

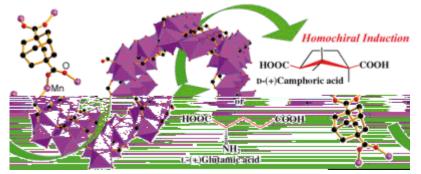
ISSUE NAVIGATION Early View | Current Issue | 2010 | 2009 | 2008 | 2007 | 2006 | ALL ISSUES (1998 - 2010)

Upcoming Hot Papers

Hot Papers are chosen by the Editors for their importance in a rapidly evolving field of high current interest. Many of the "Very Important Papers" (VIPs) would certainly qualify to be included here, but such a duplication is avoided.

Chirality Induction

A Tale of Three Carboxylates: Cooperative Asymmetric Crystallization of a Three-Dimensional Microporous Framework from Achiral Precursors



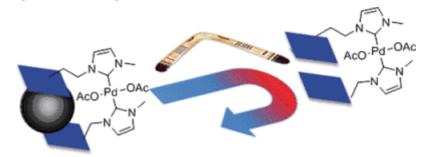
Jian Zhang, Shumei Chen, Ruben A. Nieto, Tao Wu, Pingyun Feng, Xianhui Bu*

Something for nothing? A chiral induction reagent catalyzes the growth of chiral crystals and controls their bulk chirality. Time-dependent experiments show that an initial achiral phase is slowly converted into enantioenriched crystals in the presence of the chiral induction agent.

Published online, DOI: 10.1002/anie.200906248 No. 7/2010.

Homogeneous Catalysis

A Recyclable Nanoparticle-Supported Palladium Catalyst for the Hydroxycarbonylation of Aryl Halides in Water



Sebastian Wittmann, Alexander Schätz, Robert N. Grass, Wendelin J. Stark, Oliver Reiser*

Boomerang catalysis: A catalyst catch–release system is established by the noncovalent attachment of a Pd N-heterocyclic carbene complex to graphene-coated magnetic Co nanoparticles. The immobilization by pyrene tags (see scheme; blue) is reversible at elevated temperatures, releasing the homogeneous catalyst. The hydroxycarbonylation of aryl halides is performed in 16 iterative reactions with this highly active catalyst.

Coming soon.

Boronic Acids





Fanyang Mo, Yubo Jiang, Di Qiu, Yan Zhang, Jianbo Wang*

Leave the metal out: Arylboronates are produced in moderate to good yields by direct borylation of readily available aryl amines (see scheme). The reaction can be carried out under air at room temperature and transition-metal catalysis is not required. The boronate products can be used without purification in Suzuki–Miyaura cross-coupling reactions.

Published online, DOI: 10.1002/anie.200905824

Easy Synthesis of Hollow Polymer, Carbon, and Graphitized Microspheres

An-Hui Lu*, Wen-Cui Li, Guang-Ping Hao, Bernd Spliethoff, Hans-Josef Bongard, Bernd Bastian Schaack, Ferdi Schüth

Balls galore! A new approach was developed for the easy synthesis of hollow microspheres with amorphous or graphitized microstructure. Starting from one type of solid polymer sphere, a simple water washing treatment led to the formation of hollow structures. Diverse products such as hollow carbon or graphitized spheres can be obtained, depending on subsequent treatment methods (see picture).

Published online, DOI: 10.1002/anie.200906445

Direct Synthesis of Imines from Alcohols and Amines with Liberation of H₂

Boopathy Gnanaprakasam, Jing Zhang, David Milstein*

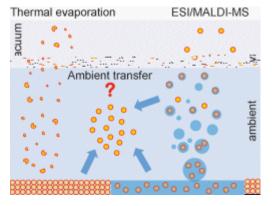
A clean sweep: Aryl and aliphatic imines can be synthesized directly and efficiently from alcohols and amines under mild, neutral conditions with the liberation of only molecular hydrogen and water (see scheme; R=isopropyl, *tert*-butyl). This general, environmentally benign reaction is catalyzed by a de-aromatized ruthenium PNP pincer complex (0.2 mol %), and can proceed in toluene under an inert atmosphere or under air.

Published online, DOI: 10.1002/anie.200907018

Indium(I)-Catalyzed Asymmetric Allylation, Crotylation, and -Chloroallylation of Hydrazones with Rare Constitutional a

Spectroscopy

Direct Access to Isolated Biomolecules at Ambient Conditions



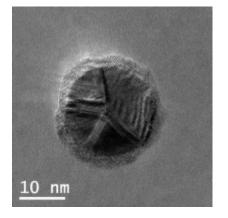
Konstantin Chingin, Vladimir Frankevich, Roman M. Balabin, Konstantin Barylyuk, Huanwen Chen, Rui Wang, Renato Zenobi*

In the transfer of nonvolatiles into the gas phase, thermal evaporation is extremely inefficient because of the rapid chemical degradation (left). Generally, nonvolatiles can be brought into the gas phase by soft-ionization methods such as ESI or MALDI for investigation by MS (right). Now a method has been developed to access isolated biomolecules in the gas phase at ambient conditions (center).

Published online, DOI: 10.1002/anie.200906213

Hydrogen Storage

Ultrahigh Hydrogen Loading in Gold–Palladium Core–Shell Nanostructures



María G. Montes de Oca, David J. Fermín*

Stuffed: An unexpectedly large amount of electrochemically produced hydrogen can be stored in thin palladium shells at gold nanoparticles (see picture). Hydrogen-loaded 1 nm Pd shells on 20 nm Au particles exhibit two orders of magnitude higher H/Pd ratios than bulk Pd electrodes.

Coming soon.

Phosphorylation-Dependent Kinase–Substrate Cross-Linking

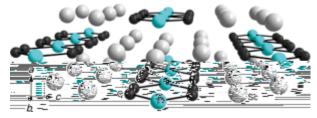
Sujit Suwal, Mary Kay H. Pflum*

Pinning down kinase substrates: The identification of substrates of a particular kinase is fundamental to the elucidation of cell-signaling cascades. This problem has now been addressed by the title approach involving kinase-catalyzed labeling coupled with photo-cross-linking (see scheme). When coupled with MS analysis, this strategy can be used to determine the sites of phosphorylation as well as the effector kinase. ADP=adenosine diphosphate.

Published online, DOI: <u>10.1002/anie.200905244</u>

Superconducting Carbides

Superconductivity in Quasi One-Dimensional Carbides



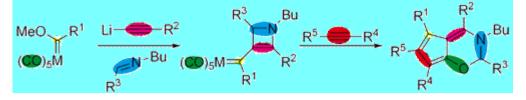
Wolfgang Scherer*, Christoph Hauf, Manuel Presnitz, Ernst-Wilhelm Scheidt, Georg Eickerling*, Volker Eyert, Rolf-Dieter Hoffmann, Ute C. Rodewald, Adrienne Hammerschmidt, Christian Vogt, Rainer Pöttgen*

Carbides and Co: The electronic structures of the isotypic carbides Sc_3TC_4 (see picture; T=Fe, Co, Ni) are investigated by theoretical and experimental charge-density studies. Even tiny differences in the electronic band structure of these solids can be found in the properties of the Laplacian of the experimental electron density. Only the cobalt carbide is superconducting below 4.5 K and displays a structural phase transition around 70 K.

Published online, DOI: 10.1002/anie.200904956

Synthetic Methods

Sequential Five-Component Construction of the Cyclopenta[e][1,3]oxazine Skeleton using Stable 2-Azetine Derivatives



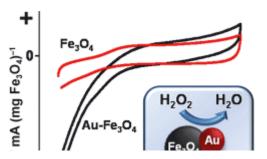
José Barluenga*, Aránzazu Gómez, Javier Santamaría, Miguel Tomás

Hawaii Five-Oxazine: The sequential one-pot reaction of a methoxy-stabilized carbene with an acetylide and an imine provides stable, metal-carbene-containing 2-azetines. Subsequent mild treatment with an alkyne affords a regioselective, three-component cyclization route to fully substituted fused 1,3-oxazines.

Published online, DOI: <u>10.1002/anie.200906357</u> No. 7/2010.

Nanoparticle Properties

Synthetic Tuning of the Catalytic Properties of Au-Fe₃O₄ Nanoparticles



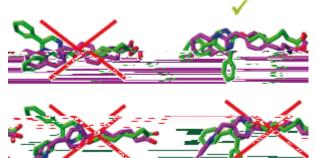
Youngmin Lee, Miguel Angel Garcia, Natalie A. Frey Huls, Shouheng Sun*

Dumbbell-like Au-Fe₃**O**₄ **nanoparticles** and their singlecomponent counterparts, Au and Fe₃O₄, were compared regarding their H₂O₂ reduction capability. The Au-Fe₃O₄ nanoparticles are catalytically more active, which is attributed to polarization effects from Au to Fe₃O₄. This activity can be further tuned by the size of the nanoparticles.

Published online, DOI: <u>10.1002/anie.200906130</u> No. 7/2010.

Drug Design

Drug Design for G-Protein-Coupled Receptors by a Ligand-Based NMR Method



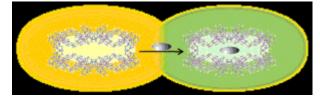
Stefan Bartoschek*, Thomas Klabunde, Elisabeth Defossa, Viktoria Dietrich, Siegfried Stengelin, Christian Griesinger, Teresa Carlomagno, Ingo Focken, K. Ulrich Wendt

A nonradioactive binding assay relying on NMR methods has been devised for a G-protein-coupled receptor; in addition the INPHARMA methods give access to the relative orientation of multiple ligands and supports ligand-based drug design (see picture of superimposed ligands). The methodology is fast and does not require any structural information from protein crystal structures.

Published online, DOI: 10.1002/anie.200905102

Luminescent Materials

Complex Iridium(III) Salts: Luminescent Porous Crystalline Materials



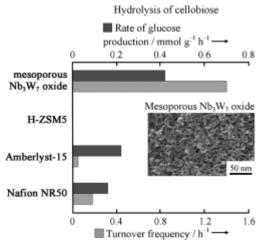
Matteo Mauro, Klaus C. Schuermann, Roger Prétôt, Andreas Hafner, Pierluigi Mercandelli, Angelo Sironi, Luisa De Cola*

Let your light shine: A new class of noncovalently linked crystalline porous materials is based on luminescent iridium complexes. Pairs complexes possessing different emission colors and complementary charges form complex salts. The crystalline materials form 3D porous motifs, and the emission color can be tuned by inclusion of a solvent or by selective quenching of one of the components of the crystal.

Published online, DOI: <u>10.1002/anie.200905713</u> No. 7/2010.

Mesoporous Solid Acid

Highly Active Mesoporous Nb–W Oxide Solid-Acid Catalyst



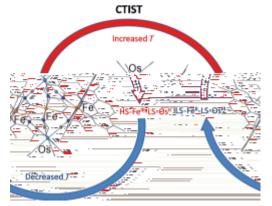
Caio Tagusagawa, Atsushi Takagaki, Ai Iguchi, Kazuhiro Takanabe, Junko N. Kondo, Kohki Ebitani, Shigenobu Hayashi, Takashi Tatsumi, Kazunari Domen*

Pore-ing acid: Mesoporous Nb–W oxides (Nb:W=3:7) are found to be a recyclable, highly active solid acid. They surpass ion-exchange resins (Nafion NR50 and Amberlyst-15) and zeolites (H-ZSM5 and H-Beta) in Friedel–Crafts alkylation and hydrolysis reactions (see picture). The high activity is due to strong acid sites and a mesoporous structure with a high surface area and easy reactant accessibility.

Published online, DOI: 10.1002/anie.200904791 No. 6/2010.

Spin Transitions

An Unprecedented Charge Transfer Induced Spin Transition in a Fe–Os Cluster



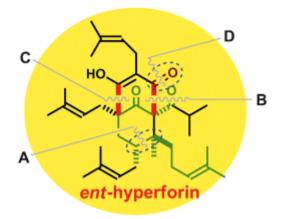
Matthew G. Hilfiger, Meimei Chen, Tatiana V. Brinzari, Tanya M. Nocera, Michael Shatruk, Doros T. Petasis, Janice L. Musfeldt, Catalina Achim*, Kim R. Dunbar*

High 'n low: The novel { $[Fe(tmphen)_2]_3[Os(CN)_6]_2$ } complex (see structure) is the first example of cluster in which a high-spin Fe^{III} ion is in a coordination environment of four imine nitrogens and two N-coordinated cyanides. Magnetic studies reveal an unprecedented type of reversible charge transfer induced spin transition (CTIST) between the low-spin Fe^{II}-N C-Os^{III} and high-spin Fe^{III}-N C-Os^{III} redox pairs.

Published online, DOI: 10.1002/anie.200906264

Total Synthesis

Catalytic Asymmetric Total Synthesis of ent-Hyperforin

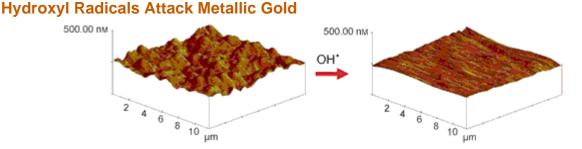


Yohei Shimizu, Shi-Liang Shi, Hiroyuki Usuda, Motomu Kanai*, Masakatsu Shibasaki*

Key to success: The first catalytic asymmetric total synthesis of *ent*-hyperforin (see picture) was accomplished by using a Diels–Alder reaction promoted by a chiral cationic iron catalyst (A; 96 % ee, d.r.>33:1), a diastereoselective Claisen rearrangement (B; 12:1 selectivity), an intramolecular aldol reaction (C), and a vinylogous Pummerer rearrangement (D) as key steps.

Published online, DOI: 10.1002/anie.200906678 No. 6/2010.

Chemical Polishing



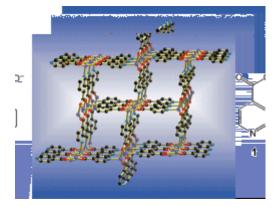
Anna Maria Nowicka*, Ulrich Hasse, Michael Hermes, Fritz Scholz*

Gold service: The asperities on a polished gold surface are quickly dissolved by the OH· radicals of Fenton's reagent. The dissolution of Au is rapid at the beginning of the reaction and is negligible when the asperities have been dissolved. Although the OH· radicals also oxidize the smooth parts of the Au surface, they do not dissolve them, but form a stable oxide monolayer.

Published online, DOI: 10.1002/anie.200906358 No. 6/2010.

Coordination Polymers

A Simple Lithium(I) Salt with a Microporous Structure and Its Gas Sorption Properties



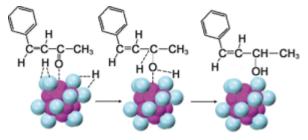
Brendan F. Abrahams*, Martin J. Grannas, Timothy A. Hudson, Richard Robson*

Thoroughly absorbing: The simple combination of lithium ions and isonicotinate anions leads to the formation of a lightweight salt (see picture; C black, O red, N blue, Li purple) that is able to reversibly sorb H_2 , N_2 , CO_2 , and CH_4 . The salt exists as a 3D network of microchannels that are occupied by solvent molecules.

Published online, DOI: <u>10.1002/anie.200906322</u> No. 6/2010.

Gold Nanocatalysts

Atomically Precise Au₂₅(SR)₁₈ Nanoparticles as Catalysts for the Selective Hydrogenation of , -Unsaturated Ketones and Aldehydes



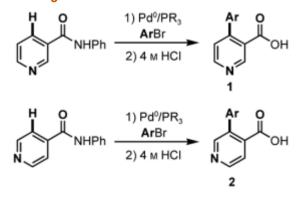
Yan Zhu, Huifeng Qian, Bethany A. Drake, Rongchao Jin*

A golden opportunity: A mechanism has been proposed to account for the chemoselective hydrogenation of , - unsaturated ketones (or aldehydes) to unsaturated alcohols catalyzed by monodisperse $Au_{25}(SR)_{18}$ particles (see picture). Now that the structure of these nanoparticles is known, structure–activity correlations can be drawn.[block]text rewritten so that it does not simply repeat the title and also so that it fits the picture better; ok?[block]

Published online, DOI: 10.1002/anie.200906249 No. 7/2010.

C–H Activation

Pd⁰/PR₃-Catalyzed Arylation of Nicotinic and Isonicotinic Acid Derivatives



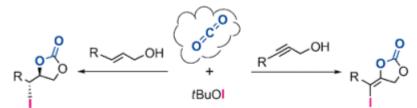
Masayuki Wasa, Brady T. Worrell, Jin-Quan Yu*

Good for your health: Intermolecular

C–H functionalization of pyridine rings at the 3- and 4-positions is described using a $Pd^{0}/PR_{3}/ArBr$ catalytic system. This reaction provides a powerful method for the preparation of structurally diverse nicotinic and isonicotinic acids that are of great importance in drug discovery.

Published online, DOI: <u>10.1002/anie.200906104</u> No. 7/2010.

Atmospheric CO₂ Fixation by Unsaturated Alcohols Using *t*BuOI under Neutral Conditions



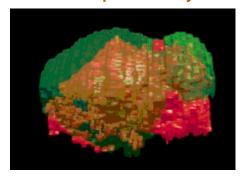
Satoshi Minakata*, Itsuro Sasaki, Toshihiro Ide

Hold on tight! Reaction of CO₂ with unsaturated alcohols and *t*BuOI to form cyclic carbonates leads to fixation of the greenhouse gas. In contrast to known CO₂ fixation methods, this process proceeds under extremely mild conditions.

Published online, DOI: 10.1002/anie.200906352 No. 7/2010.

Imaging Mass Spectrometry

Three-Dimensional Vizualization of Mouse Brain by Lipid Analysis Using Ambient Ionization Mass Spectrometry



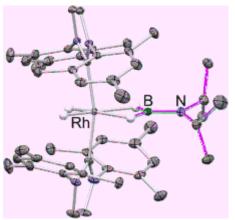
Livia S. Eberlin, Demian R. Ifa, Chunping Wu, R. Graham ${\rm Cooks}^{\star}$

Imaging, not imagination: Three-dimensional (3D) images can be constructed from a set of 2D data acquired by desorption electrospray ionization (DESI) mass spectrometry. The 3D images show the spatial distributions of specific biomolecules in substructures of the mouse brain (see picture).

Published online, DOI: 10.1002/anie.200906283 No. 5/2010.

Aminoborane Complexes

Rhodium and Iridium Aminoborane Complexes: Coordination Chemistry of BN Alkene Analogues



Christina Y. Tang, Amber L. Thompson, Simon Aldridge*

Side-on or end-on? Rhodium and iridium complexes featuring aminoboranes ($R_2N=BH_2$) as ligands have been synthesized and structurally characterized. Crystallographic measurements show that the ligands—in contrast to isoelectronic alkene donors—bind in an end-on fashion through a bis(-borane) binding motif (see structure).

Published online, DOI: <u>10.1002/anie.200906171</u> No. 5/2010.

Molecular Devices

Controlling Molecular Rotary Motion with a Self-Complexing Lock



Da-Hui Qu, Ben L. Feringa*

The key to motion: A second-generation molecular rotary motor, which contains a DB24C8 macrocycle ring incorporated into the lower stator half and a dialkyl ammonium ion attached to the upper rotor half, forms a [1]pseudorotaxane in less polar solvents such as CH_2CI_2 . In this self-complexing system, acid–base-controlled threading–dethreading movements can be utilized to unlock or lock the molecular motor (see picture).

Published online, DOI: 10.1002/anie.200906064 No. 6/2010.

Immunotherapeutic Bisphosphonates

Yonghui Zhang, Roi Wang, Kilannin Krys Kevin Houlihan, Jiku Chain gang: Lipoph long alkyl chains (se

Lipophilic Pyridinium Bisphosphonates: Potent T Cell Stimulators

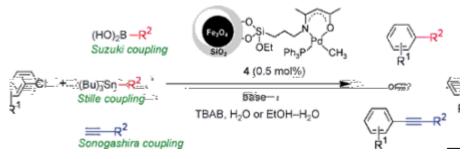
Yonghui Zhang, Rong Cao, Fenglin Yin, Fu-Yang Lin, Hong Wang, Kilannin Krysiak, Joo-Hwan No, Dushyant Mukkamala, Kevin Houlihan, Jikun Li, Craig T. Morita*, Eric Oldfield*

Chain gang: Lipophilic pyridinium bisphosphonates containing long alkyl chains (see picture, P red, N blue, C orange, H gray) stimulate human T cells expressing the V 2V 2 T cell receptor. Stimulation with such compounds is more potent than with zoledronate, which is active against breast and prostate cancer. The lipophilic bisphosphonates bind poorly to bone and are thus less likely to cause side effects associated with bisphosphonates in clinical use.

Published online, DOI: <u>10.1002/anie.200905933</u> No. 6/2010.

Heterogeneous Catalysis

A Practical Heterogeneous Catalyst for the Suzuki, Sonogashira, and Stille Coupling Reactions of Unreactive Aryl Chlorides



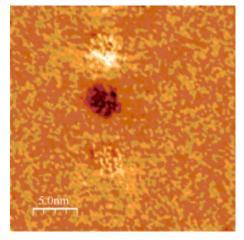
Myung-Jong Jin*, Dong-Hwan Lee

Practical catalyst: A magnetic nanoparticle-supported palladium catalyst was developed for the highly efficient heterogeneous Suzuki, Sonogashira, and Stille couplings of a wide variety of aryl chlorides. Furthermore, the catalyst could be recycled by facile magnetic separation without any loss of activity.

Published online, DOI: 10.1002/anie.200905626 No. 6/2010.

Spinn Crossover

Spin-State Patterns in Surface-Grafted Beads of Iron(II) Complexes



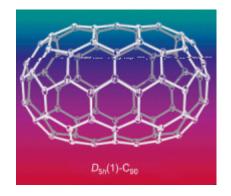
Mohammad S. Alam, Michael Stocker, Klaus Gieb, Paul Müller*, Marco Haryono, Katja Student, Andreas Grohmann*

Strung out: Fe^{II} complexes containing pairs of planar terdentate N ligands form regular one-dimensional aggregates on highly oriented pyrolytic graphite, on a length scale of hundreds of nanometers. STM spectroscopy was used to probe the molecular conductance and thus the spin state. The distribution of spin states is random in the single-molecule chain, but local cooperativity sets in when the chain is made up of oligonuclear "beads" (see picture).

Published online, DOI: 10.1002/anie.200905062 No. 6/2010.

Fullerenes

Isolation of a Small Carbon Nanotube: The Surprising Appearance of $D_{5h}(1)$ -C₉₀



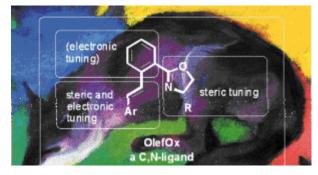
Hua Yang, Christine M. Beavers, Zhimin Wang, An Jiang, Ziyang Liu*, Hongxiao Jin*, Brandon Q. Mercado, Marilyn M. Olmstead*, Alan L. Balch*

Totally tubular: The previously undetected higher fullerene $D_{5h}(1)$ -C₉₀ (see structure) was isolated as the major C₉₀ isomer produced from Sm₂O₃-doped graphite rods and identified structurally by X-ray crystallography.

Published online, DOI: 10.1002/anie.200906023 No. 5/2010.

Ligand Design

Olefin–Oxazolines (OlefOx): Highly Modular, Easily Tunable Ligands for Asymmetric Catalysis



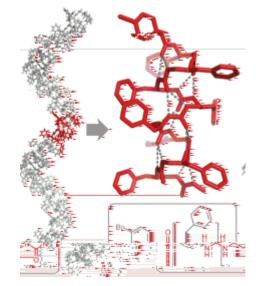
Björn T. Hahn, Friederike Tewes, Roland Fröhlich, Frank Glorius*

Foxy ligands: An efficient three-step synthesis allows the new highly modular family of olefin–oxazoline ligands (OlefOx; see picture) to be exploited in asymmetric catalysis. The ease of electronic and steric variation and the successful application in the highly enantioselective rhodium-catalyzed conjugate addition of aryl boronic acids to cylic enones demonstrate the importance of this new ligand class.

Published online, DOI: <u>10.1002/anie.200905712</u> No. 6/2010.

Helical Foldamers

The Canonical Helix of Urea Oligomers at Atomic Resolution: Insights Into Folding-Induced Axial Organization



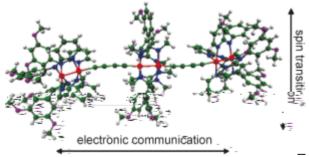
Lucile Fischer, Paul Claudon, Nagendar Pendem, Emeric Miclet, Claude Didierjean, Eric Ennifar, Gilles Guichard*

Helical by nature: Urea-basng-heptidomimetics with proteinogenic side chains are fully helical in the crystalline state (see picture). Four acyclic residues are sufficient to drive complete helix formation with all complementary H-bonding sites being satisfied (up to 14 for a 8-mer). Helices pack headto-tail to create infinite H-bondng-networks with different topologies.

Published online, DOI: <u>10.1002/anie.200905592</u> No. 6/2010.

Organometallic Wires

Linear Trimer of Diruthenium Linked by Butadiyn-Diyl Units: A Unique Electronic Wire



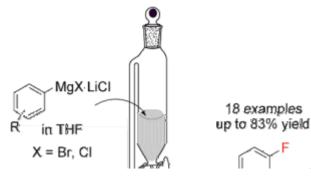
Jie-Wen Ying, Isiah Po-Chun Liu, Bin Xi, You Song, Charles Campana, Jing-Lin Zuo, Tong Ren*

Ru communicating? Butadiyn-diyl bridges link three Ru₂ moieties together to give a molecular wire (see structure, red Ru, green C, blue N, purple O). Voltammetric, spectroscopic, and magnetic data all point to extensive electronic delocalization across the linear trimer.

Published online, DOI: 10.1002/anie.200904674 No. 5/2010.

Selective Fluorination

Efficient Synthesis of Aryl Fluorides



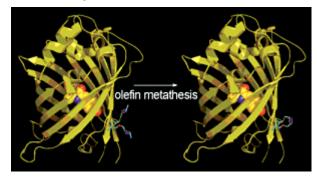
Pazhamalai Anbarasan, Helfried Neumann, Matthias Beller*

Creating C–F bonds: A novel electrophilic fluorination of aryl and heteroaryl Grignard reagents has been discovered and was used for the efficient synthesis of various aryl fluoride derivatives (see picture; THF=tetrahydrofuran).

Published online, DOI: <u>10.1002/anie.200905855</u>

Expanded Genetic Code

Genetically Encoded Alkenes in Yeast



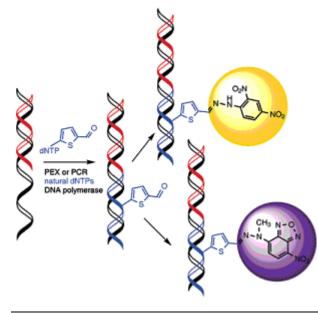
Hui-wang Ai, Weijun Shen, Eric Brustad, Peter G. Schultz*

Olefin-containing amino acids have been genetically introduced into proteins in *Saccharomyces cerevisiae* by orthogonal tRNA/aminoacyl-tRNA synthetase pairs. These nonnatural amino acids can be used for selective protein modification through olefin metathesis reactions.

Published online, DOI: 10.1002/anie.200905590 No. 5/2010.

Functionalized DNA

Direct Polymerase Synthesis of Reactive Aldehyde-Functionalized DNA and Its Conjugation and Staining with Hydrazines



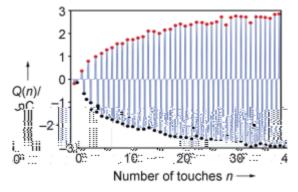
Veronika Raindlová, Radek Pohl, Miloslav Šanda, Michal Hocek*

Reactive aldehyde-modified DNA was prepared in two steps by Suzuki cross-coupling of halogenated nucleoside triphosphates (dNTPs) with 4-formylthiophene-2-boronic acid and subsequent polymerase incorporation of the modified nucleotides into DNA (see scheme; PEX=primer extension, PCR=polymerase chain reaction). Formation of hydrazones with arylhydrazines under aqueous conditions was used for DNA staining.

Published online, DOI: <u>10.1002/anie.200905556</u> No. 6/2010.

Electrostatics

Contact Electrification between Identical Materials



Mario M. Apodaca, Paul J. Wesson, Kyle J. M. Bishop, Mark A. Ratner, Bartosz A. Grzybowski*

Ch-ch-charges: Pieces of identical, atomically flat insulators separate a charge *Q* when brought into contact and then parted. Repeated contacts cause the magnitudes of the separated charges to increase monotonically (see picture). A theoretical model is presented that explains these phenomena by the inherent, molecular-scale fluctuations in the composition of the seemingly identical contacting surfaces.

Published online, DOI: <u>10.1002/anie.200905281</u> No. 5/2010.

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