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:

*G. V. Zyryanov, M. A. Palacios, P. Anzenbacher, Jr.**
Rational Design of a Fluorescence Turn-On Sensor Array for Phosphates in Blood Serum

S. Shimizu, T. Kiuchi, Na Pan*
A Teflon-Footed Resorcinarene: Hexameric Capsule in Fluorous Solvents and Fluorophobic Effects on Molecular Encapsulation

P. Mukhopadhyay, G. Zuber, P. Wipf, D. N. Beratan
Contribution of a Chiral Solvent Imprint of a Solute to Optical Rotation

J. Fölling, V. Belov, R. Kunetsky, R. Medda, A. Schönle, A. Egner, C. Eggeling, M. Bossi, S. Hell
Photochromic Rhodamines Provide Fluorescence Nanoscopy with Optical Sectioning

*O. Vendrell, F. Gatti, H.-D. Meyer**
Dynamics and Infrared Spectroscopy of the Protonated Water Dimer

*J. L. Stymiest, G. Dutheuil, A. Mahmood, V. K. Aggarwal**
Lithiated Carbamates: Chiral Carbenoids for Iterative Homologation of Boranes and Boronic Esters

News

Organometallic Chemistry:
T. Marks ———— **5826**

Honored Biological Chemistry:
C. Walsh ———— **5826**

Awarded Organic Chemistry:
H. Schwarz elected ———— **5826**

Books

Green Chemistry and Catalysis
Roger A. Sheldon, Isabel Arends
Ulf Hanefeld
reviewed by B. Cornils ———— **5827**

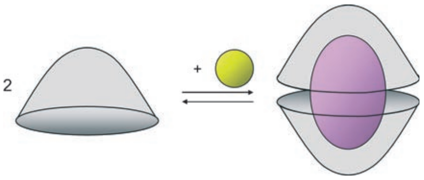
Highlights

Supramolecular Chemistry

C. Schmuck* ———— **5830–5833**

Guest Encapsulation within Self-Assembled Molecular Containers

Molecular hospitality: Self-assembled molecular containers provide a very specific geometric as well as chemical environment for a bound guest, which allows for selective guest binding or the stabilization of unstable molecules or unstable conformations within the capsule (see scheme). The geometric constraints imposed by the container can even change the outcome of a chemical reaction.

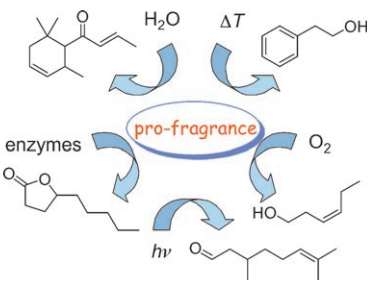


Reviews

Pro-fragrances

A. Herrmann* ———— **5836–5863**

Controlled Release of Volatiles under Mild Reaction Conditions: From Nature to Everyday Products



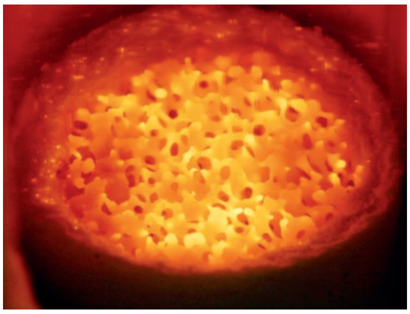
Picking up the scent: Volatile organic compounds found in nature for communication between species are also used as flavors and fragrances in numerous consumer products. As a consequence of their high volatility, their longevity is limited. The development of pro-fragrances now allows the controlled release of volatiles by the cleavage of a chemical bond under mild, everyday conditions (see scheme).

Communications

Heterogeneous Catalysis

P. J. Dauenhauer, B. J. Dreyer,
N. J. Degenstein,
L. D. Schmidt* ______ 5864 – 5867

Millisecond Reforming of Solid Biomass for Sustainable Fuels

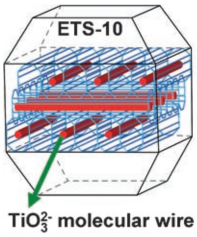


Breaking the coke habit: By coupling thermal decomposition with catalytic partial oxidation, an effective method has been developed to convert solid biomass such as cellulose into synthesis gas (see photo of a hot Rh catalyst surface). Not only is the process fast (<70 ms), it also avoids the formation of coke, which is known to deactivate catalyst surface sites and block surface reactions.

Electronic Properties

N. C. Jeong, M. H. Lee,
K. B. Yoon* ______ 5868 – 5872

Length-Dependent Band-Gap Shift of TiO_3^{2-} Molecular Wires Embedded in Zeolite ETS-10

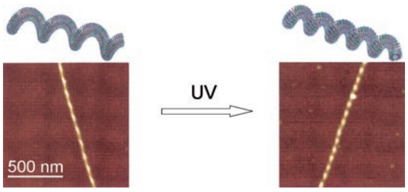


Mind the gap! The titanosilicate zeolite ETS-10 contains TiO_3^{2-} molecular wires (see picture). A reliable method has been developed to synthesize high-quality ETS-10 crystals of various sizes. Measurements on the crystals allow the dependence of the band-gap energy on the length of the TiO_3^{2-} wires to be elucidated.

Helical structures

L.-S. Li, H. Jiang, B. W. Messmore,
S. R. Bull, S. I. Stupp* ______ 5873 – 5876

A Torsional Strain Mechanism To Tune Pitch in Supramolecular Helices

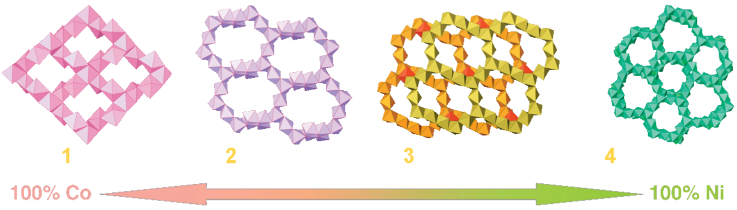


On the turn: Torsional strain has been used to control the pitch of helical nanostructures in the range of tens to hundreds of nanometers. In this method, sterically induced torsional strain on the primary helices forces the secondary helices into superhelices, with the pitch tunable depending on the magnitude of the strain. UV radiation can be used to switch the pitch of specific helical nanostructures (see AFM images).

Metal–Organic Frameworks

C. Livage,* P. M. Forster, N. Guillou,
M. M. Tafoya, A. K. Cheetham,
G. Férey ______ 5877 – 5879

Effect of Mixing of Metal Cations on the Topology of Metal Oxide Networks



Four distinct phases were isolated by adjusting the Co/Ni ratio in the hydrothermal system $CoCl_2/NiCl_2$/succinic acid/KOH/H_2O. In addition to clarifying the relationships between known hybrid inorganic–organic materials **1**, **2**, and **4**, $[M_7(OH)_2(H_2O)_2(C_4H_4O_4)_6]\cdot 3.5\,H_2O$ (**3**), a hybrid metal oxide with a rare three-dimensional metal–oxygen–metal framework, was discovered.

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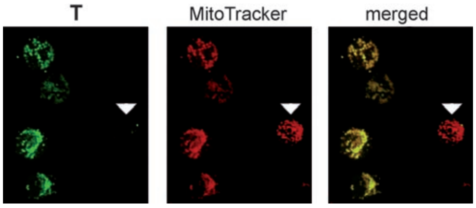
Drug Delivery

K. K. Maiti, W. S. Lee, T. Takeuchi,
C. Watkins, M. Fretz D.-C. Kim, S. Futaki,
A. Jones, K.-T. Kim,
S.-K. Chung* **5880–5884**

Guanidine-Containing Molecular Transporters: Sorbitol-Based Transporters Show High Intracellular Selectivity toward Mitochondria



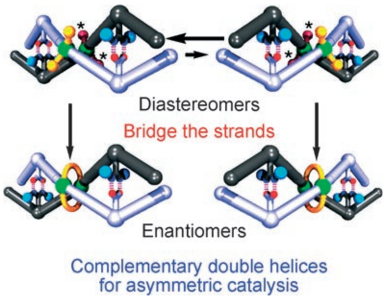
Special delivery: Transporters constructed on a sorbitol scaffold with eight guanidine residues show significant translocation across the cell membrane and the blood–brain barrier and high affinities toward mitochondria in HeLa and KG1a leukemia cells. The picture shows colocalisation of one such transporter (**T**) with MitoTracker red in KG1a cells (scale bars: 10 µm).

Helical Structures

T. Hasegawa, Y. Furusho,* H. Katagiri,
E. Yashima* **5885–5888**

Enantioselective Synthesis of Complementary Double-Helical Molecules that Catalyze Asymmetric Reactions

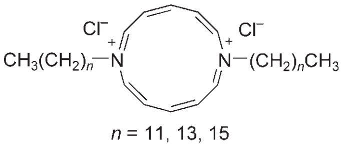
Two twisted: Optically active double helices were synthesized through a twist-sense bias induced by a chiral phosphine ligand on one of the complementary metallostrands followed by a ligand-exchange reaction with an achiral bidentate ligand, which replaces the chiral ligand, to bridge the two strands. Furthermore, the double helices can efficiently catalyze asymmetric cyclopropanation.



Self-Assembly

L. Shi, D. Lundberg, D. G. Musaev,
F. M. Menger* **5889–5891**

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

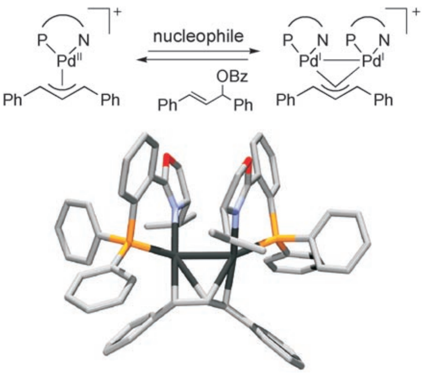


The long and short of it: Gemini surfactants with a non-Hückel diaza[12]annulene core have been synthesized (see picture). DFT computations give a minimum-energy conformation with alternate shorter and longer bonds, and with the two N substituents pointing away from each other. Studies on the aggregation of the molecules in water show they encounter packing difficulties, with no evidence for ring/ring interactions at the micelle surfaces.

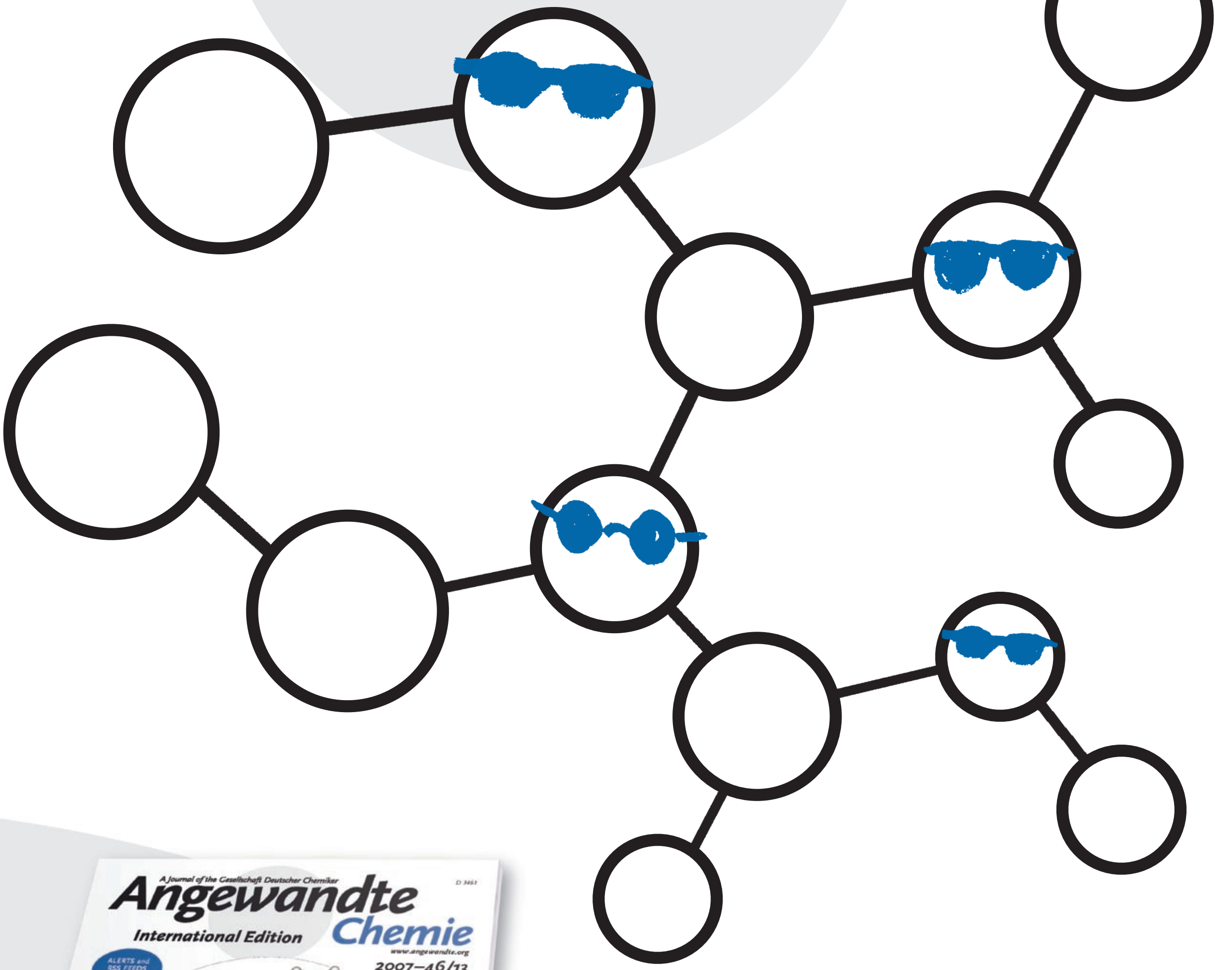
Homogeneous Catalysis

C. Markert, M. Neuburger, K. Kulicke,
M. Meuwly, A. Pfaltz* **5892–5895**

Palladium-Catalyzed Allylic Substitution: Reversible Formation of Allyl-Bridged Dinuclear Palladium(I) Complexes



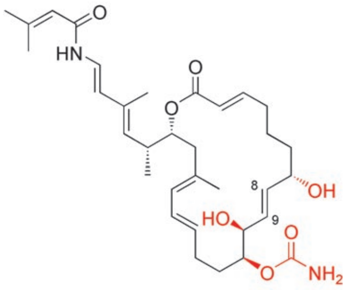
ESI-MS monitoring of the title reaction has led to the discovery that dinuclear allyl-bridged Pd^I complexes are formed reversibly in substantial amounts during catalysis (see scheme; Bz = benzoyl). The structure of one such complex was determined by X-ray analysis (see picture; P yellow, N blue, O red, Pd dark gray). Upon consumption of the starting materials a new dinuclear complex resulting from reductive C–Cl bond cleavage of CH_2Cl_2 was observed.



Natural Products

K. C. Nicolaou,* R. Guduru, Y.-P. Sun,
B. Banerji, D. Y.-K. Chen* **5896–5900**

Total Synthesis of the Originally Proposed and Revised Structures of Palmerolide A



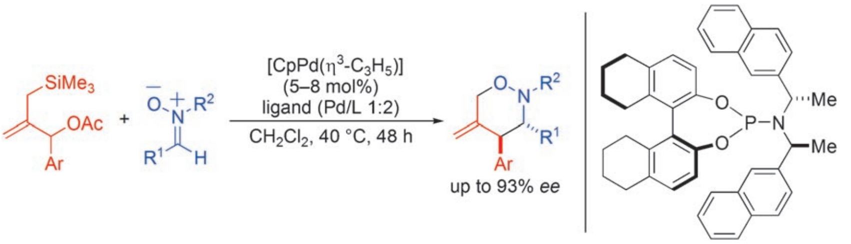
palmerolide A (revised structure)

In the palm of your hand: Total syntheses of the originally proposed and revised structures of the marine antitumor agent palmerolide A (see picture, originally proposed structure had opposite configurations at the positions indicated in red) were accomplished through a modular strategy that features a ring-closing metathesis to stereoselectively form the C8=C9 bond and concurrently form the macrocycle.

Asymmetric Catalysis

R. Shintani,* S. Park, W.-L. Duan,
T. Hayashi* **5901–5903**

Palladium-Catalyzed Asymmetric [3+3] Cycloaddition of Trimethylenemethane Derivatives with Nitrones

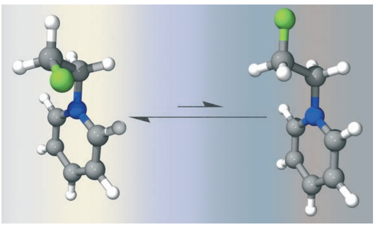


Rounding up the reactants: Functionalized 1,2-oxazines can be obtained in high yield by a palladium-catalyzed asymmetric [3+3] cycloaddition of trimethylenemethane derivatives with nitrones. The use of a modified phosphoramidite ligand has led to the formation of these compounds with high stereoselectivity (see scheme, Cp = cyclopentadienyl).

Conformation Analysis

N. E. J. Gooseman, D. O'Hagan,*
M. J. G. Peach, A. M. Z. Slawin,
D. J. Tozer,* R. J. Young **5904–5908**

An Electrostatic *Gauche* Effect in β-Fluoro- and β-Hydroxy-*N*-ethylpyridinium Cations

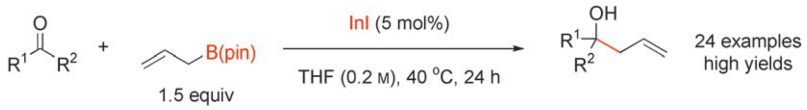


Left-leaning molecules: As shown by X-ray crystallography, NMR spectroscopy, and DFT calculations, *N*-(2-fluoroethyl)pyridinium (see picture; C gray, H white, N blue, F green) and related cations prefer a *gauche* conformation. In these systems, the *gauche* effect is attributed to an electrostatic interaction that does not involve hydrogen bonding.

Indium(I) Catalysis

U. Schneider, S. Kobayashi* **5909–5912**

Catalytic Activation of Pinacolyl Allylboronate with Indium(I): Development of a General Catalytic Allylboration of Ketones



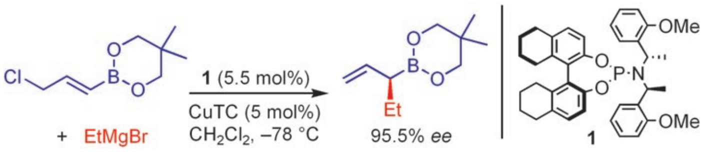
Have to B In it to win it! The unprecedented catalytic activation of a Group 13 metal reagent (boron) with a Group 13 metal catalyst in its low oxidation state (indium) was employed for the development of a general catalytic allylboration of ketones. This efficient C–C bond-forming reaction displays high functional group tolerance (see scheme; B(pin) = pinacolyl boronate).

Contents

Asymmetric Catalysis

L. Carosi, D. G. Hall* ______ **5913 – 5915**

Catalytic Enantioselective Preparation of α-Substituted Allylboronates: One-Pot Addition to Functionalized Aldehydes and a Route to Chiral Allylic Trifluoroborate Reagents

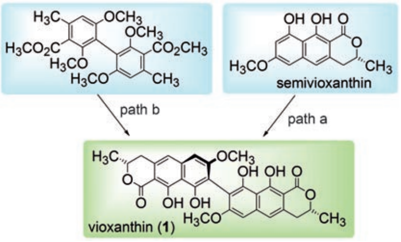


Well B-haved! Boronyl groups are fully compatible in the copper-catalyzed asymmetric alkylation with chiral phosphoramidites to afford acyclic α-substituted allylic boronate reagents (see scheme, CuTC = copper(I) thiophene-2-carboxylate). This represents the first highly enantioselective catalytic approach to these boronate compounds, which are useful reagents in synthesis.

Oxidative Phenol Coupling

S. E. Bode, D. Drochner, M. Müller* ______ **5916 – 5920**

Synthesis, Biosynthesis, and Absolute Configuration of Vioxanthin

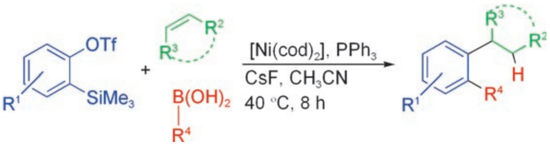


Seeing double: The biosynthesis (path a) of the biarylic compound vioxanthin (**1**) by regio- and stereoselective intermolecular oxidative phenol coupling is explored in *Penicillium citreoviride* and the first enantioselective total synthesis of **1** is described (path b). The absolute configuration of (*P*,*R*,*R*)-**1** and its stereoisomer (*M*,*R*,*R*)-**1** was elucidated by combining synthetic methods and feeding experiments with ^{13}C-labeled substrates.

Multicomponent Reactions

T. T. Jayanth, C.-H. Cheng* _ **5921 – 5924**

Nickel-Catalyzed Coupling of Arynes, Alkenes, and Boronic Acids: Dual Role of the Boronic Acid



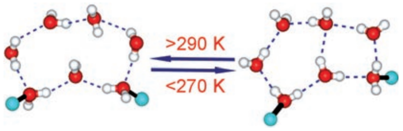
Taking on a second job: Nickel catalyzes the three-component coupling of arynes, alkenes, and boronic acids in very high yields under mild conditions. The boronic acid also acts as the proton source in this reaction. cod = 1,5-cyclooctadiene

Water Clusters

M. H. Mir, J. J. Vittal* ______ **5925 – 5928**

Phase Transition Accompanied by Transformation of an Elusive Discrete Cyclic Water Heptamer to a Bicyclic $(H_2O)_7$ Cluster

Trapped, then transformed: A discrete cyclic water heptamer with a twisted nonplanar conformation is trapped inside a 3D coordination polymeric crystal lattice with diamondoid topology. When a single crystal is cooled from 296 K to 223 K, it undergoes a phase transition accompanied by structural transformation of the cyclic water heptamer to a bicyclic structure (see scheme; Cu blue, O red, H white).



An unexpected acceleration of the insertion of terminal alkynes into the S–Pt bond of complexes **1** was observed when an *o*-halogen substituent was present in the SAr moiety (see scheme). The reaction rates for G = *o*-Cl, *o*-Br, or *o*-I were much greater than for electron-donating or electron-withdrawing groups. This "*o*-halogen effect" was also found to be relevant to the Pd-catalyzed addition of $(ArS)_2$ to alkynes.

Insertion Reactions

H. Kuniyasu,* F. Yamashita, J. Terao, N. Kambe* ______ **5929 – 5933**

Definitive Evidence for the Insertion of Terminal Alkynes into ArylS–Pt Bonds: "*o*-Halogen Effect" in Stoichiometric and Catalytic Reactions

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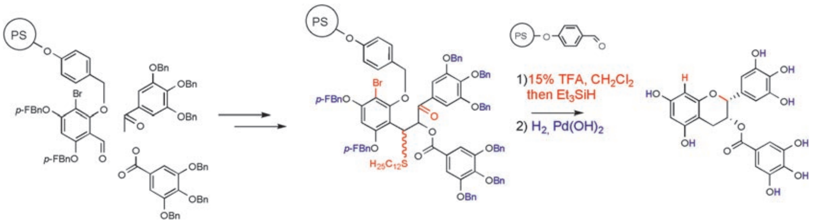


Without a trace... The natural product epigallocatechin gallate (see scheme, right) and a library of derivatives were synthesized on a solid phase. Reductive etherification upon the release of the α-acyloxy ketone intermediate from the resin provided the desired epicatechin derivatives. Bn = benzyl, PS = polystyrene, TFA = trifluoroacetic acid.

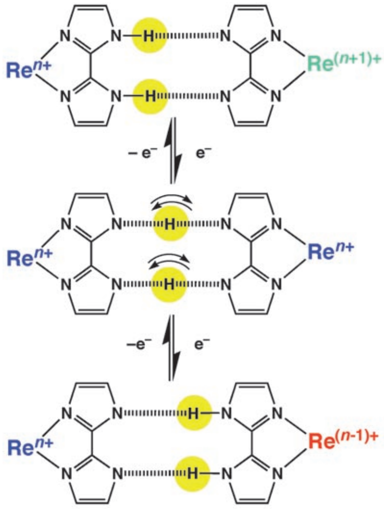
Diversity-Oriented Synthesis

H. Tanaka, H. Miyoshi, Y.-C. Chuang, Y. Ando, T. Takahashi* ______ **5934 – 5937**

Solid-Phase Synthesis of Epigallocatechin Gallate Derivatives

---

Di-Re straits: Synchronized motion of protons and electrons, as shown in the scheme, has been observed in a hydrogen-bonded Re dimer complex. The mixed-valence states obtained by electrochemical redox reactions are stabilized by proton transfer within the dual hydrogen-bonding site between 2,2′-biimidazolate ligands.



Proton–Electron Transfer

M. Tadokoro,* T. Inoue, S. Tamaki, K. Fujii, K. Isogai, H. Nakazawa, S. Takeda, K. Isobe, N. Koga, A. Ichimura, K. Nakasuji ______ **5938 – 5942**

Mixed-Valence States Stabilized by Proton Transfer in a Hydrogen-Bonded Biimidazolate Rhenium Dimer

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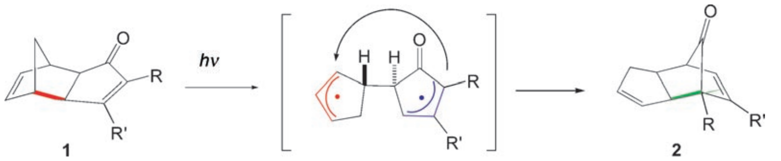


The bis-allylic nature of the diradical intermediate is the basis of a novel photochemical rearrangement of cycloadducts **1**, which are easily obtained by intermolecular Pauson–Khand reaction of norbornadiene with alkynes, to tricyclo[5.2.1.0^{2,6}]deca-3,8-dien-10-ones **2** in good yields. This photorearrangement tolerates a wide variety of functional groups.

Photorearrangement

A. Lledó, J. Benet-Buchholz, A. Solé, S. Olivella, X. Verdaguer,* A. Riera* ______ **5943 – 5946**

Photochemical Rearrangements of Norbornadiene Pauson–Khand Cycloadducts

Contents

Carbenoid Compounds

T. Cantat, X. Jacques, L. Ricard,
X. F. Le Goff, N. Mézailles,
P. Le Floch* ____________ **5947 – 5950**

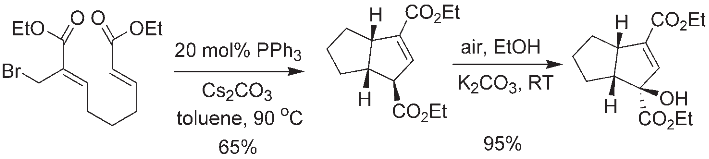
From a Stable Dianion to a Stable Carbenoid

Robust, but reactive: The first example of a Li/Cl carbenoid that is stable at room temperature has been prepared by mild oxidation of a geminal dianion (see scheme). The electronic reasons behind this unusual thermal stability are presented on the basis of DFT calculations. The reactivity of this carbenoid was investigated in the formation of a palladium carbene complex.

Intramolecular Cyclization

L.-W. Ye, X.-L. Sun, Q.-G. Wang,
Y. Tang* ____________ **5951 – 5954**

Phosphine-Catalyzed Intramolecular Formal [3+2] Cycloaddition for Highly Diastereoselective Synthesis of Bicyclo[*n*.3.0] Compounds

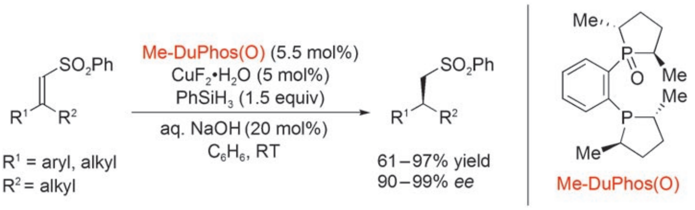


Two rings for the price of one: A catalytic intramolecular ylide annulation has been developed for the construction of bicyclo[*n*.3.0] ring systems with three continuous stereogenic centers in a single manipulation. The highly diastereoselective formation of the products and the potential for further facile chemical transformations (see scheme) make this method potentially useful in organic synthesis.

Asymmetric Catalysis

J.-N. Desrosiers,
A. B. Charette* ____________ **5955 – 5957**

Catalytic Enantioselective Reduction of β,β-Disubstituted Vinyl Phenyl Sulfones by Using Bisphosphine Monoxide Ligands

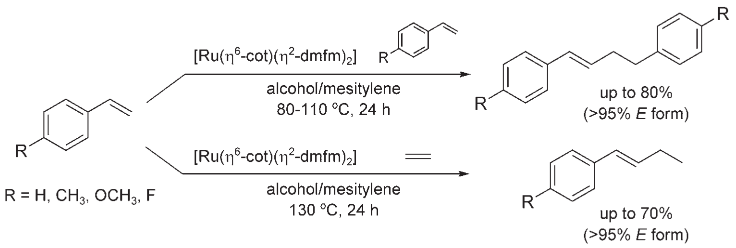


Synthesis of chiral sulfones: A copper–phosphine complex efficiently provided optically active alkyl phenyl sulfones by hydrosilylation at room temperature. The reduction of β,β-disubstituted vinyl sulfones in the presence of the Me-DuPhos monoxide ligand lead to excellent enantiomeric excesses and high yields (see scheme). The prepared chiral sulfones were desulfonylated and subjected to Julia olefination conditions.

Homogeneous Catalysis

T. Kondo,* D. Takagi, H. Tsujita, Y. Ura,
K. Wada, T. Mitsudo ______ **5958 – 5961**

Highly Selective Dimerization of Styrenes and Linear Co-dimerization of Styrenes with Ethylene Catalyzed by a Ruthenium Complex



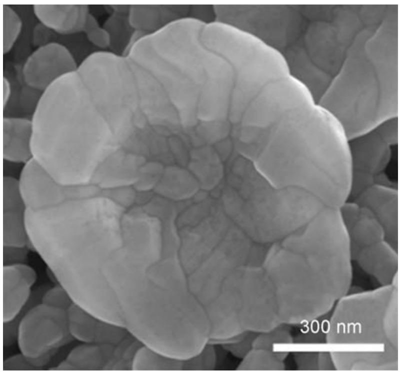
Heads you win: An unusual head-to-head dimerization of styrenes has been developed using the zero-valent ruthenium catalyst [Ru(η^6-cot)(η^2-dmfm)$_2$] (cot = 1,3,5-cyclooctatriene, dmfm = dimethyl fumarate) in the presence of primary alcohols to give the homo-dimer in high regio- and stereoselectivity. The catalyst system is also effective for the selective co-dimerization of styrenes with ethylene to give the co-dimer in high yield.

Nanostructures

K. S. Krishna, U. Mansoori, N. R. Selvi, M. Eswaramoorthy* ______ **5962 – 5965**

Form Emerges from Formless Entities: Temperature-Induced Self-Assembly and Growth of ZnO Nanoparticles into Zeptoliter Bowls and Troughs

Shaping up: Unusual bowl-, trough-, and ring-shaped structures result from the temperature-induced self-assembly of nanoparticles (see picture for bowl). The obtained ZnO bowls and rings also serve as a template to make metal or metal oxide replicas. The tiny bowls are envisaged not only to hold fluids of ultralow volume, but also to grow nanoparticles, immobilize biomolecules, and screen submicrometer-sized particles.

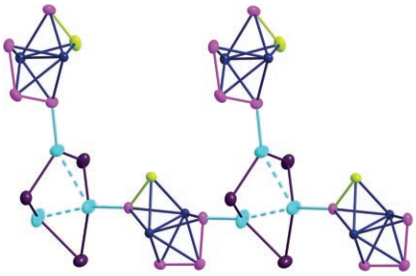


Coordination Polymers

L. J. Gregoriades, G. Balázs, E. Brunner, C. Gröger, J. Wachter, M. Zabel, M. Scheer* ______ **5966 – 5970**

An Unusual Building Block for Supramolecular Aggregates: The Mixed Group 15/16 Element Ligand Complex $[(\mathrm{Cp^*Mo})_2(\mu,\eta^3\text{-}\mathrm{P}_3)(\mu,\eta^2\text{-}\mathrm{PS})]$

Unusual suspect: The complex $[(\mathrm{Cp^*Mo})_2(\mu,\eta^3\text{-}\mathrm{P}_3)(\mu,\eta^2\text{-}\mathrm{PS})]$ reacts with CuI and $\mathrm{Ag[Al\{OC(CF_3)_3\}_4]}$ to form two novel linear polymers (see structure of CuI derivative; Cu light blue, I violet, Mo blue, P pink, S yellow). Even with X-ray crystallographic data available, the fact that the sulfur atoms in these polymers do not coordinate to the Group 11 metal centers could only be established with the help of ^{31}P MAS NMR spectroscopy. $\mathrm{Cp^*} = \mathrm{C_5Me_5}$



Asymmetric Catalysis

J. Bayardon, J. Holz, B. Schäffner, V. Andrushko, S. Verevkin, A. Preetz, A. Börner* ______ **5971 – 5974**

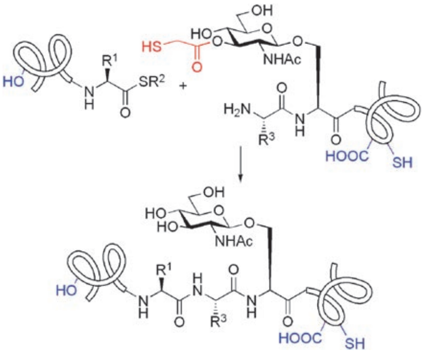
Propylene Carbonate as a Solvent for Asymmetric Hydrogenations

A penny saved is a penny earned: The use of propylene carbonate as the solvent in iridium-catalyzed hydrogenations of nonfunctionalized olefins allows efficient catalyst recycling through the formation of two-phase mixtures with nonpolar solvents such as *n*-hexane. In the picture, the hydrogenated tetrahydronaphthalene derivative is extracted into the hydrocarbon phase.

Glycopeptide Synthesis

S. Ficht, R. J. Payne, A. Brik, C.-H. Wong* ______ **5975 – 5979**

Second-Generation Sugar-Assisted Ligation: A Method for the Synthesis of Cysteine-Containing Glycopeptides



Sweet ligations: A second-generation sugar-assisted ligation is described that incorporates a sugar moiety with an ester-linked thiol auxiliary. Efficient auxiliary removal leads to native glycopeptides without the use of protecting groups. Extended glycopeptides also facilitate efficient ligation reactions by this method, therefore making it possible to scan a target sequence until a synthetically viable ligation junction is found.

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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