



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:

K. Ohmori, T. Shono, Y. Hatakoshi, T. Yano, K. Suzuki*

An Integrated Synthetic Strategy for Higher Catechin Oligomers

K. Nakano, S. Hashimoto, M. Nakamura, T. Kamada, K. Nozaki*
Synthesis of Stereogradient Poly(propylene carbonate) by Stereo- and Enantioselective Copolymerization of Propylene Oxide with Carbon Dioxide

X. Wurzenberger, H. Piotrowski, P. Klüfers*

A Stable Square-Planar High-Spin- d^6 Molecular $\text{Fe}^{\text{II}}\text{O}_4$ Chromophore From Rare Iron(II) Minerals

I. Piel, M. Steinmetz, K. Hirano, R. Fröhlich, S. Grimme,*
 F. Glorius*

Highly Asymmetric NHC-Catalyzed Hydroacylation of Unactivated Alkenes and Mechanistic Insights

Y. Han-ya, H. Tokuyama, T. Fukuyama*

Total Synthesis of (–)-Conophylline and (–)-Conophyllidine

N. Dietl, C. van der Linde, M. Schlangen, M. K. Beyer, H. Schwarz*
The Final Piece in an Intriguing Puzzle: Diatomic $[\text{CuO}]^+$ and Its Role in Spin-Selective Hydrogen- and Oxygen-Atom Transfer in the Thermal Activation of Methane

I. Garcia-Bosch, A. Company, C. W. Cady, S. Styring, W. R. Browne,
 X. Ribas, M. Costas*

Evidence for a Precursor Complex in C–H Hydrogen-Atom-Transfer Reactions Mediated by a Manganese(IV) Oxo Complex

G. N. Newton, S. Yamashita, K. Hasumi, J. Matsuno, N. Yoshida,
 M. Nihei, T. Shiga, M. Nakano, H. Nojiri, W. Wernsdorfer,
 H. Oshio*

Redox-Controlled Optimization of the Magnetic Properties of Keggin-Type $\{\text{Mn}_{13}\}$ Clusters

S. Zhou, S. Fleischer, K. Junge, M. Beller*

Cooperative Transition-Metal and Chiral Brønsted Acid Catalysis: Enantioselective Hydrogenation of Imines to Amines

J. M. Lee, W. Shim, J.-S. Noh, W. Lee*

Highly Mobile Thin Films on an Elastomeric Substrate as Gas Sensors: Palladium-Based Nanogap Hydrogen-Gas Sensors

C. C. Lee, Y. Hu,* M. W. Ribbe*

Tracing the Hydrogen Source of Hydrocarbons Formed by Vanadium Nitrogenase



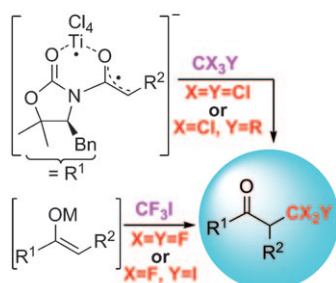
“My favorite piece of research is Günther Maier’s tetrahedrane synthesis.

The biggest challenge facing scientists is to not surrender in fighting the growing importance of business strategies in science ...”

This and more about A. Dieter Schlüter can be found on page 4540.

Author Profile

A. Dieter Schlüter _____ 4540



Radically unconventional: Natural products with di- and trichloromethyl groups and trifluoromethylated pharmaceuticals and agrochemicals are interesting compounds, often with intriguing properties. These types of compounds can be prepared by the direct perhaloalkylation of carbonyl compounds in which enolate reactivity and radical reactivity are merged (see scheme; Bn = benzyl).

Highlights

Perhaloalkylation

T. Amatov, U. Jahn* _____ 4542–4544

Perhaloalkylation of Metal Enolates—Unconventional and Versatile

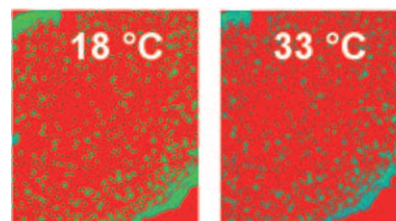
Minireviews

Upconverting Nanoparticles

L. H. Fischer, G. S. Harms,
O. S. Wolfbeis* — 4546–4551

Upconverting Nanoparticles for
Nanoscale Thermometry

Cell fever: Lanthanoid-ion-doped upconverting nanoparticles (UCNPs) display a strongly temperature-dependent luminescence that can be used to sense temperature in sub-micrometer dimensions, for example in cells or nanofluidics. The picture shows how green- and red-emitting UCNPs can be used to measure the temperature in kidney cells. The intensity ratio of two of these bands provides a referenced signal.



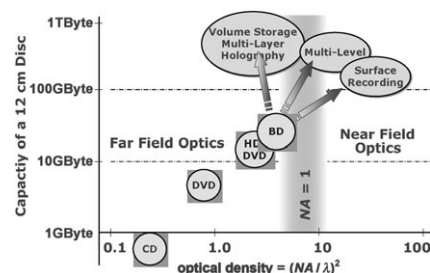
Reviews

Holographic Data Storage

F.-K. Bruder, R. Hagen, T. Rölle,
M.-S. Weiser, T. Fäcke* — 4552–4573

From the Surface to Volume: Concepts for
the Next Generation of Optical–
Holographic Data-Storage Materials

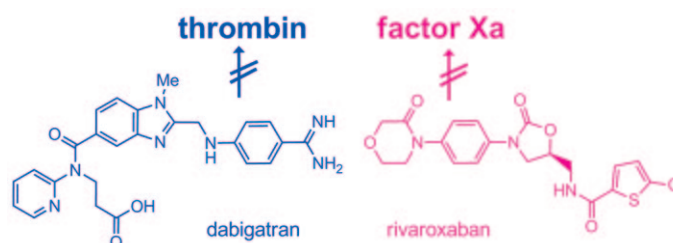
From surface to volume: Starting with the CD, optical data storage has shaped our lives. For the next generation of optical data-storage devices with robust data transfer characteristics, the development of new materials is necessary. This Review focuses on the material requirements for data-storage media and the chemical concepts they are based on and presents recent progress in the development of holographic read–write devices.



Protease Inhibitors

A. Straub,* S. Roehrig,
A. Hillisch — 4574–4590

Oral, Direct Thrombin and Factor Xa
Inhibitors: The Replacement for Warfarin,
Leeches, and Pig Intestines?



The race for orally available antithrombotic agents is in full swing. Several novel inhibitors of the blood-clotting cascade have been recently introduced to the market. The new factor Xa and thrombin

inhibitors (for examples see scheme) should herald a new generation of anti-thrombotic therapy. The history of their development is described here from the viewpoint of medicinal chemistry.

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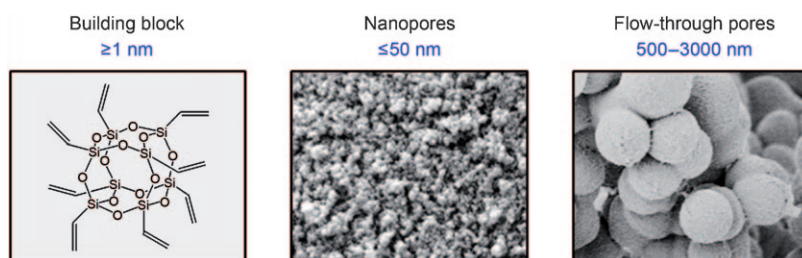
Communications

Polyhedral Silsesquioxanes



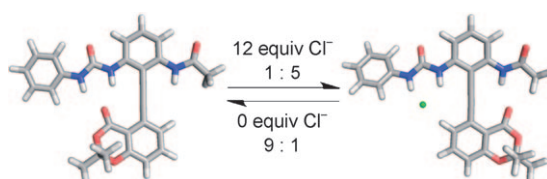
I. Nischang,* O. Brüggemann,
I. Teasdale _____ 4592 – 4596

Facile, Single-Step Preparation of
Versatile, High-Surface-Area,
Hierarchically Structured Hybrid
Materials



Strict hierarchy: A facile route to porous hybrid polymeric materials based on the vinyl polymerization of nanohybrid building blocks leads to a 3D nanoporous network with a high surface area. Through

the use of porogenic solvents, hierarchically structured porous materials with excellent flow-through properties and microfluidic dimensions were prepared with surface areas up to $900 \text{ m}^2 \text{ g}^{-1}$.



With a grain of salt: An anion-dependent switch based on an intramolecularly H-bonded diphenylacetylene is reported. The addition of Cl^- causes the conformation of the H-bond acceptor to switch from the

urea protons to the amide proton (see scheme; blue N, red O, green Cl), suggesting the use of such systems as fluorescent anion sensors.

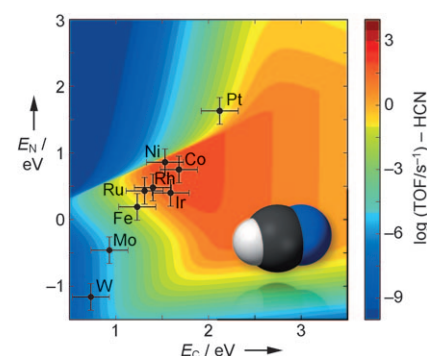
Molecular Switches

I. M. Jones,
A. D. Hamilton* _____ 4597 – 4600

Anion-Dependent Switching: Dynamically
Controlling the Conformation of
Hydrogen-Bonded Diphenylacetylenes



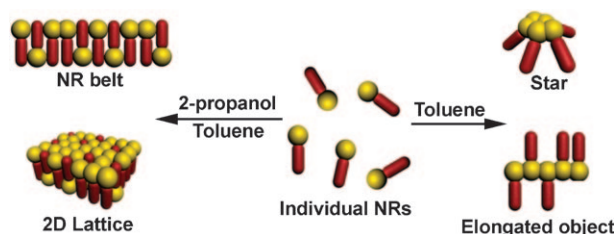
A trendy volcano: By the example of HCN synthesis from NH_3 and CH_4 , it is demonstrated how scaling relations for intermediates and transition states provide a basis for the prediction of trends in heterogeneous catalysis (see logarithmic turnover frequency, TOF). These trends include not only the activity but also selectivity and the dominant reaction mechanism. This general approach can be applied to a large number of catalytic systems.



Heterogeneous Catalysis

L. C. Grabow, F. Studt, F. Abild-Pedersen,
V. Petzold, J. Kleis, T. Bligaard,
J. K. Nørskov* _____ 4601 – 4605

Descriptor-Based Analysis Applied to
HCN Synthesis from NH_3 and CH_4



Belts, stars, 2D lattices, and elongated objects are formed by solution-based tip-to-tip or side-by-side self-assembly of single-tip Au–CdSe nanorods (see pic-

ture). Assembly was mediated by attraction between the Au or CdSe segments in selective solvents.

Nanorod Self-Assembly

N. Zhao, J. Vickery, G. Guerin, J. I. Park,
M. A. Winnik,
E. Kumacheva* _____ 4606 – 4610

Self-Assembly of Single-Tip Metal–
Semiconductor Nanorods in Selective
Solvents

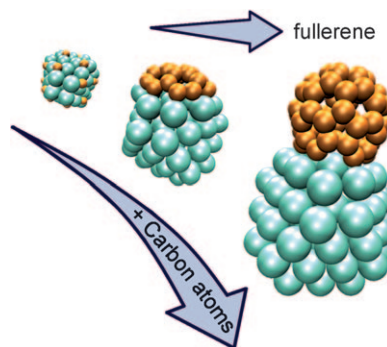


Fullerene Synthesis

F. Viñes,* A. Görling — 4611–4614



Template-Assisted Formation of Fullerenes from Short-Chain Hydrocarbons by Supported Platinum Nanoparticles



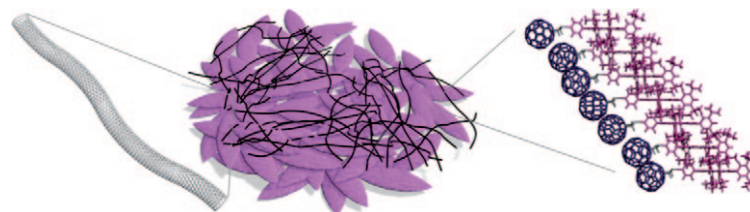
A C₆₀ bubble-maker: Induced by platinum nanoparticle templates, carbon atoms formed during the dehydrogenation of small hydrocarbon molecules gather and, reaching a certain coverage on the nanoparticle templates, form fullerenes (see picture). The tailor-made Pt nanoparticle templates exhibit defined shapes and sizes and are supported on inert or basic oxide supports.

Nanocarbon Materials

T. Umeyama, N. Tezuka, F. Kawashima, S. Seki,* Y. Matano, Y. Nakao, T. Shishido, M. Nishi, K. Hirao, H. Lehtivuori, N. V. Tkachenko,* H. Lemmetyinen, H. Imahori* — 4615–4619



Carbon Nanotube Wiring of Donor–Acceptor Nanograins by Self-Assembly and Efficient Charge Transport



Grain wiring: Functionalized single-wall carbon nanotube wiring between the nanograins of porphyrin (donor)–C₆₀ (acceptor) dyads results in efficient charge transport between them, leading

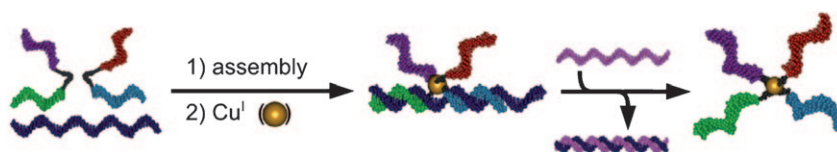
to the highest incident photon-to-current efficiency (22 %) ever reported for analogous photoelectrochemical devices utilizing donor–acceptor linked dyads.

DNA Nanostructures

H. Yang, F. Altvater, A. D. de Bruijn, C. K. McLaughlin, P. K. Lo, H. F. Sleiman* — 4620–4623



Chiral Metal–DNA Four-Arm Junctions and Metalated Nanotubular Structures



Daring to be different: Chiral DNA junctions with a transition metal at the branch point and four different DNA single-stranded arms were assembled by a combination of DNA templating and metal coordination in an approach that

enabled chirality transfer from DNA to the metal center (see picture). The intrinsic chirality of the junctions and their information density make them effective building blocks for 3D metal–DNA structures.

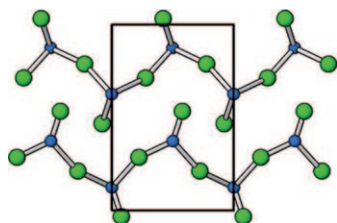
Energetic Materials

J. J. Sabatini,* J. C. Poret, R. N. Broad — 4624–4626

Boron Carbide as a Barium-Free Green Light Emitter and Burn-Rate Modifier in Pyrotechnics

Friendly green giant: A pyrotechnic with green-light emission for both military use and civilian fireworks has been developed without the need to use barium or chlorinated compounds. Boron carbide serves as a green colorant and fuel in the presence of potassium nitrate oxidizer and an epoxy binder. This environmentally friendly formulation is very stable to impact, friction, and electrostatic discharge, and has a high thermal stability.



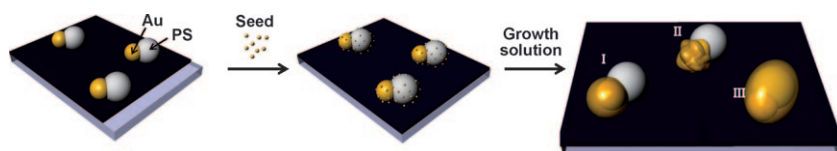


Randomness helps: Ab initio calculations were used to conduct global searches for local minima on the energy landscape of GeF_2 to predict stable configurations that can serve as targets for solid-state synthesis. The approach is able to reproduce reasonable structures showing lone pair effects without recourse to any preinformation.

Computational Chemistry

K. Doll, M. Jansen* — 4627 – 4632

Ab Initio Energy Landscape of GeF_2 :
A System Featuring Lone Pair Structure
Candidates



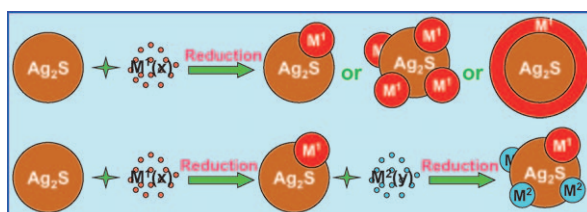
A closer look: The growth mechanism of nanoparticles is difficult to elucidate by common UV/Vis and TEM methods, owing to ensemble averaging and 2D projection effects. Single-particle scatter-

ing spectra were now used to investigate the overgrowth of gold on gold/polystyrene nanoparticles. Three patterns are readily differentiated, and corresponding overgrowth mechanisms are proposed.

Hybrid Nanoparticles

Y. I. Yang, E. Jeong, I. Choi, S. Lee,
H. D. Song, K. Kim, Y. Choi,* T. Kang,*
J. Yi* — 4633 – 4636

Simultaneous Optical Monitoring of the
Overgrowth Modes of Individual
Asymmetric Hybrid Nanoparticles



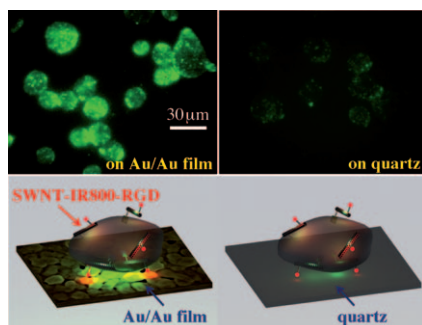
With a little help from my friends: Successive deposition of different noble metals on Ag_2S nanocrystals yields binary, ternary, and quaternary hybrid nanocom-

posites (see picture). In particular, the platinum-containing systems were found to exhibit superior catalytic activity toward methanol oxidation.

Composite Nanomaterials

J. Yang,* J. Y. Ying* — 4637 – 4643

Nanocomposites of Ag_2S and Noble
Metals



In the best light: Plasmonic gold substrates were used to image cells by near-infrared fluorescence microscopy. Two fluorophores (single-walled carbon nanotubes (SWNTs) functionalized by the RGD sequence as well as the organic fluorophore IR800) tag cells in two different spectral regions. The fluorescence of SWNTs sandwiched between a cell membrane and a gold film was enhanced relative to the fluorescence observed on a quartz substrate (see picture).

Live-Cell Imaging

G. Hong, S. M. Tabakman, K. Welsher,
Z. Chen, J. T. Robinson, H. Wang,
B. Zhang, H. Dai* — 4644 – 4648

Near-Infrared-Fluorescence-Enhanced
Molecular Imaging of Live Cells on Gold
Substrates

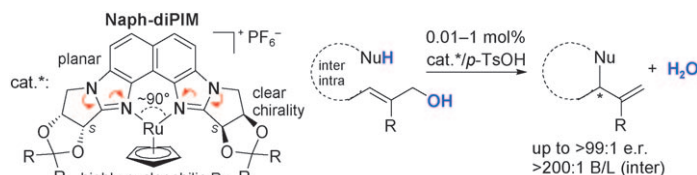


Asymmetric Catalysis

K. Miyata, H. Kutsuna, S. Kawakami,
M. Kitamura* — 4649–4653



A Chiral Bidentate sp^2 -N Ligand, Naph-diPIM: Application to CpRu-Catalyzed Asymmetric Dehydrative C-, N-, and O-Allylation



A handy new ligand: The CpRu complex (Cp = cyclopentadienyl) of a new type of chiral bisamidine ligand with a naphtho[1,2-*b*:7,8-*b'*]dipyrroloimidazole (Naph-diPIM) skeleton with a Brønsted acid efficiently catalyzes dehydrative intermo-

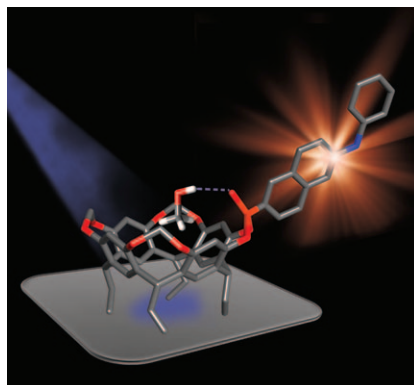
lecular C-allylation with high enantio- and regioselectivity. The catalytic system also gives nearly enantiomerically pure cycloalkanes and N- and O-heterocycles with a substrate/catalyst ratios of up to 10000.

Supramolecular Sensors

F. Maffei, P. Betti, D. Genovese,
M. Montalti, L. Prodi,* R. De Zorzi,
S. Geremia, E. Dalcanale* — 4654–4657



Highly Selective Chemical Vapor Sensing by Molecular Recognition: Specific Detection of C_1 – C_4 Alcohols with a Fluorescent Phosphonate Cavitand



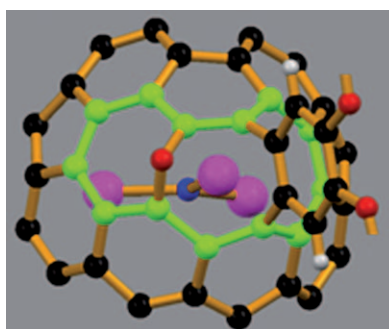
Fiat lux on alcohols: Molecular-level resolution was achieved for the detection of short-chain alcohols in the vapor phase using a fluorescent cavitand sensor. The transduction mechanism, activated exclusively by the complexation mode, is provided by the change of the electronic density on the fluorophore caused by the formation of an intracavity hydrogen bond between the cavitand P=O and the alcohol OH group.

Fullerene Chemistry

G.-W. Wang,* T.-X. Liu, M. Z. Jiao,
N. Wang, S.-E. Zhu, C. B. Chen,
S. F. Yang,* F. L. Bowles, C. M. Beavers,
M. M. Olmstead,* B. Q. Mercado,
A. L. Balch* — 4658–4662



The Cycloaddition Reaction of I_h - $Sc_3N@C_{80}$ with 2-Amino-4,5-diisopropoxybenzoic Acid and Isoamyl Nitrite to Produce an Open-Cage Metallofullerene



Opening a filled cage: Under an aerobic atmosphere, the reaction of I_h - $Sc_3N@C_{80}$ with 4,5-diisopropoxybenzyne generated in situ afforded an unprecedented open-cage metallofullerene with an oxygen atom and a benzyne addend spanning a 13-membered orifice (see picture, green; N blue, Sc pink, C black, O red, H white).

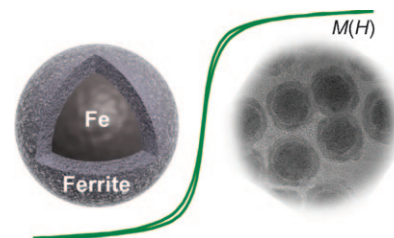
Nanoparticles for MR Imaging

T.-J. Yoon, H. Lee,* H. Shao,
R. Weissleder* — 4663–4666

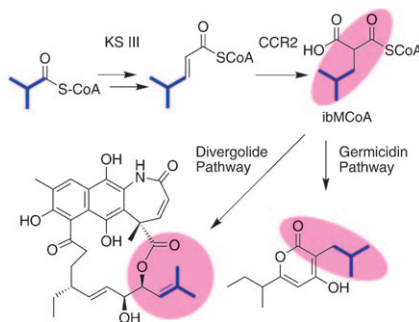


Highly Magnetic Core–Shell Nanoparticles with a Unique Magnetization Mechanism

The potent core: A new approach to preparing highly magnetic nanoparticles consisting of a ferromagnetic core (Fe) and an artificial ferrite shell was developed. The monometallic core contributes to high overall magnetization. The superparamagnetic ferrite shell protects the core against oxidation and further increases magnetization while minimizing particle aggregation.



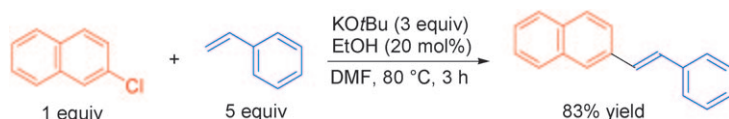
Sharing a branch: The first biosynthesis of an unprecedented branched PKS extender unit from valine/isobutyrate was unveiled, involving a designated ketosynthase III and a crotonyl reductase/carboxylase (CCR2). Isobutylmalonyl-CoA (ibMCoA) is not only employed in divergolide biosynthesis but is also incorporated into novel, antibacterial germicidins (see scheme). Such natural biocombinatorics are unparalleled in polyketide biosynthesis.



Polyketides

Z. Xu, L. Ding, C. Hertweck* 4667–4670

A Branched Extender Unit Shared between Two Orthogonal Polyketide Pathways in an Endophyte



In the absence of transition-metal catalysts, a Mizoroki-Heck-type reaction proceeded to give stilbene derivatives in a simple manner using an aryl halide, a

styrene derivative, KOtBu, EtOH, and DMF (see scheme; DMF = *N,N*-dimethylformamide).

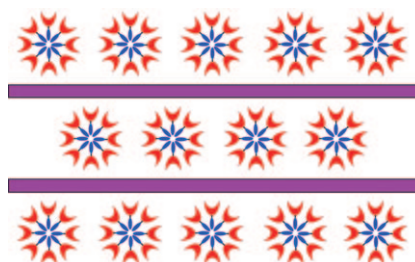
Synthetic Methods

E. Shirakawa,* X. Zhang, T. Hayashi* 4671–4674

Mizoroki-Heck-Type Reaction Mediated by Potassium *tert*-Butoxide



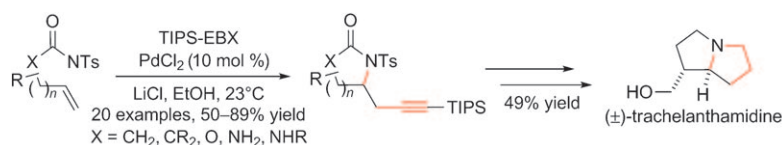
Supramolecular string of pearls: Polycationic ligands are designed to self-assemble into spherical pseudo-dendrimers that are capable of binding polyanionic heparin with affinities and binding modes similar to covalent nanostructures such as dendrimers and proteins (see picture; purple: heparin, red/blue: self-assembling ligand). Binding of the ligands to heparin induces nanoscale organization of the formed nanostructures.



Nanostructures

A. C. Rodrigo, A. Barnard, J. Cooper, D. K. Smith* 4675–4679

Self-Assembling Ligands for Multivalent Nanoscale Heparin Binding



Sweet cyclizations: The synthesis of pyrrolizidines and indolizidines has been achieved. Olefins were subjected to an intramolecular palladium-catalyzed aminoalkynylation with the hypervalent iodine reagent TIPS-EBX. After removal of

the protecting group, a two-step cyclization sequence and subsequent reduction led to the natural product (±)-trachelanthamidine (see scheme; TIPS-EBX = triisopropylsilyl ethynylbenziodoxolone).

Heterocyclic Synthesis

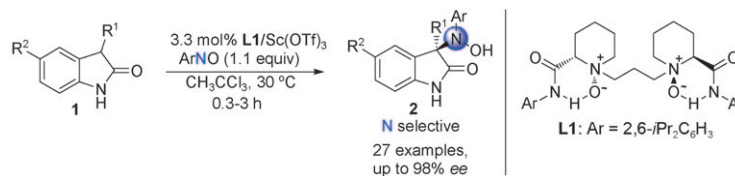
S. Nicolai, C. Piemontesi, J. Waser* 4680–4683

A Palladium-Catalyzed Aminoalkynylation Strategy towards Bicyclic Heterocycles: Synthesis of (±)-Trachelanthamidine



Asymmetric Catalysis

K. Shen, X. H. Liu, G. Wang, L. L. Lin,
X. M. Feng* — 4684–4688



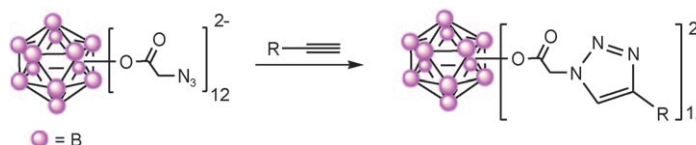
Facile and Efficient Enantioselective Hydroxyamination Reaction: Synthesis of 3-Hydroxyamino-2-Oxindoles Using Nitrosoarenes

Sc takes action: The highly enantioselective hydroxyamination reaction of N-unprotected 2-oxindoles with nitrosoarenes has been realized using the Sc(OTf)₃/L1 complex. The catalyst system exhibited remarkably broad substrate

scope and high efficiency. This transformation is the first example of a chiral Sc^{III}/enolate activating a nitrosoarene, and can be conducted on a gram scale without loss in the ee values.

Polyhedral Boranes

L. N. Goswami, S. Chakravarty, M. W. Lee,
S. S. Jalisatgi,
M. F. Hawthorne* — 4689–4691



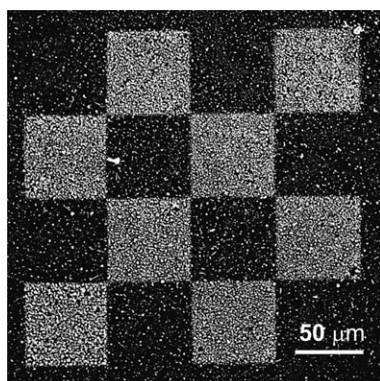
Extensions of the Icosahedral Closomer Structure by Using Azide–Alkyne Click Reactions

Clusters with a click: The chemistry of icosahedral borane closomers has been combined with click chemistry for the first time. This approach provided a facile

syntheses of diverse 12-fold closomer nanoparticles (see scheme; R = alkyl or aryl) which could be adapted for biomedical and material applications.

Electron-Beam Lithography

V. Halka, M. J. Schmid, V. Avrutskiy, X. Ma,
R. Schuster* — 4692–4695

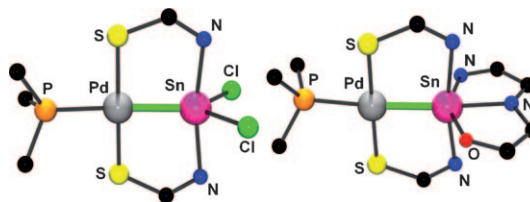


Electron-Beam-Induced Deposition of Metallic Microstructures from a Molten-Salt Film on Conductive and Nonconductive Substrates

Microscale checkerboard: A thin liquid electrolyte layer can serve as the precursor for the direct electron-beam-induced deposition of metal on conductive and nonconductive substrates. Mass transport in the film is the key for nucleation and growth of Ag crystallites, which are strongly attached to the substrate surface. The precision of the structures is of the order of the film dimensions (picture: checkerboard pattern of Ag particles on Si).

Coordination Chemistry

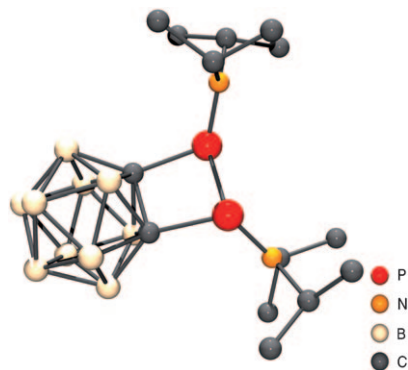
E. Brendler, E. Wächter, T. Heine,
L. Zhechkov, T. Langer, R. Pöttgen,
A. F. Hill, J. Wagler* — 4696–4700



Stannylene or Metallastanna(IV)ocane: A Matter of Formalism

Pushmi-pullyu with palladium: Although created by σ donation from SnCl₂ to a Pd complex, the Sn–Pd bonds in the compounds depicted exhibit formal σ donation in the opposite direction. Computa-

tional and spectroscopic data support stannylpalladium (Pd^I–Sn^{III}) and palladastanna(IV)ocane (Pd⁰→Sn^{IV}) descriptions over stannylene coordination.

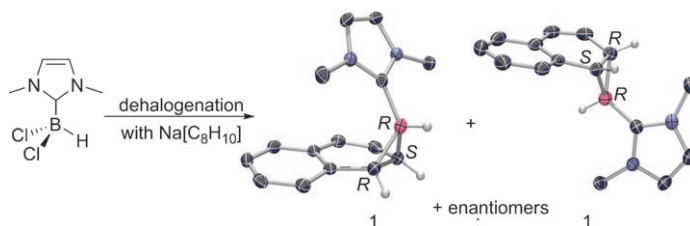


The ring and I: Air- and water-stable 1,2-diphosphetanes (see structure) were prepared in high yield utilizing the unique electronic and structural properties of 1,2-dicarba-*closo*-dodecaborane(12)s. Ring-opening reactions with elemental iodine gave the first 1,2-bis(iodophosphanyl)-1,2-dicarba-*closo*-dodecaborane(12)s.

Phosphorus Heterocycles

A. Kreienbrink, M. B. Sárosi, E. G. Rys,
 P. Lönnecke,
 E. Hey-Hawkins* _____ 4701 – 4703

Carbaborane-Substituted
 1,2-Diphosphetanes



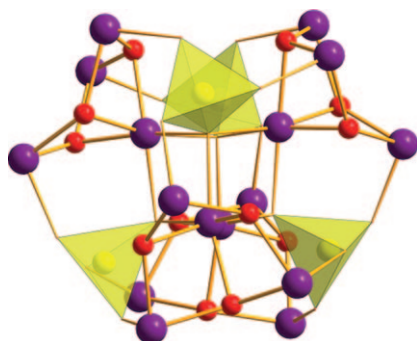
The taming of borylene: Dehalogenation of $\text{BHCl}_2\cdot\text{IMe}$ ($\text{IMe} = 1,3\text{-dimethylimidazol-2-ylidene}$) leads to a carbene-stabilized elusive B–H borylene. A *syn*-selective [2+1] cycloaddition with naphthalene enabled the isolation and full character-

ization of the resulting diastereomeric products. These findings along with calculations provide clear evidence for the existence of borylenes (crystal structures: B violet, C black, H gray, N blue).

B–H Borylenes

P. Bissinger, H. Braunschweig,* K. Kraft,
 T. Kupfer _____ 4704 – 4707

Trapping the Elusive Parent Borylene



POMs, magnets, and Co: The tetrameric 36-tungsto-8-phosphate $[\{\text{Co}_4(\text{OH})_3\text{PO}_4\}_4\text{-(PW}_9\text{O}_{34})_4\}]^{28-}$ containing 16 cobalt(II) centers was prepared by a simple, one-pot synthetic procedure. The $\{\text{Co}_{16}(\text{OH})_{12}\text{-(PO}_4)_4\}^{8+}$ core (see picture) exhibits single-molecule magnetic behavior.

Polyoxometalates

M. Ibrahim, Y. Lan, B. S. Bassil, Y. Xiang,
 A. Suchopar, A. K. Powell,*
 U. Kortz* _____ 4708 – 4711

Hexadecacobalt(II)-Containing
 Polyoxometalate-Based Single-Molecule
 Magnet



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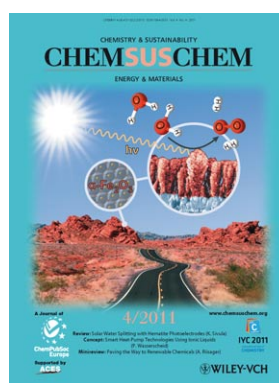
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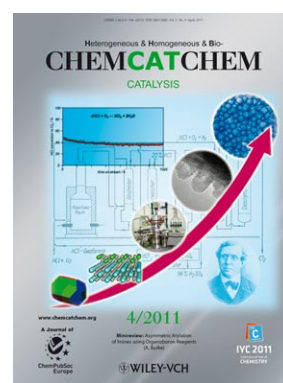
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