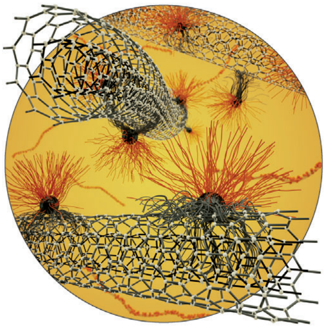
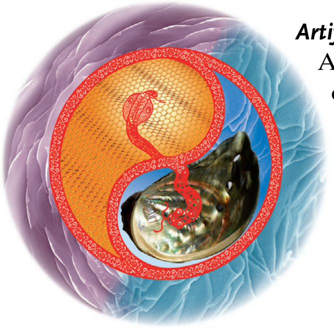
The direct alkynylation …

… of electron-rich aromatic heterocycles with terminal alkynes was accomplished in high yields and good selectivity when using a low loading of palladium catalyst, as described by W. Su and co-workers in their Communication on page 3630 ff. A high loading of palladium catalyst led to poor yields because of the undesired homocoupling of alkynes.

Dispersants for Nanotubes

Polymer-based Janus micelles provide excellent stabilization for carbon nanotubes in a variety of solvents. The “Janus balance” is critical for good stabilization properties as A. H. Gröschel, A. H. E. Müller et al. explain in their Communication on page 3602 ff.



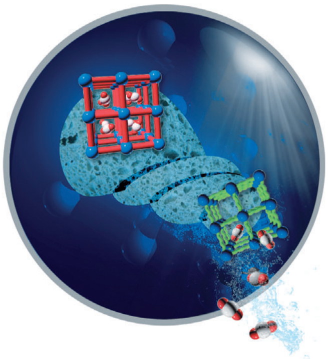


Artificial Nacre

An ultratough artificial nacre based on graphene oxide sheets is presented by Q. F. Cheng, M. Z. Li, Z. Y. Tang et al. in their Communication on page 3750 ff. This conductive nacre shows excellent mechanical properties and a hierarchical microstructure.

Metal–Organic Framework

In their Communication on page 3695 ff., R. Lyndon, M. R. Hill, et al. report a metal–organic framework constructed with light-responsive linkers, which are activated upon exposure to light and release the stored carbon dioxide.



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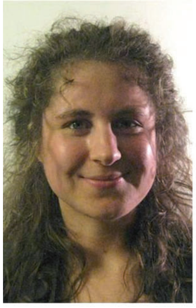
Service

Author Profile

"My favorite way to spend a holiday is fishing.
My favorite painter is Joan Miró …"
This and more about Claudio Palomo can be found on page 3562.

News



F. Schoenebeck

M. Alcarazo

G. Clever

C. Nevado

C. Mazet

U. Pischel

S. Dagorne

S. Bellemin-Laponnaz

Books

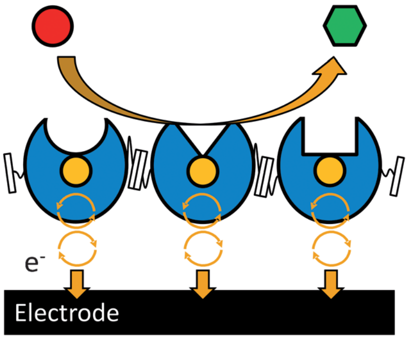
From the Molecular World — Alan J. Rocke — *reviewed by S. Mauskopf* ________ **3565**

Highlights

Bioelectrocatalysis

U. Schröder* ________ **3568 – 3569**

Self-Assembling Enzyme Networks—A New Path towards Multistep Bioelectrocatalytic Systems



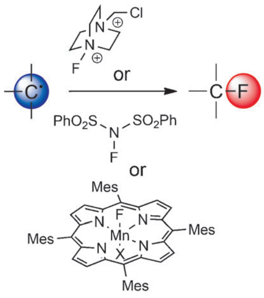
Enzymes for energy: Recently, an elegant and efficient protein-engineering approach was proposed to create self-assembling enzyme arrays. This approach paves the way for efficient biofuel cells and for complex bioelectrocatalytic processes (general scheme shown; blue: enzyme, red: substrate, green: product).

Synthetic Methodology

M. P. Sibi,* Y. Landais* ____ **3570 – 3572**

C_{sp^3}–F Bond Formation: A Free-Radical Approach

Totally rad: Synthetic methods have been developed for the formation of C_{sp3}–F bonds by reaction of C-centered radicals with fluorine sources. Three complementary strategies, which differ in the mode of generation of the alkyl radical intermediate, are described. These include olefin hydrofluorination, decarboxylative fluorination, and aliphatic C–H fluorination.

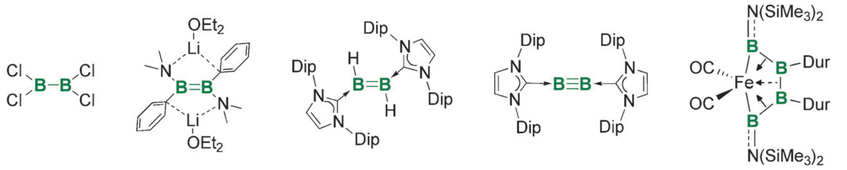


Minireviews

Boron Chemistry

H. Braunschweig,*
R. D. Dewhurst ________ **3574 – 3583**

Single, Double, Triple Bonds and Chains: The Formation of Electron-Precise B–B Bonds



Boron bond construction: Despite the intense synthetic interest in diboranes and the high B–B bond enthalpy, the formation of boron–boron bonds is still difficult, uncontrollable, and unpredictable. Methods for B–B multiple bonds are rarer still. These problems have witnessed some progress in recent years, and recent results are presented along with a background to the history of B–B bond synthesis. Dip = 2,6-diisopropylphenyl, Dur = 2,3,5,6-tetramethylphenyl.

For the USA and Canada:
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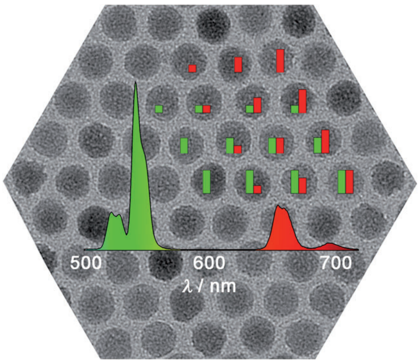
Reviews

Photon Upconversion

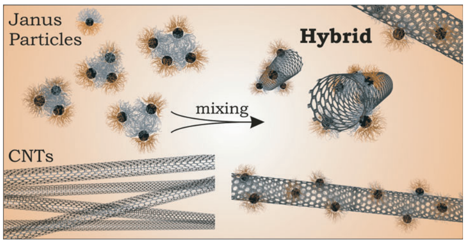


Code makers: Photon-upconverting nanoparticles show multiple emission of visible light under near-IR excitation and thus avoid autofluorescence and light scattering associated with other forms of optical encoding. The emission lines can be tuned individually to yield larger sets and more photostable optical codes than conventional fluorescent codes. A combination of two emission lines each adjusted to four intensity levels yields 15 codes (see picture, background TEM image of $NaYF_4$ nanoparticles).

Communications

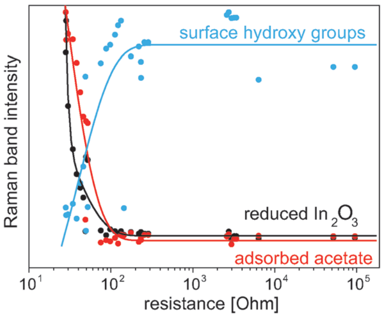
Colloidal Surfactants

Frontispiece



Supracolloidal hybrids: Soft polymer-based Janus micelles provide excellent stabilization for multi-walled carbon nanotubes (see scheme) in a variety of solvents, including water. The size ratio of the micelle's stabilizing corona to adsorbing corona (Janus balance) is decisive for good physisorption and stabilization. The supracolloidal interaction preserves the structural integrity of the nanotubes, which is essential for maintaining their useful properties.

Gas Sensors

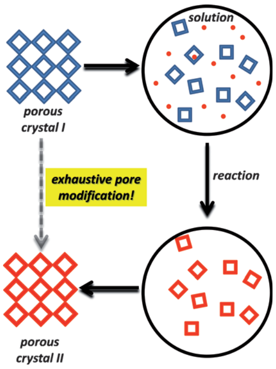


Gas sensors at work: The mode of operation of metal-oxide gas sensors can be studied by simultaneous measurement of the sensor response, adsorbates, changes in the metal-oxide material, and gas-phase composition by operando Raman–FTIR spectroscopy. Depending on the gas environment and temperature, for EtOH sensing by In_2O_3, a correlation has been found between the sensor signal, presence of adsorbates, oxidation state of the sensor material, and intensity of surface hydroxy groups.

Porous Organic Cage Compounds

M. W. Schneider, I. M. Oppel, A. Griffin,
M. Mastalerz* ____________ **3611 – 3615**

Post-Modification of the Interior of Porous Shape-Persistent Organic Cage Compounds



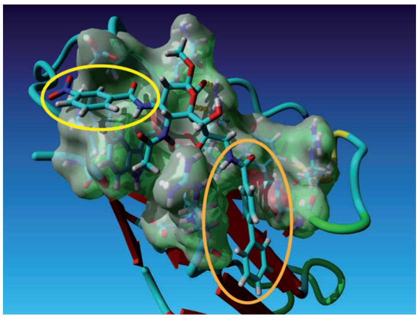
Interior decorating: A post-synthetic method allows porous organic cage compounds to be prepared with functionalized interior cavities. The approach produces modified cage compounds in quantitative yield and opens the possibility of preparing organic alloys with different functionality. The solution-based technique shows the advantage of solubility, an inherent property of porous materials derived from discrete organic molecules.

Immunoglycotherapy

S. Kelm,* P. Madge, T. Islam, R. Bennett,
H. Koliwer-Brandl, M. Waespy,
M. von Itzstein,
T. Haselhorst* ____________ **3616 – 3620**

C-4 Modified Sialosides Enhance Binding to Siglec-2 (CD22): Towards Potent Siglec Inhibitors for Immunoglycotherapy

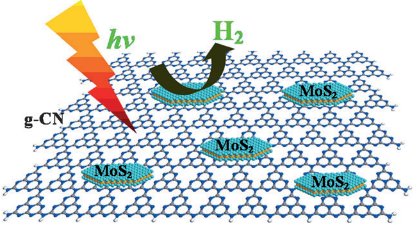
Two changes for the better: A novel class of sialic acid derivatives is prepared by modifying both the C-4 and C-9 positions of Neu5Aα2Me (see structure). This approach gives a lead compound that has sub-micromolar affinity for Siglec-2 and may provide a pathway for immunoglycotherapy strategies for autoimmune diseases and B cell derived non-Hodgkin's lymphoma.



Organic–Inorganic Hybrid Compounds

Y. Hou, A. B. Laursen, J. Zhang, G. Zhang,
Y. Zhu, X. Wang,* S. Dahl,
I. Chorkendorff* ____________ **3621 – 3625**

Layered Nanojunctions for Hydrogen-Evolution Catalysis

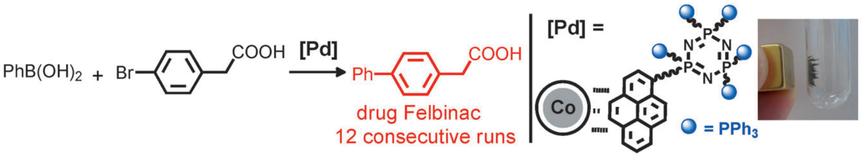


Brought to light: Thin, planar nanojunctions between layered MoS_2 and graphitic CN (g-CN) were constructed and allowed fast charge separation across the junction interfaces to facilitate hydrogen photosynthesis. This research represents a proof of concept for the rational fabrication of thin interfacial junctions between co-catalysts and semiconductors having similar layered geometric structures.

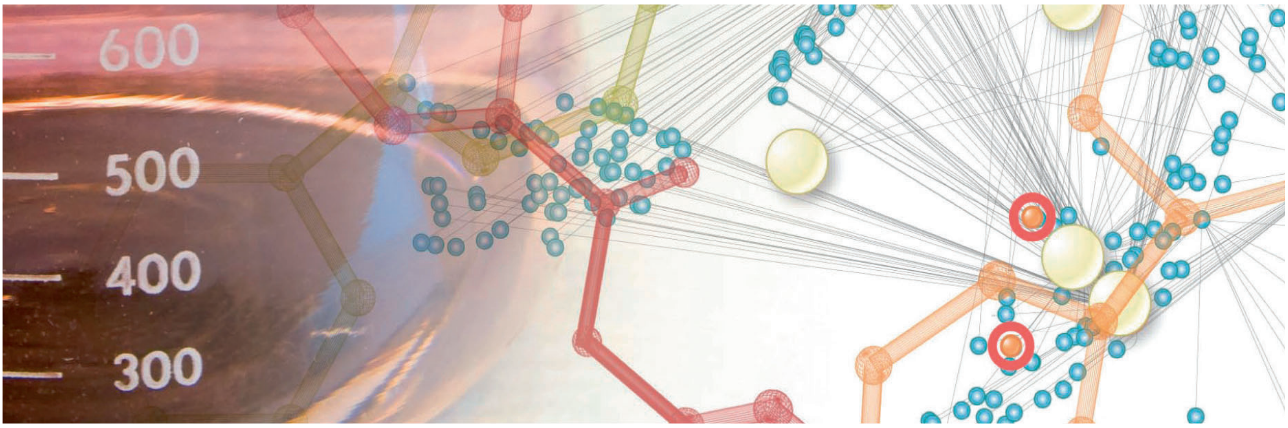
Synthetic Methods

M. Keller, V. Collière, O. Reiser,
A.-M. Caminade,* J.-P. Majoral,*
A. Ouali* ____________ **3626 – 3629**

Pyrene-Tagged Dendritic Catalysts Noncovalently Grafted onto Magnetic Co/C Nanoparticles: An Efficient and Recyclable System for Drug Synthesis



Hold on to your palladium! Phosphines have been grafted on magnetic Co/C nanoparticles through π–π interactions. The resulting Pd complexes showed high activity for Suzuki couplings and the system involving a dendritic ligand was recyclable, allowing the preparation of the drug Felbinac over 12 consecutive runs with minimal Pd leaching. After extraction with CH_2Cl_2, Felbinac met the requirements of the pharmaceutical industry (< 5 ppm Pd).



Call for Nominations 2013

Novartis Early Career Award in Organic Chemistry

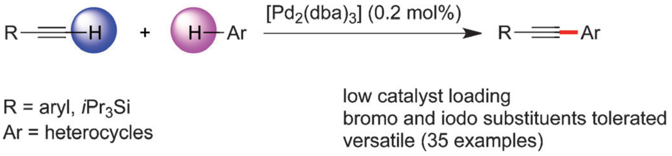
The Novartis Early Career Award in Organic Chemistry marks Novartis' commitment to science and innovation. This annual award recognizes outstanding scientists in the area of organic or bioorganic chemistry and provides funding support for academics early in their career. Eligible candidates will have started their independent academic career after Jan 1st 2003. Two winners will each receive an unrestricted research grant of $150,000 payable over three years. Nominations by curriculum vitae and a letter of recommendation, should be submitted to Dr Tom Hunt (tom.hunt@novartis.com) by May 31st 2013.

Past Awardees:

2012	Sarah E. Reisman and Corey R.J. Stephenson
2011	David Chen and David Spiegel
2010	Karl Gademann and Jin-Quan Yu
2009	Christopher J. Chang and Magnus Rueping
2008	Matthew J. Gaunt and Jeffrey S. Johnson
2007	Lukas J. Goossen and Anna K. Mapp
2006	Armido Studer and F. Dean Toste
2005	Benjamin List and Dirk Trauner
2004	J. Stephen Clark and Jonathan P. Clayden
2003	Thorsten Bach
2002	Bernhard Breit and Thomas Carell
2001	Tim Donohoe
2000	Andrew Miller
1999	Alan Armstrong
1998	Mark Bradley

NOVARTIS

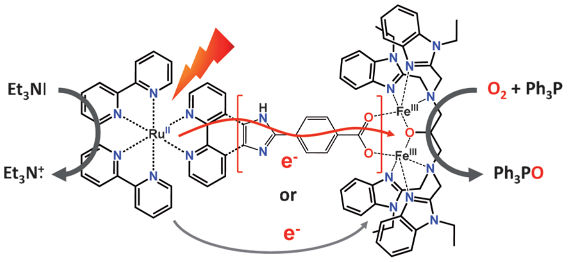
Dehydrogenative Coupling



Direct: With [$Pd_2(dba)_3$] as a catalyst, the direct alkynylation of thiophenes bearing a variety of substituents has been accomplished by using terminal alkynes as alkynylating reagents. This protocol is also applicable to other electron-rich aromatic heterocycles. dba = dibenzylidenacetone.

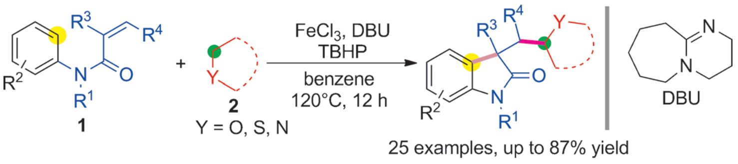
Front Cover

Dioxygen Activation



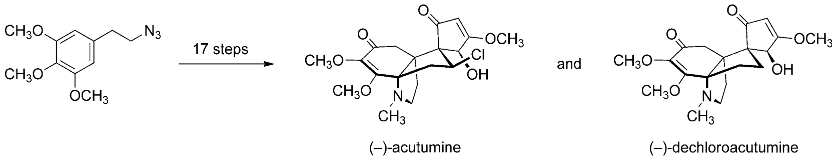
Closing the loop: Light absorption by a sensitizer–diiron(III) complex in the presence of a sacrificial electron donor and subsequent exposure to O_2 led to the formation of the corresponding active diiron(III)–peroxo species, which can transfer an oxygen atom to a substrate (see scheme).

Synthetic Methods



Difunctionalization: Inexpensive and environmentally benign $FeCl_3$ catalyzes the oxidative 1,2-alkylarylation of activated alkenes with an aryl C(sp^2)—H bond and a C(sp^3)—H bond adjacent to a heteroatom. This reaction is a new strategy for the synthesis of oxindoles and makes use of DBU as ligand and TBHP as oxidant (see scheme, TBHP = *tert*-butyl hydrogenperoxide).

Natural Products

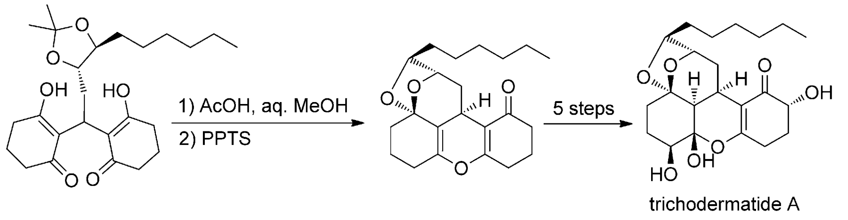


One route fits all: Syntheses of the title complex tetracyclic alkaloids are described. The routes feature the strategic application of 5-trimethylsilylcyclopentadiene, a selective hydrostannylation of a complex enyne, a Hosomi–Sakurai cyclization to form the skeleton of the targets, an allylic formate rearrangement to construct the spirocyclopentenone rings, and a selective hydrogenation to establish the alkyl chloride functional group of (−)-acutumine.

Natural Product Synthesis

H. Shigehisa, Y. Suwa, N. Furiya,
Y. Nakaya, M. Fukushima, Y. Ichihashi,
K. Hiroya* ―――――― **3646 – 3649**

Stereocontrolled Synthesis of Trichodermatide A

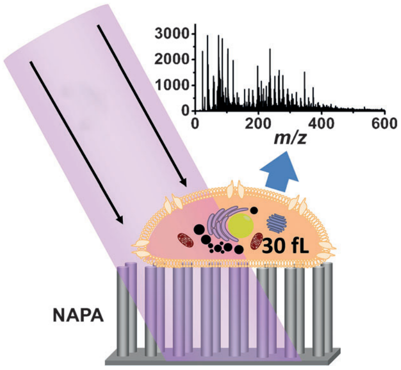


Hard core made easy: The pentacyclic core of trichodermatide A was stereoselectively synthesized from a bis(1,3-cyclohexanedione) derivative by a ring-closing reaction followed by an intramolecular ketal formation (see scheme; PPTS = pyridinium *p*-toluenesulfonate). The first total synthesis of trichodermatide A was then completed by the introduction of three hydroxy groups.

Analytical Methods

B. N. Walker, C. Antonakos, S. T. Retterer,
A. Vertes* ―――――― **3650 – 3653**

Metabolic Differences in Microbial Cell Populations Revealed by Nanophotonic Ionization

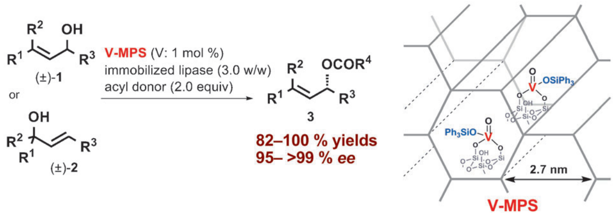


Playing (yeast) laser tag: Laser desorption ionization mass spectrometry (LDI-MS) with nanopost arrays (NAPA, see scheme) was shown to quantitatively analyze trace amounts of intracellular metabolites from single cells of *Saccharomyces cerevisiae* (baker's yeast). The upregulation and downregulation of metabolites because of external stress (such as oxidative stress) are also observed, even at the single-cell level.

Heterogeneous Catalysis

M. Egi, K. Sugiyama, M. Saneto,
R. Hanada, K. Kato, S. Akai* **3654 – 3658**

A Mesoporous-Silica-Immobilized Oxovanadium Cocatalyst for the Lipase-Catalyzed Dynamic Kinetic Resolution of Racemic Alcohols

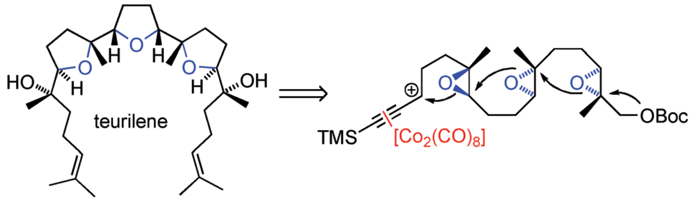


V for resolution: A new oxovanadium catalyst (V-MPS; see scheme) immobilized in the pores of mesoporous silica has been developed. The combined use of V-MPS and lipases achieved the dynamic kinetic resolution of a wide range of racemic alcohols (**1** or **2**) to produce optically active esters **3** in high chemical and optical yields. The paired catalysts retained high catalytic activity when reused up to six times.

Natural Products

J. Rodríguez-López,
F. Pinacho Crisóstomo, N. Ortega,
M. López-Rodríguez, V. S. Martín,*
T. Martín* ―――――― **3659 – 3662**

Epoxide-Opening Cascades Triggered by a Nicholas Reaction: Total Synthesis of Teurilene

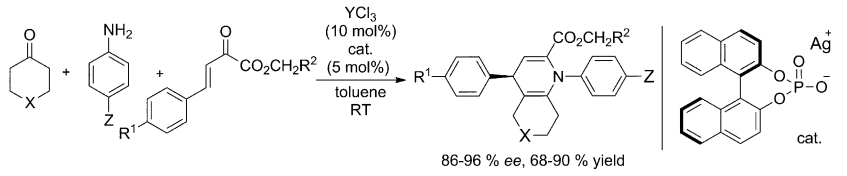


Natural inspiration: Based on the biosynthesis of squalene-derived polyethers, a total synthesis of teurilene is described. The carbocation formation in the Nicholas reaction serves to control the initiation of a polyepoxide ring-opening cascade. The three furan rings present in teurilene were obtained in excellent yield in one step. Boc = *tert*-butoxycarbonyl, TMS = trimethylsilyl.

Cooperative Catalysis

Y.-M. Deng, L. Liu, R. G. Sarkisian,
K. Wheeler, H. Wang,*
Z.-H. Xu* ______ **3663 – 3667**

Arylamine-Catalyzed Enamine Formation: Cooperative Catalysis with Arylamines and Acids

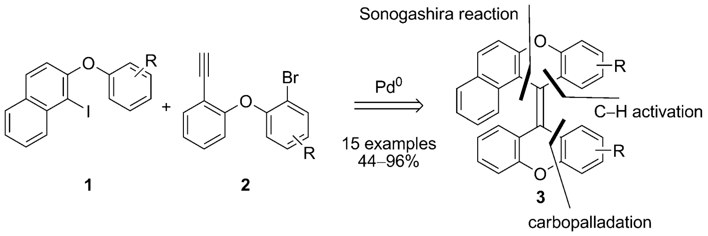


Powerful combination: Arylamines and metal Lewis acids are used as catalysts in the highly chemo- and enantioselective three-component inverse-electron-demand aza-Diels–Alder reaction of cyclic ketones with enones. The enantioselectivity is introduced by a simple chiral anion (see scheme). Arylamines can also serve as effective enamine catalysts in combination with either a metal Lewis acid or a Brønsted acid.

Domino Reaction

L. F. Tietze,* T. Hungerland, C. Eichhorst,
A. Düfert, C. Maaß,
D. Stalke ______ **3668 – 3671**

Efficient Synthesis of Helical Tetrasubstituted Alkenes as Potential Molecular Switches: A Two-Component Palladium-Catalyzed Triple Domino Process

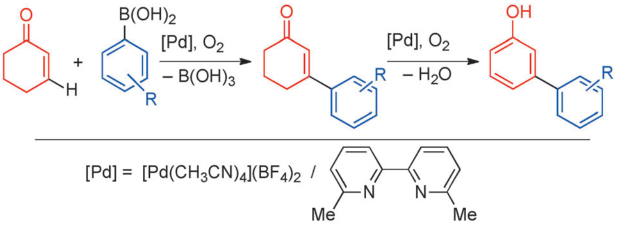


Fast and easy: Various helical tetrasubstituted alkenes were synthesized by a palladium-catalyzed domino process. The domino process consists of a Sonogashira reaction, a carbopalladation, and a direct C—H functionalization.

Synthetic Methods

Y. Izawa, C. W. Zheng,
S. S. Stahl* ______ **3672 – 3675**

Aerobic Oxidative Heck/Dehydrogenation Reactions of Cyclohexenones: Efficient Access to *meta*-Substituted Phenols

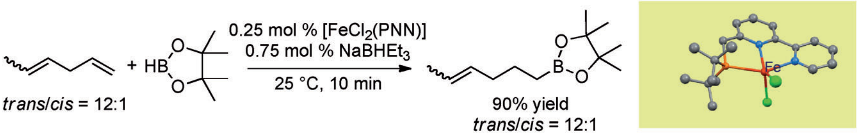


Jockeying for the (*meta*)position: A new dicationic palladium(II) catalyst, employing a 6,6′-dimethyl-2,2′-bipyridine ligand, promotes both the aerobic oxidative Heck coupling and dehydrogenation reactions of cyclohexenones. These reactions may be combined in a one-pot sequence to enable the straightforward synthesis of *meta*-substituted phenols (see scheme).

Organometallic Catalysis

L. Zhang, D. Peng, X. Leng,
Z. Huang* ______ **3676 – 3680**

Iron-Catalyzed, Atom-Economical, Chemo- and Regioselective Alkene Hydroboration with Pinacolborane



[$FeCl_2$(PNN)]

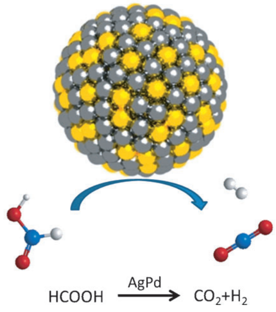
Precious iron: A new PNN iron complex has been developed for use in an iron-catalyzed alkene hydroboration reaction under mild conditions. The environmentally friendly and earth-abundant iron catalyst system is superior to precious-metal systems in terms of efficiency and selectivity for α-olefin hydroborations with pinacolborane.

Heterogeneous Catalysis

VIP

S. Zhang, Ö. Metin,* D. Su, S. Sun* ———— 3681 – 3684

Monodisperse AgPd Alloy Nanoparticles and Their Superior Catalysis for the Dehydrogenation of Formic Acid

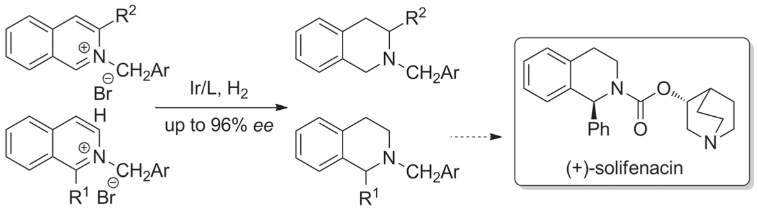


A facile approach to the composition-controlled synthesis of monodisperse 2.2 nm AgPd alloy nanoparticles (NPs) is reported. The 2.2 nm AgPd NPs are highly active and durable catalysts for the dehydrogenation of formic acid. The study proves the unique approach in using alloying effects to enhance the catalytic activity of the NPs for hydrogen generation from formic acid (see picture).

Synthetic Methods

Z.-S. Ye, R.-N. Guo, X.-F. Cai, M.-W. Chen, L. Shi, Y.-G. Zhou* ———— 3685 – 3689

Enantioselective Iridium-Catalyzed Hydrogenation of 1- and 3-Substituted Isoquinolinium Salts

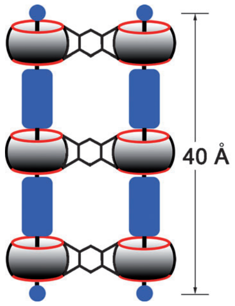


Asymmetric hydrogenation: The title reaction provides an efficient and rapid access to chiral 1- and 3-substituted 1,2,3,4-tetrahydroisoquinolines with excellent enantioselectivity (see scheme; L = ligand). A preliminary mechanistic study indicates that the 1,2-hydride addition might be the initial step in the reaction. The method has been used in the synthesis of urinary antispasmodic drug (+)-solifenacin.

Self-Assembly

J. B. Wittenberg, P. Y. Zavalij, L. Isaacs* ———— 3690 – 3694

Supramolecular Ladders from Dimeric Cucurbit[6]uril



Climbing the cucurbit ladder: Cucurbit[6]uril dimers (connected gray cylinders; see scheme) were prepared by condensation of glycoluril hexamer with the appropriate tetraaldehydes. The self-assembly process between these dimers and oligoviologen compounds (blue) in water leads to a supramolecular ladder with the dimensions and molecular weight typical of small proteins.

Metal–Organic Frameworks

VIP

R. Lyndon,* K. Konstas, B. P. Ladewig, P. D. Southon, P. C. J. Kepert, M. R. Hill* ———— 3695 – 3698

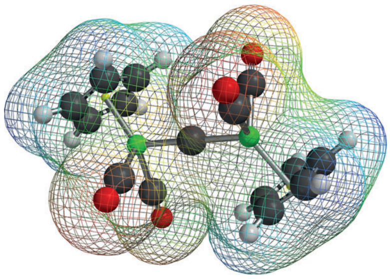
Dynamic Photo-Switching in Metal–Organic Frameworks as a Route to Low-Energy Carbon Dioxide Capture and Release

Like wringing out a sponge, a metal–organic framework loaded with structure-changing light-responsive groups can squeeze out captured CO_2. Because of the groups being structurally integral, there is oscillation between native and excited states. Pairing with CO_2 capture from coal-based power generation could reduce the parasitic energy load of adsorbent regeneration.

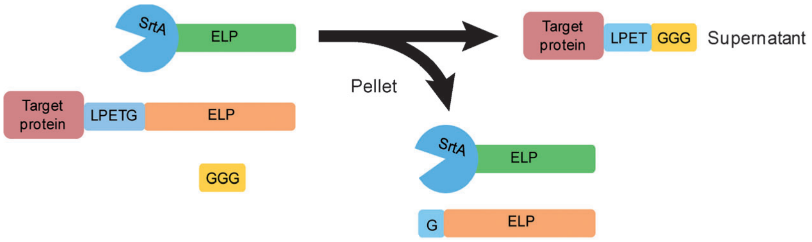
Back Cover

Homonuclear Carbides

It's easy to C: The reaction of $[Re(CO)_2(CS)(\eta\text{-}C_5H_5)]$ with $[Re(CO)_2(thf)(\eta\text{-}C_5H_5)]$ affords the disulfur complex $[Re(CO)_2(\eta^2\text{-}S_2)(\eta\text{-}C_5H_5)]$ and the remarkably simple μ-carbido complex $[(\mu\text{-C})\{Re(CO)_2(\eta\text{-}C_5H_5)\}_2]$, which has been structurally characterized and computationally investigated (see picture; black C, white H, red O, green Re).



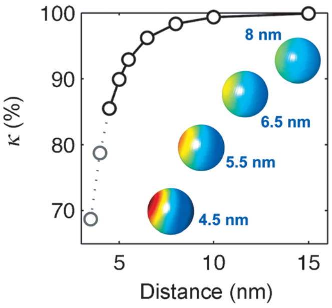
Protein Expression



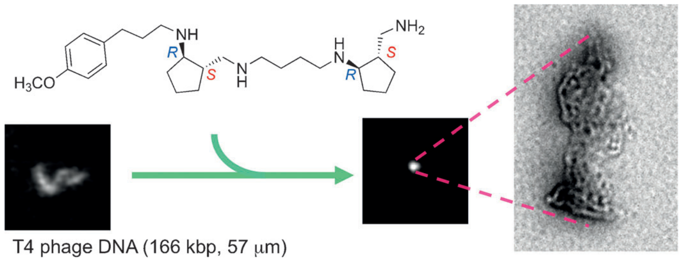
Sorting it out: Applied in tandem, elastin-like polypeptides (ELPs, see scheme) and the Sortase A (SrtA) transpeptidase provide a method for chromatography-free purification of recombinant proteins and optional, site-specific conjugation of the protein to a small molecule (yellow). This system provides an efficient mechanism for generating bioactive proteins at high yields and purities.

Protein–Protein Interactions

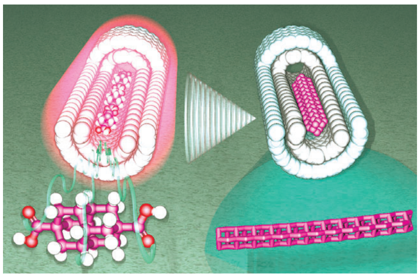
Meeting your match: The early molecular recognition event of ubiquitin with the ubiquitin-interacting motif (UIM) of Hrs protein starts out with a directional bias in the position of UIM, increasingly favoring directions facing the binding interface of ubiquitin as the distance decreases (see figure). This process, which is driven by electrostatic long-range interactions, precedes an internal conformational population shift.



DNA Structure



Normal doughnuts or lots of little ones? Among four stereoisomers of a tetravalent polyamine, the isomer pictured was the most potent at inducing DNA compaction, whereby the DNA molecules adopted a unique morphology of minitoroid clusters. The nonchiral polyamine spermine induced the formation of typical, larger toroidal structures.



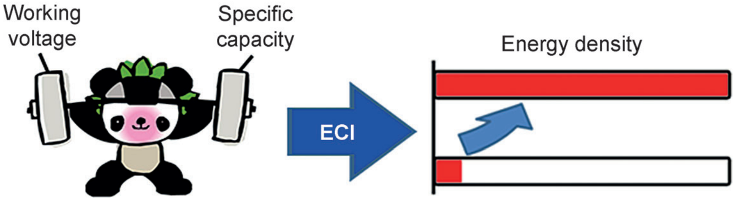
Carbon is a girl's best friend: Carbon-based nanowires have been produced during thermal annealing of diamantane-4,9-dicarboxylic acid in carbon nanotubes under hydrogen atmosphere (see scheme). HR-TEM images, Raman spectra, and structural transformations observed under an intense electron beam suggest that the as-produced carbon-based nanowires are sp^3 diamond nanowires, consistent with our computational results.

Nanodiamonds

J. Zhang, Z. Zhu, Y. Feng, H. Ishiwata, Y. Miyata, R. Kitaura, J. E. P. Dahl, R. M. K. Carlson, N. A. Fokina, P. R. Schreiner, D. Tománek, H. Shinohara* ______ **3717 – 3721**

Evidence of Diamond Nanowires Formed inside Carbon Nanotubes from Diamantane Dicarboxylic Acid

Inside Cover

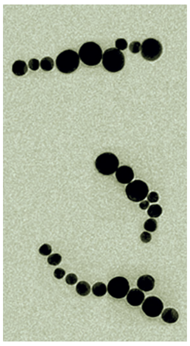


Maximized energy density: Controlled electrochemical charge injection (ECI) can be used for maximizing the energy density of supercapacitors (SCs). The electrode potential is tuned by the surface chemical structure of the electrode material to increase both the working voltage and the specific capacity of the SCs. As a result, the energy density of carbon SCs is significantly improved close to the level of lithium-ion batteries (see picture).

Energy Storage

Z. Weng, F. Li,* D.-W. Wang, L. Wen, H.-M. Cheng* ______ **3722 – 3725**

Controlled Electrochemical Charge Injection to Maximize the Energy Density of Supercapacitors

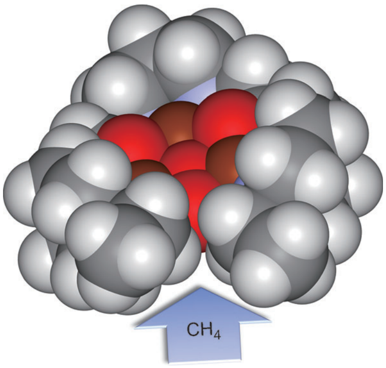


Big and small, short and tall: Nanoparticles (NPs) coated with pH-sensitive polymers underwent reversible chain growth as a result of varying electrostatic interparticle repulsion as determined by the pH value. Tuning of the pH value also enabled the coupling of differently sized NPs to form linear composite chains reminiscent of block copolymers (see picture).

Nanoparticle Self-Assembly

H. Xia,* G. Su, D. Wang* __ **3726 – 3730**

Size-Dependent Electrostatic Chain Growth of pH-Sensitive Hairy Nanoparticles



TONs of copper fun: There is considerable interest in developing catalysts to harness the abundant natural supply of methane for various industrial applications. Two tricopper complexes capable of mediating efficient oxidation of methane to methanol under ambient conditions were tested: a biomimetic tricopper complex (see figure) and a tricopper-peptide species derived from the particulate methane monooxygenase (pMMO) protein.

Methane Oxidation

VIP

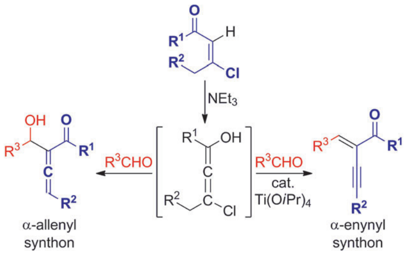
S. I. Chan,* Y.-J. Lu, P. Nagababu, S. Maji, M.-C. Hung, M. M. Lee, I.-J. Hsu, P. D. Minh, J. C.-H. Lai, K. Y. Ng, S. Ramalingam, S. S.-F. Yu,* M. K. Chan* ______ **3731 – 3735**

Efficient Oxidation of Methane to Methanol by Dioxygen Mediated by Tricopper Clusters

Synthetic Methods

H. Y. Kim, J.-Y. Li, K. Oh* ___ 3736 – 3740

A Soft Vinyl Enolization Approach to α-Acylvinyl Anions: Direct Aldol/Aldol Condensation Reactions of (*E*)-β-Chlorovinyl Ketones



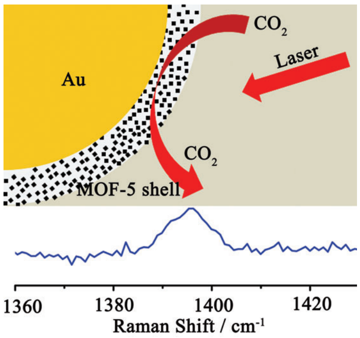
Synthesizing the synthons: The development of α-acylvinyl anion synthons has been achieved using direct α-vinyl enolization of α,β-unsaturated ketones under mild reaction conditions. The synthetic utility of such synthons has been demonstrated in intermolecular aldol and aldol condensation reactions, which provide synthetically useful allenyl ketone and enyne derivatives.

Functional Nanoparticles

L. He, Y. Liu, J. Liu, Y. Xiong, J. Zheng, Y. Liu,* Z. Tang* ___ 3741 – 3745

Core–Shell Noble-Metal@Metal-Organic-Framework Nanoparticles with Highly Selective Sensing Property

Of cores! Core–shell Au@metal-organic-framework-5 (MOF-5) nanoparticles (NPs), in which a single Au NP core is coated with a uniform MOF-5 shell, were prepared by a facile one-pot method. The diameter of the Au NP core and the thickness of the MOF-5 shell are easily tuned by controlling the reaction conditions. These nanoparticles are selective sensors of CO_2 in gas mixtures.



DOI: 10.1002/anie.201301280

50 Years Ago …

Angewandte Chemie International Edition was first published in 1962, the mother journal first in 1888. In this monthly flashback, we feature some of the articles that appeared 50 years ago. This look back can open our eyes, stimulate discussion, or even raise a smile.

Shock waves and detonations were the subject of a Review by W. Jost and T Just. These methods were used to achieve high temperatures and thus permit the kinetic investigation of fast reactions in the gas phase.

Albert Eschenmoser and co-workers reported the esterification of carboxylic acids with aminoacetals of *N*,*N*-dimethylformamide. A range of amino acid and peptide derivatives were studied and the reaction was assumed to proceed by alkylation of the carboxylate oxygen atom. Eschenmoser later published two comprehensive Reviews in *Angewandte Chemie* on the origin of biomolecular structures, including Vitamin B_{12} and nucleic acids (see *Angew. Chem. Int. Ed.* **1988**, *27*, 5 and *Angew. Chem. Int. Ed.* **2011**, *50*, 12412).

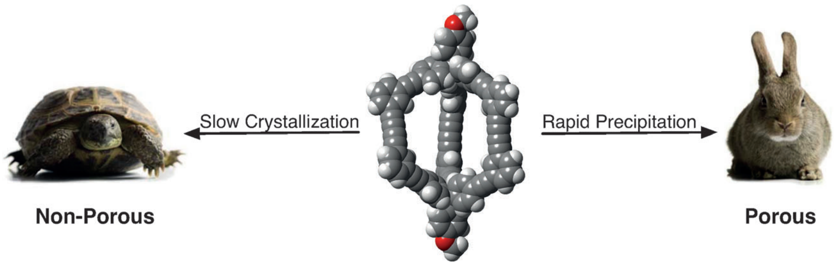
NMR spectroscopy was used by Heinz A. Staab and co-workers to investigate the tautomeric forms of 4 (or 5)-substituted imidazoles. The magnitude of the spin–spin coupling constants of deuterated compounds showed that they exist predominantly in one form. Staab was for many years Director at the Max Planck Institute for Medical Research in Heidelberg, and pioneered the synthesis of rigid phenylacetylene-based macrocycles and cyclophanes (see his recent Obituary: *Angew. Chem. Int. Ed.* **2012**, *51*, 12404).

Read more in Issue 4/1963

Porous Molecular Solids

A. Avellaneda, P. Valente, A. Burgun, J. D. Evans, A. W. Markwell-Heys, D. Rankine, D. J. Nielsen, M. R. Hill, C. J. Sumby,* C. J. Doonan* **3746 – 3749**

Kinetically Controlled Porosity in a Robust Organic Cage Material



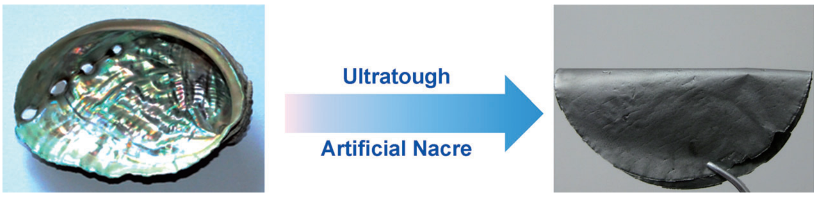
Won by the hare: A new crystalline microporous solid was prepared that is composed of discrete organic cages made entirely from carbon–carbon bonds. The porosity of this material can be controlled by simple kinetic methods, which afford reproducible access to either a non-porous or porous polymorph.

Artificial Nacre

Q. F. Cheng,* M. X. Wu, M. Z. Li,* L. Jiang, Z. Y. Tang* ______ **3750 – 3755**

Ultratough Artificial Nacre Based on Conjugated Cross-linked Graphene Oxide

Inside Back Cover

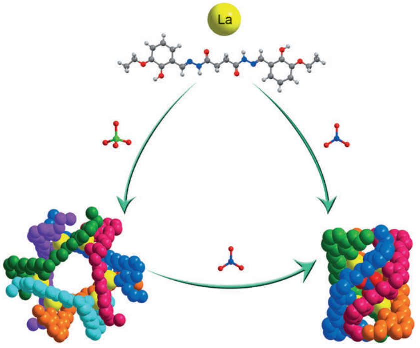


Inspired by natural nacre, layered composites based on graphene oxide (GO) and 10,12-pentacosadiyn-1-ol (PCDO) have been successfully fabricated. PCDO molecules are grafted onto GO sheets and cross-linked with each other, resulting in a superior toughness that is two times higher than that of the natural nacre.

Supramolecular Chemistry

B. Wang, Z. P. Zang, H. H. Wang, W. Dou, X. L. Tang, W. S. Liu,* Y. L. Shao, J. X. Ma, Y. Z. Li, J. Zhou ______ **3756 – 3759**

Multiple Lanthanide Helicate Clusters and the Effects of Anions on Their Configuration

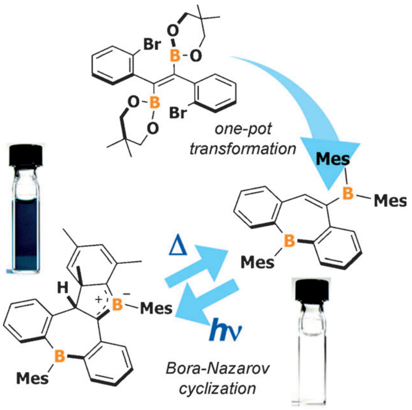


Shaping up your clusters: Two supramolecular clusters of multiple lanthanide helicates have been synthesized. Cluster structure is controlled by the choice of anion, with tetrahedral ClO_4^- producing larger circular helicates, and trigonal-planar NO_3^- leading to a compact quadruple-stranded helicate (see picture).

Structure Elucidation

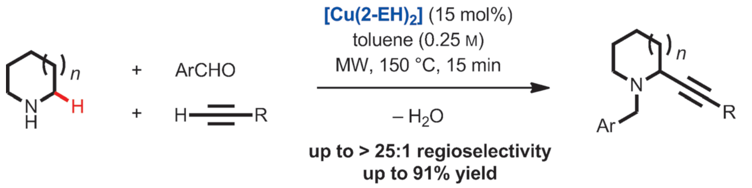
A. Iida, S. Saito, T. Sasamori, S. Yamaguchi* ______ **3760 – 3764**

Borylated Dibenzoborepin: Synthesis by Skeletal Rearrangement and Photochromism Based on Bora-Nazarov Cyclization



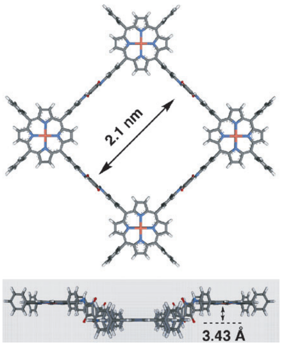
It's a boron kind of magic: A complex reaction sequence involving a skeletal rearrangement leads to 10-dimesitylboryl-substituted dibenzoborepin in a one-pot transformation in good yield. The borylborepin shows remarkable photochromic properties and undergoes a bora-Nazarov cyclization to give a deep-blue compound with an allyl cation-like C–B–C substructure.

C–H Functionalization



Cocktail of three: A new strategy for iminium ion isomerization was applied to the direct, redox-neutral α-alkynylation of amines. Copper(II) 2-ethylhexanoate $[Cu(2\text{-}EH)_2]$ was identified as the optimal catalyst for this three-component coupling reaction of secondary amines, aldehydes, and alkynes. MW = microwave.

Organic Frameworks



π in the sky: A squaraine-linked, conjugated two-dimensional porphyrin covalent organic framework (COF; see scheme; C: gray, H: white, N: blue, Cu: red) was synthesized. Owing to the π-conjugated linkage together with the eclipsed stacking of the units, this COF exhibits enhanced chemical and thermal stabilities. It absorbs a broad range of light, from the ultraviolet to the visible, and near-infrared regions, and shows potential as a photocatalyst.

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).

This article is available online free of charge (Open Access).

This article is accompanied by a cover picture (front or back cover, and inside or outside).

Angewandte Corrigendum

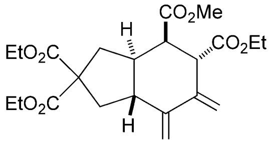
Rhodium(I)-Catalyzed Ene–Allene–Allene [2+2+2] Cycloadditions: Stereoselective Synthesis of Complex *trans*-Fused Carbocycles

A. T. Brusoe,
E. J. Alexanian* ___________ 6596–6600

Angew. Chem. Int. Ed. **2011**, *50*

DOI: 10.1002/anie.201100272

In Table 2 of this Communication, a wrong structure is shown for cycloadduct **9**. The correct structure of cycloadduct **9** is depicted below and in the Supporting Information.



9

Angewandte Corrigendum

In this Communication the acknowledgement part should be corrected as follows:

"Research at UCSB including the fabrication and testing of solar cells and the measurements and analysis were supported by the Air Force Office of Scientific Research, (AFOSR FA9550-11-1-0063), Dr. Charles Lee, Program Officer. J.H.P. acknowledges the support from NRF grants (2010-0029321)."

Transferable Graphene Oxide by Stamping Nanotechnology: Electron-Transport Layer for Efficient Bulk-Heterojunction Solar Cells

D. H. Wang, J. K. Kim, J. H. Seo, I. Park, B. H. Hong, J. H. Park, A. J. Heeger* ____________ **2874–2880**

Angew. Chem. Int. Ed. **2013**, *52*

DOI: 10.1002/anie.201209999

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