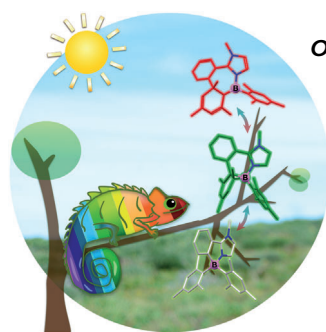


... using the [NiFe]hydrogenase (H_2ase) S-77 as the hydrogen anode is described by P. Ogo et al. in their Communication on page 8895 ff. The enzyme has a mass activity that is over 600 times greater than that of platinum, is stable to air, and can be recovered after CO poisoning.

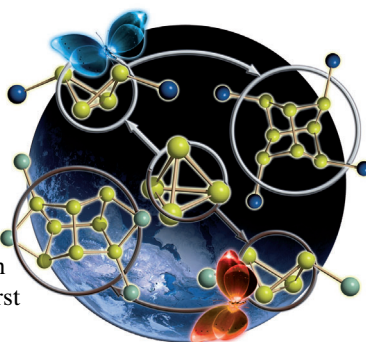
Conjugated Polymers

K. Sugiyasu, M. Takeuchi, et al. describe micro-phase separation in polythiophene copolymers with unfunctionalized and “fenced” blocks in their Communication on page 8870 ff. π - π stacking of the unfunctionalized block results in an ensemble of stacked and isolated polythiophenes.



Organoboron Compounds

In their Communication on page 9086 ff., H. Braunschweig, S. Wang, et al. describe the isolation of the first example of azaborabenzotropolilidenes and the direct observation of an unprecedented photothermal interconversion between azaborabenzotropolilidene and azaborabenzotropolilidene.



Phosphorus and Arsenic Complexes

P_4 and As_4 butterfly complexes of iron and chromium can be prepared. As described by M. Scheer et al. in their Communication on page 9077 ff., they can react further afford the first examples of As_8 cuneane complexes.

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Service

Spotlight on Angewandte's Sister Journals

8812–8815

Author Profile



"My worst nightmare is to have to stop promising scientific work.

The most exciting thing about my research is a lot of wonderful (chemical) surprises ..."

This and more about Sergey Troyanov can be found on page 8816.

Sergey Troyanov ————— 8816

Books

Photochemistry and Photophysics

Vincenzo Balzani, Paola Ceroni, Alberto Juris

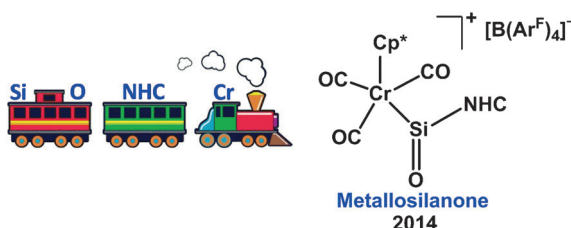
reviewed by X. Ma, H. Tian ————— 8817

Highlights

Si=O Bonds

S. S. Sen* ————— 8820–8822

A Stable Silanone with a Three-Coordinate Silicon Atom: A Century-Long Wait is Over



Mission accomplished: More than 100 years after first attempts at isolating a stable silanone, this task has finally been completed with the isolation of a metallosilanone complex (see Scheme). The elusive bare Si=O bond was made acces-

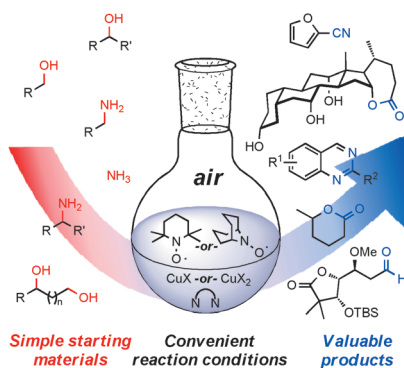
sible by utilizing the coordination sphere of an electron-rich chromium fragment in combination with a sterically demanding saturated N-heterocyclic carbene (NHC) to protect the reactive site.

Minireviews

Aerobic Oxidation

B. L. Ryland, S. S. Stahl* — 8824–8838

Practical Aerobic Oxidations of Alcohols and Amines with Homogeneous Copper/TEMPO and Related Catalyst Systems



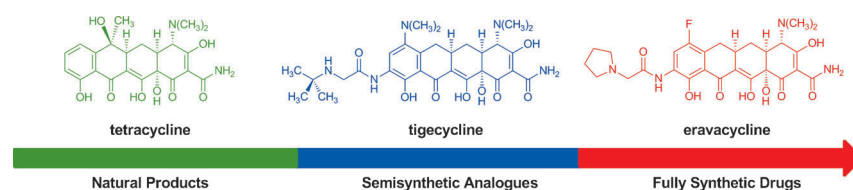
Coming up for air: Cu/nitroxyl catalysts for aerobic alcohol oxidation have been developed that exhibit near-ideal reaction conditions: operation at room temperature, use of ambient air as the oxidant, and complete reaction within one hour. These methods, together with related amine oxidations, have the potential to be the first class of aerobic oxidation reactions widely used in organic chemistry.

Reviews

Antibiotic Development

P. M. Wright, I. B. Seiple,
A. G. Myers* — 8840–8869

The Evolving Role of Chemical Synthesis in Antibacterial Drug Discovery



Chemical synthesis enabled the development of the first antibacterial substances, but these were soon outshone by more powerful antibiotics from nature. Many antibiotics are now significantly less effective due to rapid evolution of resist-

ance within pathogenic bacteria. It is believed that the strategic application of modern synthesis to antibacterial drug discovery can avert a crisis of potentially global proportions.

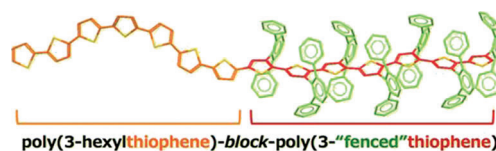
Communications

Conjugated Polymers

C. Pan, K. Sugiyasu,* J. Aimi, A. Sato,
M. Takeuchi* — 8870–8875



Picket-Fence Polythiophene and its Diblock Copolymers that Afford Microphase Separations Comprising a Stacked and an Isolated Polythiophene Ensemble



Stack control: All-polythiophene diblock copolymers, comprising one unsheathed block (left) and one fenced block (right), were synthesized through catalyst-transfer polycondensation. The unsheathed block

self-assembles through π - π stacking, thereby inducing microphase separation. As a consequence, a microphase separation is created with an ensemble of stacked and isolated polythiophenes.

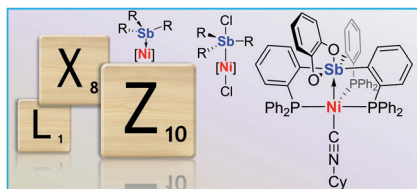
Frontispiece

For the USA and Canada:

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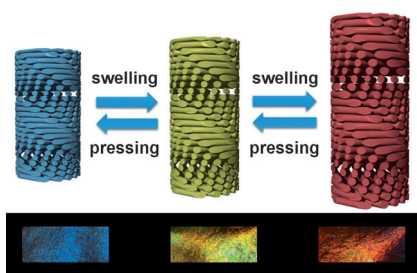
Pick a letter: A series of redox and anion exchange reactions carried out on a novel SbNi complex can be used to transform the starting stibine ligand (L-type) into a stiboranyl (X-type) and stiborane (Z-type) ligand without dissociation of the coordinated nickel atom (see picture). These results provide the first example of a complex in which the ligating atom can adopt all three ligand functions of the covalent bond classification.

Coordination Chemistry

J. S. Jones, C. R. Wade,
F. P. Gabbaï* _____ **8876–8879**

Redox and Anion Exchange Chemistry of a Stibine–Nickel Complex: Writing the L, X, Z Ligand Alphabet with a Single Element

Inside Cover



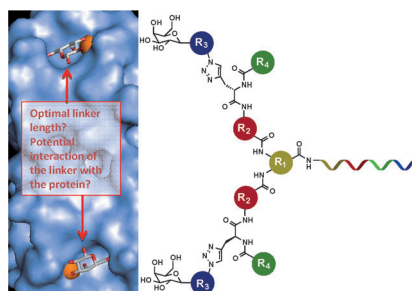
Eye-catching photonic origami: The invention of a supramolecular cotemplating method led to photonic cellulose material—an active form of “paper” with mesopores and dynamic structural colors. The high flexibility and rapid response upon swelling or pressing of these cellulose-based materials (see picture) make them suitable for applications in pressure or polarity sensing as well as for optical filters.

Mesoporous Materials

M. Giese, L. K. Blusch, M. K. Khan,
W. Y. Hamad,*
M. J. MacLachlan* _____ **8880–8884**

Responsive Mesoporous Photonic Cellulose Films by Supramolecular Cotemplating

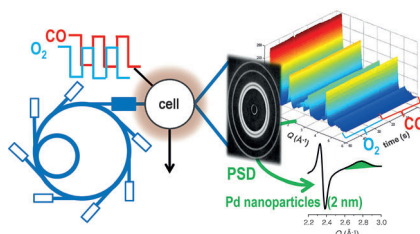
Optimal combination: Lectin LecA is a pathogenicity factor from *P. aeruginosa* involved in lung injury and cellular invasion. A novel divalent ligand identified from a focused glycan array binds to LecA with very high affinity and shows a strong inhibition of host cell invasion. Cocystal structures provided a rationale for its binding affinity.



Drug Discovery

A. Novoa, T. Eierhoff, J. Topin, A. Varrot,
S. Barluenga, A. Imberty,* W. Römer,*
N. Winssinger* _____ **8885–8889**

A LecA Ligand Identified from a Galactoside-Conjugate Array Inhibits Host Cell Invasion by *Pseudomonas aeruginosa*



Take a good look: By combining time-resolved high-energy X-ray diffraction (XRD) with a modulation approach, the sensitivity can be increased so that subtle structural changes during a reaction become visible. Therefore, palladium particles with a diameter of approximately 2 nm could be detected by XRD, and their dynamic behavior under CO/O₂ pulses was analyzed.

Heterogeneous Catalysis

D. Ferri,* M. A. Newton,* M. Di Michiel,*
G. L. Chiarello, S. Yoon, Y. Lu,
J. Andrieux _____ **8890–8894**

Revealing the Dynamic Structure of Complex Solid Catalysts Using Modulated Excitation X-ray Diffraction

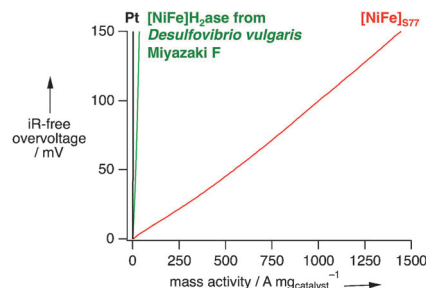
Fuel Cells

T. Matsumoto, S. Eguchi, H. Nakai,
T. Hibino, K.-S. Yoon,
S. Ogo* 8895–8898



[NiFe]Hydrogenase from *Citrobacter* sp.
S-77 Surpasses Platinum as an Electrode
for H₂ Oxidation Reaction

Outperforming Pt: An electrode for the H₂ oxidation reaction is based on [NiFe]Hydrogenase from *Citrobacter* sp. S-77 ([NiFe]_{S77}). It has a 637 times higher mass activity than Pt at 50 mV in a hydrogen half-cell, is stable in air and, unlike Pt, can be recovered 100% after poisoning by CO. A fuel cell comprising a [NiFe]_{S77} anode and Pt cathode was constructed and thus demonstrated a higher power density than that of Pt.



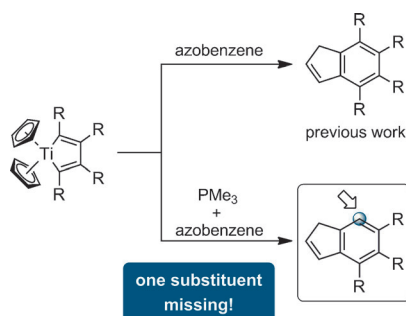
Front Cover

C–C Bond Cleavage

Y. Mizukami, H. Li, K. Nakajima, Z. Song,
T. Takahashi* 8899–8903



Coupling of Titanacyclopentadienes with
a Cp Ligand and Elimination of One
Substituent



On the trail of the one that got away: 4,5,6-Trisubstituted indene derivatives were formed in good yields by the treatment of titanacyclopentadienes with PMe₃ and then azobenzene. The coupling of a Cp ligand with the diene moiety of the complex was accompanied by the removal of one substituent, in sharp contrast to the formation of 4,5,6,7-tetrasubstituted indene derivatives without the loss of a substituent in the absence of PMe₃ (see scheme).

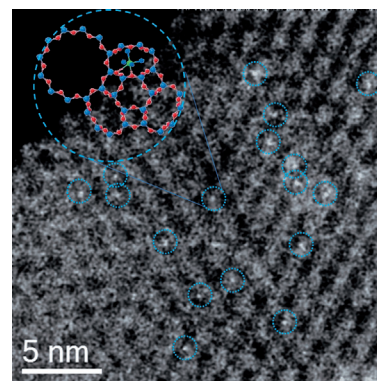
Platinum in Zeolites

J. D. Kistler, N. Chotigkrai, P. Xu,
B. Enderle, P. Praserttham, C. Y. Chen,
N. D. Browning,
B. C. Gates* 8904–8907



A Single-Site Platinum CO Oxidation
Catalyst in Zeolite KLTL: Microscopic and
Spectroscopic Determination of the
Locations of the Platinum Atoms

In the right spot: A site-isolated mono-nuclear platinum catalyst is supported in the zeolite KLTL with a stable and well-defined structure. This catalyst was examined spectroscopically and imaged with STEM (see picture) to show locations of the platinum complexes (blue circles) within the zeolite pores.

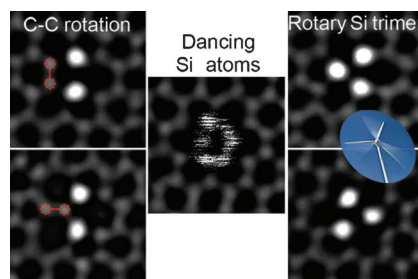


Doping Graphene

Z. Q. Yang,* L. C. Yin, J. Lee, W. C. Ren,
H.-M. Cheng, H. Q. Ye, S. T. Pantelides,
S. J. Pennycook,
M. F. Chisholm* 8908–8912

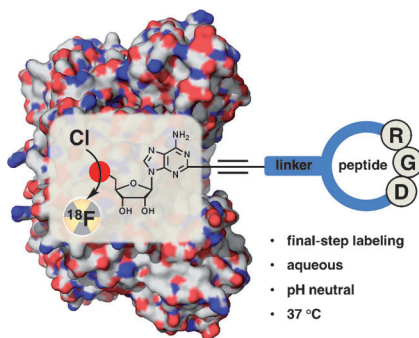


Direct Observation of Atomic Dynamics
and Silicon Doping at a Topological
Defect in Graphene



Atomic competition: The dynamic atomic processes during the formation of a rotary Si trimer in monolayer graphene were monitored using aberration-corrected scanning-transmission electron microscopy. An incoming Si atom competes with and replaces a metastable C dimer next to a pair of Si substitutional atoms at a topological defect in graphene, producing a Si trimer.

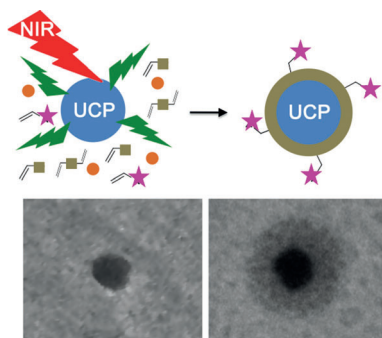
Leave it 'til the last minute: Direct “last-step” ^{18}F radiolabeling of bioactive peptides is achieved by exploiting an “Achilles heel” in the substrate specificity of the fluorinase enzyme. These isotopically labeled biomolecules can be prepared under ambient pH neutral conditions using aqueous (H_2^{18}O) cyclotron-generated [^{18}F]fluoride and are suitable for application as tracers in positron emission tomography.



Radiolabeling

S. Thompson, Q. Zhang, M. Onega, S. McMahon, I. Fleming, S. Ashworth, J. H. Naismith, J. Passchier, D. O'Hagan* **8913–8918**

A Localized Tolerance in the Substrate Specificity of the Fluorinase Enzyme enables “Last-Step” ^{18}F Fluorination of a RGD Peptide under Ambient Aqueous Conditions

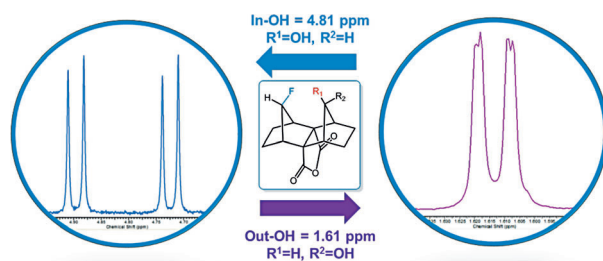


An IRregular initiator: The UV or visible light emitted by photoexcited (by near-infrared light) upconverting nanoparticles (UCPs) was used to photopolymerize a thin polymer coating around the UCPs for their protection, functionalization, and conjugation (see picture). The method has the advantages of ease of application and rapid surface functionalization, and the polymer-encapsulated UCPs are suitable for applications in bioassays, imaging, and drug delivery.

Upconversion Nanoparticles

S. Beyazit, S. Ambrosini, N. Marchyk, E. Palo, V. Kale, T. Soukka, B. Tse Sum Bui,* K. Haupt* **8919–8923**

Versatile Synthetic Strategy for Coating Upconverting Nanoparticles with Polymer Shells through Localized Photopolymerization by Using the Particles as Internal Light Sources



Close encounters: The spectroscopic properties of a caged fluorine molecule with a strong $\text{C}-\text{F}\cdots\text{H}-\text{O}$ interaction were studied. While computations and NMR data afford evidence for a strong inter-

action, almost no shift of the OH stretch in the IR spectrum was detected. These data point to a rare no-shift hydrogen bond, in which the bond's red- and blue-shift character cancels.

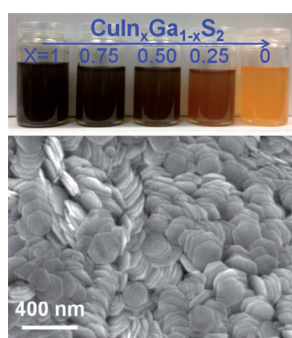
Noncovalent Interactions

M. D. Struble, C. Kelly, M. A. Siegler, T. Lectka* **8924–8928**

Search for a Strong, Virtually “No-Shift” Hydrogen Bond: A Cage Molecule with an Exceptional $\text{OH}\cdots\text{F}$ Interaction



Step up to the nanoplate: A facile and general method was used to synthesize monodispersed copper-based ternary and quaternary semiconducting nanoplates (i.e., $\text{CuIn}_x\text{Ga}_{1-x}\text{S}_2$ and $\text{Cu}_2\text{ZnSnS}_4$) with pre-synthesized ultrathin CuS nanoplates as a template. The obtained nanoplates had tunable optical properties, and a photoelectrochemical device based on $\text{Cu}_2\text{ZnSnS}_4$ nanoplates demonstrated promise for photovoltaic devices.



Nanostructures

X.-J. Wu, X. Huang, X. Y. Qi, H. Li, B. Li, H. Zhang* **8929–8933**

Copper-Based Ternary and Quaternary Semiconductor Nanoplates: Templated Synthesis, Characterization, and Photoelectrochemical Properties



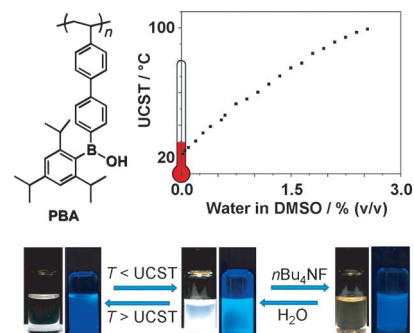
Smart Polyacids

W. Wan, F. Cheng, F. Jäkle* . 8934–8938



A Borinic Acid Polymer with Fluoride Ion- and Thermo-responsive Properties that are Tunable over a Wide Temperature Range

Reversibly multi-responsive: A new type of smart polymer with borinic acid moieties has been developed. Polymer PBA has an upper critical solution temperature (UCST) that is tunable from 20 to 100 °C; it also responds to the binding of fluoride to the Lewis acidic boron centers, enabling potential applications in trace water detection and anion recognition.

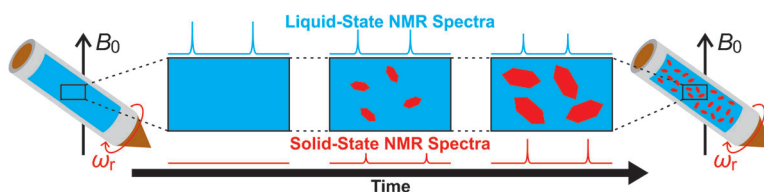


Crystallization

C. E. Hughes, P. A. Williams, K. D. M. Harris* . 8939–8943



“CLASSIC NMR”: An In-Situ NMR Strategy for Mapping the Time-Evolution of Crystallization Processes by Combined Liquid-State and Solid-State Measurements



Killing two birds with one stone: A new in-situ NMR strategy (termed CLASSIC NMR) for mapping the evolution of crystallization processes is reported, involving simultaneous measurement of both liquid-state and solid-state NMR

spectra as a function of time. This combined strategy allows complementary information to be obtained on the evolution of the solid phase during the crystallization process as well as the corresponding changes in the solution phase.



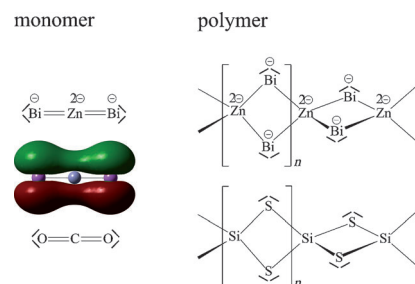
Zintl Ions

C. B. Benda, T. Köchner, R. Schäper, S. Schulz, T. F. Fässler* . 8944–8948



Bi–Zn Bond Formation in Liquid Ammonia Solution: $[\text{Bi}–\text{Zn}–\text{Bi}]^{4-}$, a Linear Polyanion that is Iso(valence)-electronic to CO_2

Metallic carbon dioxide: The metal atoms Bi and Zn form two isomers, molecular $[\text{Bi}–\text{Zn}–\text{Bi}]^{4-}$ and polymeric $[\text{ZnBi}_2]^{4-}$, whereas iso(valence)-electronic CO_2 and SiS_2 adopt only one form under standard conditions. The linear anion $[\text{Bi}–\text{Zn}–\text{Bi}]^{4-}$ found in the compound $\text{K}_4[\text{ZnBi}_2](\text{NH}_3)_{12}$ is formed in the reaction of a low-valent Zn^{I} compound with a solution of the neat solid K_3Bi_2 in liquid ammonia under mild reaction conditions.



Zeolites

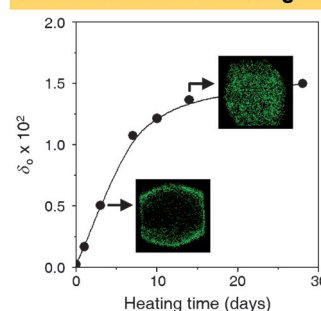
J. Shin, N. H. Ahn, M. A. Camblor, S. J. Cho, S. B. Hong* . 8949–8952

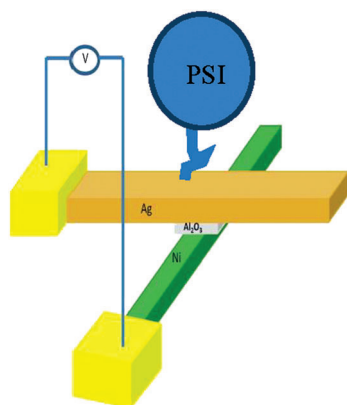


Intraframework Migration of Tetrahedral Atoms in a Zeolite

Migration in natrolite: Clear experimental evidence for the intraframework migration of tetrahedral atoms (T-atoms) in natrolite-type zeolites is presented. This process is triggered by species in solution, accompanied by T-atom ordering, and occurs without Ostwald ripening or “classical” dissolution–recrystallization processes. δ_o = orthorhombic distortion.

Intraframework T-atom migration



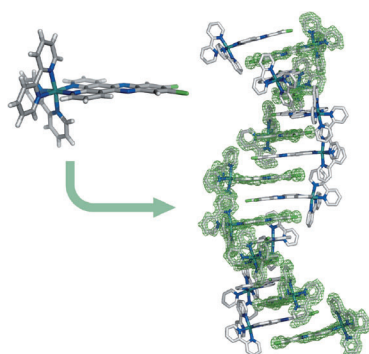


Unexpected influence: By using a newly developed spintronic device it is shown that the electron transfer (ET) efficiency of photosystem I (PSI) is affected by the electrons' spin. High-spin selectivity is found throughout the entire ET path, and the spins of the electrons being transferred are aligned parallel to their momenta.

Spintronics

I. Carmeli, K. S. Kumar, O. Heifler,
C. Carmeli, R. Naaman* — **8953–8958**

Spin Selectivity in Electron Transfer in Photosystem I



Unprecedented crystal structures of a ruthenium(II) complex were obtained, showing a left-handed double helical assembly of only the Δ -enantiomer, leading to an alternating tread stairs-like arrangement, which mimics the DNA double helix structure. Two different polymorphs could be distinguished: a crossed woodpile structure versus a parallel columnar stacking.

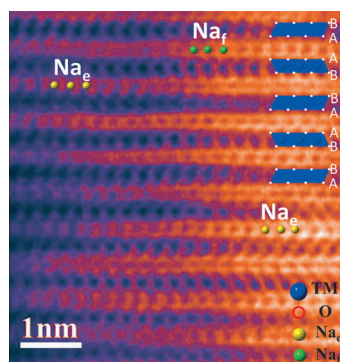
Helical Self-Assembly

K. Van Hecke,* T. Cardinaels,
P. Nockemann, J. Jacobs, L. Vanpraet,
T. N. Parac-Vogt, R. Van Deun,
K. Binnemans,
L. Van Meervelt — **8959–8962**

Enantioselective Assembly of a Ruthenium(II) Polypyridyl Complex into a Double Helix



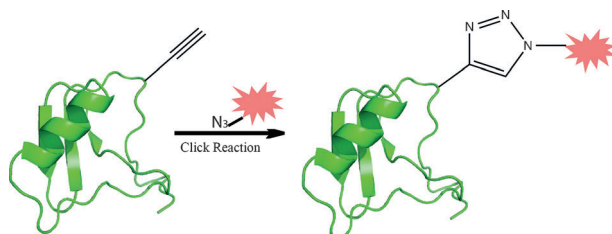
Cycle stability: When a novel and ultra-stable P2-type titanium-based material was used as the anode, a sodium-ion battery with a long cycle life was obtained. A capacity retention of 84.84% after 3000 cycles and a small volume contraction of only 0.046% after 500 cycles lead to the outstanding cycle stability.



Sodium-Ion Batteries

H. J. Yu, Y. Ren, D. D. Xiao, S. H. Guo,
Y. B. Zhu, Y. M. Qian, L. Gu,*
H. S. Zhou* — **8963–8969**

An Ultrastable Anode for Long-Life Room-Temperature Sodium-Ion Batteries



Modern ligation methods were used to establish the total chemical synthesis of the Ts1 protein. By using click chemistry the synthetic Ts1 molecule was site-spe-

cifically labeled with fluorescent dyes. Dye-labeled Ts1 protein bound to the voltage-gated sodium channel Na_v and modified its voltage dependence.

Dye-Labeled Ts1 toxin

B. Dang, T. Kubota, A. M. Correa,
F. Bezanilla, S. B. H. Kent* — **8970–8974**

Total Chemical Synthesis of Biologically Active Fluorescent Dye-Labeled Ts1 Toxin



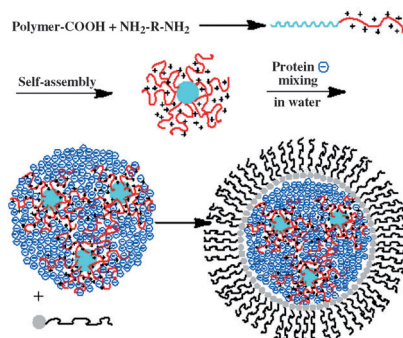


Nanomedicine

J. Wu, N. Kamaly, J. Shi, L. Zhao, Z. Xiao,
G. Hollett, R. John, S. Ray, X. Xu, X. Zhang,
P. W. Kantoff,
O. C. Farokhzad* — 8975–8979



Development of Multinuclear Polymeric
Nanoparticles as Robust Protein
Nanocarriers



Polymer–polycation nanoparticles have been used as nuclei to readily adsorb large amounts of protein (> 20% of the nanoparticles by weight) to form new hybrid nanospheres with diameters < 200 nm in aqueous solutions without organic solvents through electrostatic interactions. This model system was used to demonstrate the relationships between nanoparticle size, surface charge, polymer–polycation composition, and protein loading.

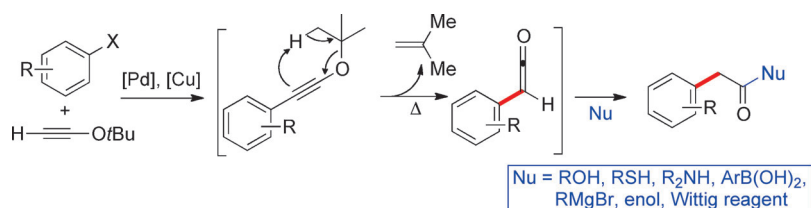


Ketenes

W. Zhang, J. M. Ready* — 8980–8984



The Ketene-Surrogate Coupling: Catalytic
Conversion of Aryl Iodides into Aryl
Ketenes through Ynol Ethers



Setting a trap: Coupling of a terminal ynol ether with aryl iodides enables a catalytic synthesis of aryl ketenes. In situ trapping with nucleophiles provides a wide array of aryl acetic acids and benzyl ketones with

only HI and isobutylene as chemical waste. The aryl ketenes additionally participate in electrocyclic ring closure to yield naphthols and quinolines.

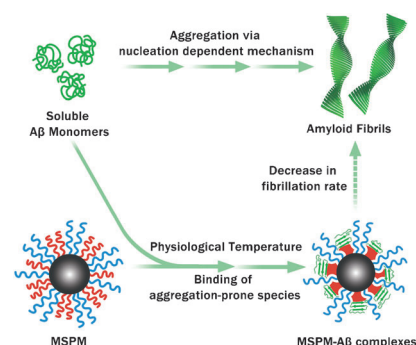
Artificial Chaperones

F. Huang, J. Wang, A. Qu, L. Shen, J. Liu,
J. Liu, Z. Zhang, Y. An,
L. Shi* — 8985–8990



Maintenance of Amyloid β Peptide
Homeostasis by Artificial Chaperones
Based on Mixed-Shell Polymeric Micelles

Maintaining homeostasis: Mixed-shell polymeric micelles (MSPMs) with tunable surface properties can act as an artificial chaperone. These chaperones can maintain amyloid β ($A\beta$) homeostasis by inhibiting $A\beta$ fibrillation and facilitating $A\beta$ aggregate clearance, and can also reduce $A\beta$ -mediated neurotoxicity.



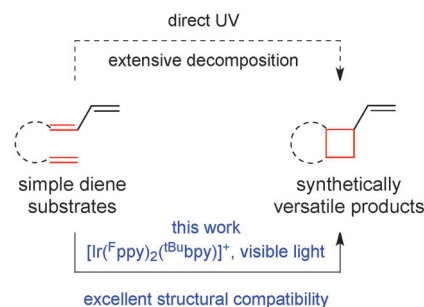
Photochemistry

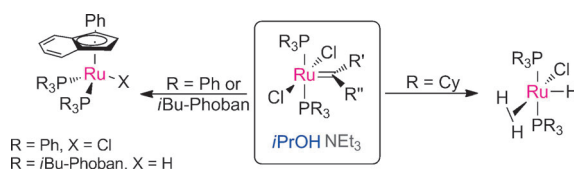
A. E. Hurtley, Z. Lu,
T. P. Yoon* — 8991–8994



[2+2] Cycloaddition of 1,3-Dienes by
Visible Light Photocatalysis

Square dance: A convenient and highly functional-group-tolerant [2+2] cycloaddition of 1,3-dienes that operates under visible light irradiation is reported. The vinylcyclobutane products serve as versatile synthetic intermediates in a range of further transformations as illustrated by a concise synthesis of the marine natural product (\pm)-epiraikovenal. bpy = bipyridyl, ppy = phenylpyridyl.





Ligands make a difference: The decomposition of olefin metathesis precatalysts in isopropyl alcohol leads to a series of differing complexes. Bis(tricyclohexylphosphane)-bearing complexes decompose to yield $[\text{RuCl}(\text{H})(\text{H}_2)(\text{PCy}_3)_2]$, while

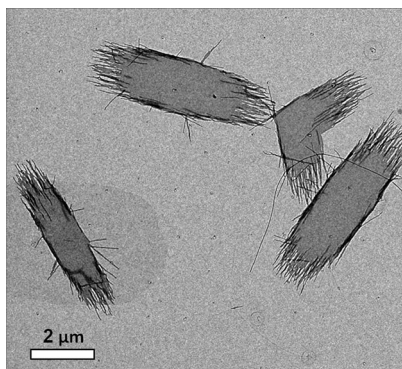
bis(triphenylphosphane) and bis(*i*Bu-Phoban)-bearing indenylidene complexes yield η^5 -(3-phenyl)indenyl complexes. The (3-phenyl)indenylidene to η^5 -indenyl rearrangement for three complexes has been probed using DFT calculations.

Reaction Mechanisms

S. Manzini, A. Poater, D. J. Nelson, L. Cavallo, A. M. Z. Slawin, S. P. Nolan* 8995 – 8999

Insights into the Decomposition of Olefin Metathesis Precatalysts

A novel mechanism of lamella formation is described, which involves the hierarchical self-assembly of poly(ethylene oxide)-*block*-polycaprolactone micelles in water. Spheres transform first into rods, which then align spontaneously and associate laterally to form extended lamellar sheets. These self-assembled lamellar “rafts” are thus quite different from the traditional chain-folded crystalline lamellae.

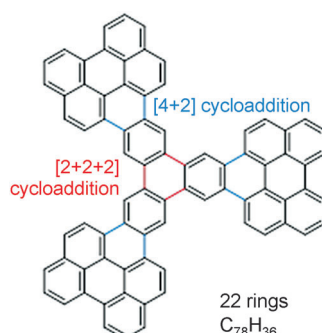


Lamellae from Rods

G. Rizis, T. G. M. van de Ven,* A. Eisenberg* 9000 – 9003

“Raft” Formation by Two-Dimensional Self-Assembly of Block Copolymer Rod Micelles in Aqueous Solution

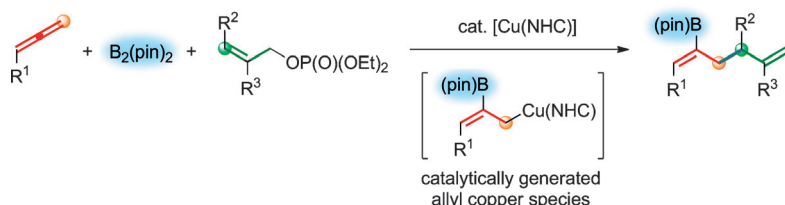
A threefold symmetric nanographene was synthesized by following a simple procedure based on two sequential aryne cycloadditions in solution starting from perylene. The clover-shaped graphene molecule was characterized with atomic resolution by scanning probe microscopy.



Nanographenes

B. Schuler, S. Collazos, L. Gross, G. Meyer, D. Pérez, E. Guitián, D. Peña* 9004 – 9006

From Perylene to a 22-Ring Aromatic Hydrocarbon in One-Pot



All in all: Borylative allyl–allyl coupling using allenes, bis(pinacolato)diboron, and allyl phosphates has been developed in the presence of a copper catalyst bearing an N-heterocyclic carbene (NHC)

ligand. The reaction affords boryl-substituted 1,5-diene derivatives in good to high yields with high regioselectivity and Z selectivity.

C–C Coupling

K. Semba, N. Bessho, T. Fujihara, J. Terao, Y. Tsuji* 9007 – 9011

Copper-Catalyzed Borylative Allyl–Allyl Coupling Reaction

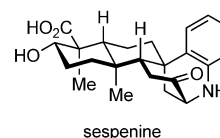
Natural Product Synthesis

Y. Sun, P. Chen, D. Zhang, M. Baunach,
C. Hertweck, A. Li* 9012–9016



Bioinspired Total Synthesis of Sespentine

Being crafty: The first total synthesis of sespentine has been accomplished by using a bioinspired aza-Prins/Friedel–Crafts/retro Friedel–Crafts cascade reaction as the key step.



Cascade Reaction

Y. Liu, J.-L. Zhang, R.-J. Song, P.-C. Qian,
J.-H. Li* 9017–9020



Cascade Nitration/Cyclization of 1,7-Enynes with *t*BuONO and H₂O: One-Pot Self-Assembly of Pyrrolo-[4,3,2-*de*]quinolinones



29 examples, up to 88% yield

Nitration cascade: The pyrrolo[4,3,2-*de*]quinolinone scaffold was synthesized by a metal-free reaction of *N*-(2-(ethynyl)-aryl)acrylamides, *tert*-butyl nitrite and H₂O. This cascade reaction is triggered

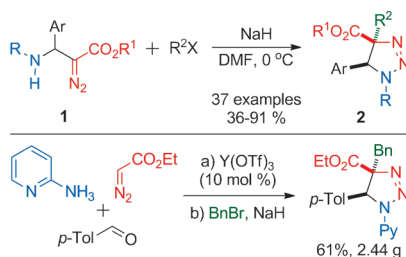
by alkene nitration followed by 1,7-enyne 6-*exo*-trig cyclization, C–H nitrations, and redox cyclization and forms the product in good yields.

Reactivity of Diazo Compounds

A. Kuznetsov, A. V. Gulevich, D. J. Wink,
V. Gevorgyan* 9021–9025



A New Reactivity Mode for the Diazo Group: Diastereoselective 1,3-Aminoalkylation Reaction of β -Amino- α -Diazoesters To Give Triazolines



Tetrasubstituted 1,2,3-triazolines were synthesized from β -amino- α -diazoesters. This aminoalkylation proceeds through the unusual 1,3-addition of a nucleophile and an electrophile to the diazo group. The reactions exhibit a broad scope and good functional group tolerance as well as excellent diastereoselectivity.

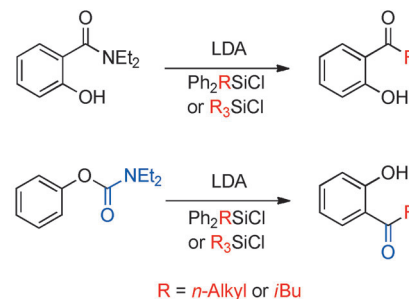
Synthetic Methods

H.-J. Lo, C.-Y. Lin, M.-C. Tseng,
R.-J. Chein* 9026–9029



Lithiation of a Silyl Ether: Formation of an *ortho*-Fries Hydroxyketone

Me gets a move on: The hydroxy-directed alkylation of an *N,N*-diethylarylamide through an anionic Si \rightarrow C alkyl migration was developed using a simple reagent combination of LDA (lithium diisopropylamide) and chlorosilane. This reaction was applied to the anionic Snieckus–Fries rearrangement and employed in a highly efficient synthesis of a phosphatidyl-inositol 3-kinase inhibitor.

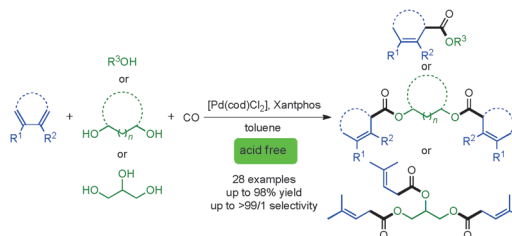


Carbonylation

X. Fang, H. Li, R. Jackstell,
M. Beller* 9030–9034



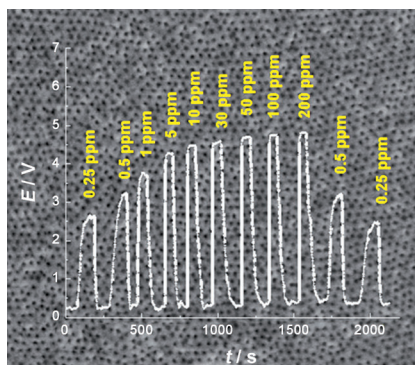
Palladium-Catalyzed Alkoxy carbonylation of Conjugated Dienes under Acid-Free Conditions: Atom-Economic Synthesis of β,γ -Unsaturated Esters



Away with acid: A benign palladium-based catalyst system for the alkoxy carbonylation of 1,3-dienes to selectively form β,γ -unsaturated esters under acid-

free conditions has been developed. This atom-efficient process is demonstrated in the straightforward synthesis of adipates from 1,3-butadiene.

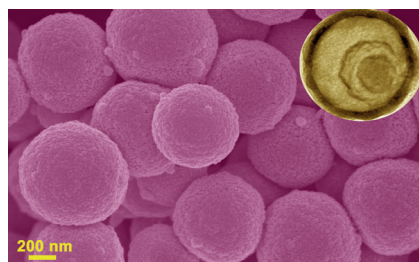
Good sense: Ordered mesoporous WO_3 materials with a crystalline framework and large pore size (ca. 11 nm) were synthesized by a template-carbonization strategy by using a high-molecular weight amphiphilic block copolymer as the structure-directing agent. The materials exhibit excellent performance for H_2S gas sensing.



Mesoporous Materials

Y. H. Li, W. Luo, N. Qin, J. P. Dong, J. Wei, W. Li, S. S. Feng, J. C. Chen, J. Q. Xu, A. A. Elzawahry, M. H. Es-Saheb, Y. H. Deng,* D. Y. Zhao — **9035 – 9040**

Highly Ordered Mesoporous Tungsten Oxides with a Large Pore Size and Crystalline Framework for H_2S Sensing

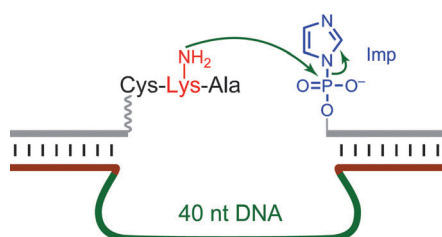


Three steps and you're there: A general "penetration–solidification–annealing" method was developed to synthesize multi-shelled hollow spheres of $\text{Co}_x\text{Mn}_{2-x}\text{O}_4$ with controllable Co/Mn molar ratios. The method can be easily extended to the synthesis of other mixed metal oxide spheres, such as ZnMn_2O_4 , ZnCo_2O_4 and NiCo_2O_4 . The carbon-coated CoMn_2O_4 triple-shelled spheres exhibit excellent lithium storage properties with nearly 100% capacity retention after 200 cycles.

Lithium Storage

G. Q. Zhang, X. W. Lou* — **9041 – 9044**

General Synthesis of Multi-Shelled Mixed Metal Oxide Hollow Spheres with Superior Lithium Storage Properties



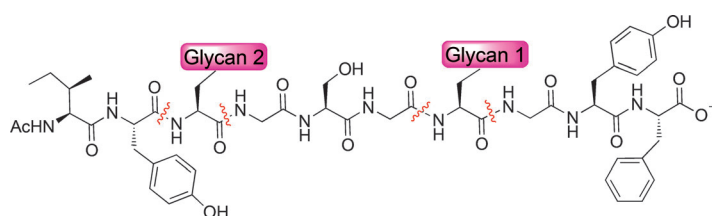
The trick for nitrogen: DNA-catalyzed modification of the lysine (Lys) side chain is achieved. The key to success is the provision of a rather reactive electrophile,

5'-phosphorimidazole (5'-Imp; see figure). This approach is effective even without preorganization of the two substrates.

Catalytic DNA

B. M. Brandsen, T. E. Velez, A. Sachdeva, N. A. Ibrahim, S. K. Silverman* — **9045 – 9050**

DNA-Catalyzed Lysine Side Chain Modification



Sweet peptides: The large size and tremendous structural complexity of glycosaminoglycan family glycopeptides poses many challenges for their synthesis. A successful strategy for the synthesis of a syndecan-3 glycopeptide (see chemical

formula) was established by constructing the partially deprotected single glycan chain containing glycopeptides first, followed by union of the glycan-bearing fragments and cleavage of the ester-type protecting groups.

Glycopeptide Synthesis

K. Yoshida, B. Yang, W. Yang, Z. Zhang, J. Zhang, X. Huang* — **9051 – 9058**

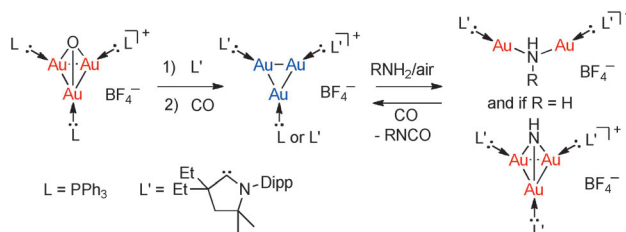
Chemical Synthesis of Syndecan-3 Glycopeptides Bearing Two Heparan Sulfate Glycan Chains





Heterogeneous Catalysis

L. Jin, D. S. Weinberger, M. Melaimi,
C. E. Moore, A. L. Rheingold,
G. Bertrand* ————— 9059 – 9063



Well-defined clusters supported by three cyclic (alkyl)(amino)carbenes (CAACs), or two CAACs and a phosphine, can be prepared by ligand exchange. These mixed-valence gold(I)/gold(0) clusters

promote the catalytic carbonylation of amines by the formation of di- or trinuclear gold(I) complexes, which can be isolated.



C–H Activation

J. Pedroni, M. Boghi, T. Saget,
N. Cramer* ————— 9064 – 9067



Strain away: Chiral β -lactams are obtained from readily accessible chloroacetamides by an asymmetric palladium(II)-catalyzed C–H functionalization in high yields and excellent enantioselectivities. Important

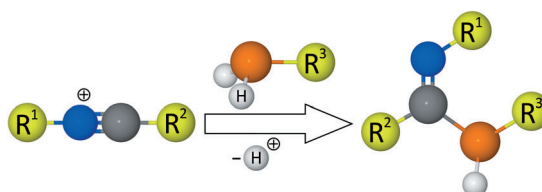
aspects of this transformation are the challenging strain-building C(sp³)–C(sp³) reductive elimination to form the four-membered ring. Ad = adamanyl.



Access to β -Lactams by Enantioselective Palladium(0)-Catalyzed C(sp³)–H Alkylation

P,N Ligands

T. van Dijk, S. Burck, M. K. Rong,
A. J. Rosenthal, M. Nieger, J. C. Slootweg,*
K. Lammertsma* ————— 9068 – 9071

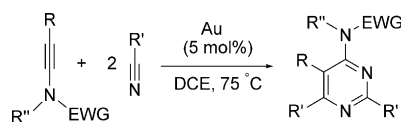


P bridges: Readily accessible nitrilium triflates are convenient imine building blocks for the expedient synthesis of phosphamidines as demonstrated for the reaction with primary phosphanes (see Scheme). Lithiation of these species

provides access to phosphamidines, of which the coordination to [AuCl(tht)] gives a unique P-bridged gold trimer, while [{RhCl(cod)}₂] gives bidentate coordination. cod = 1,5-cyclooctadiene, tht = tetrahydrothiophene.

Synthetic Methods

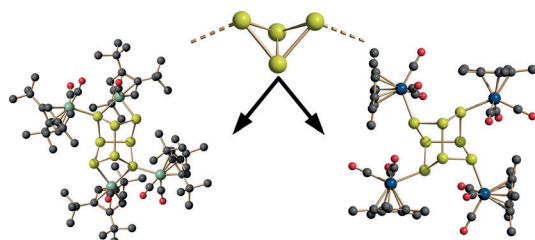
S. N. Karad, R.-S. Liu* ————— 9072 – 9076



In addition: A novel gold-catalyzed intermolecular [2+2+2] cycloaddition of ynamides with two discrete nitriles leads to monomeric 4-aminopyrimidines. The utility of this cycloaddition is demonstrated by the excellent regioselectivity obtained by using a variety of ynamides and nitriles. DCE = 1,2-dichloroethane, EWG = electron-withdrawing group.



Regiocontrolled Gold-Catalyzed [2+2+2] Cycloadditions of Ynamides with Two Discrete Nitriles to Construct 4-Aminopyrimidine Cores



As a butterfly: The selective formation of the dinuclear butterfly complexes $[\{\text{Cp}^*\text{Fe}(\text{CO})_2\}_2(\mu, \eta^{1:1}\text{-E}_4)]$ and $[\{\text{Cp}^*\text{Cr}(\text{CO})_3\}_2(\mu, \eta^{1:1}\text{-E}_4)]$ ($\text{E} = \text{P}, \text{As}$) results from the reaction of E_4 with the corresponding dimeric carbonyl com-

plexes. The As complexes are the first As_4 butterfly compounds with a bridging coordination mode. First studies of their reactivity show the formation of unprecedented As_8 cuneane complexes.

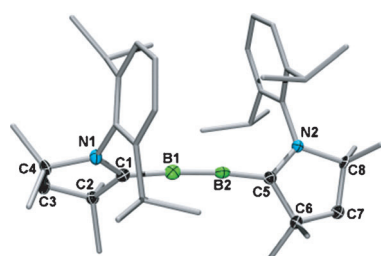
As₄ Activation

C. Schwarzmaier, A. Y. Timoshkin,
G. Balázs, M. Scheer* — 9077–9081

Selective Formation and Unusual
Reactivity of Tetraarsabicyclo[1.1.0]butane
Complexes



Back Cover

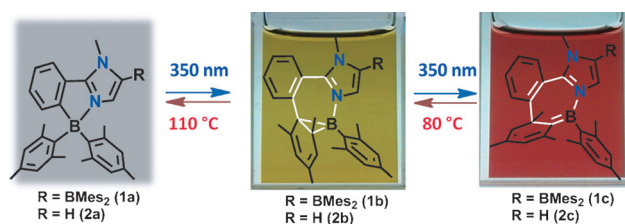


The use of π -acidic carbenes as stabilizing ligands on a central diboron unit has enabled the synthesis and characterization of a diborabutatriene, an inorganic/organic electron-deficient cumulene with a linear CBBC core. Structural characterization, theoretical analysis, and electrochemical investigation each indicated even sharing of electrons across the four-membered center.

Cumulenes

J. Böhnke, H. Braunschweig,*
W. C. Ewing, C. Hörl, T. Kramer,
I. Krummenacher, J. Mies,
A. Vargas — 9082–9085

Diborabutatriene: An Electron-Deficient
Cumulene



Boron chameleon: The exceptional ability of the boron atom to facilitate molecular transformations upon external stimuli has led to the isolation of the first example of azaborabenzotropolidenes and the direct

observation of an unprecedented photo-thermal interconversion between azoratabisnorcaradiene and azorabenzotropolidene.

Photoisomerization

Y.-L. Rao, C. Hörl, H. Braunschweig,*
S. Wang* — 9086–9089

Reversible Photochemical and Thermal
Isomerization of
Azoratabisnorcaradiene to
Azorabenzotropolidene



Inside Back Cover



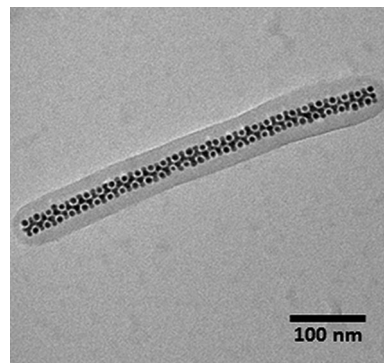
Helical Packing

S. Sanwaria, A. Horechyy,* D. Wolf,
C.-Y. Chu, H.-L. Chen, P. Formanek,
M. Stamm, R. Srivastava,
B. Nandan* _____ **9090–9093**



Helical Packing of Nanoparticles Confined
in Cylindrical Domains of a Self-
Assembled Block Copolymer Structure

Packing makes coated screws: Silver nanoparticles confined in the self-assembled cylindrical domains of polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) pack in an interesting helical morphology. This observation opens up possibilities for the discovery of novel hierarchical structures in such composite systems and also provides new opportunities for the application of such materials in nanotechnology.



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
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The Hot Papers are articles that the Editors
have chosen on the basis of the referee
reports to be of particular importance for
an intensely studied area of research.

Angewandte Corrigendum



Total Synthesis of (–)-Lycoposerramine-S
N. Shimada, Y. Abe, S. Yokoshima,
T. Fukuyama* _____ **11824–11826**

Angew. Chem. Int. Ed. **2012**, 51

DOI: 10.1002/anie.201206863

Some of the NMR spectra shown in the Supporting Information of this manuscript have not been properly processed. Copies of the correct spectra are available as Supporting Information for this Corrigendum.

Angewandte Corrigendum



Total Synthesis of Tryprostatins A and B
T. Yamakawa, E. Ideue, J. Shimokawa,
T. Fukuyama* _____ **9262–9265**

Angew. Chem. Int. Ed. **2010**, 49

DOI: 10.1002/anie.201004963

Some of the NMR spectra shown in the Supporting Information of this manuscript have not been properly processed. Copies of the correct spectra are available as Supporting Information for this Corrigendum.

Angewandte Corrigendum

The authors of this Communication request that Mirco Sorci be inserted as an additional author. The author list should read as follows:

Joseph Imbrogno, Arpan Nayak, Mirco Sorci, and Georges Belfort

The affiliation for Mirco Sorci is:

Howard P. Isermann Department of Chemical and Biological Engineering
Rensselaer Polytechnic Institute, 110 8th Street, Troy, NY 12180 (US'A)

Egg White Varnishes on Ancient
Paintings: A Molecular Connection to
Amyloid Proteins

J. Imbrogno, A. Nayak, G.
Belfort* _____ **7014–7017**

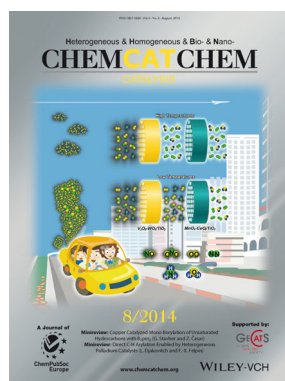
Angew. Chem. Int. Ed. **2014**, 53

DOI: 10.1002/anie.201400251

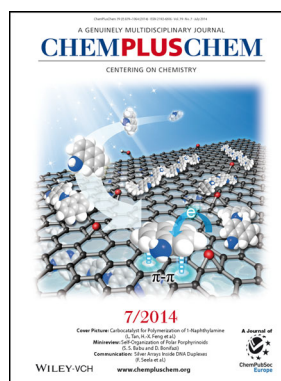
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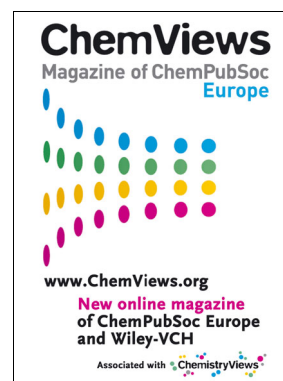
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