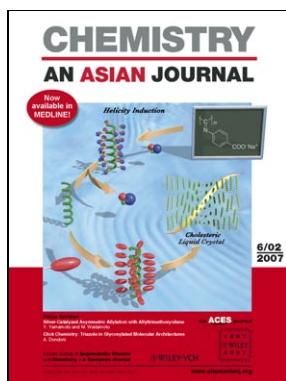
**Spotlights Angewandte's
Sister Journals** _____ **5050 – 5051**

Keywords _____ **5242**

Authors _____ **5243**

Vacancies _____ **5055**

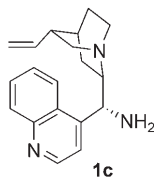
Preview _____ **5245**



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Corrigenda

In Scheme 2 of this Communication, structure **1c** was shown incorrectly. The correct structure of this chiral primary amine catalyst is shown below.



Highly Asymmetric Michael Addition to α,β -Unsaturated Ketones Catalyzed by 9-Amino-9-deoxyepiquinine

J.-W. Xie, W. Chen, R. Li, M. Zeng, W. Du, L. Yue, Y.-C. Chen,* Y. Wu, J. Zhu, J.-G. Deng* **389–392**

Angew. Chem. Int. Ed. **2007**, 46

DOI 10.1002/anie.200603612

In our Review, we described only work of D. M. Adams et al. (*J. Am. Chem. Soc.* **1993**, 115, 8221–8229) as an example of solid-state valence tautomerism (p. 2154). However, we should note that solid-state valence tautomerism has also been reported by G. A. Abakumov et al. (*Dokl. Akad. Nauk SSSR* **1993**, 328, 332–335). Furthermore, the pioneering works of G. A. Abakumov et al. in which metal–ligand electron transfer in *o*-semiquinonic copper complexes was first reported are not cited (*Dokl. Akad. Nauk SSSR* **1982**, 266, 361–363; *Dokl. Akad. Nauk SSSR* **1989**, 304, 107–111).

It has been suggested that our interpretation of photomechanical effects on p. 2158 is wrong. We proposed that bending is induced by the expansion of the irradiated region of the crystals. If this were the case, irradiation of the opposite side of the crystal should cause bending in the other direction. However, the crystal actually bends according to its own axis, and the bending is independent of the side from which the crystal is irradiated.

Furthermore, the title of Chapter 3.1 on p. 2162 should read “Metal-to-Metal Charge Transfer in FeCo *Pentanuclear* Compounds”.

Control of Magnetic Properties through External Stimuli

O. Sato,* J. Tao, Y.-Z. Zhang **2152–2187**

Angew. Chem. Int. Ed. **2007**, 46

DOI 10.1002/anie.200602205

The authors of this Communication have noticed that Equation (2) appears incorrectly in print. The authors apologize for the oversight, but point out that this mistake has no bearing on the discussion of their results as the correct equation [Eq. (2)] was used in their calculations.

$$P_{\text{off}}(\Delta t) = e^{-k_d \Delta t} = e^{-v_{\text{off}} \Delta t} \quad (2)$$

Direct Monitoring of Formation and Dissociation of Individual Metal Complexes by Single-Molecule Fluorescence Spectroscopy

A. Kiel, J. Kovacs, A. Mokhir, R. Krämer, D.-P. Herten* **3363–3366**

Angew. Chem. Int. Ed. **2007**, 46

DOI 10.1002/anie.200604965