

Spotlight on Angewandte's Sister Journals

11928 – 11931

Service

Author Profile



"I like refereeing because it is the only way to keep scientific publishing working. The biggest problem that scientists face is distractions from outside science. ..."
This and more about Shu-Li You can be found on page 11934.

Shu-Li You _____ 11934

News



F. Kraus



H. W. Roesky



P. Couvreur



J. S. Figueroa

Wöhler Prize for Young Scientists:
F. Kraus _____ 11935

Heinrich Roessler Prize:
H. W. Roesky _____ 11935

Médaille de l'innovation du CNRS:
P. Couvreur _____ 11935

Presidential Early Career Award:
J. S. Figueroa _____ 11935

Obituaries



Horst Prinzbach, Professor Emeritus at the Institute of Organic Chemistry at the Albert-Ludwigs-Universität, Freiburg, passed away at the age of 81, after a short but serious illness, on September 18th, 2012. The scientific community has lost a distinguished chemist who significantly influenced the post World War 2 chemical landscape in Germany.

Horst Prinzbach (1931–2012)

W.-D. Fessner* _____ 11936 – 11937

Books

Characterization of Solid Materials and Heterogeneous Catalysts

Michel Che, Jacques C. Védrine

reviewed by R. A. Schoonheydt _____ 11938

Diffusion in Nanoporous Materials

Jörg Kärger, Douglas M. Ruthven,
Doros N. Theodorou

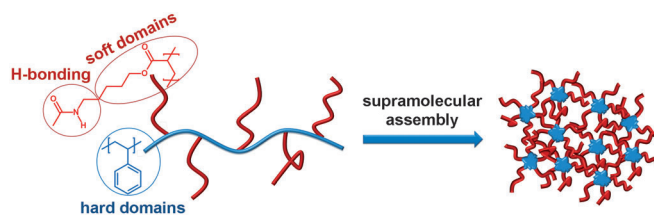
reviewed by H. Koller _____ 11939

Highlights

Supramolecular Materials

R. Hoogenboom* — 11942 – 11944

Hard Autonomous Self-Healing
Supramolecular Materials—A
Contradiction in Terms?



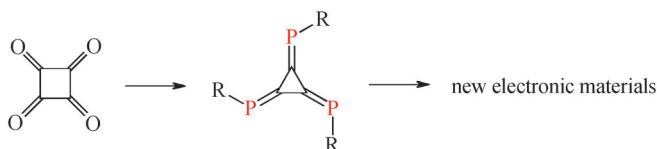
Achieving the unachievable: Hard supramolecular materials displaying autonomous self-healing have been considered unachievable because of the mobility required to reconstitute supramolecular interactions after rupture. Now, relatively

hard thermoplastic elastomers have been reported that meet these requirements. The picture shows a triblock copolymer containing soft supramolecular “self-healing” domains and hard, structure-giving domains.

Heteroradialenes

H. Hopf* — 11945 – 11947

Phosporadialenes—A New Kid in Town



A bright future: The realization that a mixture of squaraine derivatives drastically improve quantum efficiency in the visible and near-IR region of organic solar

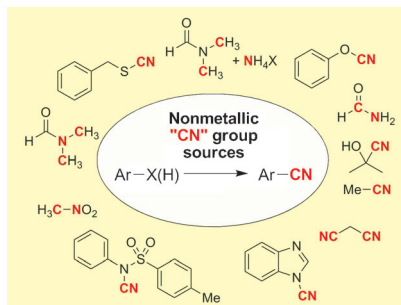
cells, and the synthesis of the first phosporadialene serve as the focus for a short overview of oxocarbons and related heteroorganic compounds.

Minireviews

Cyano-Group Sources

J. Kim, H. J. Kim,
S. Chang* — 11948 – 11959

Synthesis of Aromatic Nitriles Using
Nonmetallic Cyano-Group Sources



Introducing CN: Recently, a range of nonmetallic organic cyano-group precursors (see scheme) have been developed as attractive alternatives to metal cyanides that have been frequently employed in the catalytic cyanation of aryl halides. This Minireview summarizes the development of organic cyano-group precursors and their application in the cyanation of aryl halides, boronates, boronic acids, arene carboxylic acids, and (hetero)arene C–H bonds.

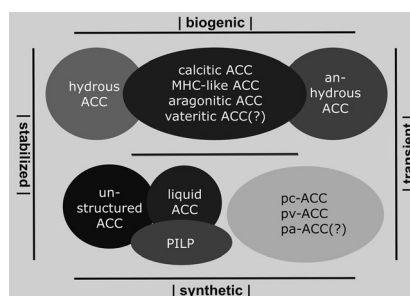
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a national chemical society prices are available
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sales tax.

Reviews

Coming in to form: A summary is given of what is known about polymorphism in calcium carbonate as well as the role of amorphous calcium carbonate in biomineralization. The amorphous forms of calcium carbonate within the physical notion of polymorphism lead to new insights when it comes to the mechanisms by which polymorphic structures can evolve. This also has implications beyond biomineralization.



Biomaterial Polymorphism

J. H. E. Cartwright,* A. G. Checa,
J. D. Gale, D. Gebauer,*
C. I. Sainz-Díaz _____ **11960–11970**

Calcium Carbonate Polymorphism and Its Role in Biomineralization: How Many Amorphous Calcium Carbonates Are There?

Communications

Chiral Circulene

L. Severa, M. Ončák, D. Koval, R. Pohl,
D. Šaman, I. Čísařová,
P. E. Reyes-Gutiérrez, P. Sázelová,
V. Kašička, F. Teplý,*
P. Slavíček* _____ **11972–11976**

A Chiral Dicationic [8]Circulene: Photochemical Origin and Facile Thermal Conversion into a Helicene Congener



Frontispiece



Wire Devices

T. Chen, L. Qiu, Z. Yang, Z. Cai, J. Ren,
H. Li, H. Lin, X. Sun,
H. Peng* _____ **11977–11980**

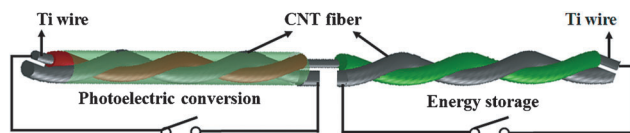
An Integrated “Energy Wire” for both Photoelectric Conversion and Energy Storage



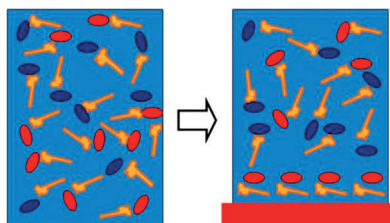
Inside Cover

Light my wire: Aligned carbon nanotube (CNT) fibers are wrapped around a TiO₂ nanowire that is several centimeters long. Treating the ends of the nanotube wire with a light-sensitive dye and an electro-

lyte, creates photoelectric-conversion and energy-storage regions in the same device (see scheme). The “wire” shows a high overall photoelectric conversion and storage efficiency of 1.5%.



A good sort: A racemate is observed to segregate in situ upon diastereoselective adsorption on an achiral surface by surface-mediated complex formation in a liquid (see picture; yellow: enantiopure resolving agents, ovals: the enantiomers of the racemate to be resolved).



Chiral Resolution

H. Xu, W. J. Saletra, P. Iavicoli,
B. Van Averbek, E. Ghijsens, K. S. Mali,
A. P. H. J. Schenning, D. Beljonne,
R. Lazzaroni,* D. B. Amabilino,*
S. De Feyter* _____ **11981–11985**

Pasteurian Segregation on a Surface Imaged In Situ at the Molecular Level



The German Chemical Society (GDCh) invites you to:



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GDCh
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Tuesday, March 12, 2013

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Speakers



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Bertozzi



François
Diederich



Alois
Fürstner



Roald Hoffmann
(Nobel Prize 1981)



Susumu
Kitagawa



Jean-Marie Lehn
(Nobel Prize 1987)



E.W. "Bert"
Meijer



Frank
Schirrmacher
(Publisher, FAZ)



Robert
Schlögl



George M.
Whitesides



Ahmed Zewail
(Nobel Prize 1999)

More information:

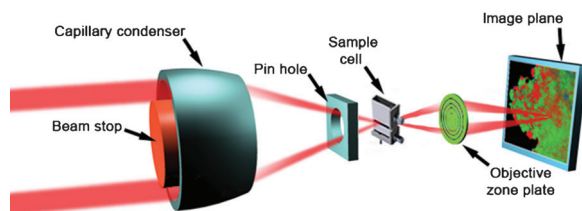


angewandte.org/symposium



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A closer look at catalysis: In situ hard X-ray nanotomography has been developed (see picture) as a method to investigate an individual iron-based Fischer–Tropsch–Olefins (FTO) catalyst particle at elevated temperatures and pressures. 3D

and 2D maps of 30 nm resolution could be obtained and show heterogeneities in the pore structure and chemical composition of the catalyst particle of about 20 μm .

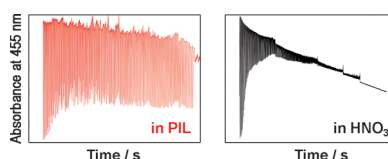
Heterogeneous Catalysis

I. D. Gonzalez-Jimenez, K. Cats, T. Davidian, M. Ruitenbeek, F. Meirer, Y. Liu, J. Nelson, J. C. Andrews, P. Pianetta, F. M. F. de Groot, B. M. Weckhuysen* — 11986 – 11990

Hard X-ray Nanotomography of Catalytic Solids at Work



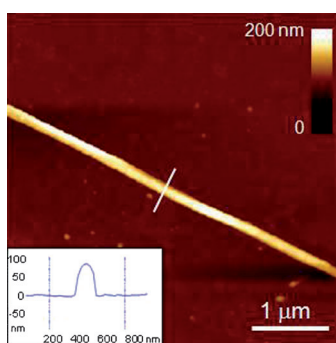
The Belousov–Zhabotinsky (BZ) reaction using hydrated protic ionic liquid (PIL) as reaction medium is reported. For the first time it is found that the BZ oscillation reaction occurred in certain hydrated PILs without adding strong acid such as HNO_3 (see red oscillation profile). Furthermore, a stable and long-lasting self-oscillation can be realized when the component concentrations of the BZ medium are optimized.



Non-Equilibrium Processes

T. Ueki, M. Watanabe, R. Yoshida* — 11991 – 11994

Belousov–Zhabotinsky Reaction in Protic Ionic Liquids

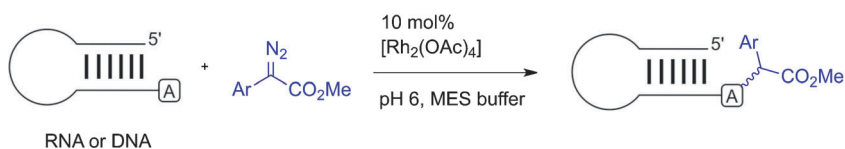


Wired for action: An alumina-based template method produces nanowires of an alkylated mononuclear spin-crossover Fe^{III} complex. The wires can be isolated by dissolving the template in acid without decomposition of the product, and have a narrow distribution of diameter widths in the range of 80–100 nm. Electronic characterization of a single wire is possible by using Raman spectroscopy coupled to AFM (see picture).

Nanostructures

P. N. Martinho, T. Lemma, B. Gildea, G. Picardi, H. Müller-Bunz, R. J. Forster, T. E. Keyes,* G. Redmond,* G. G. Morgan* — 11995 – 11999

Template Assembly of Spin Crossover One-Dimensional Nanowires



Nuc'em: A variety of nucleic acids can be catalytically alkylated with rhodium-carbenoids generated from diazo compounds in aqueous buffer through an N–H insertion process (see scheme; MES = 2-(N-morpholino)ethanesulfonic

acid). The method specifically targets unpaired bases such as those present in single strands, turn regions, and overhangs while leaving double-stranded sequences untouched.

Synthetic Methods

K. Tishinov, K. Schmidt, D. Häussinger, D. G. Gillingham* — 12000 – 12004

Structure-Selective Catalytic Alkylation of DNA and RNA



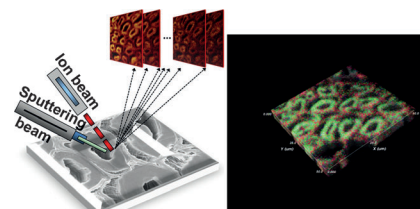
3D Chemical Imaging

S. Jung, M. Foston, U. C. Kalluri,
G. A. Tuskan,
A. J. Ragauskas* — 12005 – 12008



3D Chemical Image using TOF-SIMS
Revealing the Biopolymer Component
Spatial and Lateral Distributions in
Biomass

Show me inside: 3D time-of-flight secondary-ion mass spectrometry (TOF-SIMS) with a dual-beam mode allows the detection of the characteristic biopolymers from surface to subsurface in plant cell walls. Lateral and vertical distribution of major components can thereby be mapped to understand the structural architecture of plant cell walls at under sub-micrometer scales (see picture: green = cellulose, red = lignin).

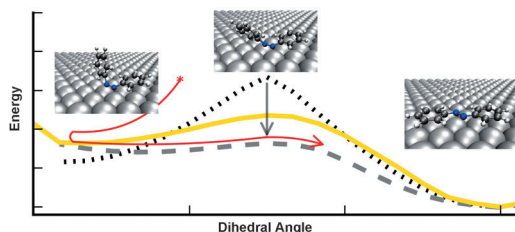


Molecular Switches

R. J. Maurer, K. Reuter* — 12009 – 12011



Bistability Loss as a Key Feature in
Azobenzene (Non-)Switching on Metal
Surfaces



Flip the switch on metals: Coinage metal adsorbed azobenzene is investigated as a prototypical molecular switch. Switching capabilities are not just lost owing to excited-state quenching, but also because of changes in the ground-state energetics

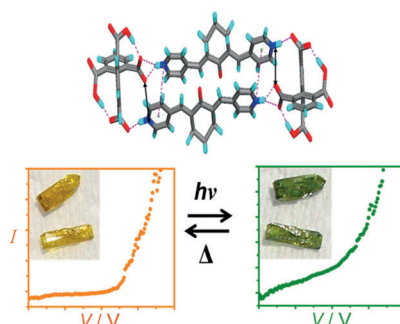
(see graph; black = gas phase, gray = Ag-(111), yellow = Au(111)). Electron-demanding coadsorbates are suggested as a strategy to regain the switching function.

Charge-Transfer Interactions

S. Roy, S. P. Mondal, S. K. Ray,
K. Biradha* — 12012 – 12015



A Photoswitchable and Photoluminescent
Organic Semiconductor Based On
Cation- π and Carboxylate-Pyridinium
Interactions: A Supramolecular Approach



More than the sum of the parts: The property of a supramolecular material can differ significantly from those of the constituent materials. Two organic components, which are nonconductive, nonphotochromic, and nonluminescent, were shown to self-assemble by cation- π , π - π , and carboxylate-pyridinium interactions. An organic semiconductor is thus produced with significant charge mobility and photochromic and photoluminescence properties.

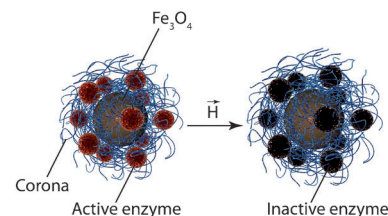
Magnetic Nanoparticles

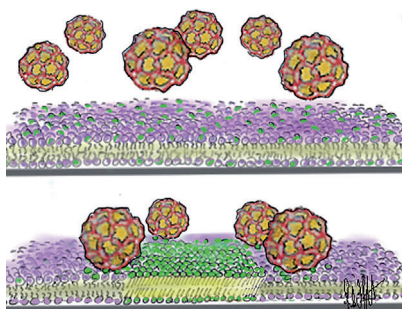
N. L. Klyachko, M. Sokolsky-Papkov,
N. Pothayee, M. V. Efremova, D. A. Gulin,
N. Pothayee, A. A. Kuznetsov,
A. G. Majouga, J. S. Riffle, Y. I. Golovin,
A. V. Kabanov* — 12016 – 12019



Changing the Enzyme Reaction Rate in
Magnetic Nanosuspensions by a Non-
Heating Magnetic Field

Deactivation and structural deformation of enzymes immobilized on magnetic nanoparticles (MNPs) are observed after exposure to magnetic fields. These changes are due to realignment of MNPs in response to the AC magnetic field, which leads to stresses in MNP-linked polymer chains. Such stresses translated to an enzyme molecule immobilized on a MNP aggregate induce deformations and irreversible (or long lasting) conformational changes.



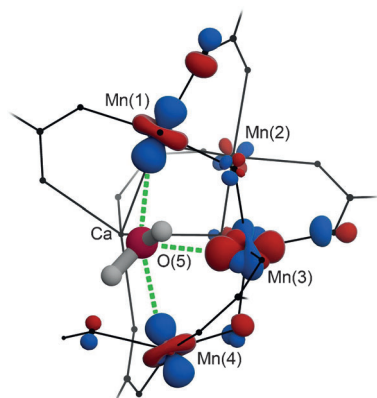


A sticky situation: Domain-dependent recognition of the glycosphingolipid galactosylceramide by norovirus-like particles (see picture; red/yellow) is shown using supported lipid bilayers (purple) as model membranes. Optimal ligand presentation is found to promote strong binding to GalCer. This presentation can be found at the edges of the glycosphingolipid-enriched domains (green) and binding is repressed in the absence of these domains.

Virus Binding

M. Bally,* G. E. Rydell, R. Zahn, W. Nasir, C. Eggeling, M. E. Breimer, L. Svensson, F. Höök, G. Larson* — 12020 – 12024

Norovirus GII.4 Virus-like Particles Recognize Galactosylceramides in Domains of Planar Supported Lipid Bilayers

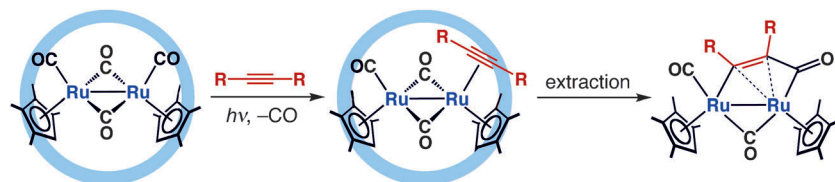


Balancing act: DFT calculations show that the structures of the water-oxidizing complex in the two most recent single crystal XRD studies of photosystem II at 2.9 Å and 1.9 Å resolution are tautomers related by a single proton transfer. The anomalous oxygen species, O(5), weakly bound to four metal centers in the 1.9 Å structure (see picture) is identified as a substrate water molecule balanced between the Jahn–Teller axes of Mn(1), Mn(3), and Mn(4).

Photosystem II Structure

P. Gatt, S. Petrie, R. Stranger,* R. J. Pace* — 12025 – 12028

Rationalizing the 1.9 Å Crystal Structure of Photosystem II—A Remarkable Jahn–Teller Balancing Act Induced by a Single Proton Transfer



Under confinement: Photosubstitution of a CO ligand with an alkyne on a dinuclear ruthenium carbonyl complex within a self-assembled cage occurs without the cleavage of the photolabile Ru–Ru bond. The resulting Ru–alkyne π complex is

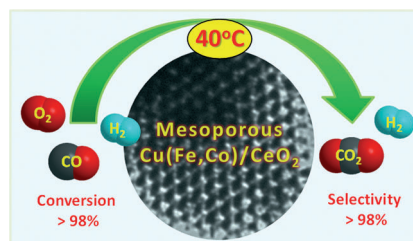
a reaction intermediate stabilized inside the cage. Outside the cage, the π complex can be further transformed to a diruthenacyclopentenone framework by intramolecular CO insertion (see scheme).

Host–Guest Systems

S. Horiuchi, T. Murase, M. Fujita* — 12029 – 12031

A Remarkable Organometallic Transformation on a Cage-Incarcerated Dinuclear Ruthenium Complex

Porosity control: Mixed metal oxides (CuM/CeO_2 , $\text{M} = \text{Co, Fe}$) with tailored porosity were prepared by improved hard templating. These materials were highly active and selective catalysts for low-temperature oxidation of CO in the presence of excess H_2 (see picture), a process which is central for the practical use of H_2 in proton-exchange membrane fuel cells.



Heterogeneous Catalysis

H. Yen, Y. Seo, S. Kaliaguine,* F. Kleitz* — 12032 – 12035

Tailored Mesostructured Copper/Ceria Catalysts with Enhanced Performance for Preferential Oxidation of CO at Low Temperature

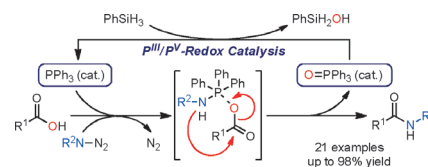
Staudinger Ligation

A. D. Kosal, E. E. Wilson,
B. L. Ashfeld* 12036 – 12040



Phosphine-Based Redox Catalysis in the Direct Traceless Staudinger Ligation of Carboxylic Acids and Azides

Redox catalysis: Aryl amides, imides, lactams, and dipeptides are obtained through a direct Staudinger ligation mediated by phosphine-based redox catalysis (see scheme). Mechanistic studies indicate the involvement of a phosphonium carboxylate intermediate that leads to a 1,3-acyl migration and thus results in C–N bond formation.

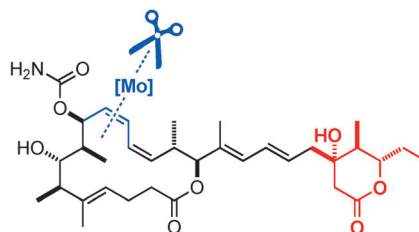


Natural Product Synthesis

J. Willwacher, N. Kausch-Busies,
A. Fürstner* 12041 – 12046



Divergent Total Synthesis of the Antimitotic Agent Leiodermatolide



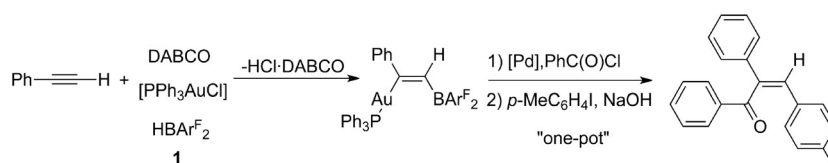
Subtle but distinctive: The stereostructure of the biologically highly promising anti-mitotic agent leiodermatolide was uncertain. A short, efficient, and flexible total synthesis based on ring-closing alkyne metathesis as the key step has now solved the puzzle. Subtle differences in the ¹H NMR spectra of the structure shown and the conceivable isomer proved invaluable for the assignment.

Borometalation

H. Ye, Z. Lu, D. You, Z. Chen, Z. H. Li,*
H. Wang* 12047 – 12050



Frustrated Lewis Pair Induced Boroauration of Terminal Alkynes



Golden frustration: The facile activation of terminal alkynes with a frustrated Lewis pair (**1** and 1,4-diazabicyclo[2.2.2]octane (DABCO)) enables the development of an efficient boroauration reaction. This pro-

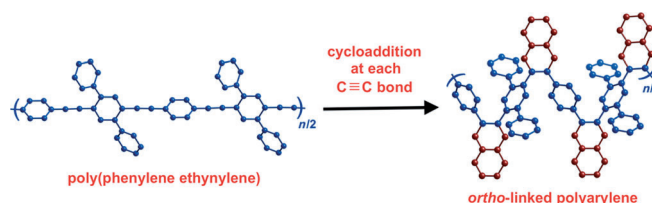
cess can be achieved directly from alkynes, a hydroborane, [PPh₃AuCl], and an organic base. Ar^F = 2,4,6-tris(trifluoromethyl)phenyl.

Conjugated Polymers

H. Arslan, J. D. Saathoff, D. N. Bunck,
P. Clancy,* W. R. Dichtel* 12051 – 12054

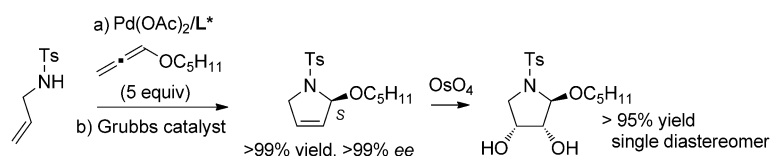


Highly Efficient Benzannulation of Poly(phenylene ethynylene)s



Put a ring on it: Sterically congested polyarylenes can be synthesized by benzannulation reactions at each C≡C bond of a poly(phenylene ethynylene) (see picture), one of the most easily synthesized and versatile classes of conjugated poly-

mers. The benzannulation reaction is highly specific and efficient, as determined by an isotopic labeling study and several complementary spectroscopic methods.



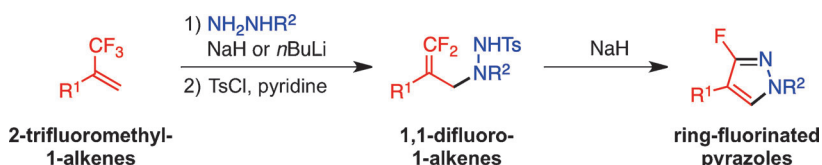
In control: A new synthetic strategy towards cyclic amines was developed and exploits a stereodefined cyclic N,O-acetal as the key stereocontrol and diversity-generating element. The cyclic N,O-acetal was prepared from the sequential asym-

metric hydroamination of an alkoxyallene with the chiral ligand L^* , and ring-closing metathesis. The stereochemical integrity of the labile N,O-acetal was conserved in all catalytic transformations.

Heterocycles

H. Kim, W. Lim, D. Im, D.-g. Kim, Y. H. Rhee* 12055 – 12058

Synthetic Strategy for Cyclic Amines: A Stereodefined Cyclic N,O-Acetal as a Stereocontrol and Diversity-Generating Element



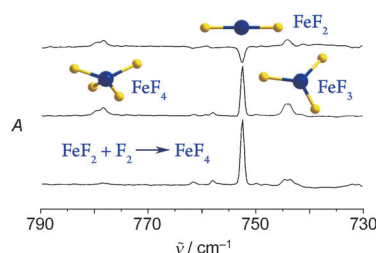
Replacing the fluorine: 3-Fluorinated pyrazoles were regioselectively synthesized by sequential substitution reactions of 2-trifluoromethyl-1-alkenes (see scheme). S_N2' -type reactions of 2-trifluoromethyl-1-

alkenes with deprotonated *tert*-butoxycarbonyl- or arylhydrazines afforded 1,1-difluoro-1-alkenes, which were tosylated and then treated with NaH to give the desired 3-fluoropyrazoles.

Heterocycle Formation

K. Fuchibe, M. Takahashi, J. Ichikawa* 12059 – 12062

Substitution of Two Fluorine Atoms in a Trifluoromethyl Group: Regioselective Synthesis of 3-Fluoropyrazoles

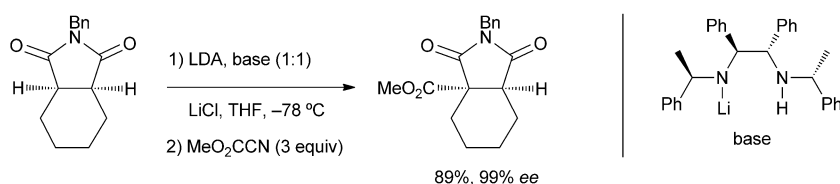


Beyond iron trifluoride: Matrix-isolation IR spectroscopy and state-of-the-art quantum-chemical calculations have led to the characterization of iron tetrafluoride, a previously unknown species. FeF_4 has been prepared by co-deposition of laser-ablated iron atoms with fluorine under excess of noble gases (neon and argon) at cryogenic temperatures.

Iron Fluorides

T. Schlöder, T. Vent-Schmidt, S. Riedel* 12063 – 12067

A Matrix-Isolation and Quantum-Chemical Investigation of FeF_4



Experiments involving competition between chiral and achiral lithium amides provide a qualitative impression of the kinetics of different amide motifs in enolization reactions. The level of enan-

tioselectivity was not diminished by the inclusion of lithium diisopropylamide (LDA; see scheme) into asymmetric enolizations mediated by a chiral lithium amide base, derived from a 1,2-diamine.

Kinetic Probes

M. R. Prestly, N. S. Simpkins* 12068 – 12071

Chiral Bases as Useful Probes of Lithium Amide Reactivity

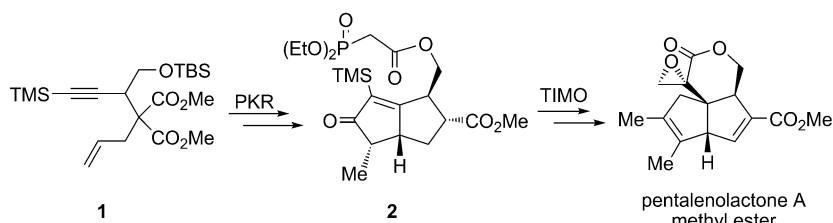


Natural Product Synthesis

Q. Liu, G. Yue, N. Wu, G. Lin, Y. Li,
J. Quan, C.-c. Li,* G. Wang,*
Z. Yang* ————— 12072 – 12076



Total Synthesis of (±)-Pentalenolactone A
Methyl Ester



Ringing it up: The methyl ester of pentalenolactone A has been obtained through the stereoselective synthesis of a cyclopentenone by a combination of the Co-mediated Pauson–Khand reaction (PKR) of enyne **1**, and the construction of

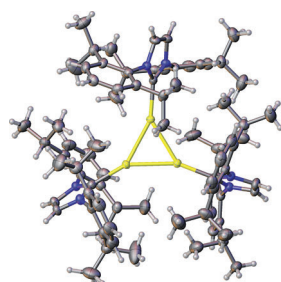
a quaternary-carbon-based strained α -methylidene- δ -pentrolactone core through a trimethylsilyl (TMS) mediated, telescoped intramolecular Michael olefination (TIMO) reaction of keto-phosphonate **2**.

Gold Clusters

T. J. Robilotto, J. Bacsá, T. G. Gray,*
J. P. Sadighi* ————— 12077 – 12080



Synthesis of a Trigold Monocation: An
Isolobal Analogue of $[H_3]^+$



Isolobal and isolatable: A triangular $[L_3Au_3]^+$ ion, bearing N-heterocyclic carbene ligands (L), is crystallographically characterized (see structure; Au yellow, C gray, N blue). Density functional theory suggests full valence delocalization among the gold atoms, with the HOMO composed largely of gold 6s orbitals and the LUMO comprising a degenerate pair. This orbital picture is analogous to that of $[H_3]^+$.

Inside Back Cover

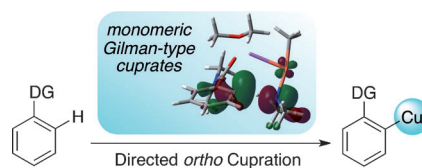
Mechanistic Studies

S. Komagawa,* S. Usui, J. Haywood,
P. J. Harford, A. E. H. Wheatley,*
Y. Matsumoto, K. Hirano, R. Takita,
M. Uchiyama* ————— 12081 – 12085



Amidocuprates for Directed *ortho*
Cupration: Structural Study, Mechanistic
Investigation, and Chemical
Requirements

The name of the game: X-ray crystallographic analysis of Gilman- and Lipshutz-type amidocuprates indicates that the presence of LiX ($X = CN, I$) and THF shifts the equilibrium between the two toward the Lipshutz-type cuprate and that this is important in generating the active species for directed *ortho* cupration. DFT calculations show that monomeric Gilman-type cuprates have an unprecedentedly high reactivity (see scheme, DG = directing group).

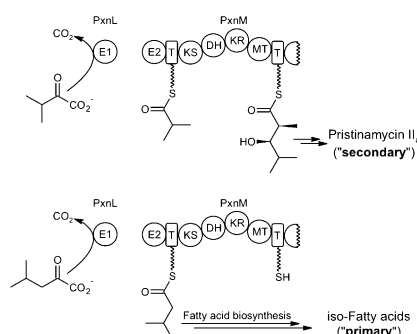


Biosynthetic Pathway

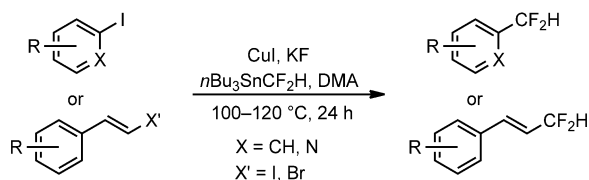
A. O. Brachmann, D. Reimer, W. Lorenzen,
E. Augusto Alonso, Y. Kopp, J. Piel,
H. B. Bode* ————— 12086 – 12089



Reciprocal Cross Talk between Fatty Acid
and Antibiotic Biosynthesis in
a Nematode Symbiont



Don't play the second fiddle! The identification of different arrangements of branched-chain keto acid dehydrogenases usually involved in the biosynthesis of cellular building blocks is demonstrated (see scheme). Direct cross talk between secondary metabolism ketosynthases (KS) and fatty acid biosynthesis is shown and the biosynthesis of odd-numbered iso-fatty acids is found to be connected to the production of pristinamycin II_a .



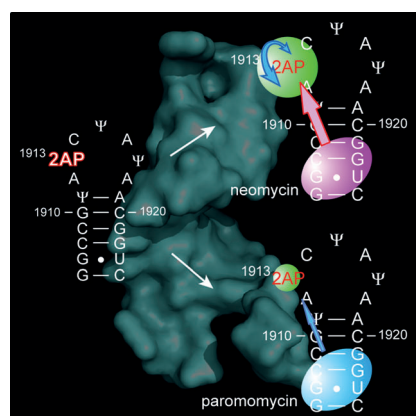
Owing to their unique properties, molecules containing the difluoromethyl group (CF_2H) are of great interest. Tributyl(difluoromethyl)stannane has now been used for the selective and efficient direct *ipso* difluoromethylation of aryl

iodides, heterocyclic iodides, and β -styryl halides (see scheme). The straightforward preparation of the difluoromethylating reagent makes this approach particularly valuable.

Organofluorine Compounds

G. K. S. Prakash,* S. K. Ganesh, J.-P. Jones, A. Kulkarni, K. Masood, J. K. Swabeck, G. A. Olah **12090–12094**

Copper-Mediated Difluoromethylation of (Hetero)aryl Iodides and β -Styryl Halides with Tributyl(difluoromethyl)stannane



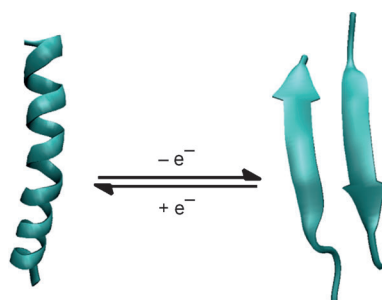
Loop conformation: The loop of the RNA domain helix 69 (H69) was modified with the fluorescent analogue 2-aminopurine (2AP), thus showing different conformational states under various conditions. The application of this model RNA reveals the unique impact of aminoglycoside neomycin, which differs from the effects of structurally related compounds paromomycin and gentamicin, on the H69 loop conformation in solution (see picture).

Ribosomes

Y. Sakakibara, S. C. Abeysirigunawardena, A.-C. E. Duc, D. N. Dremann, C. S. Chow* **12095–12098**

Ligand- and pH-Induced Conformational Changes of RNA Domain Helix 69 Revealed by 2-Aminopurine Fluorescence

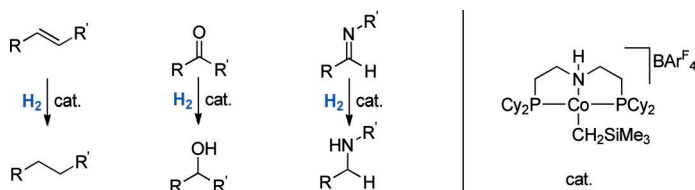
Secondary structures are critical regulators of protein structure and function. Switchable peptides that can adopt multiple defined conformations in response to stimuli are attractive model systems for the study of protein folding and misfolding. A peptide is presented that can be reversibly reconfigured between an α -helical monomer and a β -sheet aggregate upon one-electron oxidation and reduction in the presence of $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$.



Peptide Switches

X. Wang, I. Bergenfeld, P. S. Arora,* J. W. Canary* **12099–12101**

Reversible Redox Reconfiguration of Secondary Structures in a Designed Peptide



A cationic cobalt(II)-alkyl complex is an effective pre-catalyst for hydrogenation of alkenes, aldehydes, ketones, and imines under mild conditions (1–4 atm H_2 ; see scheme). The catalyst shows a high func-

tional-group tolerance across a broad range of substrates. Experiments suggest that the active catalytic species is a cobalt(II)-hydride complex.

Cobalt Catalysts

G. Zhang, B. L. Scott, S. K. Hanson* **12102–12106**

Mild and Homogeneous Cobalt-Catalyzed Hydrogenation of $\text{C}=\text{C}$, $\text{C}=\text{O}$, and $\text{C}=\text{N}$ Bonds

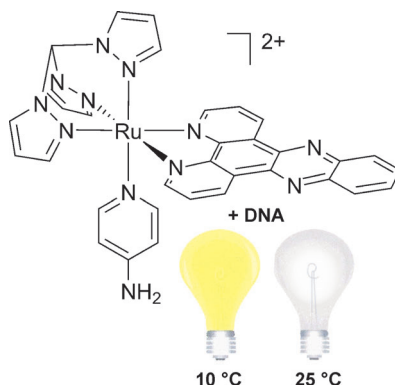
Front Cover

DNA Binding

M. G. Walker, V. Gonzalez,
E. Chekmeneva,
J. A. Thomas* 12107–12110



Temperature-Switched Binding of
a Ru^{II}(dppz)/DNA Light-Switch Complex



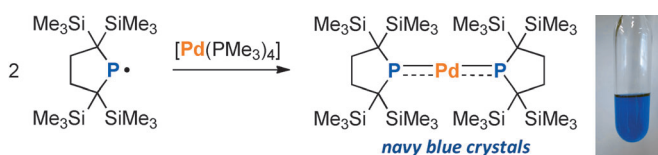
Cool to switch on: Although a Ru(dppz)-based complex binds to the grooves of duplex DNA at room temperature and above, it intercalates into duplex DNA at 10 °C, thus displaying a light-switch effect (see picture, dppz = dipyridylphenazine). Furthermore, once intercalated at low temperatures, emission does not disappear, even after the bound complex is warmed up to 35 °C for several hours.

Palladium Complexes

T. Iwamoto,* F. Hirakawa,
S. Ishida* 12111–12114



A Two-Coordinate Palladium Complex
with Two Dialkylphosphinyl Ligands



Navy blue crystals of a two-coordinate homoleptic palladium complex with two phosphinyl radical ligands was synthesized by a simple ligand-exchange reaction. Significant π interactions between orbitals of Pd and the SOMO of phosphinyl radicals are responsible for the diamagnetic character, the intense blue color, and short P–Pd distances. Hydrogenation of the complex gave the corresponding bis(dialkylhydrophosphine)palladium complex.

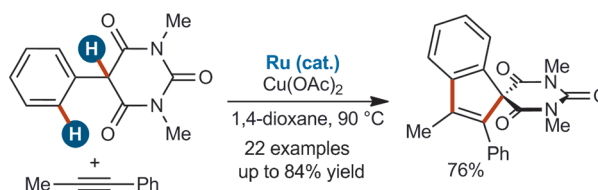
phenyl radicals are responsible for the diamagnetic character, the intense blue color, and short P–Pd distances. Hydrogenation of the complex gave the corresponding bis(dialkylhydrophosphine)palladium complex.

C–H Functionalization

S. Reddy Chidipudi, I. Khan,
H. W. Lam* 12115–12119



Functionalization of C_{sp}³–H and C_{sp}²–H Bonds: Synthesis of Spiroindenes by Enolate-Directed Ruthenium-Catalyzed Oxidative Annulation of Alkynes with 2-Aryl-1,3-dicarbonyl Compounds



Ru(de) awakening: The synthesis of carbocycles by the ruthenium-catalyzed oxidative annulation of alkynes with 2-aryl cyclic 1,3-dicarbonyl substrates is described. Proceeding by the functionaliza-

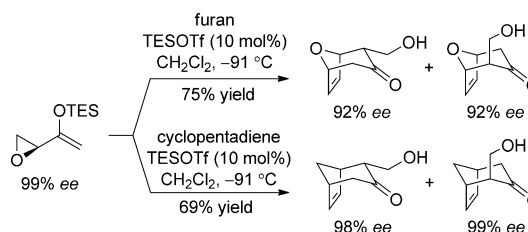
tion of C_{sp}³–H and C_{sp}²–H bonds, and the formation of an all-carbon quaternary center, the reaction provides a diverse range of spiroindenes in good yields with high levels of regioselectivity.

Synthetic Methods

B. Lo, S. Lam, W.-T. Wong,
P. Chiu* 12120–12123



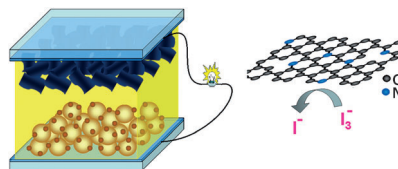
Asymmetric (4+3) Cycloadditions of
Enantiomerically Enriched Epoxy
Enolsilanes



A f(oxy) allyl: The intermolecular (4+3) cycloaddition of enantiomerically enriched epoxy enolsilanes produces cycloadducts with up to 99% ee, thus implying the reaction does not proceed by the putative achiral oxyallyl cation inter-

mediate, but through a transiently chiral electrophile which retains the stereochemical information of the epoxide (see scheme; TES = triethylsilyl, Tf = trifluoromethanesulfonyl).

Efficient without metal: Nitrogen-doped graphene foams with a nitrogen content up to 7.6% have been prepared and used as counter electrodes in dye-sensitized solar cells (DSSCs; see picture). The doping with nitrogen leads to a power conversion efficiency of 7.07%. This is one of the highest values reported for DSSCs with carbon-based metal-free counter electrodes.



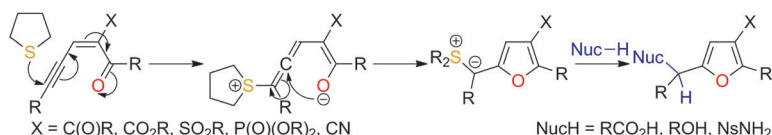
Energy Conversion

Y. Xue, J. Liu, H. Chen, R. Wang, D. Li, J. Qu,* L. Dai* 12124–12127

Nitrogen-Doped Graphene Foams as Metal-Free Counter Electrodes in High-Performance Dye-Sensitized Solar Cells



Back Cover



Top cat! Tetrahydrothiophene is an efficient organocatalyst for the synthesis of highly substituted furfuryl products from readily accessible electron-poor enynes

under neutral reaction conditions. This process is applicable to a wide range of nucleophiles and enynes and can be used in a domino organocatalysis sequence.

Organocatalysis

J. S. Clark,* A. Boyer, A. Aimon, P. Engel García, D. M. Lindsay, A. D. F. Symington, Y. Danoy 12128–12131

Organocatalytic Synthesis of Highly Substituted Furfuryl Alcohols and Amines



Supporting information is available on www.angewandte.org (see article for access details).



A video clip is available as Supporting Information on www.angewandte.org (see article for access details).



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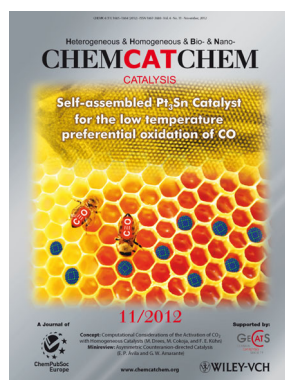


This article is accompanied by a cover picture (front or back cover, and inside or outside).

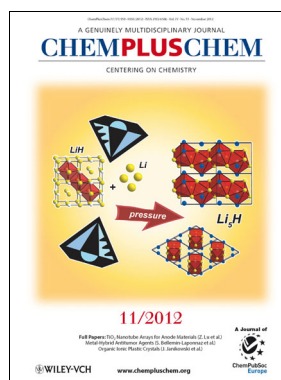
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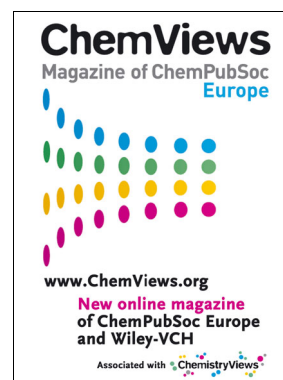
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Angewandte Corrigendum

Enantioselective Oxidation of Aldehydes
Catalyzed by Alcohol Dehydrogenase

P. Könst, H. Merkens, S. Kara,
S. Kochius, A. Vogel,* R. Zuhse,
D. Holtmann, I. W. C. E. Arends,
F. Hollmann* **9914–9917**

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

DOI: 10.1002/anie.201203219

The address given for Dr. Andreas Vogel in this communication is wrong. His correct address is given below. Dr. Vogel is also joint correspondence author of this communication.

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Angewandte Corrigendum

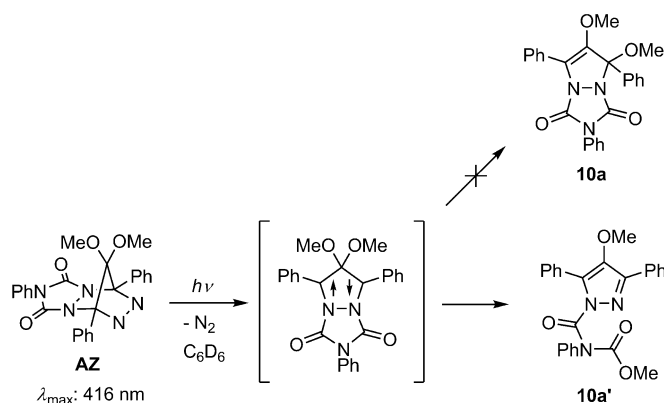
An Extremely Long-Lived Singlet 4,4-
Dimethoxy-3,5-diphenylpyrazolidine-3,5-
diyl Derivative: A Notable Nitrogen-Atom
Effect on Intra- and Intermolecular
Reactivity

M. Abe,* E. Kubo, K. Nozaki, T. Matsuo,
T. Hayashi **7828–7831**

Angew. Chem. Int. Ed. **2006**, 45

DOI: 10.1002/anie.200603287

In Scheme 1 of this Communication, formation of the MeO-migrated compound **10a** was reported for the photochemical denitrogenation of azoalkane **AZ** in benzene. 2D NMR spectroscopic analyses (HMBC, HMQC) of this reaction have now revealed that the product is not compound **10a** but compound **10a'**.



The HMBC spectrum (see the Supporting Information) shows a clear correlation between the protons of one MeO group ($\delta = 3.31$ ppm) and one carbonyl carbon atom ($\delta = 154.74$ ppm) as well as the protons of another MeO group ($\delta = 3.14$ ppm) and the enolic C4 carbon atom ($\delta = 144.37$ ppm). These correlations are not consistent with structure **10a** but with structure **10a'**.