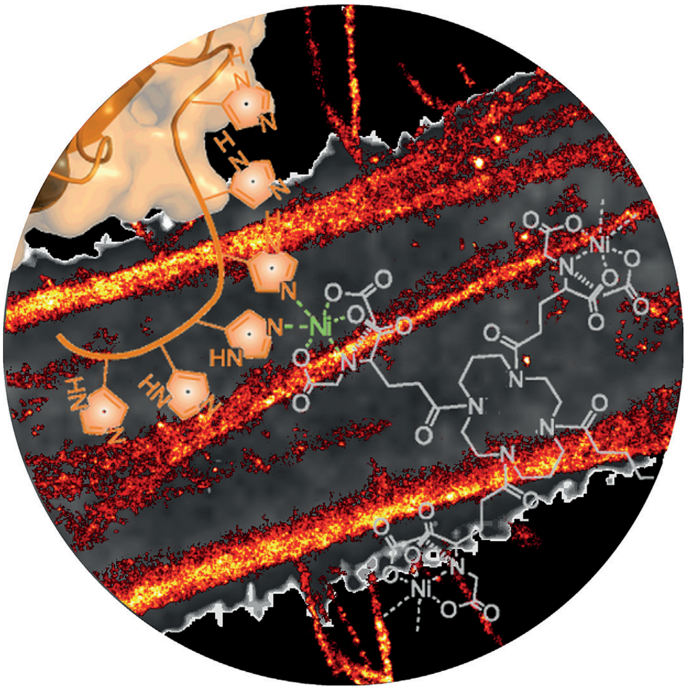
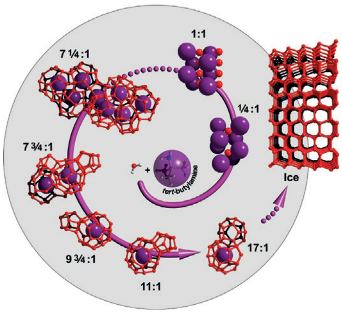
A Small Labeling Pair (SLAP) …

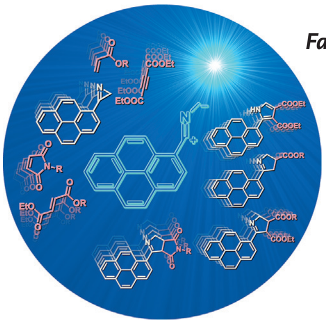


… for single-molecule imaging techniques is reported by M. Heilemann, R. Tampé, and co-workers in their Communication on page 10216 ff. The small-molecule recognition unit (Ni-trisNTA) and the genetically encoded minimal protein (His6-10-tag) enable rapid, site-specific, and stoichiometric labeling with high density. The proximity achieved with SLAP accounts for the higher spatial resolution with nanoscopy (orange) compared to wide-field imaging (gray).

Clathrates

Ł. Dobrzycki, R. Boese et al. analyze in their Communication on page 10138 ff. seven single-crystal structures that were obtained by diluting *tert*-butylamine with water and can be considered as frozen stages of hydration.



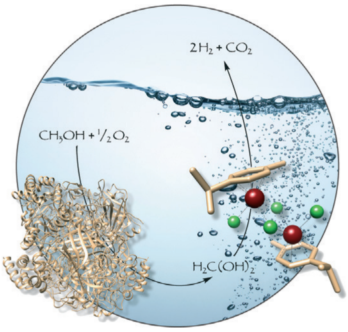


Fast Photoreactions

A rapid, highly efficient, and catalyst-free method for the conjugation of an azirine moiety and diverse dipolarophiles under blue-light irradiation is described by C. Barner-Kowollik and co-workers in their Communication on page 10284 ff.

Methanol Economy

In their Communication on page 10308 ff. J. Deska, M. Prechtl et al. employ an organometallic formaldehyde dehydrogenase mimic to liberate hydrogen gas from aqueous methanol at room temperature.



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Editorial

Klaus Müllen
Direktor am Max-Planck-Institut für Polymerforschung

"... Chemists are expected more and more to explain their contributions to the public. This could be straightforward since there is no new technology without improved materials, especially in fields of immense societal importance such as energy, health, water, or sustainability. Can't these unsolved scientific and technical challenges motivate chemists to offer their superior abilities in synthesis and join the field of materials? ..."
Read more in the Editorial by Klaus Müllen.

Service

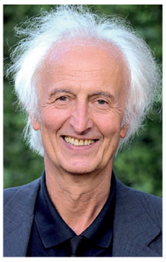
Author Profile

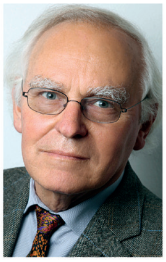
*"In a spare hour, I finally get some sleep.
My favorite way to spend a holiday is to travel to Australia. ..."*
This and more about A. Stephen K. Hashmi can be found on page 10066 – 10067.

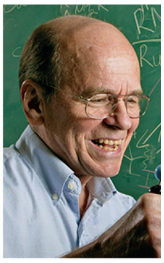
News


C. Bolm

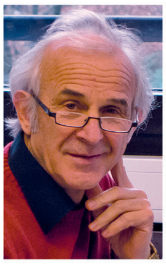

M. Beller


H. Schwarz

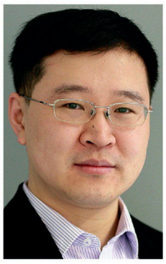

H. Hopf


K. B. Sharpless


T. F. Fässler


M. Tausch


C. P. Grey


J. Yuan


R. Zenobi


B. Chaudret


L. Latos-Grażyński


D. Koziej


D. Summerer

Obituaries

Heinrich Nöth, who was President of the Gesellschaft Deutscher Chemiker (GDCh; German Chemical Society) from 1988–1989 and 1992–1993, passed away on June 26, 2015. His research was focused on boron chemistry, including low-coordinate boron compounds, species with boron–transition-metal bonds, and boron-containing heterocycles. He was instrumental in the promotion of science in Germany and held several influential positions in the German scientific community.

For the USA and Canada:
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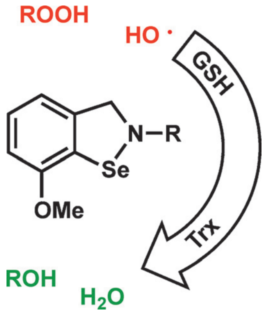
Highlights

Antioxidants

T. Wirth* **10074 – 10076**

Small Organoselenium Compounds: More than just Glutathione Peroxidase Mimics



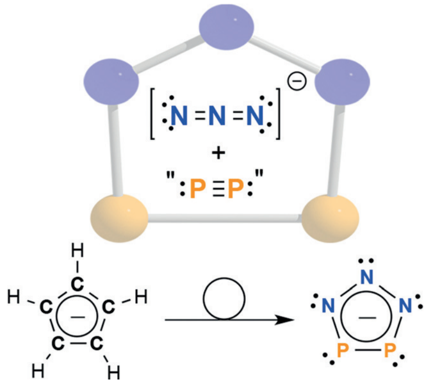
Se-ing and doing: Isoselenazoles are novel, very potent antioxidant derivatives offering remarkable cytoprotection to human cells. Synthetically available in only a few steps, these compounds have the potential to fight diseases caused by oxidative stress.

P,N Heterocycles

C. Hering-Junghans,*
E. Rivard* **10077 – 10079**

Accessing an Aromatic Diphosphatriazolate Anion by Formal Inorganic "Click" Chemistry

High five: A formal cycloaddition reaction between a chemical source of P_2 and azide $(N_3)^-$ affords the novel $[P_2N_3]^-$ ion. Experimental and computational investigations confirm the presence of substantial aromaticity within this exciting new building block in inorganic chemistry.

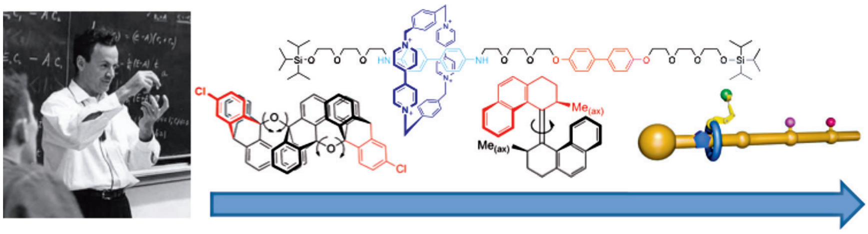


Essays

Supramolecular Systems

E. R. Kay,* D. A. Leigh* **10080 – 10088**

Rise of the Molecular Machines



They're coming! From Feynman to ribosome mimics, the evolution of artificial molecular machines is told in terms of key inventions and the questions the field continues to face, including design philosophies and what to make and why.

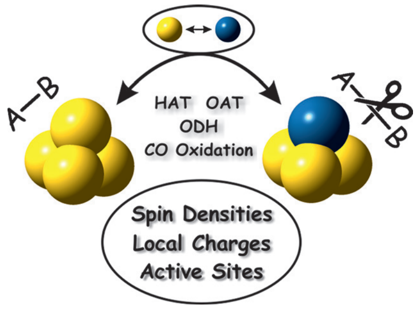
Minireviews

Gas-Phase Processes

H. Schwarz* **10090 – 10100**

Doping Effects in Cluster-Mediated Bond Activation

Excellent clusters: Gas-phase investigations of doped oxide clusters can provide answers to fundamental questions, for example, regarding the low-temperature oxidation of CO and the selective conversion of hydrocarbons. Such clusters can be considered model systems for catalysis. They can thus be used to identify the active site of a catalyst and to unravel mechanistic details of catalyzed reactions.



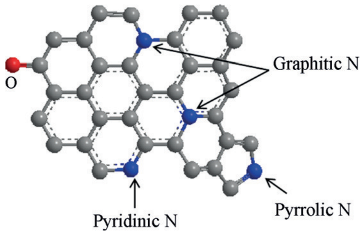
Reviews

Electrocatalysts

J. Masa, W. Xia, M. Muhler,*
W. Schuhmann* ———— 10102 – 10120

On the Role of Metals in Nitrogen-Doped Carbon Electrocatalysts for Oxygen Reduction

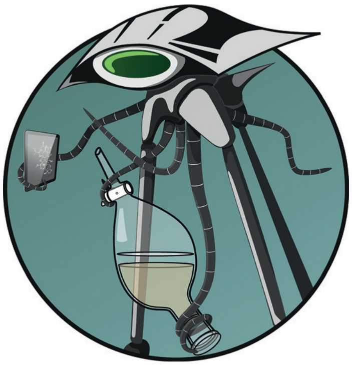
A free agent: Nitrogen-modified carbon (NC) materials (see scheme) are of emerging importance for electrocatalysis of the oxygen reduction reaction (ORR). However, trace-metal residues in NC catalysts can significantly influence the ORR, which has raised concerns regarding the validity of the notion of a metal-free catalyst. A critical discussion of the role of metals in NC catalysts is given to reconcile divergent views.



Machine-Assisted Synthesis

S. V. Ley,* D. E. Fitzpatrick, R. M. Myers,
C. Battilocchio,
R. J. Ingham ———— 10122 – 10136

Machine-Assisted Organic Synthesis



Machines making molecules: This Review discusses upstream equipment that is assisting chemists to create molecules at the time of reaction. By adopting a machine-assisted approach, new reactivities have been unlocked and previously impossible conditions have been utilized.

Communications

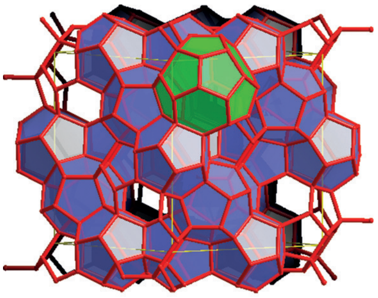
Clathrates

Ł. Dobrzycki,* P. Taraszewska, R. Boese,*
M. K. Cyrański,
S. A. Cirkel ———— 10138 – 10144

Towards Clathrates: Frozen States of Hydration of *tert*-Butylamine

Frontispiece

Seven single-crystal structures were determined by diluting the liquid *tert*-butylamine with water and using in situ crystallization techniques. In this series of structures, considered as frozen stages of hydration, water first acts as a linker between the amines whereas for intermediary ratios, no single crystals could be obtained. At high water concentrations, water acts as a host, which leads to clathrate structures (see picture).



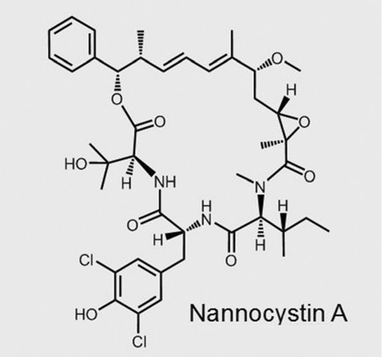
$t\mathrm{BuNH_2{\bullet}17H_2O}$

Natural Products

H. Hoffmann, H. Kogler, W. Heyse,
H. Matter, M. Caspers, D. Schummer,
C. Klemke-Jahn, A. Bauer, G. Penarier,
L. Debussche,
M. Brönstrup* ———— 10145 – 10148

Discovery, Structure Elucidation, and Biological Characterization of Nannocystin A, a Macrocyclic Myxobacterial Metabolite with Potent Antiproliferative Properties

Nanomolar inhibitor Nannocystin A: A little-explored myxobacterial *Nannocystis* sp. was found to produce a novel macrocyclic natural product, nannocystin A. Its relative and absolute configuration was elucidated by NMR, molecular dynamics calculations, and X-ray crystallography. Nannocystin A inhibits cell proliferation at low nanomolar concentrations through the early induction of apoptosis.

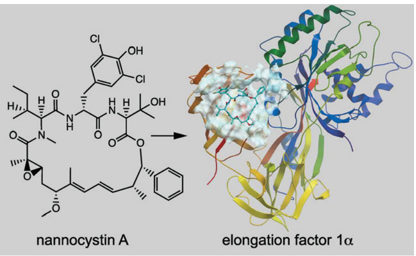


Cancer Therapeutics

P. Krastel, S. Roggo, M. Schirle, N. T. Ross, F. Perruccio, P. Aspesi, Jr., T. Aust, K. Buntin, D. Estoppey, B. Liechty, F. Mapa, K. Memmert, H. Miller, X. Pan, R. Riedl, C. Thibaut, J. Thomas, T. Wagner, E. Weber, X. Xie, E. K. Schmitt, D. Hoepfner* ______ **10149 – 10154**

Nannocystin A: an Elongation Factor 1 Inhibitor from Myxobacteria with Differential Anti-Cancer Properties

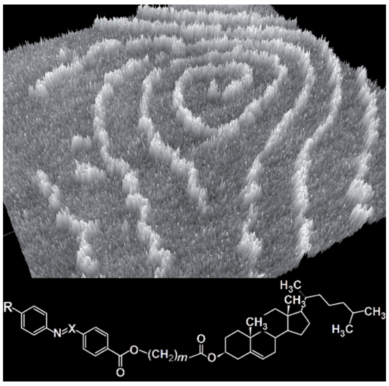
The cyclic lactone nannocystin A was isolated from myxobacteria of the *Nannocystis* species. Combined genetic and proteomic approaches identified the eukaryotic translation elongation factor 1α (EF-1α) as the primary target for this compound class.



Liquid Crystals

E. Gorecka,* N. Vaupotič, A. Zep, D. Pociecha, J. Yoshioka, J. Yamamoto, H. Takezoe ______ **10155 – 10159**

A Twist-Bend Nematic (N_{TB}) Phase of Chiral Materials

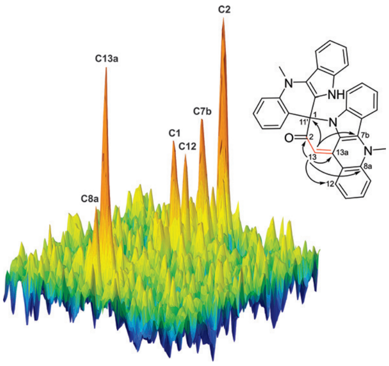


Crystal clear: Chiral dimers consisting of rod-like and cholesteric units form a chiral twist-bend nematic phase (N_{TB}*; see picture). The compressibility of the N_{TB} phase made of bent dimers was found to be as large as in smectic phases. Atomic force microscopy observations showed a periodicity of about 50 nm in the chiral N_{TB} phase of bent dimers.

NMR Techniques

J. Saurí, W. Bermel, A. V. Buevich, E. C. Sherer, L. A. Joyce, M. H. M. Sharaf, P. L. Schiff, Jr., T. Parella, R. T. Williamson,* G. E. Martin* ______ **10160 – 10164**

Homodecoupled 1,1- and 1,n-ADEQUATE: Pivotal NMR Experiments for the Structure Revision of Cryptospirolepine

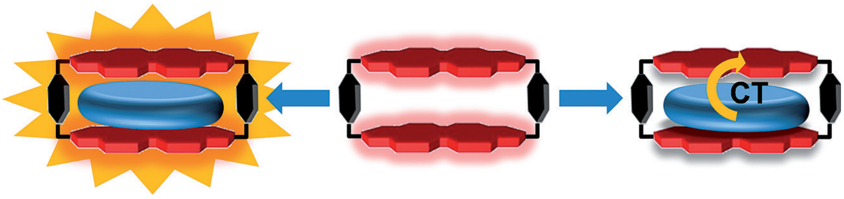


Taking a second look: Development of an improved, homodecoupled 1,1- and 1,n-ADEQUATE (HD-ADEQUATE) technique is reported and applied to the revision of the structure of a 700 μg sample of the complex, spiro nonacyclic alkaloid cryptospirolepine whose structure was first reported in 1993.

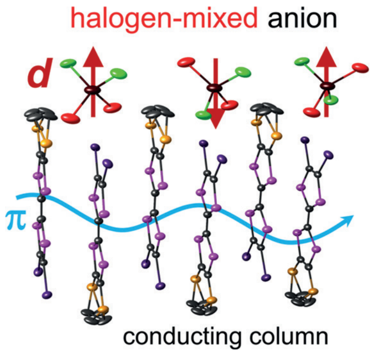
Host–Guest Chemistry

P. Spenst, F. Würthner* _ **10165 – 10168**

A Perylene Bisimide Cyclophane as a "Turn-On" and "Turn-Off" Fluorescence Probe



Boxed in: A perylene bisimide cyclophane can intercalate large planar aromatic hydrocarbons. The fluorescence properties of the corresponding host–guest complexes are strongly dependent on the electronic structure of the guest molecules. The system serves as "turn-on" and "turn-off" fluorescence probe that distinguishes electron-poor from electron-rich aromatic hydrocarbons (see figure; CT = charge transfer).



Blend halogens: A radical cation salt was synthesized using halogen-mixed magnetic anions. The crystal structure is robust against random halogen substitution due to iodine bonds. The material shows unprecedented hysteresis in both magnetic moment and magnetoresistance associated with a spin-flop transition.

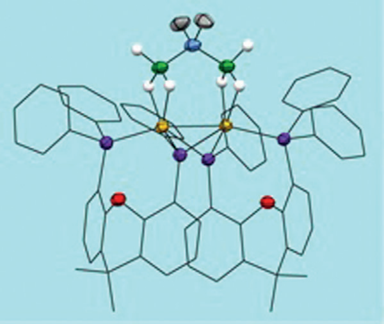
Spintronic Materials

G. Kawaguchi, M. Maesato,* T. Komatsu,
H. Kitagawa, T. Imakubo, A. Kiswandhi,
D. Graf, J. S. Brooks ——— **10169 – 10172**

Unconventional Magnetic and Resistive Hysteresis in an Iodine-Bonded Molecular Conductor

---

Doubling up: {Rh(xantphos)}-based phosphido dimers, such as $[Rh_2(\kappa^2\text{-}_{P,P}\text{-xantphos}')_2(\eta^2,\eta^2\text{-}H_3BNMe_2BH_3)]^+$ (see picture), form by P–C activation of xantphos (4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) in the presence of amine–borane. The dimers are active dehydrocoupling catalysts, forming polymeric $[H_2BNMeH]_n$ from $H_3B{\cdot}NMeH_2$ and $[H_2BNMe_2]_2$ from $H_3B{\cdot}NMe_2H$ at low catalyst loadings. Atom colors: Rh = yellow; P = purple; B = green; N = blue; C = gray; H = white.



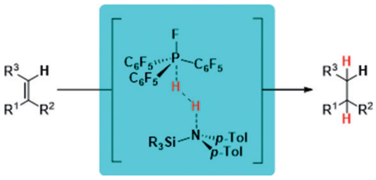
Amine–Boranes

H. C. Johnson,*
A. S. Weller* ——— **10173 – 10177**

P–C-Activated Bimetallic Rhodium Xantphos Complexes: Formation and Catalytic Dehydrocoupling of Amine–Boranes

---

FLP hydrogenation: The combination of a phosphorus(V)-based Lewis acid with diaryl amines or diaryl silylamines promotes reversible activation of dihydrogen and can be further exploited in metal-free catalytic olefin hydrogenation. Combined experimental and density functional theory (DFT) studies suggest a frustrated Lewis pair (FLP)-type activation mechanism.



Olefin Hydrogenation

T. vom Stein, M. Peréz, R. Dobrovetsky,
D. Winkelhaus, C. B. Caputo,
D. W. Stephan* ——— **10178 – 10182**

Electrophilic Fluorophosphonium Cations in Frustrated Lewis Pair Hydrogen Activation and Catalytic Hydrogenation of Olefins

---

Selection process: Self-assembled cationic clusters that complex DNA through multivalent interactions are expressed in situ by means of chemoselective ligations. Template effects have been characterized whereby DNA imposes component selection, and component exchange was exploited for triggering DNA release.

DNA Recognition

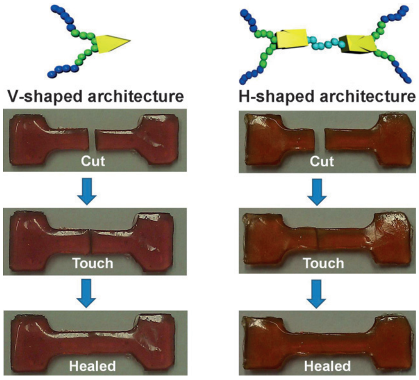
E. Bartolami, Y. Bessin, V. Gervais,
P. Dumy, S. Ulrich* ——— **10183 – 10187**

Dynamic Expression of DNA Complexation with Self-assembled Biomolecular Clusters

Block Copolymers

S. Chen, N. Mahmood, M. Beiner,
W. H. Binder* ________ **10188 – 10192**

Self-Healing Materials from V- and H-Shaped Supramolecular Architectures

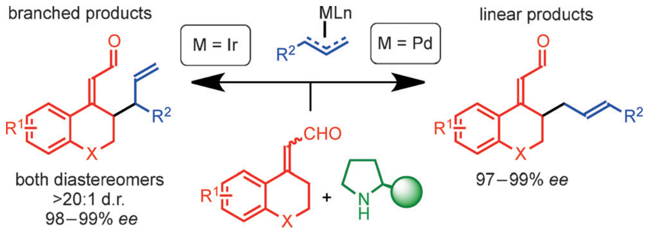


Unbreakable: Incorporation of a barbiturate unit in the center of soft–hard–soft triblock copolymers results in V-shaped supramolecular architectures with multiple self-healing properties. Self-assembly with the heterocomplementary α,ω-Hamilton wedge functionalized polyisoprene results in an H-shaped supramolecular architecture that can recover around 95% of its original performance after 24 h at 30°C.

Asymmetric Catalysis

L. Næsborg, K. S. Halskov, F. Tur,
S. M. N. Mønsted,
K. A. Jørgensen* ________ **10193 – 10197**

Asymmetric γ-Allylation of α,β-Unsaturated Aldehydes by Combined Organocatalysis and Transition-Metal Catalysis

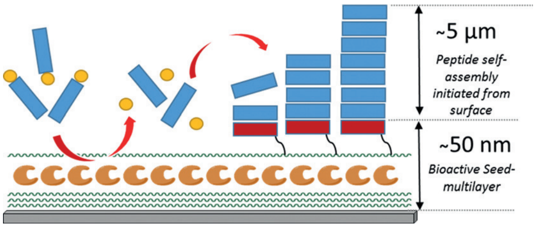


Catalyst combo: By combining an aminocatalyst with an iridium catalyst, both diastereomers of branched allylated products can be achieved in good yields and excellent regio- and stereoselectivities. By replacing the iridium catalyst with a palladium catalyst, the linear allylated products are formed in good yields and excellent regio- and enantioselectivities. Thus, all six isomers of the γ-allylated product can be accessed.

Surface Chemistry

C. Vigier-Carrière, T. Garnier, D. Wagner,
P. Lavalle, M. Rabineau, J. Hemmerlé,
B. Senger, P. Schaaf,* F. Boulmedais,*
L. Jierry ________ **10198 – 10201**

Bioactive Seed Layer for Surface-Confined Self-Assembly of Peptides

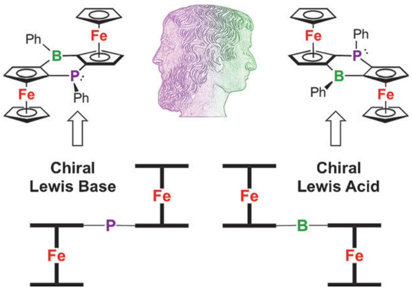


Peptidic hydrogel assembly line: The growth of peptide-based hydrogel exclusively from the surface can be realized and controlled by using a bioactive seed layer. Confined into the seed layer, an enzyme ensures the gradient production of self-assembling peptides from the surface in a continuous and autonomous way (see scheme).

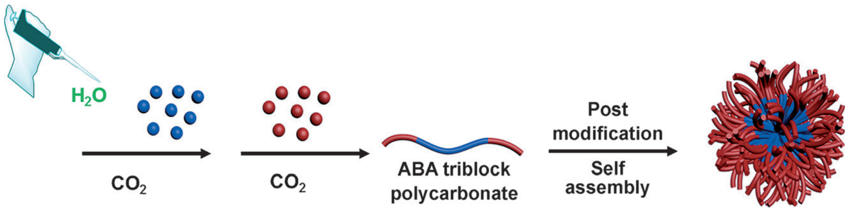
Ambiphilic Ligands

J. Chen, D. A. Murillo Parra,
R. A. Lalancette, F. Jäkle* **10202 – 10205**

Diferrocenophosphaborin:
A Planar-Chiral, Redox-Active and Anion-Responsive Ambiphilic Ligand



Janus ligands: Ambiphilic ligands with an unprecedented stereochemical environment that is determined solely by the spatial orientation of fused ferrocenes are introduced. The Lewis acidic B site is a mirror image of the Lewis basic P site. Mutual interactions are demonstrated and the redox- and fluoride anion-responsive properties investigated.



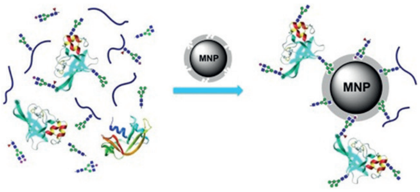
A two step, one-pot synthesis of an amphiphilic triblock polycarbonate from CO_2 and propylene oxide is described. The poly(propylene carbonate) diols produced in the first step serve as macroinitiators in the subsequent allyl glycidyl ether/CO_2 coupling reaction leading to self-assembled triblock PC nanoparticles following postmodification by thiol–ene click chemistry.

CO_2-Based Materials

Y. Wang, J. Fan,
D. J. Darensbourg* ______ **10206 – 10210**

Construction of Versatile and Functional Nanostructures Derived from CO_2-based Polycarbonates

---



Sweet-test thing: Boronate-affinity glycan-oriented surface imprinting was used to prepare molecularly imprinted polymers (MIPs) with lectin-like binding properties. As a proof of principle, glycan-imprinted magnetic nanoparticles (MNPs) that enable the recognition of an intact glycoprotein and its characteristic fragments through binding to the attached glycans were prepared.

Molecular Imprinting

Z. Bie, Y. Chen, J. Ye, S. Wang,
Z. Liu* ______ **10211 – 10215**

Boronate-Affinity Glycan-Oriented Surface Imprinting: A New Strategy to Mimic Lectins for the Recognition of an Intact Glycoprotein and Its Characteristic Fragments

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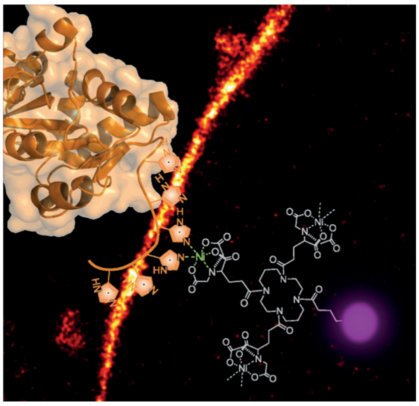
A sharp SLAP: A sensitive and efficient protein labeling method was developed on the basis of a synthetic small-molecule recognition unit (Ni-*tris*NTA) and the genetically encoded minimal protein His$_{6\text{-}10}$-tag. This small labeling pair (SLAP) technique enables super-resolution fluorescence imaging and fulfills the necessary sampling criteria for single-molecule localization-based imaging techniques.

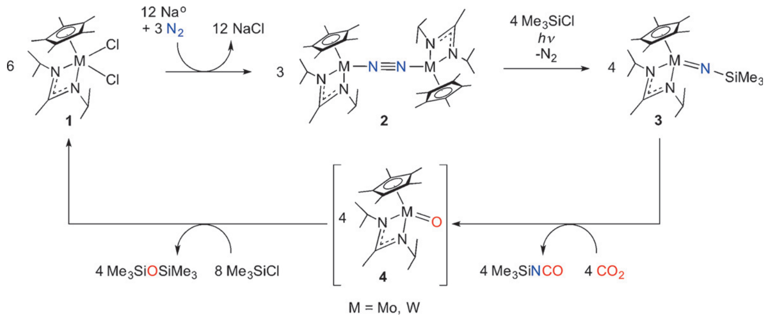


Super-resolution Microscopy

R. Wieneke, A. Raulf, A. Kollmannsperger,
M. Heilemann,*
R. Tampé* ______ **10216 – 10219**

SLAP: Small Labeling Pair for Single-Molecule Super-Resolution Imaging

Front Cover



Tandem fixation: A highly efficient and versatile chemical cycle has been developed for the production of isocyanates through the molecular fixation of N_2, CO_2, and R_3ECl (E = C, Si and Ge). Key steps include a simultaneous nitrene-group transfer and oxygen-atom transfer.

Nitrogen Fixation

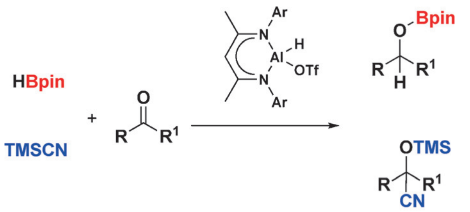
A. J. Keane, W. S. Farrell, B. L. Yonke,
P. Y. Zavalij, L. R. Sita* ___ **10220 – 10224**

Metal-Mediated Production of Isocyanates, $R_3EN{=}C{=}O$ from Dinitrogen, Carbon Dioxide, and R_3ECl

Homogeneous Catalysis

Z. Yang,* M. Zhong, X. Ma, S. De,
C. Anusha, P. Parameswaran,*
H. W. Roesky* ________ **10225 – 10229**

An Aluminum Hydride That Functions like a Transition-Metal Catalyst

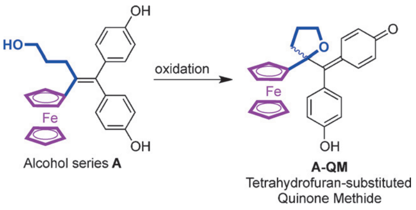


Canned catalysis: The aluminum hydride [LAlH(OTf)] has an excellent catalytic activity both in the hydroboration and the addition of trimethylsilyl cyanide (TMSCN) to aldehydes and ketones. The compound was synthesized by the reaction of [LAlH$_2$] (L = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) with MeOTf (Tf = SO$_2$CF$_3$). Theoretical calculations show that the catalyst initially acts as a hydride donor to the carbonyl group. HBPin = pinacolborane.

Antitumor Agents

Y. Wang, P. Pigeon, S. Top,*
M. J. McGlinchey,
G. Jaouen* ________ **10230 – 10233**

Organometallic Antitumor Compounds: Ferrocifens as Precursors to Quinone Methides



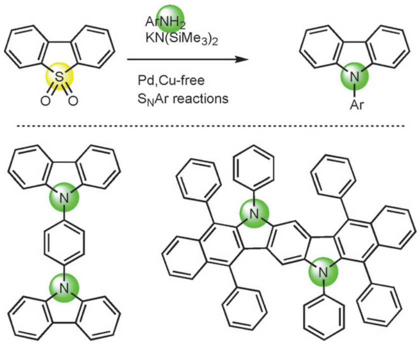
The bifunctional role of ferrocenyl as both an intramolecular reversible redox “antenna” and a stabilized carbenium ion “modulator” encourages the oxidation of compound **A** to give an unprecedented tetrahydrofuran-substituted quinone methide (QM) via an internal cyclization of the hydroxyalkyl chain. The chemical metabolic profile reveals crucial clues for deciphering the mechanism of the exceptional antiproliferative activity of **A**.

Aromatic Substitution

M. Bhanuchandra, K. Murakami, D. Vasu,
H. Yorimitsu,* A. Osuka _ **10234 – 10238**

Transition-Metal-Free Synthesis of Carbazoles and Indoles by an S$_N$Ar-Based “Aromatic Metamorphosis” of Thiaarenes

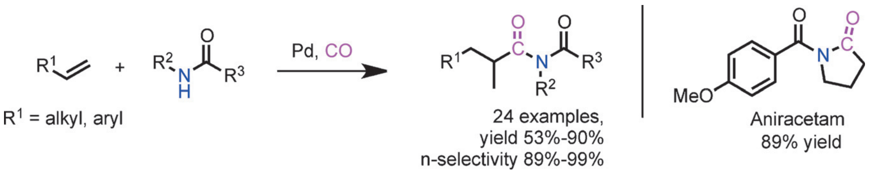
Lite on the metal: Dibenzothiophene dioxides undergo sequential inter- and intramolecular nucleophilic aromatic substitution with anilines to yield the corresponding carbazoles in a single operation. One advantage of this protocol is that heavy metals are not required. Coupling a thiaarene-dioxide-specific reaction with the S$_N$Ar carbazole synthesis allows construction of difficult-to-access carbazoles.



Synthetic Methods

H. Li, K. Dong, H. Neumann,
M. Beller* ________ **10239 – 10243**

Palladium-Catalyzed Hydroamidocarbonylation of Olefins to Imides

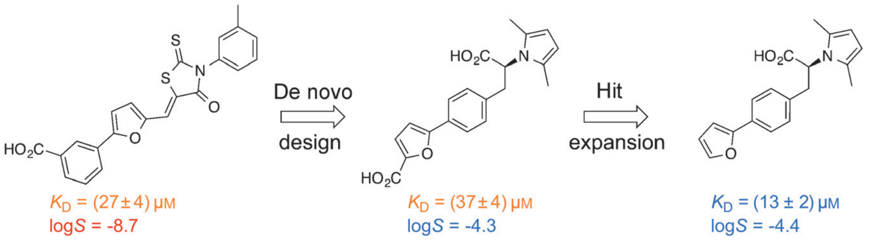


Efficiency drive: The direct and efficient synthesis of imides from simple alkenes and amides can be achieved in good yield and with linear selectivity by employing the title reaction. As an example, the synthesis of the anxiolytic drug Aniracetam has been accomplished in an atom-economic manner by an intramolecular carbonylative ring-closing reaction.

De Novo Design

A. M. Perna, T. Rodrigues, T. P. Schmidt, M. Böhm, K. Stutz, D. Reker, B. Pfeiffer, K.-H. Altmann, S. Backert, S. Wessler, G. Schneider* ———— **10244 – 10248**

Fragment-Based De Novo Design Reveals a Small-Molecule Inhibitor of *Helicobacter Pylori* HtrA

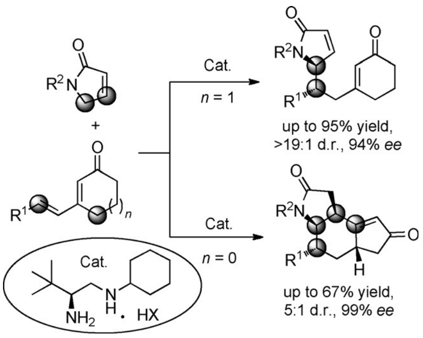


The current best-in-class inhibitor of *Helicobacter pylori* HtrA was discovered using fragment-based de novo design and hit expansion. This combination allows rapid prototyping of new chemical entities, and the new inhibitor can be seen as a pioneering tool for chemical biology and potential lead structure for anti-cancer and anti-infective drug discovery.

Asymmetric Catalysis

X. Gu, T. Guo, Y. Dai, A. Franchino, J. Fei, C. Zou, D. J. Dixon,* J. Ye* ———— **10249 – 10253**

Direct Catalytic Asymmetric Doubly Vinylogous Michael Addition of α,β-Unsaturated γ-Butyrolactams to Dienones

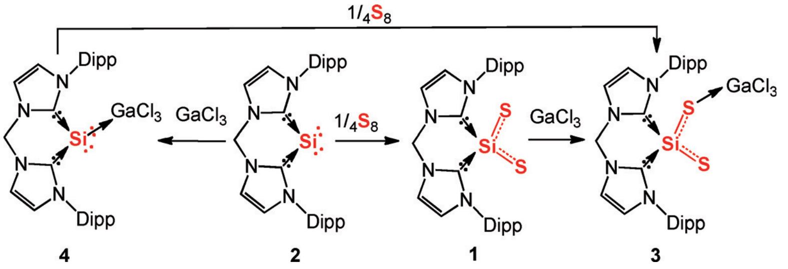


Doubled up: The title reaction of α,β-unsaturated γ-butyrolactams and sterically congested β-substituted cyclic dienones proceeds with high site-, diastereo-, and enantioselectivity. An unprecedented cascade reaction takes place with five-membered dienones, leading to complex tricyclic γ-lactams with four newly formed stereocenters.

Silicon Compounds

Y. Xiong, S. Yao, R. Müller, M. Kaupp, M. Driess* ———— **10254 – 10257**

From Silylone to an Isolable Monomeric Silicon Disulfide Complex

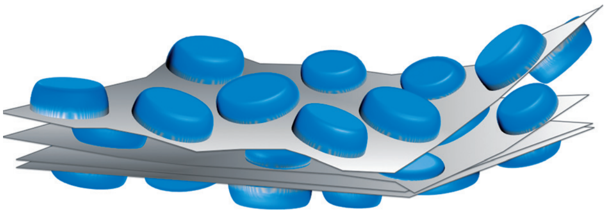


Family catching: The elusive monomeric silicon disulfide SiS_2 could be stabilized in the chelating pocket of a bis-N-heterocyclic carbene (bis-NHC) donor, resulting in the first silicon disulfide complex **1**. Compound **1** reacts with $GaCl_3$ to form the corresponding (bis-NHC)Si(=S)S→$GaCl_3$ adduct **3** which is also accessible from the unprecedented silylone→$GaCl_3$ adduct **4**.

Layered Material Exfoliation

J. Texter* ———— **10258 – 10262**

A Kinetic Model for Exfoliation Kinetics of Layered Materials

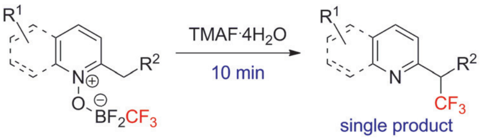


Splitting sheets: A simple kinetic model for exfoliation is presented that postulates random and irreversible sheet separation in the presence of highly effective stabilizers. This model appears to quantitatively fit graphene exfoliation data, and it illuminates mechanistic aspects of exfoliation: Thicker sheets exfoliate much faster than trilayer and bilayer sheets.

Heterocycle Synthesis

Y. Kuninobu,* M. Nagase,
M. Kanai* ———— **10263 – 10266**

Benzylic C(sp^3)–H Perfluoroalkylation of Six-Membered Heteroaromatic Compounds



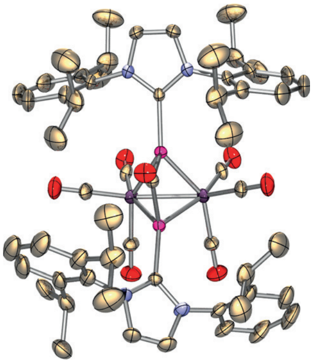
Go for it–3,5,7: Benzylic C(sp^3)–H trifluoromethylation, pentafluoroethylation, and heptafluoropropylation of the title compounds is described. This is the first practical benzylic C(sp^3)–H perfluoroalkylation, and it was used to regioselectively trifluoromethylate a bioactive compound, as well as introduce a CF_3 group into a bioactive molecular skeleton. TMAF = tetramethylammonium fluoride.

Silicon Complexes

H. P. Hickox, Y. Wang, Y. Xie, M. Chen,
P. Wei, H. F. Schaefer III,
G. H. Robinson* ———— **10267 – 10270**

Transition-Metal-Mediated Cleavage of a Si=Si Double Bond

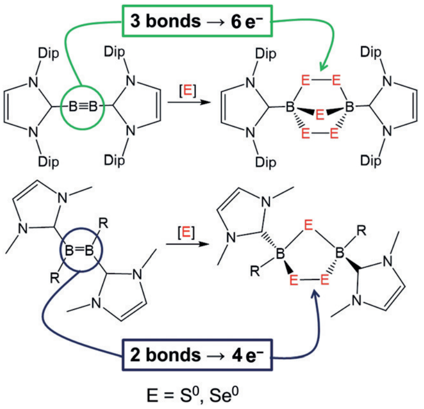
Dual insertions: Iron pentacarbonyl is demonstrated to cleave the Si=Si double bond in L:Si=Si:L (L: = C{N(2,6-$Pr^i_2C_6H_3$)CH}$_2$) through insertion of both CO and $Fe_2(CO)_6$ between the two carbene-stabilized silicon atoms, giving L:Si-[μ-$Fe_2(CO)_6$](μ-CO)Si:L (pink Si, blue N, purple Fe, red O). This represents the first experimental realization of transition metal-carbonyl-mediated cleavage of a Si=Si double bond.



Main-Group Chemistry

H. Braunschweig,* T. Dellermann,
W. C. Ewing, T. Kramer, C. Schneider,
S. Ullrich ———— **10271 – 10275**

Reductive Insertion of Elemental Chalcogens into Boron–Boron Multiple Bonds

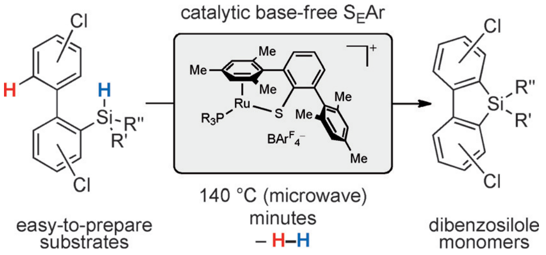


Bond order determined by reactivity: Polychalcogenido bi- and monocyclic compounds have been synthesized through use of the reducing equivalents stored in the form of boron–boron multiple bonds. The triple bond of the diboryne is capable of initiating six-electron reductions, while the boron–boron double bond of a diborene provides four reducing equivalents.

C–H Silylation

L. Omann, M. Oestreich* **10276 – 10279**

A Catalytic S$_E$Ar Approach to Dibenzosiloles Functionalized at Both Benzene Cores

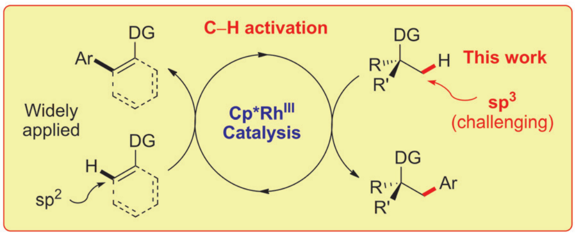


Silole, not silanol: Catalytic access to directly polymerizable dibenzosiloles can be accomplished through intramolecular electrophilic aromatic substitution (S$_E$Ar) starting from easy-to-prepare *ortho*-silylated biphenyls. This Friedel–Crafts-type C–H bond silylation features broad functional-group tolerance, including ethers and amines.

Synthetic Methods

X. Wang, D.-G. Yu,
F. Glorius* ——— 10280 – 10283

Cp*Rh^{III}-Catalyzed Arylation of C(sp^3)–H Bonds



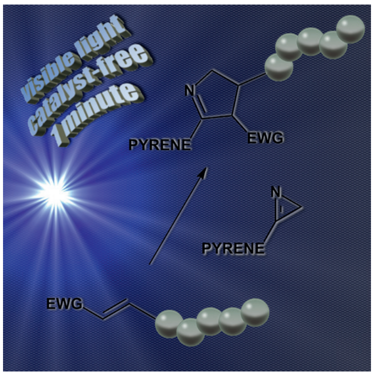
Unactivated! The unactivated primary C(sp^3)–H bond of 2-alkylpyridines can be activated by Rh^{III} and then react with triarylboroxines to efficiently build new C(sp^3)–aryl bonds (see scheme, DG = directing group, FG = functional group). The methodology also provides a facile and efficient synthesis of unsymmetrical triarylmethanes by Rh^{III}-catalyzed C(sp^3)–H arylation.

Fast Photoreactions

J. O. Mueller, F. G. Schmidt, J. P. Blinco,*
C. Barner-Kowollik* ——— 10284 – 10288

Visible-Light-Induced Click Chemistry

Inside Back Cover

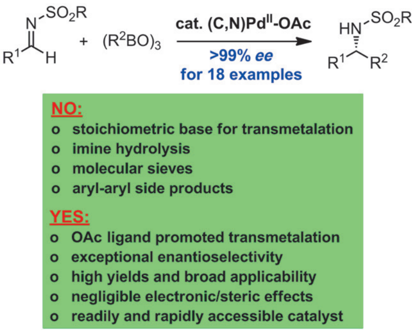


Quick as a flash: A rapid and catalyst-free cycloaddition system for visible-light-induced click chemistry at ambient conditions is reported. Irradiation of a 2*H*-azirine moiety with low-energy light sources enables efficient small-molecule synthesis with a diverse range of multiple-bond-containing compounds, as well as rapid quantitative ligation of the photoactivatable chromophore with polymeric substrates.

1,2-Additions

C. Schrapel, R. Peters* ——— 10289 – 10293

Exogenous-Base-Free Palladacycle-Catalyzed Highly Enantioselective Arylation of Imines with Arylboroxines



NO:
- stoichiometric base for transmetalation
- imine hydrolysis
- molecular sieves
- aryl-aryl side products

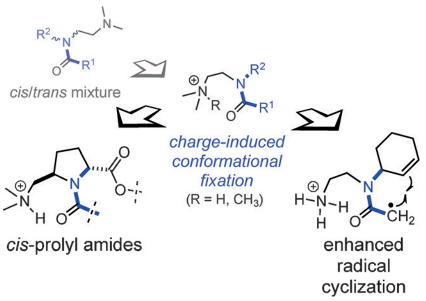
YES:
- OAc ligand promoted transmetalation
- exceptional enantioselectivity
- high yields and broad applicability
- negligible electronic/steric effects
- readily and rapidly accessible catalyst

A ferrocene-based planar-chiral palladacycle is a very efficient catalyst for the enantioselective 1,2-addition of arylboroxines to both aromatic and aliphatic imines. A broad range of substrates are generally converted into benzylic amines in high yields and in almost enantiomerically pure form. Crucial is the use of an acetate ligand, which promotes the transmetalation step and prevents imine hydrolysis.

Amide Conformation

A. L. Bartuschat, K. Wicht,
M. R. Heinrich* ——— 10294 – 10298

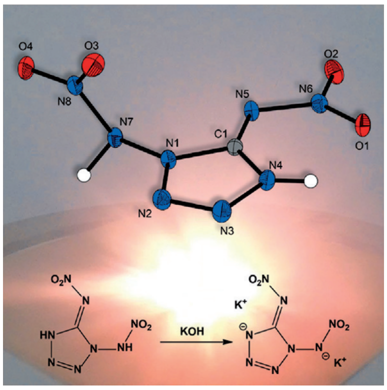
Switching and Conformational Fixation of Amides Through Proximate Positive Charges



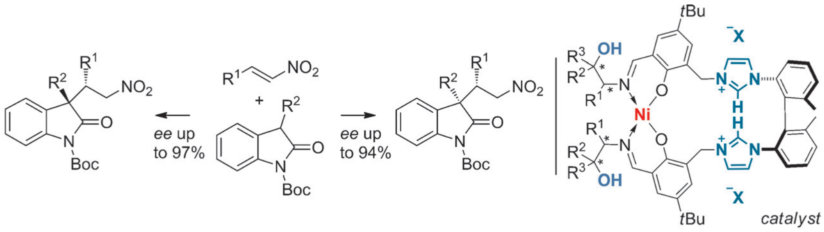
Taking charge of conformation: Tertiary amides, which usually occur as *cis/trans* mixtures, can be effectively shifted to the *cis* conformation by placing a positive charge in close proximity to the amide carbonyl. This effect was used to prepare *cis*-configured prolyl amides and to facilitate a strongly rotamer-dependent radical cyclization.

Energetic Materials

N + O = 92.62 %: The solid 1,5-di(nitramino)tetrazole consists of 92.62 % nitrogen and oxygen and is one of the most powerful chemical explosives to date. Owing to its high sensitivities toward impact and friction, it is hard to tame. The picture shows its molecular structure in front of its thermally induced detonation on a hot copper plate.



Cooperative Catalysis



Overwriting the preference for one diastereomer by means of a catalyst is a challenge and requires precise control over the spatial arrangement of both reacting substrates. A polyfunctional catalyst type has been developed in which a Ni^{II} center, OH groups, and a bisimidazolium participate in the stereocontrol of direct 1,4-additions of oxindoles to nitroolefins. Both product epimers are accessible on demand with high *ee* values. Boc = *tert*-butoxycarbonyl.

DOI: 10.1002/anie.201583514

Flashback: 50 Years Ago . . .

1965 saw the 100th anniversary of Kekulé's rationalization of the benzene ring structure. In a Review, Hermann Hartmann described the history of the benzene formula, including a discussion of Hückel's theory of aromaticity. To mark the 150th anniversary, this journal published an Essay earlier this year by Alan Rocke that gives a comprehensive history of how Kekulé approached the problem (see *Angew. Chem. Int. Ed.* **2015**, *54*, 46).

The structure of benzene was the subject of further Reviews: Georg Wittig discussed the generation and reactions of 1,2-didehydrobenzene, and Eugen E. van Tamalen and Heinz G. Viehe discussed valence-bond isomers of aromatic systems and substituted benzenes (such as Dewar benzene and prismane), respectively.

Hans Bock reported on a new aromatic substitution reaction in the form of dialkylamination. The reaction of N-chlorodialkylamines with aromatic compounds could be achieved by heating or irradiating the reactants in sulfuric acid, or by heating with a Lewis acid catalyst. For Bock's Obituary, see *Angew. Chem.* **2008**, *47*, 2912.

Max Schmidt described the reactions of diphenylphosphinotriphenyltin with compounds such as CS_2, COS, and $CSCl_2$. The reactions were postulated to proceed by a four-centered concerted mechanism at the Sn–P bond.

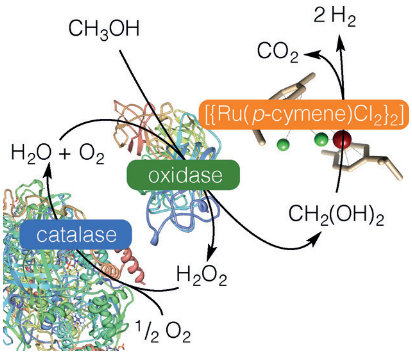
Read more in Issue 9/1965.

Methanol Economy

L. E. Heim, D. Thiel, C. Gedig, J. Deska,* M. H. G. Prechtl* ——— **10308 – 10312**

Bioinduced Room-Temperature Methanol Reforming

Back Cover

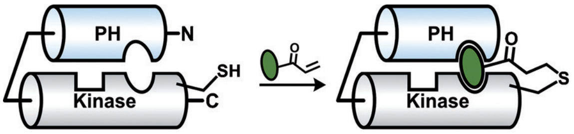


Imitating nature's approach for nucleophile-activated formaldehyde dehydrogenation: Air-stable ruthenium complexes are catalysts for the dehydrogenation of formaldehyde hydrate as well as for transfer hydrogenation to unsaturated organic substrates. In combination with an oxidase-mediated activation of methanol, an artificial methylotrophic in vitro metabolism provides hydrogen gas in a room-temperature methanol-reforming pathway.

Drug Design

J. Weisner, R. Gontla, L. van der Westhuizen, S. Oeck, J. Ketzer, P. Janning, A. Richters, T. Mühlenberg, Z. Fang, A. Taher, V. Jendrossek, S. C. Pelly, S. Bauer, W. A. L. van Otterlo, D. Rauh* ——— **10313 – 10316**

Covalent-Allosteric Kinase Inhibitors

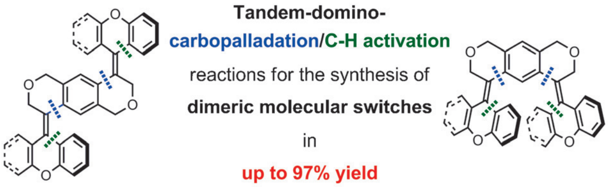


Modulating protein kinases with allosteric ligands may allow improved target selectivity compared to ATP-competitive binders. Exploiting suitable cysteines, we developed covalent-allosteric Akt inhibitors. These ligands irreversibly stabilize the inactive enzyme conformation and provide novel methods for chemical biology research.

Helical Structures

L. F. Tietze,* B. Waldecker, D. Ganapathy, C. Eichhorst, T. Lenzer, K. Oum, S. O. Reichmann, D. Stalke ——— **10317 – 10321**

Four- and Sixfold Tandem-Domino Reactions Leading to Dimeric Tetrasubstituted Alkenes Suitable as Molecular Switches

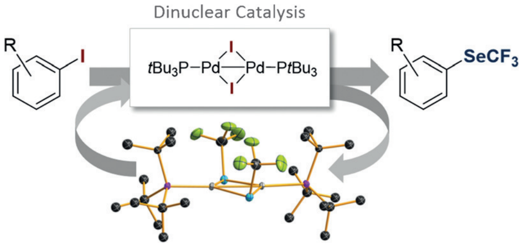


Highly efficient palladium-catalyzed fourfold tandem-domino reactions consisting of two carbopalladation and two C–H-activation steps were developed for the synthesis of two types of tetrasubstituted alkenes with intrinsic helical chirality. 20 different substrates were prepared with yields of up to 97%. Photophysical investigations revealed light-induced switching properties of the products.

Pd^{I} Catalysts

M. Aufiero, T. Sperger, A. S.-K. Tsang, F. Schoenebeck* ——— **10322 – 10326**

Highly Efficient C–SeCF$_3$ Coupling of Aryl Iodides Enabled by an Air-Stable Dinuclear Pd^{I} Catalyst

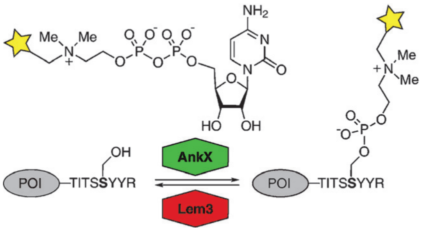


It takes two: The first catalytic trifluoromethylselenolation of aryl iodides is made possible by the readily prepared, air-stable dinuclear Pd^{I} catalyst [{(PtBu$_3$)PdI}$_2$]. The method is simple, mild, and shows high functional-group tolerance. A novel SeCF$_3$-bridged dinuclear Pd^{I} complex was isolated. Experimental and computational data suggest a mechanism involving dinuclear Pd^{I} catalysis.

Protein Labeling

K. Heller, P. Ochtrop, M. F. Albers,
F. B. Zauner, A. Itzen,*
C. Hedberg* **10327 – 10330**

Covalent Protein Labeling by Enzymatic Phosphocholination



Infectious labeling strategy! A new protein labeling method is based on the covalent enzymatic phosphocholination of octapeptide amino acid sequences in intact proteins. The labeling method utilizes the bacterial enzymes AnkX (transferase) and Lem3 (hydrolase) from *Legionella pneumophila*.

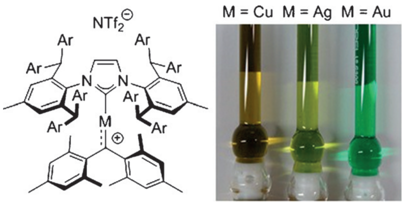
Carbene versus Carbenoid

M. W. Hussong, W. T. Hoffmeister,
F. Rominger,
B. F. Straub* **10331 – 10335**

Copper and Silver Carbene Complexes without Heteroatom-Stabilization: Structure, Spectroscopy, and Relativistic Effects

Inside Cover

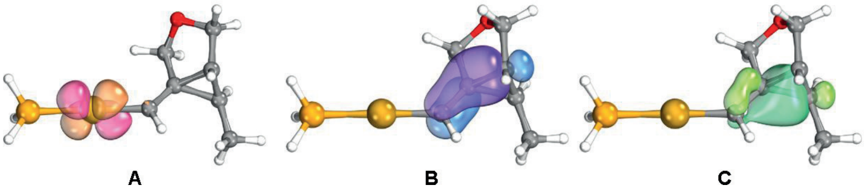
Relatively labile relatives: Isostructural Group 11 element carbene complexes have been prepared and characterized. Thermolability, deshielded carbene NMR spectroscopy signals, and bathochromic light absorption of the copper and silver complexes reflect their increased carbenoid character compared to the gold analogue, whose remarkable stability is explained by strong relativistic effects on gold's valence shell.



Gold Complexes

L. Nunes dos Santos Comprido,
J. E. M. N. Klein, G. Knizia, J. Kästner,*
A. S. K. Hashmi* **10336 – 10340**

The Stabilizing Effects in Gold Carbene Complexes

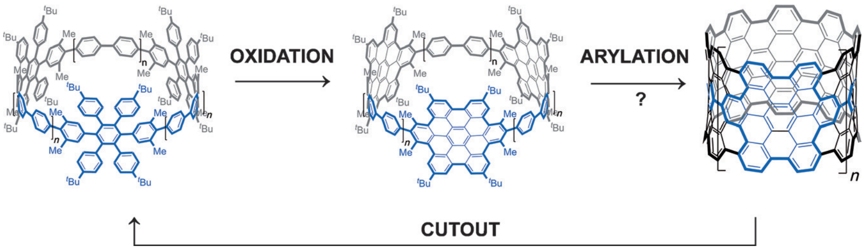


Is anybody there? Intrinsic bond orbital analyses based on DFT calculations on gold carbene complexes indicate little π backbonding from gold (**A**) and π stabilization from organic fragments even in cyclopropyl-substituted gold carbene complex intermediates (**B**, **C**).

Polycyclic Aromatic Hydrocarbons

M. Quernheim, F. E. Golling, W. Zhang,
M. Wagner, H.-J. Räder, T. Nishiuchi,*
K. Müllen* **10341 – 10346**

The Precise Synthesis of Phenylene-Extended Cyclic Hexa-*peri*-hexabenzocoronenes from Polyarylated [*n*]Cycloparaphenylenes by the Scholl Reaction



All that it's cutout to be: Polyarylated [*n*]cycloparaphenylenes are intermediates on the way to ultra-short carbon nanotubes (CNT). Different polyarylated [*n*]CPPs can be prepared and their oxidative cyclodehydrogenation leads to CPPs that are cutouts from CNTs.

NMR spectroscopy

H. Kadavath, M. Jaremko, Ł. Jaremko,
J. Biernat, E. Mandelkow,
M. Zweckstetter* ——— 10347 – 10351

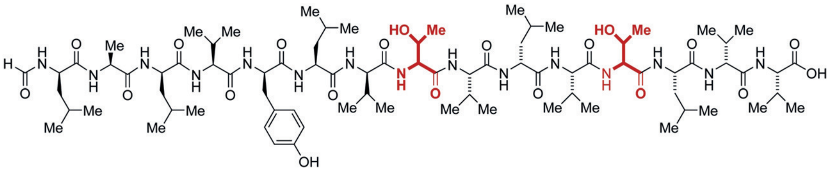
Folding of the Tau Protein on Microtubules

Tau the line: NMR spectroscopy shows that the protein Tau, which is intrinsically disordered in solution, locally folds into a stable structure upon binding to microtubules. While Tau is highly flexible in solution and forms a β-sheet structure in amyloid fibrils, the conserved hexapeptides at the beginning of the second and third repeats in Tau adopt a hairpin conformation when bound to microtubules. Thus, binding to microtubules stabilizes a unique conformation in Tau.

Nonribosomal Peptides

H. B. Bode,* A. O. Brachmann,
K. B. Jadhav, L. Seyfarth, C. Dauth,
S. W. Fuchs, M. Kaiser, N. R. Waterfield,
H. Sack, S. H. Heinemann,
H.-D. Arndt* ——— 10352 – 10355

Structure Elucidation and Activity of Kolossin A, the D-/L-Pentadecapeptide Product of a Giant Nonribosomal Peptide Synthetase



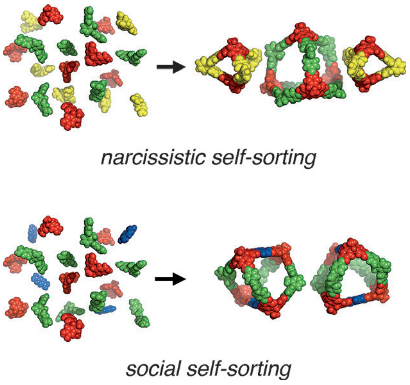
Sleeping giant: A 1.8 MDa nonribosomal peptide synthetase (NRPS) was identified in the entomopathogenic bacterium *Photorhabdus luminescens* and its production was activated. Its 15-mer D-/L-peptide product kolossin A was structurally characterized by combining genomic analysis of the silent gene cluster, molecular biology, LC–MS, and total synthesis. A stereoisomer of kolossin A was found to be active against the pathogen that causes African sleeping sickness.

Self-Sorting

S. Klotzbach, F. Beuerle* 10356 – 10360

Shape-Controlled Synthesis and Self-Sorting of Covalent Organic Cage Compounds

Tailor-made cages: A series of covalent organic cage compounds was synthesized with precise control over their geometric shapes being obtained by a rational building-block design. Both narcissistic and social self-sorting was observed for reaction mixtures containing competitive precursors.

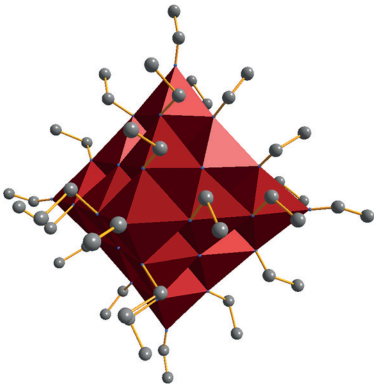


Solvothermal Syntheses

O. Nachtigall, M. Kusserow, R. Clérac,
W. Wernsdorfer, M. Menzel, F. Renz,
J. Mrozinski, J. Spandl* — 10361 – 10364

[Fe_{19}] "Super-Lindqvist" Aggregate and Large 3D Interpenetrating Coordination Polymer from Solvothermal Reactions of [$Fe_2(OtBu)_6$] with Ethanol

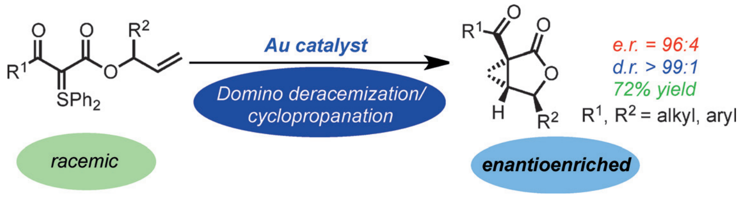
By temperature control, the solvothermal reaction of [$Fe_2(OtBu)_6$] with ethanol yields either a [Fe_{19}] "super-Lindqvist" aggregate or a mixed-valence iron coordination polymer. The [Fe_{19}] aggregate contains a [$Fe(\mu_6\text{-}O)_6$] core with a NaCl structure. The homoleptic coordination polymer consists of three 3D interpenetrating nets with hexagonal loops of ca. 50 × 16 Å.



Enantioselective Synthesis

S. Klimczyk, A. Misale, X. Huang,
N. Maulide* ______ **10365 – 10369**

Dimeric TADDOL Phosphoramidites in Asymmetric Catalysis: Domino Deracemization and Cyclopropanation of Sulfonium Ylides

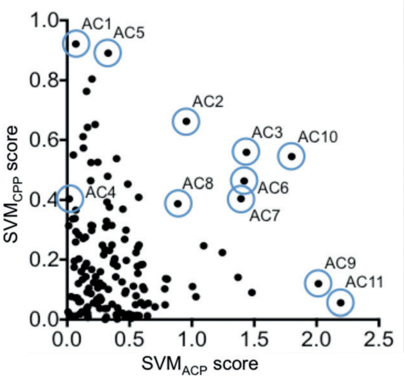


Master of all trades: A gold-catalyzed asymmetric cyclopropanation of unactivated olefins with sulfonium ylides has been developed that employs a bimetallic catalyst with a novel dimeric TADDOL ligand. This transformation allows a unique gold-catalyzed dynamic deracemization of chiral racemic substrates, with the products being useful building blocks in synthesis.

Peptide Design

Y.-C. Lin, Y. F. Lim, E. Russo, P. Schneider, L. Bolliger, A. Edenharter, K.-H. Altmann, C. Halin, J. A. Hiss,
G. Schneider* ______ **10370 – 10374**

Multidimensional Design of Anticancer Peptides



Ex machina: A computational method for the design of bioactive peptides was developed and applied to the discovery of minimalist linear membrane-active amino acid sequences with strong killing activity against cancer cells and a negligible effect on non-transformed cells. The technique considers several design objectives in parallel and is broadly applicable to rational peptide optimization.

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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