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:

*S. T. Scroggins, Y. Chi, J. M. J. Fréchet**
Polarity-Directed One-Pot Asymmetric Cascade Reactions Mediated by Two Catalysts in an Aqueous Buffer

D. Loffreda, F. Delbecq, F. Vigné, P. Sautet*
Fast Prediction of Selectivity in Heterogeneous Catalysis from Extended Brønsted–Evans–Polanyi Relations: A Theoretical Insight

*P. Eisenberger, R. O. Ayinla, J. M. P. Lauzon, L. L. Schafer**
Ta–Amidate Complexes for the Hydroaminoalkylation of Secondary Amines: Enhanced Substrate Scope and Enantioselective Chiral Amine Synthesis

*T. Ichino, S. M. Villano, A. J. Gianola, D. J. Goebbert, L. Velarde, A. Sanov, S. J. Blanksby, X. Zhou, D. A. Hrovat, W. T. Borden, W. C. Lineberger**
The Lowest Singlet and Triplet States of the Oxyallyl Diradical

*S. Joseph, M. Hamberger, F. Mutzbauer, O. Härtl, M. Meier, N. Korber**
Chemistry with Bare Silicon Clusters in Solution: A Transition Metal Complex of a Polysilicide Anion

*M. H. Kox, K. F. Domke, J. P. Day, G. Rago, E. Stavitski, M. Bonn, B. M. Weckhuysen**
Label-Free Chemical Imaging of Catalytic Solids by Coherent Anti-Stokes Raman Scattering and Synchrotron-Based Infrared Microscopy

*M. Griesser, D. Neshchadin, K. Dietliker, N. Moszner, R. Liska, G. Gescheidt**
Decisive Reaction Steps at Initial Stages of Photoinitiated Radical Polymerizations

*P. Ceroni, G. Bergamini, V. Balzani**
Old Molecules, New concepts: $[Ru(bpy)_3]^{2+}$ as a Molecular Encoder–Decoder

Author Profile

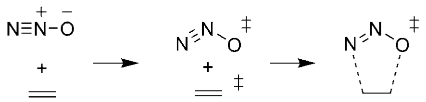
"The most significant advances in chemistry of this century have been the advances made in organocatalysis. The biggest challenge facing chemists is to regain acceptance in the general public. …"
This and more about Gerhard Hilt can be found on page 7964.

Books

Highlights

1,3-Dipolar Cycloadditions

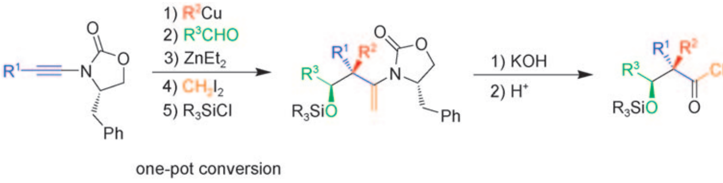
Reaction rates of 1,3-dipolar cycloadditions correlate closely with the energy required to distort the 1,3-dipole and dipolarophile to the transition-state geometry (see scheme). A bridge can be built connecting these new findings to the traditional frontier molecular orbital theory, which was and still is enormously successful in the rationalization of 1,3-dipolar cycloadditions.



Stereoselective Synthesis

D. C. Koester, D. B. Werz* **7971 – 7973**

Creating Aldols Differently: How to Build up Aldol Products with Quaternary Stereocenters Starting from Alkynes

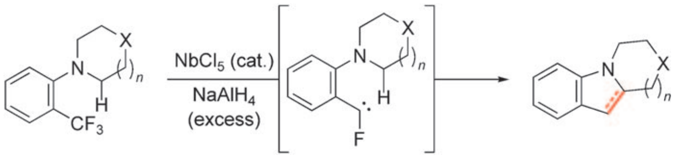


New approaches! Sometimes there is no harm in questioning established protocols and to think about completely new strategies. Here a new method makes possible the construction of all-carbon quaternary stereocenters within aldol patterns in a sequential, one-pot procedure starting from simple compounds such as alkynes (see scheme).

C–F Bond Activation

T. G. Driver* **7974 – 7976**

Niobium-Catalyzed Activation of Aryl Trifluoromethyl Groups and Functionalization of C–H Bonds: An Efficient and Convergent Approach to the Synthesis of N-Heterocycles



Activate that bond! The functionalization of the CF_3 groups is an ongoing synthetic challenge owing to the inert nature of the C–F bond. The aryl trifluoromethyl group can be reduced by a low-valent niobium catalyst to produce a carbenoid that inserts into a C(sp^3)–H bond to produce complex, functionalized N-fused indoles (see scheme).

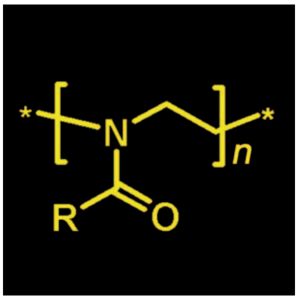
Reviews

Poly(2-oxazoline)s

R. Hoogenboom* **7978 – 7994**

Poly(2-oxazoline)s: A Polymer Class with Numerous Potential Applications

Versatile polymers: Poly(2-oxazoline)s have recently gained renewed interest because of their potential use as biomaterials, their thermoresponsive behavior, and the easy access to amphiphilic structures for self-assembly studies. These new trends are discussed together with recent efforts to combine poly(2-oxazoline)s with click chemistry.



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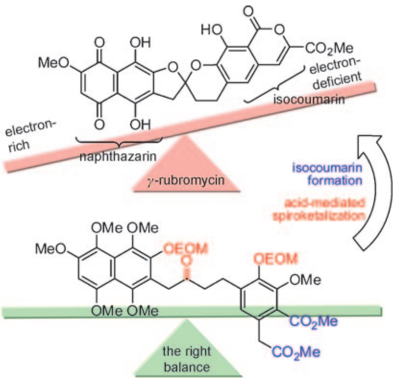
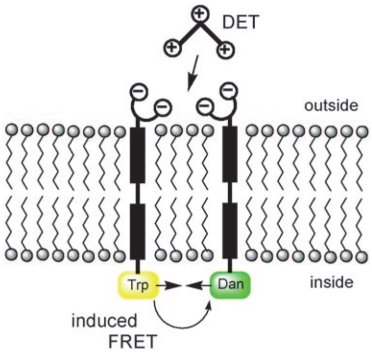
Communications

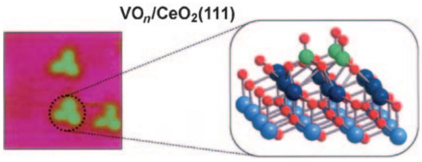


Balancing act: The correct balance of electronic factors in the naphthazarin and isocoumarin fragments facilitates the acid-mediated spiroketalization step to afford the key densely functionalized spiroketal (see picture; EOM = ethoxymethyl) in the formal synthesis of (±)-γ-rubromycin. A novel regioselective allyloxylation/Claisen rearrangement of 2-azido-1,4-naphthoquinone provides access to the highly oxygenated naphthazarin fragment.

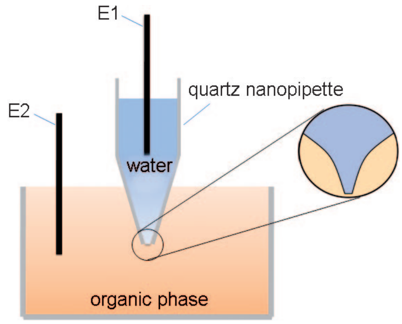
I saw the sign: An artificial system allows messenger-induced transmembrane signaling. External addition of a primary messenger molecule (DET, see picture) leads to formation of a heterodimeric complex of transmembrane units bearing tryptophan–dansyl (Trp–Dan) donor–acceptor pairs, which in turn stimulates a strong FRET on the opposite side of the membrane.



On top of old ceria: Vanadyl-terminated monomers, trimers (see picture), and oligomers form on a $CeO_2(111)$ surface, and their atomic structure is resolved using a combination of high-level experimental and theoretical results. Ceria surfaces stabilize vanadia species in a +5 oxidation state, which wet and chemically reduce the ceria surface and probably play a crucial role in the reactivity of ceria-supported vanadia in oxidation reactions.



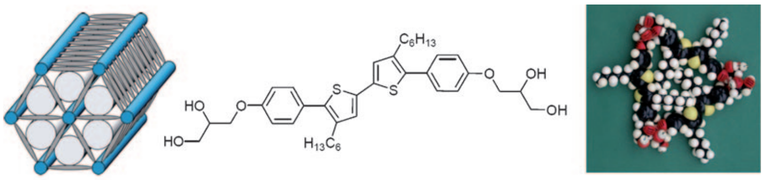
Keeping up: The fastest kinetic data for ion transfer at a liquid/liquid interface were evaluated by nanopipette voltammetry. The steady-state voltammograms can be explained by theoretical models. In previous electrochemical measurements the systematic underestimation of k^0 is probably a result of inefficient mass transfer to the relatively large interface.



Liquid Crystals

X. Cheng,* X. Dong, G. Wei, M. Prehm,
C. Tschierske* ———— **8014 – 8017**

Liquid-Crystalline Triangle Honeycomb Formed by a Dithiophene-Based X-Shaped Bolaamphiphile

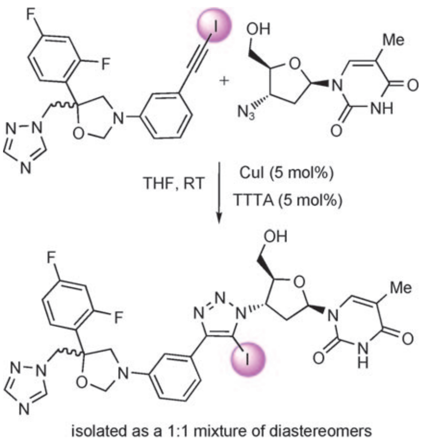


Soft supramolecular triangles: The molecule shown displays a new liquid-crystalline phase formed by a periodic array of triangular cylinders. The cylinders are fused to form a honeycomb by hydrogen-bonding networks running along the vertices, and the cells are filled by molten alkyl chains. The thickness of the walls separating the compartments is equal to the width of the π-conjugated rods.

Click Chemistry

J. E. Hein,* J. C. Tripp, L. B. Krasnova,
K. B. Sharpless, V. V. Fokin* **8018 – 8021**

Copper(I)-Catalyzed Cycloaddition of Organic Azides and 1-Iodoalkynes

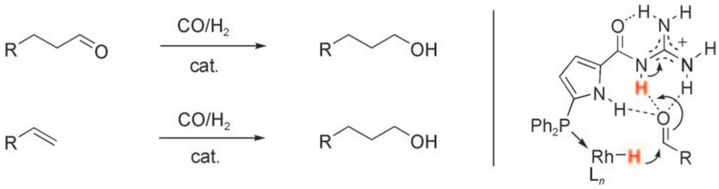


High fidelity: 1-Iodoalkynes react rapidly and selectively with organic azides in the presence of copper(I) catalysts (see scheme; TTTA = tris((1-*tert*-butyl-1*H*-1,2,3-triazolyl)methyl)amine). The reaction is compatible with many functional groups and solvents, and 5-iodotriazole products were usually obtained in excellent yield. These products can be further functionalized to give fully substituted 1,2,3-triazoles.

Catalytic Hydrogenation

L. Diab, T. Šmejkal, J. Geier,
B. Breit* ———— **8022 – 8026**

Supramolecular Catalyst for Aldehyde Hydrogenation and Tandem Hydroformylation–Hydrogenation



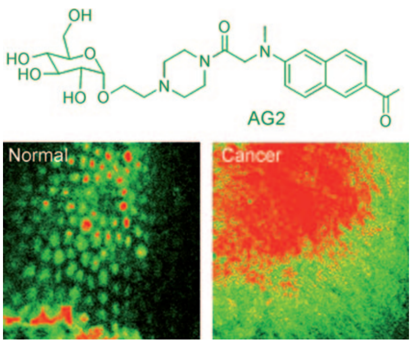
The chemoselective reduction of aldehydes and the tandem hydroformylation–hydrogenation of terminal alkenes are possible with a supramolecular catalyst that operates by a novel mechanism involving substrate activation by hydrogen bonding and subsequent metal–ligand bifunctional hydrogenation (see scheme).

Fluorescent Probes

Y. S. Tian, H. Y. Lee, C. S. Lim, J. Park,
H. M. Kim, Y. N. Shin, E. S. Kim,
H. J. Jeon, S. B. Park,*
B. R. Cho* ———— **8027 – 8031**

A Two-Photon Tracer for Glucose Uptake

It takes two: Two-photon tracers (AG1, AG2) have been developed that can be excited by 780 nm fs laser pulses, can be easily loaded into cancer cells and tissues, show high photostability and negligible toxicity, and can visualize glucose uptake in living cells and tissues by two-photon microscopy (TPM). Moreover, AG2 can screen anticancer agents in cancer cells and cancer tissues at 75–150 mm depth by TPM.

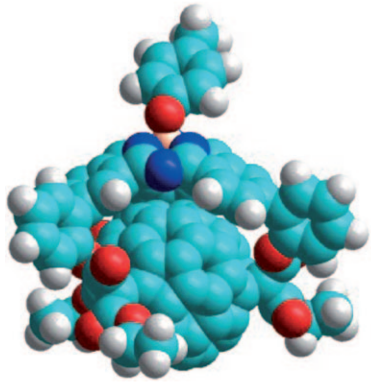


Electron Transfer

D. González-Rodríguez, E. Carbonell, D. M. Guldi,* T. Torres* ___ 8032 – 8036

Modulating Electronic Interactions between Closely Spaced Complementary π Surfaces with Different Outcomes: Regio- and Diastereomerically Pure Subphthalocyanine–C_{60} Tris Adducts

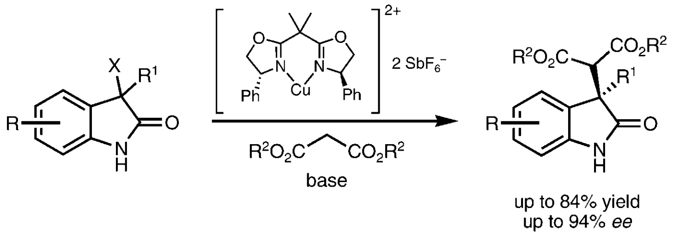
Tightly coupled, regio- and diastereomerically pure subphthalocyanine–C_{60} dyads (see space-filling depiction; B orange, C light blue, H gray, N blue, O red), tethered by means of a tris-addition reaction, can follow different mechanisms on photoexcitation (electron transfer or energy transfer), depending on the spacing between the two complementary π surfaces.



Asymmetric Catalysis

S. Ma, X. Han, S. Krishnan, S. C. Virgil, B. M. Stoltz* ___ 8037 – 8041

Catalytic Enantioselective Stereoablative Alkylation of 3-Halooxindoles: Facile Access to Oxindoles with C3 All-Carbon Quaternary Stereocenters

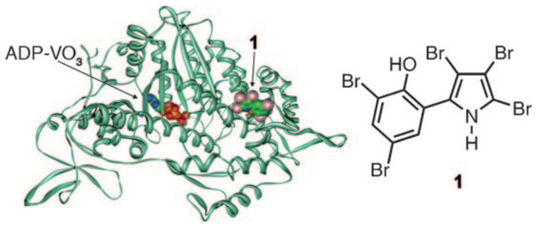


From 2 to 1! Racemic tertiary halooxindoles proceed to enantioenriched oxindoles bearing all-carbon quaternary stereocenters as a result of a catalytic enantioselective stereoablative process (see scheme). The application of this procedure allows for the rapid asymmetric construction of biologically significant alkaloid core motifs.

Myosin Inhibition

R. Martin, A. Jäger, M. Böhl, S. Richter, R. Fedorov, D. J. Manstein, H. O. Gutzeit, H.-J. Knölker* ___ 8042 – 8046

Total Synthesis of Pentabromo- and Pentachloropseudilin, and Synthetic Analogues—Allosteric Inhibitors of Myosin ATPase

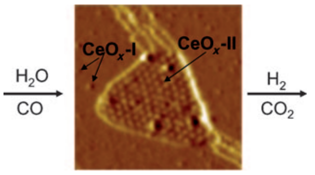


Stopping myo: The total syntheses of the title compounds have been achieved using a highly efficient silver(I)-catalyzed cyclization of *N*-tosyl-homopropargylamines. The pseudilin derivatives represent a novel class of myosin inhibitors. A new allosteric binding pocket of the *Dictyostelium* myosin-2 motor domain has been identified for pentabromopseudilin (**1**) by using an X-ray crystal structure determination of the inhibitor–protein complex.

Heterogeneous Catalysis

J. A. Rodriguez,* J. Graciani, J. Evans, J. B. Park, F. Yang, D. Stacchiola, S. D. Senanayake, S. Ma, M. Pérez, P. Liu, J. F. Sanz, J. Hrbek ___ 8047 – 8050

Water-Gas Shift Reaction on a Highly Active Inverse CeO_x/Cu(111) Catalyst: Unique Role of Ceria Nanoparticles

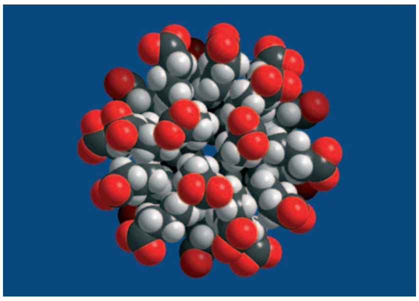


CeO takes charge: Ceria grows forming small islands on terraces (2–5 nm, CeO_x-I) and large islands on steps of a copper substrate (30–50 nm, CeO_x-II; see scheme; 100 × 100 nm^2). The resulting CeO_x/Cu(111) systems display an extraordinary water-gas shift activity and illustrate the role that an oxide can play in improving the performance of copper-based catalysts.

Nanoscale Assemblies

C. Schäffer, H. Bögge, A. Merca,
I. A. Weinstock, D. Rehder,
E. T. K. Haupt,* A. Müller* **8051 – 8056**

A Spherical 24 Butyrate Aggregate with a Hydrophobic Cavity in a Capsule with Flexible Pores: Confinement Effects and Uptake–Release Equilibria at Elevated Temperatures

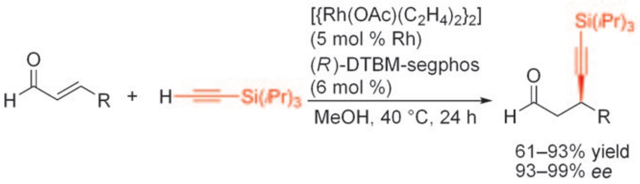


Forced interaction: The encapsulation of a large assembly of organic species—the 24 butyrate unit, which exhibits a remarkable central spherical hydrophobic cavity spanned by 72 H atoms—in a porous capsule (see picture) leads to interesting interactions between the butyrates under the confined conditions. The quarantine for the guests is lifted upon temperature increase: guests can easily leave and return.

Synthetic Methods

T. Nishimura,* T. Sawano,
T. Hayashi* **8057 – 8059**

Asymmetric Synthesis of β-Alkynyl Aldehydes by Rhodium-Catalyzed Conjugate Alkynylation

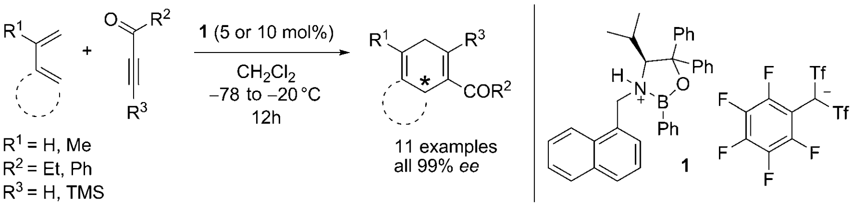


To the point: The rhodium-catalyzed asymmetric conjugate alkynylation of α,β-unsaturated aldehydes with triisopropylsilyl acetylene proceeded efficiently in methanol to give the β-alkynyl aldehydes in high yields with high enantioselectivity (see Scheme).

Asymmetric Catalysis

J. N. Payette,
H. Yamamoto* **8060 – 8062**

Cationic-Oxazaborolidine-Catalyzed Enantioselective Diels–Alder Reaction of α,β-Unsaturated Acetylenic Ketones

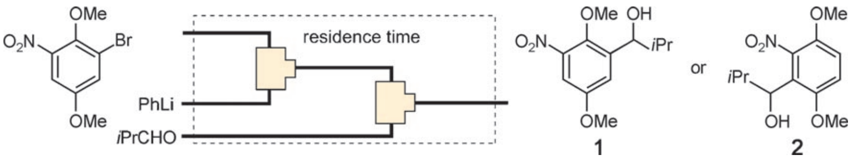


Yne also a good dienophile: The cationic oxazaborolidine **1** promoted the formation of Diels–Alder adducts between acetylenic ketones and both cyclic and acyclic dienes in excellent yield with 99 % *ee* (see scheme; Tf = trifluoromethanesulfonyl, TMS = trimethylsilyl). Importantly, high levels of asymmetric induction were also observed with dienophiles that lacked the typical hydrogen-bonding motif required for other oxazaborolidinium-mediated reactions.

Microreactors

A. Nagaki, H. Kim,
J. Yoshida* **8063 – 8065**

Nitro-Substituted Aryl Lithium Compounds in Microreactor Synthesis: Switch between Kinetic and Thermodynamic Control



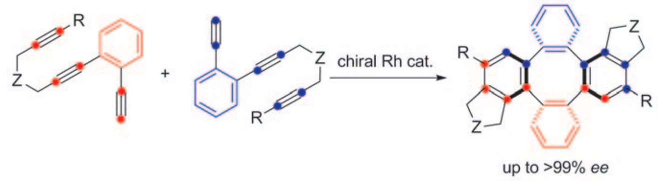
Be quick or take your time, depending on your goal: A microflow method for the generation and transformation of *o*-, *m*-, and *p*-nitro-substituted aryl lithium compounds enabled the selective use of either the kinetically or the thermodynamically preferred intermediate. In the example pictured, a residence time of 0.06 s at −48 °C led to the formation of **1**, whereas **2** was obtained exclusively when the residence time was extended to 63 s.

Contents

Annulated Rings

T. Shibata,* T. Chiba, H. Hirashima,
Y. Ueno, K. Endo ———— **8066 – 8069**

Catalytic Enantioselective Synthesis of Chiral Tetraphenylenes: Consecutive Inter- and Intramolecular Cycloadditions of Two Triynes

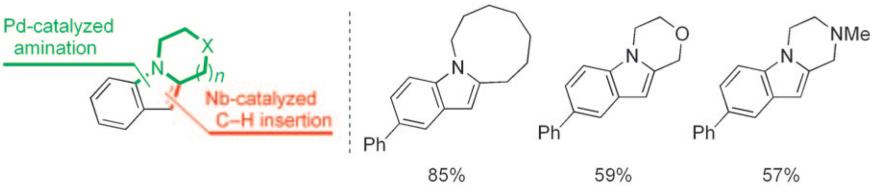


Triynes having a phenylene-bridged 1,5-diyne moiety were transformed into substituted tetraphenylenes by the title sequence. A cationic Rh–ligand species catalyzed this highly enantioselective reaction. This protocol is a new and easy approach to the construction of the tetraphenylene skeleton and enables an efficient asymmetric synthesis (see scheme; R = H; Z = NTs, $C(CO_2Me)_2$, O).

Synthetic Methods

K. Fuchibe, T. Kaneko, K. Mori,
T. Akiyama* ———— **8070 – 8073**

Expedient Synthesis of N-Fused Indoles: A C–F Activation and C–H Insertion Approach

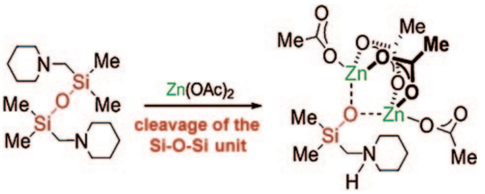


Easy does it: A wide range of N-fused indole skeletons, which are core structures of many biologically potent molecules, are successfully furnished by a niobium-catalyzed $C(sp^3)$–H insertion reaction (see picture). The precursors are readily prepared by a palladium-catalyzed amination reaction of bromotrifluorotoluenes with cyclic amines.

Siloxane Chemistry

C. Däschlein, J. O. Bauer,
C. Strohmann* ———— **8074 – 8077**

From the Selective Cleavage of the Si-O-Si Bond in Disiloxanes to Zwitterionic, Water-Stable Zinc Silanolates

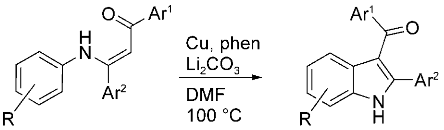


Zinc salts do Si–O's: Organosilicon chemistry is crucially determined by the high stability and chemical resistance of the Si-O-Si bond. The formation and structural existence of water-stable metallasilanolates demonstrate both the possibility to cleave the Si-O-Si bond with simple zinc compounds under mild conditions as well as the existence of such molecular metallasilanolates in the presence of water.

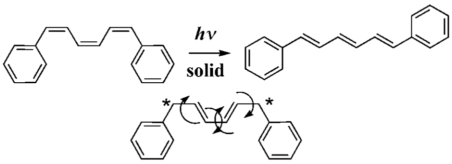
Synthesis Design

R. Bernini, G. Fabrizi, A. Sferrazza,
S. Cacchi* ———— **8078 – 8081**

Copper-Catalyzed C–C Bond Formation through C–H Functionalization: Synthesis of Multisubstituted Indoles from *N*-Aryl Enaminones



A variety of functionalities, including the whole range of halogen substituents, are tolerated in the title reaction, an intramolecular approach for the construction of a multisubstituted indole skeleton from readily available enaminones (see scheme; phen = 1,10-phenanthroline). The indole products are also prepared directly in high yield from α,β-ynones and primary amines.



Disrotatory bicycle pedals: Irradiation of the title compound in the solid state gives the all-*trans* isomer directly in a crystal-to-crystal reaction. This threefold *cis*–*trans* photoisomerization is proposed to proceed by a two-stage mechanism that is consistent with two simultaneous bicycle-pedal processes occurring in disrotatory fashion about the central bond.

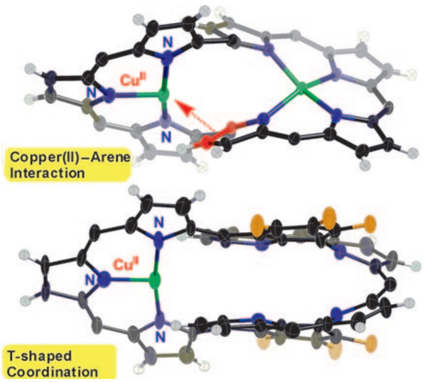
Trienes

J. Saltiel,* D. Papadimitriou,
T. S. R. Krishna, Z.-N. Huang,
G. Krishnamoorthy, S. Laohhasurayotin,
R. J. Clark ________ **8082 – 8085**

Photoisomerization of All-*cis*-1,6-diphenyl-1,3,5-hexatriene in the Solid State and in Solution: A Simultaneous Three-Bond Twist Process

---

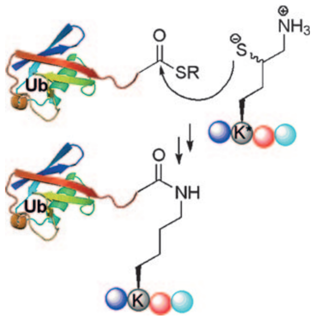
T for two: The use of [32]heptaphyrin ligands allows the synthesis of T-shaped three-coordinate copper(II) complexes. For a relatively flexible nonfused [32]heptaphyrin ligand, a copper(II)–arene interaction supplements the coordination deficiency, whereas a highly rigid quadruply N-fused heptaphyrin ligand allows the formation of a three-coordinate copper(II) complex with T-shaped planar symmetry (see picture).



Expanded Porphyrins

S. Saito, K. Furukawa,
A. Osuka* ________ **8086 – 8089**

T-Shaped Three-Coordinate Copper(II) Heptaphyrin Complexes

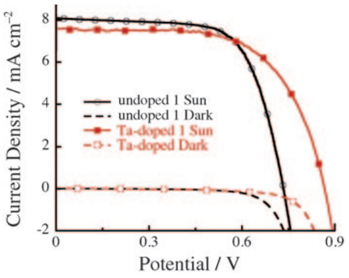


Loving kiss of death: A highly efficient and chemoselective method for ubiquitylation of peptides using δ-mercaptolysine to assist isopeptide formation between the ε-NH_2 of the lysine residue and the activated C-terminal glycine of ubiquitin (Ub) is presented.

Protein Modifications

K. S. Ajish Kumar, M. Haj-Yahya,
D. Olschewski, H. A. Lashuel,
A. Brik* ________ **8090 – 8094**

Highly Efficient and Chemoselective Peptide Ubiquitylation



Nanowires in the sun: Hydrothermal synthesis yields homogeneously tantalum-doped titania nanowire arrays on transparent conducting oxide substrates. The methodology should allow doping of titania nanowires with different transition metals. This advance in materials synthesis translates into enhanced device performance, as demonstrated by dye-sensitized solar cells with very high open-circuit photovoltage (see picture).

Nanowire Solar Cells

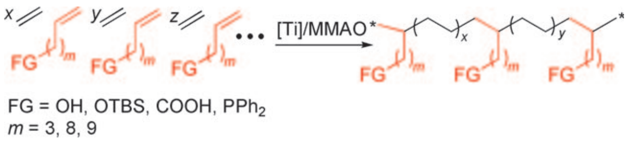
X. J. Feng, K. Shankar, M. Paulose,
C. A. Grimes* ________ **8095 – 8098**

Tantalum-Doped Titanium Dioxide Nanowire Arrays for Dye-Sensitized Solar Cells with High Open-Circuit Voltage

Olefin Polymerization

X.-H. Yang, C.-R. Liu, C. Wang, X.-L. Sun, Y.-H. Guo, X.-K. Wang, Z. Wang, Z. Xie, Y. Tang* ______ **8099 – 8102**

$[O^-NS^R]TiCl_3$-Catalyzed Copolymerization of Ethylene with Functionalized Olefins

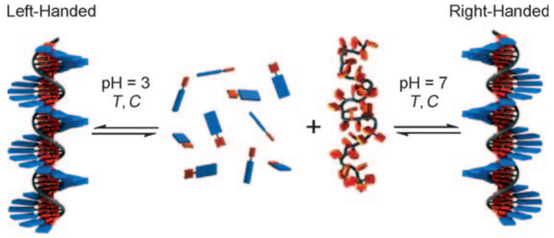


All zipped up: Titanium complexes are designed as efficient catalysts for the copolymerization of ethylene with polar olefins, such as ω-alkenol and ω-alkenoic acid. An organophosphine catalyst can be zippered on the polyethylene (see scheme; TBS = *tert*-butyldimethylsilyl, FG = functional group, MMAO = modified methylaluminoxane) to form an efficient and recoverable initiator for [3+2] cycloaddition.

Host–Guest Systems

P. G. A. Janssen, A. Ruiz-Carretero, D. González-Rodríguez, E. W. Meijer, A. P. H. J. Schenning* ______ **8103 – 8106**

pH-Switchable Helicity of DNA-Templated Assemblies

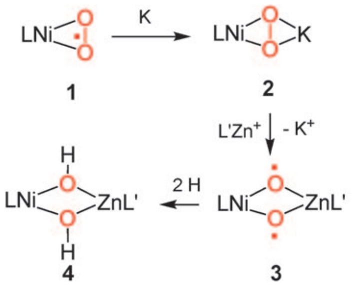


Coming together: Oligothymine is used as a template to self-assemble complementary nonchiral naphthalene guests. Depending on the protonated state of the guest, left- or right-handed DNA-templated self-assemblies are formed (see picture). The templated assembly processes were studied in detail with temperature-dependent circular dichroism and UV/Vis spectroscopy.

Dioxygen Activation

S. Yao, Y. Xiong, M. Vogt, H. Grützmacher, C. Herwig, C. Limberg,* M. Driess* ______ **8107 – 8110**

O–O Bond Activation in Heterobimetallic Peroxides: Synthesis of the Peroxide $[LNi(\mu,\eta^2:\eta^2\text{-}O_2)K]$ and its Conversion into a Bis(μ-Hydroxo) Nickel Zinc Complex

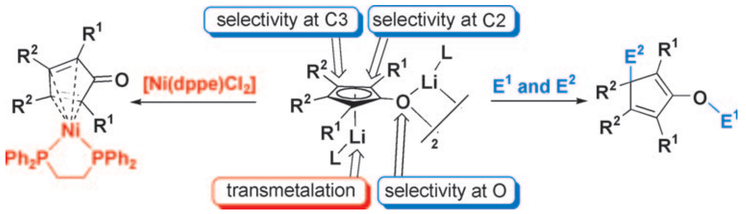


O_2 takes activation lessons: O–O bond activation can be achieved depending on the nature of the heterometal M in $[LNi(\mu,\eta^2:\eta^2\text{-}O_2)M]$ complexes. The reduction of the nickel(II) superoxide **1** with potassium affords the peroxide **2**, which, upon replacement of the K^+ ion in **2** by the non-redox-active $L'Zn^+$ ion, leads to transient **3**, which subsequently abstracts two solvent hydrogen atoms to give the heterobimetallic complex **4**. L, L′ = β-diketiminates.

Dianion Chemistry

L. Liu, W.-X. Zhang, C. Wang, C. Y. Wang, Z. Xi* ______ **8111 – 8114**

Isolation, Structural Characterization, and Synthetic Application of Oxycyclopentadienyl Dianions

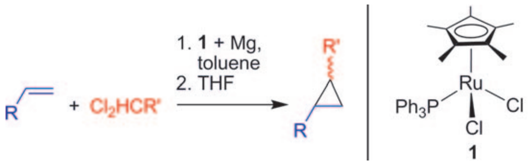


A new building block? Lithium complexes of novel oxycyclopentadienyl dianions were isolated in high yield and characterized by X-ray crystallography. Cyclopentadienes and transition-metal complexes could be prepared from these intriguing intermediates (see scheme).

Synthetic Methods

K. Thommes, G. Kiefer, R. Scopelliti,
K. Severin* ______________ 8115 – 8119

Olefin Cyclopropanation by a Sequential Atom-Transfer Radical Addition and Dechlorination in the Presence of a Ruthenium Catalyst

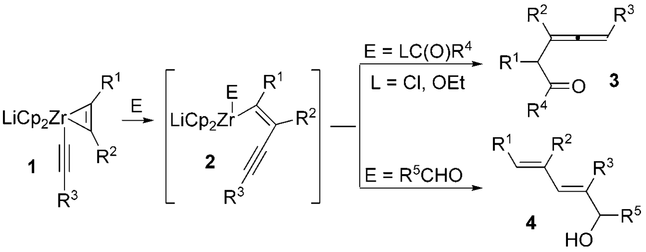


Without diazo: The reductive coupling of olefins with dichloro compounds in the presence of a ruthenium catalyst and magnesium gives cyclopropanes in good yield (see scheme).

Organozirconate Chemistry

C. Xi,* X. Yan, W. You,
T. Takahashi* ______________ 8120 – 8123

Coupling Reactions of Zirconate Complexes Induced by Carbonyl Compounds

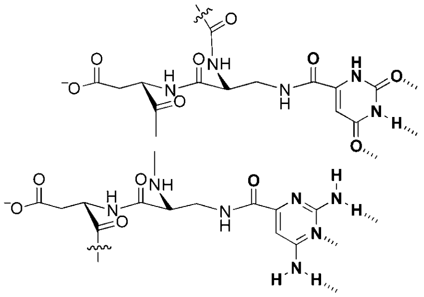


Multifaceted organozirconate: The novel coupling reaction of organozirconates **1** and carbonyl compounds (through intermediate **2**) selectively affords highly substituted allene **3** and dienol **4** derivatives.

Oligopeptides

X. Zhang,
R. Krishnamurthy* ______________ 8124 – 8128

Mapping the Landscape of Potentially Primordial Informational Oligomers: Oligo-dipeptides Tagged with Orotic Acid Derivatives as Recognition Elements

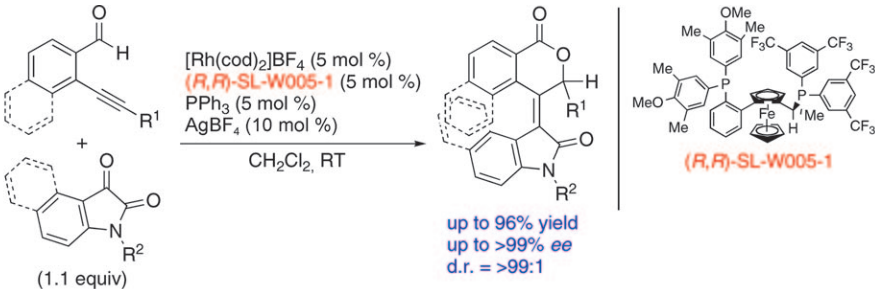


Partner up! Base-pairing properties of oligo-dipeptides tagged with orotic acid and its 2,4-diamino counterpart (see structure) are found to be consistent with previously observed correlations between ΔpK_a values and the pairing strength of complementary bases. The combined results provide a general justification for anticipating the base-pairing propensity of a recognition element based on its pK_a value and the pH of the medium.

Asymmetric Catalysis

D. Hojo, K. Noguchi,
K. Tanaka* ______________ 8129 – 8132

Synthesis of Chiral Tetrasubstituted Alkenes by an Asymmetric Cascade Reaction Catalyzed Cooperatively by Cationic Rhodium(I) and Silver(I) Complexes



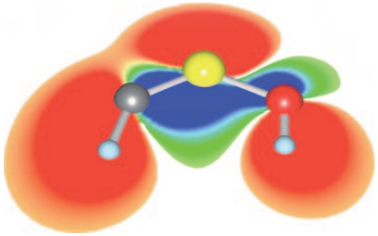
Fantastic four: Tetrasubstituted alkenes have been prepared with high enantioselectivity by the title transformation. This reaction was successfully applied to the enantio- and diastereoselective synthesis of tetrasubstituted helical alkenes possessing both central and helical chirality (see scheme).

Reactive Intermediates

P. R. Schreiner,* H. P. Reisenauer,
J. Romanski, G. Mloston* **8133 – 8136**

A Formal Carbon–Sulfur Triple Bond: H–C≡S–O–H

Extremely rare: A CS triple bond can be assigned to HCSOH, a new molecule prepared from $H_2C{=}S{=}O$ by a photochemical [1,3]H-shift. But does this formal description agree with analyses on the basis of IR vibrations, bond lengths, bond orders, molecular orbitals, and compliance constants? Molecules like this challenge and refine our current understanding of chemical bonding.

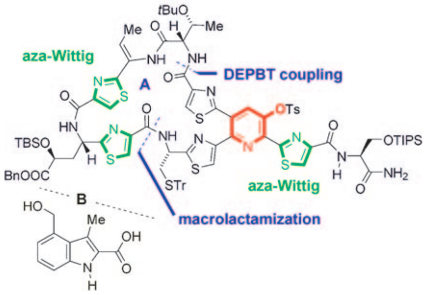


Natural Products

J.-Y. Lu, M. Riedrich, M. Mikyna,
H.-D. Arndt* **8137 – 8140**

Aza-Wittig-Supported Synthesis of the A Ring of Nosiheptide

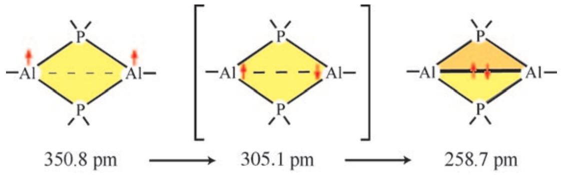
An array of aza-Wittig reactions: In the unique synthesis of the A ring of the potent thiopeptide antibiotic nosiheptide, mild aza-Wittig thiazole ring closure, a Sc^{III}-mediated regioselective ester hydrolysis, and a highly efficient macrolactam formation have enabled the assembly of the fully functionalized scaffold, with its 3-hydroxypyridine nucleus orthogonally protected (see scheme).



Al–Al σ Bonds

P. Henke, T. Pankewitz, W. Klopper,*
F. Breher, H. Schnöckel* **8141 – 8145**

Snapshots of the Al–Al σ-Bond Formation Starting from $\{AlR_2\}$ Units: Experimental and Computational Observations



The approach of two atoms with an unpaired electron each results in the formation of a σ bond. Snapshots of the primary step with a large atom-to-atom distance and a parallel spin of both electrons and of the final product, consisting of a butterfly structure with a short Al–Al σ bond, have been identified for a $[R_2P{-}Al(PR_2)Al{-}PR_2]$ compound using quantum chemical calculations and X-ray crystallography (see scheme).

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

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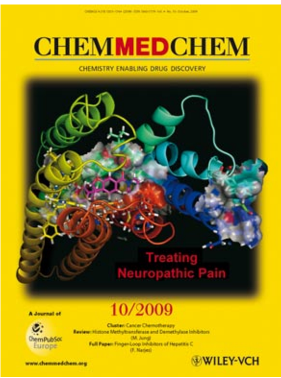
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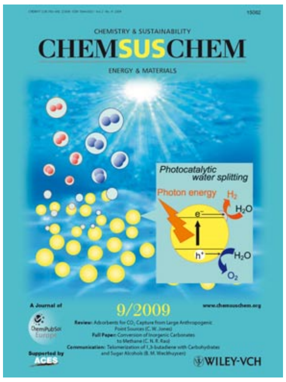
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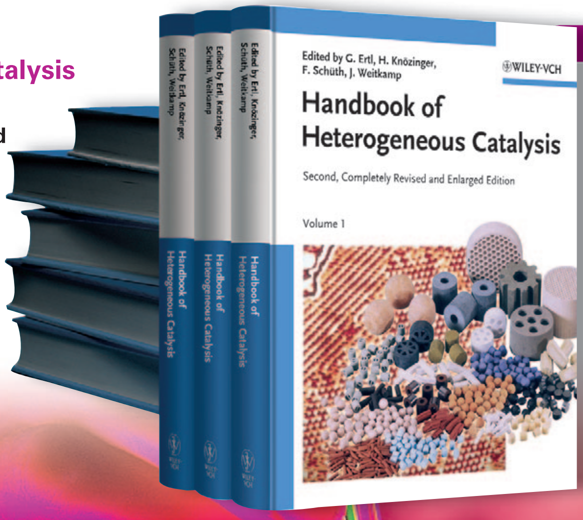
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