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. Mascal, E. B. Nikitin*
Direct, High-Yield Conversion of Cellulose into Biofuel

P. García-Álvarez, D. V. Graham, E. Hevia, A. R. Kennedy, J. Klett, R. E. Mulvey, C. T. O Hara, S. Weatherstone*
Unmasking Representative Structures of TMP-Active Hauser and Turbo Hauser Bases

*T. Robert, J. Velder, H.-G. Schmalz**
Enantioselective Copper-Catalyzed 1,4-Addition of Grignard Reagents to Cyclohexenone Using Taddol-Derived Phosphine–Phosphite Ligands and 2-Methyl-THF as a Solvent

*A. D. Shaller, W. Wang, H. Gan, A. D. Q. Li**
Tunable Molecular Assembly Codes Direct Reaction Pathways

K. C. Nicolaou, Y.-P. Sun, X.-S. Peng, D. Polet, D. Y.-K. Chen**
Total Synthesis of (+)-Cortistatin A

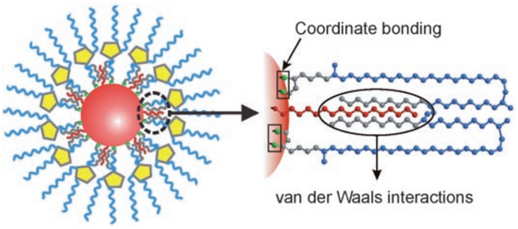
D. Staack, A. Fridman, A. Gutsol, Y. Gogotsi, G. Friedman**
Nanoscale Corona Discharge in Liquids Enabling Nanosecond Optical Emission Spectroscopy

*C. Hawner, K. Li, V. Cirriez, A. Alexakis**
Copper-Catalyzed Asymmetric Conjugate Addition of Aryl Aluminum Reagents to Trisubstituted Enones: Construction of Aryl-Substituted Quaternary Centers

Books

Highlights

Nano-Biotechnology



The preparation of nanoparticles with sufficient chemical and thermal stability for bio-related applications has long been a major issue in nanobiotechnology. New types of highly stable Au, CdSe/ZnS, and F_3O_4 nanoparticles have been stabilized with Tween derivatives through coordination to the particle surface as well as van der Waals interaction with the primary ligands on the nanoparticle surface. The Au nanoparticles are more stable than the corresponding Au nanoparticles functionalized with thiolated DNA.

Gold Catalysis

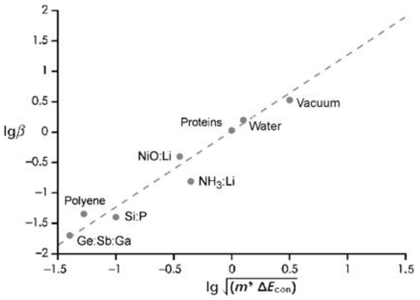
What is the nature of the gold–carbon bond—double, single? The structure of a crucial intermediate of many gold-catalyzed reactions has become a matter of debate. A current study demonstrates that the carbocationic form determines the outcome of many cycloisomerizations.

Contents

Essays

Electron Transfer

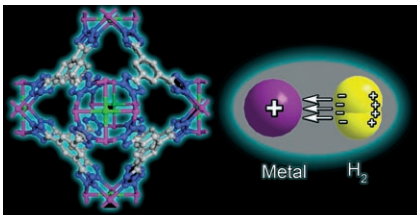
A new vision for ET: Electron-transfer (ET) processes in biological and synthetic materials (such as proteins and semiconductors, respectively) are of immense importance. A unified approach to describe these processes is useful in understanding, and controlling the various facets of electron transfer in condensed matter. The diagram shows a plot of the decay constant for the electron-tunneling process against the effective tunneling barrier in different materials.



Reviews

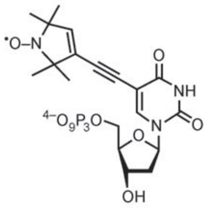
Hydrogen Storage

Getting a grip on hydrogen: Hydrogen typically adsorbs very weakly in physisorptive systems. In microporous materials, however, coordinatively unsaturated metal centers can contribute to an increase in the enthalpy of H_2 adsorption. Strategies to incorporate such metal sites in metal–organic frameworks have led to remarkable results within a short period, thus promising to deliver new materials with improved H_2 affinity in the near future.



Communications

Spectroscopic Probes

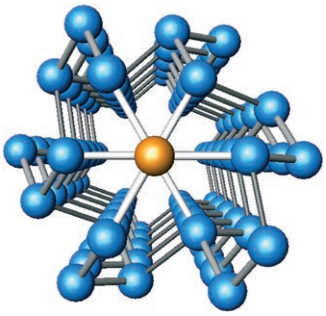


Multi-spinning: The use of modified triphosphates and DNA polymerases has resulted in the multiple spin-labeling of DNA (see picture). A DNA helix entirely labeled with paramagnetic centers has been generated in this way and investigated by EPR spectroscopy.

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.

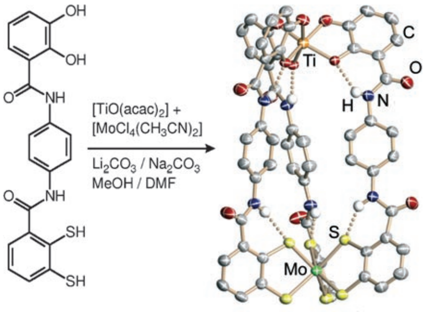
Smart writing by electrons: A new technique enables the fabrication of full-coverage polymer brush patterns of variable shape on a nanometer length scale. The key to this technique is electron-beam activation of amino groups, which serve as the nucleation centers for surface-initiated polymerization. The technique untangles chemistry and morphology, and it is possible to monitor only morphology effects on chemically homogeneous surfaces and interfaces.

Polymer Nanostructures



Under pressure: The new modification Ge(*hR*8) is obtained upon pressurization of clathrate-type Ge(*cF*136) or controlled decompression of a Ge(*tI*4)-type high-pressure phase. The atomic arrangement comprises four-bonded germanium atoms with a topological organization bearing remarkable similarity to high-pressure host–guest assemblies of other main-group elements.

Germanium Modifications

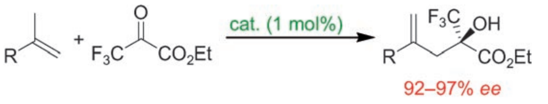


H_4-**1**

$[\mathrm{TiMo}(\mathbf{1})_3]^{4-}$

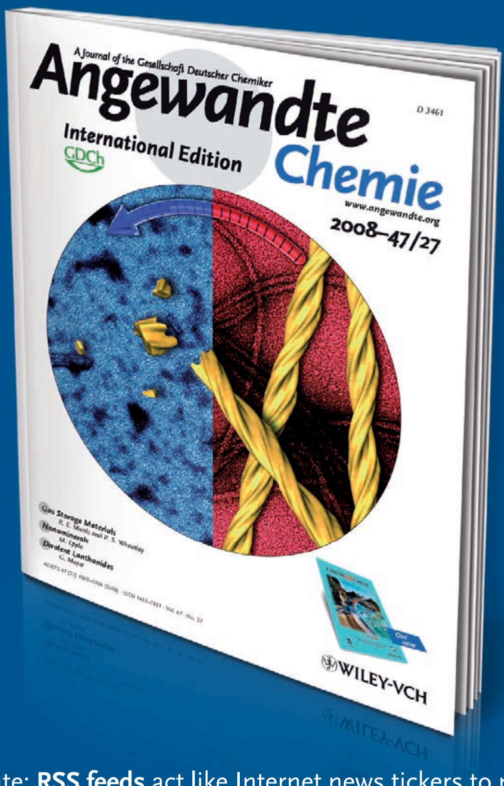
It takes two to tango: When ligand H_4-**1** (see scheme) reacts with $\mathrm{Mo^{IV}}$ and $\mathrm{Ti^{IV}}$, the different binding preferences of the O–O and S–S donor groups lead to the formation of the helicate $[\mathrm{TiMo}(\mathbf{1})_3]^{4-}$ with a parallel orientation of the ligand strands. With different cations, the supramolecular complexes $\{\Lambda,\Lambda\text{-}[\mathrm{TiMo}(\mathbf{1})_3]\text{-}(\mathrm{PNP})\text{-}\Delta,\Delta\text{-}[\mathrm{TiMo}(\mathbf{1})_3]\}^{7-}$ and $\{\Delta,\Delta\text{-}[\mathrm{TiMo}(\mathbf{1})_3]\text{-}\mathrm{Na}\text{-}\Delta,\Delta\text{-}[\mathrm{TiMo}(\mathbf{1})_3]\}^{7-}$ can be crystallized. PNP = bis(triphenylphosphoranylidene)ammonium.

Helical Structures



You can count on the counterion in ion-pair intermediates to induce high levels of asymmetry in the title reaction. The efficient transformation proceeds under mild reaction conditions in the presence of an air-stable *N*-triflylphosphoramide in a low catalyst loading of just 1 mol% to give substituted α-hydroxyesters in good yields and with excellent *ee* values (see scheme; R = aryl).

Asymmetric Synthesis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Gas Storage Materials
Nanominerals
Divalent Lanthanides
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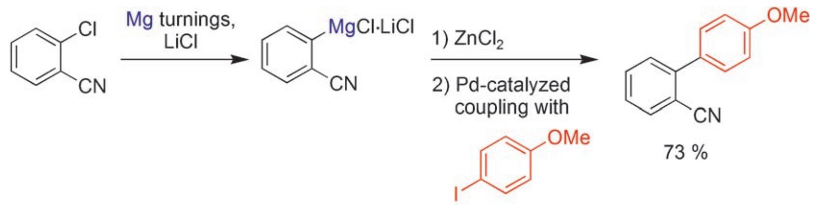
Grignard Reagents

F. M. Piller, P. Appukkuttan,
A. Gavryushin, M. Helm,
P. Knochel* ——— **6802 – 6806**

Convenient Preparation of Polyfunctional Aryl Magnesium Reagents by a Direct Magnesium Insertion in the Presence of LiCl

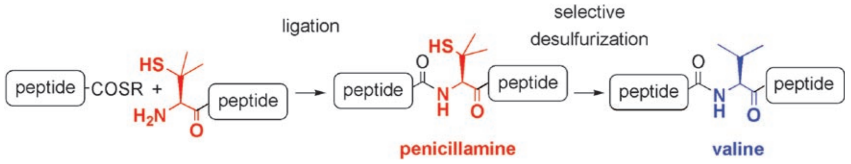


In the footsteps of Victor Grignard: The simple LiCl-mediated insertion of magnesium into aryl chlorides and bromides at moderate temperatures leads to functionalized organomagnesium reagents (see scheme). An unprecedented range of functional groups may be present in the substrates (e.g. CN, CO_2R, OTs, OBoc; Ts = *p*-toluenesulfonyl, Boc = *tert*-butylcarbonyloxy).

Peptide Ligation without Cysteine

C. Haase, H. Rohde,
O. Seitz* ——— **6807 – 6810**

Native Chemical Ligation at Valine

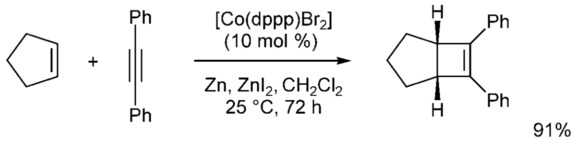


Peptide ligation at hydrophobic sites is possible with a ligation–desulfurization strategy in which penicillamine serves as a precursor of valine. The β,β-dimethylcysteine peptides reacted surprisingly fast in native chemical ligation reactions. Even the sterically crowded and unpolar Leu–Val bond can be formed in high yield.

Synthetic Methods

J. Treutwein, G. Hilt* ——— **6811 – 6813**

Cobalt-Catalyzed [2+2] Cycloaddition



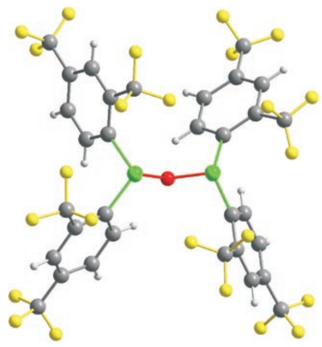
Three's a charm, but four's not half bad either: A simple cobalt–diphosphine complex facilitates the synthesis of cyclobutene derivatives through the chemoselective transformation of strained five-membered unsaturated rings with internal alkynes (see scheme). This atom-efficient, intermolecular reaction generates polycyclic products in excellent yields and with excellent *exo* selectivity. dppp = 1,3-bis(diphenylphosphanyl)propane.

Acid Anhydrides

B. Hoge,* B. Kurscheid ——— **6814 – 6816**

Tetrakis[2,4-bis(trifluoromethyl)phenyl]-diphosphoxane: An Anhydride of a Phosphinous Acid

Steric and electronic characteristics of the bulky, strongly electron-withdrawing 2,4-$(CF_3)_2C_6H_3$ group are ideally suited to stabilize the unusual form of a diphosphoxane, R_2POPR_2, the anhydride of a phosphinous acid. The high-yield synthesis and first structural characterization of a tetraorganyl diphosphoxane are described (see structure; C gray, H white, O red, F yellow, P green).

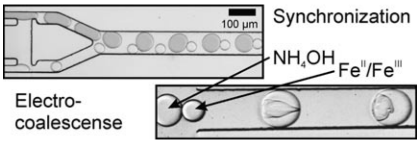


Contents

Microfluidics

L. Frenz, A. El Harrak, M. Pauly,
S. Bégin-Colin, A. D. Griffiths,*
J.-C. Baret* ——— **6817 – 6820**

Droplet-Based Microreactors for the Synthesis of Magnetic Iron Oxide Nanoparticles

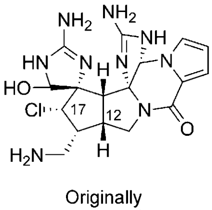


Microdroplets for nanoparticles: An extremely reliable method to create droplet pairs, based on hydrodynamic coupling of two spatially separated nozzles, has been developed. Droplets containing the reagents for the precipitation of iron oxide are electrocoalesced to synthesize iron oxide nanoparticles in a very fast (millisecond-scale) and reproducible reaction (see picture).

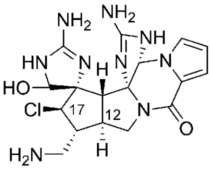
Natural Products

M. S. Bultman, J. Ma,
D. Y. Gin* ——— **6821 – 6824**

Synthetic Access to the Chlorocyclopentane Cores of the Proposed Original and Revised Structures of Palau'amine



Originally proposed structure



Revised structure

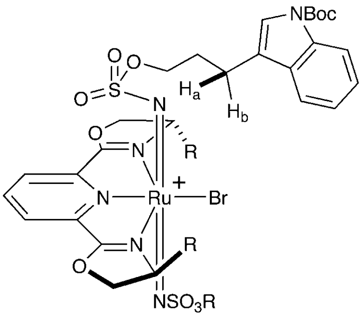
Core knowledge: The synthesis of the functionalized cores of both the originally proposed and revised structures of palau'amine have been achieved (see structures). A Diels–Alder/[3,3]-sigmatropic rearrangement sequence and a Beckmann rearrangement enable the stereocontrolled formation of the highly congested cores.

Asymmetric Catalysis

E. Milczek, N. Boudet,
S. Blakey* ——— **6825 – 6828**

Enantioselective C–H Amination Using Cationic Ruthenium(II)–pybox Catalysts

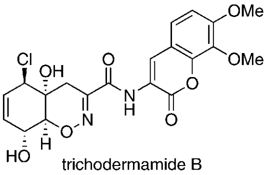
The whole "pybox" and dice: Highly enantioselective amination reactions of both allylic and benzylic C–H bonds are catalyzed by cationic ruthenium(II)–pybox complexes (see structure). A novel mode of stereocontrol, which is induced by the versatile pybox ligand, is proposed to account for the excellent enantioselectivity in these reactions. Boc = *tert*-butoxycarbonyl, pybox = pyridine bisoxazoline.



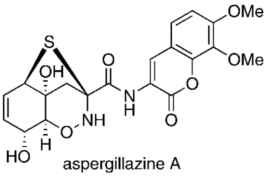
Natural Product Synthesis

C.-D. Lu, A. Zakarian* ——— **6829 – 6831**

Total Synthesis of (±)-Trichodermamide B and of a Putative Biosynthetic Precursor to Aspergillazine A Using an Oxaza-Cope Rearrangement



trichodermamide B



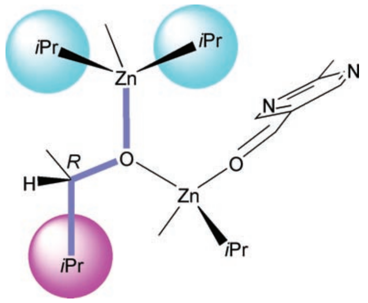
aspergillazine A

Coping with tandem reactions: The total synthesis of marine fungal metabolite, trichodermamide B, is accomplished using a tandem nitrosation/oxaza-Cope rearrangement as the key step to establish the characteristic heterocyclic ring system of the natural product. Preparation of the putative biosynthetic precursor of aspergillazine A provides further insight into the possible biosynthetic pathway to aspergillazines.

Asymmetric Autocatalysis

L. Schiaffino, G. Ercolani* — **6832–6835**

Unraveling the Mechanism of the Soai Asymmetric Autocatalytic Reaction by First-Principles Calculations: Induction and Amplification of Chirality by Self-Assembly of Hexamolecular Complexes

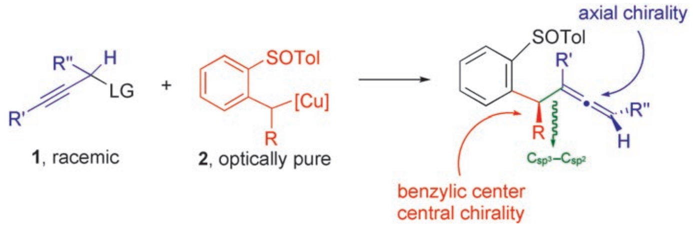


Soai, so good: The Soai reaction is the sole reported case of amplifying asymmetric autocatalysis. A mechanism is proposed for this reaction, supported by first-principle calculations, clarifying not only the reasons for the detected chiral induction and amplification, but also the roles performed by isopropyl groups, γ-pyridinic nitrogen atoms, and the δ-substituent.

Asymmetric Synthesis

J. L. García Ruano,* V. Marcos, J. Alemán — **6836–6839**

Configurational Control of Benzyl Carbanion–Copper Complexes by Sulfinyl Groups: Synthesis of Optically Pure Allenes with Central and Axial Chirality

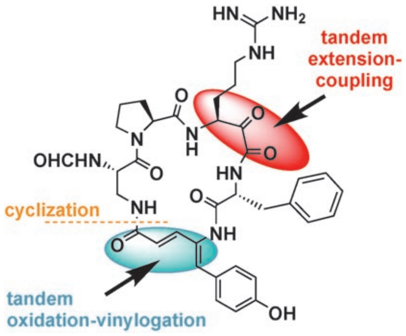


Lean, mean, chiral allene: Optically pure complexes **2** react with propargyl bromides and mesylates **1** to afford the title products (see scheme; LG = leaving group). The regioselectivity and the configuration of the chiral axis are completely controlled, and the stereoselectivity at the benzylic position is high. Kinetic resolution of racemic propargyl mesylates can also be achieved with these reagents.

Natural Products Synthesis

S. P. Roche, S. Faure, D. J. Aitken* — **6840–6842**

Total Synthesis of Cyclotheonamide C using a Tandem Backbone-Extension–Coupling Methodology

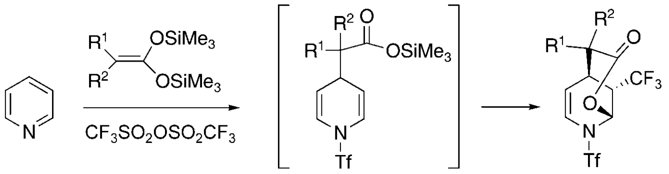


Mastering unusual amino acids: The first total synthesis of the potent protease inhibitor cyclotheonamide C (see structure representation) has been achieved. The key features of the synthesis are a three-component tandem procedure to create a masked α-keto-β-arginine within a peptide chain, and the control of the extended conjugation of a vinylogous α,β-dehydrotyrosine.

Synthetic Methods

H. Rudler,* A. Parlier, C. Sandoval-Chavez, P. Herson, J.-C. Daran — **6843–6846**

Overall "Pseudocationic" Trifluoromethylation of Dihydropyridines with Triflic Anhydride



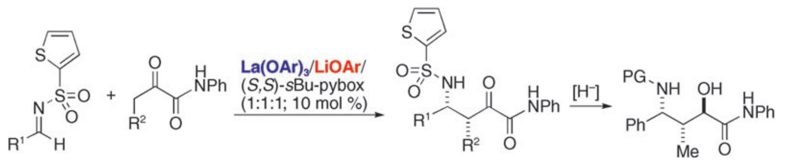
A triflic reaction: The role of triflic anhydride is not limited to the transfer of a triflyl group to the nitrogen atom during the interaction of pyridine with bis(trimethylsilyl)ketene acetals: it can also provide an electrophilic CF_3 group able to transform the formed dihydropyridines substituted with trimethylsilyl ester groups into α-trifluoromethyllactones (see scheme).

Contents

Synthetic Methods

G. Lu, H. Morimoto, S. Matsunaga,*
M. Shibasaki* ____________ **6847 – 6850**

Chiral γ-Amino Amide Synthesis by Heterobimetallic Lanthanum/Lithium/Pybox-Catalyzed Direct Asymmetric Mannich-Type Reactions of α-Keto Anilides

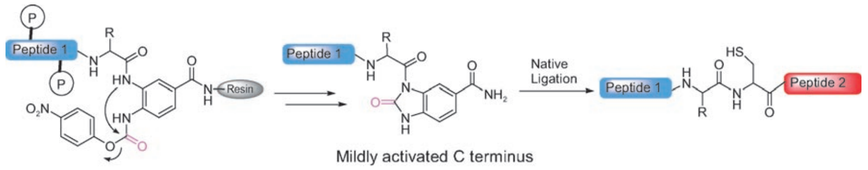


Not so Mannich now: A heterobimetallic La/Li/pybox complex was key in direct catalytic asymmetric Mannich-type reactions, using α-keto anilides as synthetic homoenolate equivalents to afford γ-amino amide products in up to >99% yield, 95% *ee*, and >97:3 *syn*-selectivity. Stereoselective reduction of the α-keto moiety afforded the β-alkyl-γ-amino-α-hydroxy amide with three contiguous stereocenters (PG = protecting group).

Peptide Ligation

J. B. Blanco-Canosa,
P. E. Dawson* ____________ **6851 – 6855**

An Efficient Fmoc-SPPS Approach for the Generation of Thioester Peptide Precursors for Use in Native Chemical Ligation

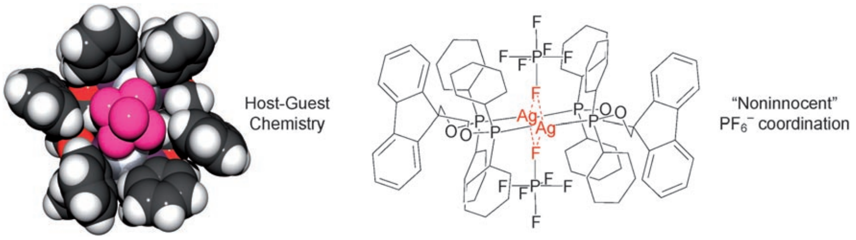


Intramolecular activation of C-terminal peptides: Mildly activated *N*-acylurea peptides are readily formed on the solid support following chain assembly, avoiding over-activation of the C-terminus. The utility of these peptides is demonstrated by the native chemical ligation of unprotected peptides (see scheme; R = amino acid side chain).

Host–Guest Chemistry

C. Li, R. Pattacini, R. Graff,
P. Braunstein* ____________ **6856 – 6859**

Diphosphinite Ag^I and Pd^{II} Dinuclear Complexes as Adaptable Anion Receptors: An Unprecedented Bridging Mode for the PF_6^- Ion

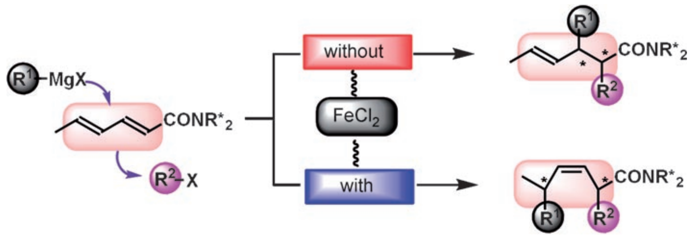


The special guest: In the host–guest chemistry of dinuclear complexes that contain the 9*H*-fluorene-9,9′-dimethanediphenylphosphinite ligand the synergy between the phenyl groups and the axial fluorene moiety leads to the formation of molecular cavities that have selective steric affinity for the anions BF_4^- or PF_6^- (see picture). An unprecedented M···F-(PF_5)···M bridging coordination mode of PF_6^- has now been established.

Homogeneous Catalysis

S. Okada, K. Arayama, R. Murayama,
T. Ishizuka, K. Hara, N. Hirone, T. Hata,
H. Urabe* ____________ **6860 – 6864**

Iron-Catalyst-Switched Selective Conjugate Addition of Grignard Reagents: α,β,γ,δ-Unsaturated Amides as Versatile Templates for Asymmetric Three-Component Coupling Processes

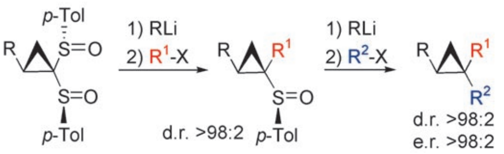


Diene for conjugate addition: Iron(II) chloride switches the reaction course of the three-component coupling of a Grignard reagent, an alkyl halide, and a dienamide, thus making the amide a simple yet versatile chiral template.

Synthetic Methods

A. Abramovitch, L. Fensterbank,
M. Malacria, I. Marek* ____ 6865 – 6868

Convergent Preparation of Enantiomerically Pure Polyalkylated Cyclopropane Derivatives

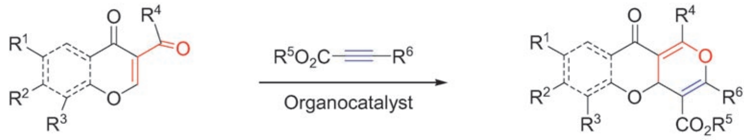


Crossroads: Selective sulfoxide/lithium exchange reactions lead to the unique preparation of diastereo- and enantiomerically pure polyalkylated cyclopropanes (see scheme). This reaction allows the independent formation of both diastereoisomers from a common starting material.

Asymmetric Synthesis

H. Waldmann,* V. Khedkar, H. Dückert,
M. Schürmann, I. M. Oppel,
K. Kumar* ____ 6869 – 6872

Asymmetric Synthesis of Natural Product Inspired Tricyclic Benzopyrones by an Organocatalyzed Annulation Reaction

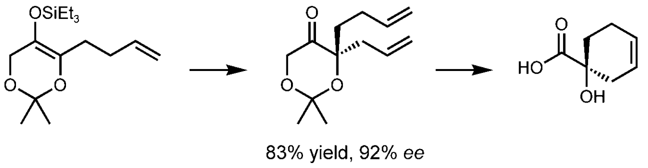


Going back to nature: Electron-deficient oxadienes and electron-poor acetylene carboxylates react in the presence of an organocatalyst to give natural product inspired tricyclic benzopyrones efficiently (up to 99% yield) and stereoselectively (up to 87% *ee*; see scheme). This efficient and operationally simple asymmetric annulation involves the generation of zwitterions from acetylene carboxylates.

Stereoselective Catalysis

M. Seto, J. L. Roizen,
B. M. Stoltz* ____ 6873 – 6876

Catalytic Enantioselective Alkylation of Substituted Dioxanone Enol Ethers: Ready Access to C(α)-Tetrasubstituted Hydroxyketones, Acids, and Esters

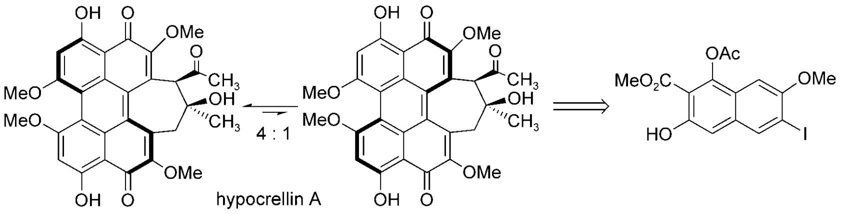


Adaptive Alkylation: Palladium-catalyzed asymmetric alkylation enables access to fully substituted enantioenriched oxygenated stereocenters, which can be transformed easily to α-hydroxyketones, esters, and acids, providing a catalytic, enantioselective synthesis for natural products.

Natural Product Synthesis

E. M. O'Brien, B. J. Morgan,
M. C. Kozlowski* ____ 6877 – 6880

Dynamic Stereochemistry Transfer in a Transannular Aldol Reaction: Total Synthesis of Hypocrellin A

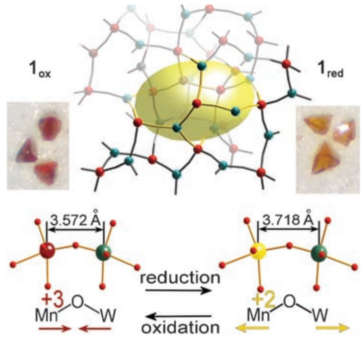


A dynamic approach: The key step in the total synthesis of hypocrellin A involves a potentially biomimetic 1,8-diketone aldol reaction, which constructs the seven-membered ring. The helical configuration is established first from an axially chiral biaryl unit and is then used in a dynamic stereochemical transfer process to form the remaining stereocenters in the intramolecular aldol reaction (see scheme).

Polyoxometalates

C. Ritchie, C. Streb, J. Thiel, S. G. Mitchell,
H. N. Miras, D.-L. Long, T. Boyd,
R. D. Peacock, T. McGlone,
L. Cronin* ____________ **6881 – 6884**

Reversible Redox Reactions in an Extended Polyoxometalate Framework Solid

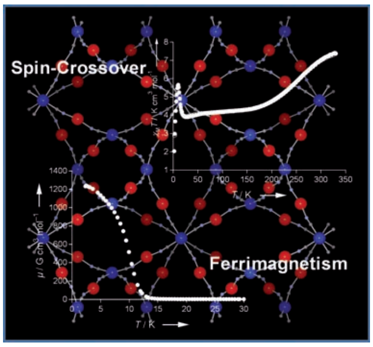


Back and forth: A concerted reversible redox reaction occurs in a pure metal oxide extended polyoxometalate framework when the accessible pockets are filled with a suitable redox agent (see picture). Direct control over the framework properties is demonstrated by repeated reversible switching between an expanded and a contracted structure. Successive recrystallizations from hot water repeatedly destroys and regenerates the framework.

Spin-Crossover Magnets

M. Arai, W. Kosaka, T. Matsuda,
S. Ohkoshi* ____________ **6885 – 6887**

Observation of an Iron(II) Spin-Crossover in an Iron Octacyanoniobate-Based Magnet



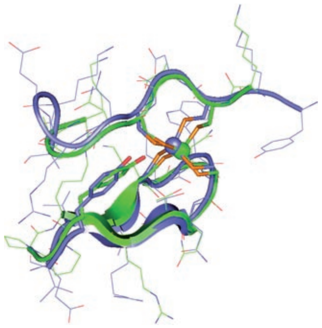
A spin-crossover from Fe^{II}(S=2)-Nb^{IV}-(S=1/2)-Fe^{II}(S=2) to Fe^{II}(S=0)-Nb^{IV}-(S=1/2)-Fe^{II}(S=2) occurs in $Fe_2[Nb(CN)_8]\cdot(3\text{-}pyCH_2OH)_8\cdot 4.6\,H_2O$ (3-py = 3-pyridyl) with decreasing temperature (see picture; red Fe, blue Nb). The low-temperature phase shows ferrimagnetism with a Curie temperature of 12 K owing to an antiferromagnetic interaction between the remaining Fe^{II} (S = 2) and the Nb^{IV} (S = 1/2) centers.

Peptide Design

O. Sénèque,* E. Bourlès, V. Lebrun,
E. Bonnet, P. Dumy,
J.-M. Latour* ____________ **6888 – 6891**

Cyclic Peptides Bearing a Side-Chain Tail: A Tool to Model the Structure and Reactivity of Protein Zinc Sites

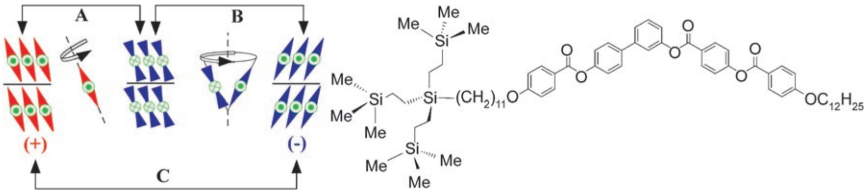
A near-perfect model: The design of short peptides with cyclic and linear components allows mimicking of the structure and reactivity of protein tetracysteinate zinc sites, as illustrated by the superposition of the $Zn(Cys)_4$ site of Hsp33 (blue) and its 20 amino acid model (green).



Liquid Crystals

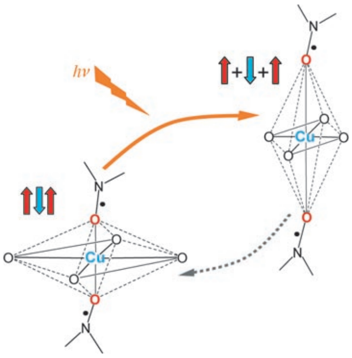
Y. Zhang,* M. J. O'Callaghan,
U. Baumeister,
C. Tschierske* ____________ **6892 – 6896**

Bent-Core Mesogens with Branched Carbosilane Termini: Flipping Suprastructural Chirality without Reversing Polarity



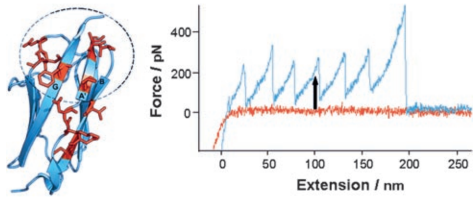
Back flip: Field-induced transformations between the two homogeneously chiral enantiomers of a bent-core mesogen (see picture) take place by two different mechanisms (A and B). Their combination leads to an unexpected field-induced chirality flipping (C) between the oppositely tilted structures without polarity reversal.

Light-Induced Spin Transitions



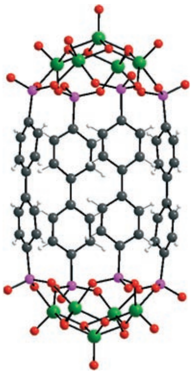
Beyond the classics: An exchange-coupled three-spin cluster of copper(II) with nitroxides can be converted by light from a strongly to a weakly coupled spin state (see picture), the latter being metastable at low temperatures. This kind of magnetic photoswitching is very similar to the LIESST effect in spin-crossover complexes of iron. Such compounds form a new class of systems capable of optical switching of their magnetic properties.

Protein Engineering



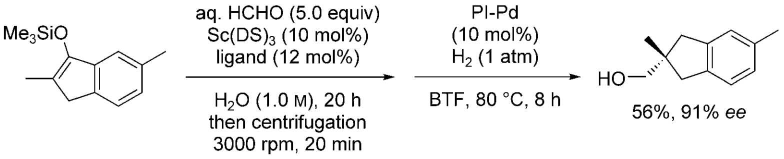
Titinic strength: The mechanical resistance of titin domain I27 (see picture, left) was increased by substituting residues from a stronger homologue in regions of the protein important for mechanical strength (red). The unfolding profile of I27st (see picture, right) shows that the mechanical strength is significantly increased compared to wild-type I27 (black arrow).

Polyoxometalate Clusters



Functionalization of polyoxovanadate clusters using phosphonate and arsonate ligands results in molecular capsules (see structure; green V, purple P, red O, black C). Through the use of extended homologous ligands, these hybrid organic-inorganic capsules can be successively elongated into tubular molecules.

Water Chemistry

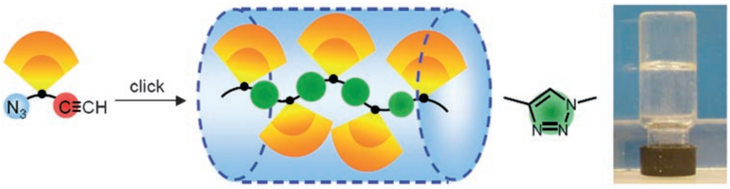


Synthesis in deep water: For the title reaction, which proceeds with high selectivities, acid–base interactions between the Sc catalyst and HCHO are important. The reaction was used in the synthesis of an odorant to demonstrate its utility (see scheme; ligand DS not shown; PI-Pd = polymer-incarcerated palladium; BTF = benzotrifluoride).

Click Chemistry

K.-N. Lau, H.-F. Chow,* M.-C. Chan, K.-W. Wong ______ 6912 – 6916

Dendronized Polymer Organogels from Click Chemistry: A Remarkable Gelation Property Owing to Synergistic Functional-Group Binding and Dendritic Size Effects

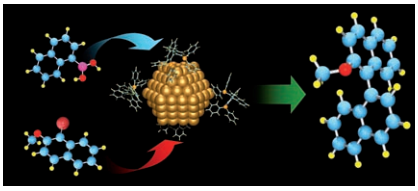


Click together and gel: Non-gelating AB-type heterobifunctional macromonomers "click" together to form polytriazole-containing dendronized polymers. These polymers form interchain hydrogen bonds, the extent of which is influenced by the size of the dendritic appendage.

Asymmetric Catalysis

K. Sawai, R. Tatumi, T. Nakahodo, H. Fujihara* ______ 6917 – 6919

Asymmetric Suzuki–Miyaura Coupling Reactions Catalyzed by Chiral Palladium Nanoparticles at Room Temperature



Similar but different: Chiral mono- and bisphosphine ligands have been used to prepare chiral stabilized palladium nanoparticles (Pd NPs). Despite the chiral Pd NPs having similar diameters of 1.2–1.7 nm, they show very different catalytic activities and enantioselectivities in the room-temperature asymmetric Suzuki–Miyaura cross-coupling reactions of aryl halides with aryl boronic acids (see picture).

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

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

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