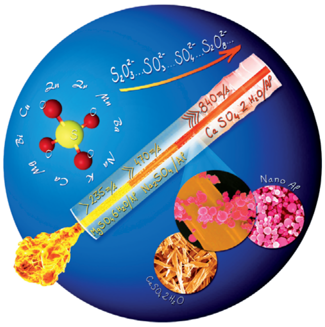
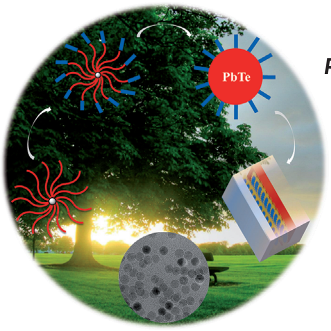
An asymmetric cross-hydroalkenylation ...

… catalyzed by [NiH] complexes provides branched *gem*-disubstituted olefins with high enantio- and chemoselectivity, depending on the steric and electronic effects of the substrates and N-heterocyclic carbene (NHC) ligands. In their Communication on page 4512 ff., C.-Y. Ho and co-workers rule out a π–π stacking mechanism and suggest that the N-aryl rings of the NHCs possibly “move like wings” to coordinate a π system with a Ni^{II} center.

Metastable Materials

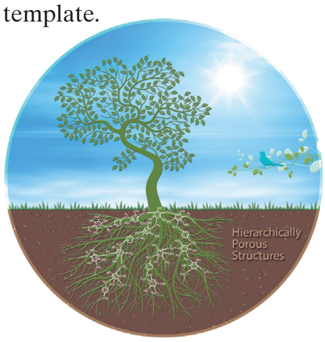
D. Spitzer et al. report in their Communication on page 4458 ff. the preparation of energetic nanothermites from metal sulfates and aluminum nanopowder. These new materials are characterized by fast combustion velocities and extremely low sensitivity to friction.





Polymer–Semiconductor Hybrids

A robust strategy to produce nanocomposites composed of PbTe nanoparticles tethered with PEDOT chains is described by H. Xia, Z. Lin et al. in their Communication on page 4636 ff. Amphiphilic star-like diblock copolymer PAA-*b*-PEDOT is used as template.



Soft Chemistry

In their Communication on page 4582 ff., S. Dai et al. describe the preparation of porous phenolic polymers through Friedel–Crafts alkylation. The resulting porous frameworks feature interconnected micro- and mesopores.

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Service

Author Profile

"My favorite painter is Jan Vermeer.
The most important thing I learned from my students is self-motivation …"
This and more about Shi Zhang Qiao can be found on page 4426.

News

T. Loiseau

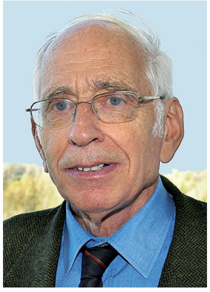
L. Fensterbank

A. Böckmann

J.-F. Carpentier

S. Zard

Obituaries

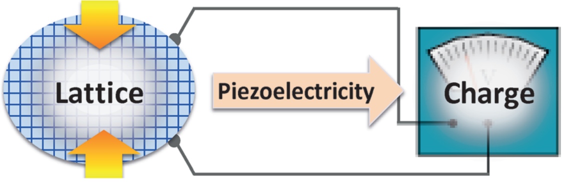


Yves Chauvin passed away at the age of 84 on January 27, 2015. Chauvin was a remarkable man and a prominent scientist, who received the Nobel Prize in Chemistry in 2005 jointly with Robert H. Grubbs and Richard R. Schrock for his discoveries relating to the mechanism of olefin metathesis. Chauvin also investigated a large number of catalytic reactions, including polymerization and oligomerization, hydrogenation, carbonylation, and asymmetric synthesis.

Books

Highlights

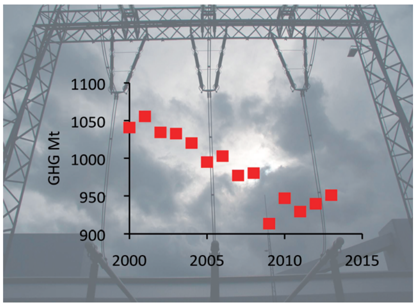
Piezoelectricity



Powering up 2D materials: Recent experimental studies confirmed the existence of piezoelectricity—the conversion of mechanical stress into electricity—in two-dimensional single-layer MoS_2 nanosheets. The results represent a milestone towards embedding low-dimensional materials into future disruptive technologies.

Essays

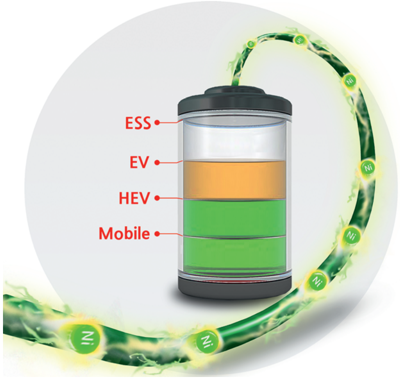
Energy Industry



You say you want a revolution: The "Energiewende", the change in energy regimes in Germany, is presently not effective. The lack of integration of renewable and conventional power generation is seen as the critical factor. Chemistry and catalysis play a decisive role in solving this systemic challenge.

Reviews

Electrode Materials



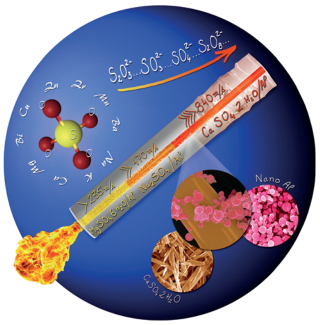
The end is Ni: Over the past two decades, nickel-rich materials have become highly promising candidates for high-energy cathode materials for lithium-ion batteries. This Review brings a new perspective to Ni-rich materials as well as providing a comprehensive account of recent progress, limits, and new utilization possibilities for these materials. ESS = energy storage systems, EV = electric vehicles, HEV = hybrid electric vehicles, Mobile = mobile appliances.

For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. US mailing agent: SPP, PO Box 437, Emigsville, PA 17318. Periodicals postage paid at Emigsville, PA. US POSTMASTER: send address changes to *Angewandte Chemie*, John Wiley & Sons Inc., C/O The Sheridan Press, PO Box 465, Hanover, PA 17331. Annual subscription price for institutions: US$ 11.738/10.206 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Communications

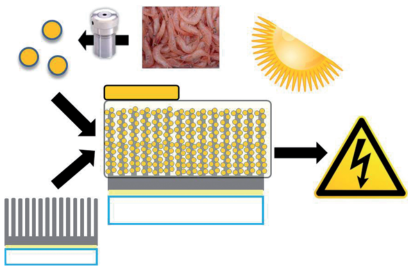
Metastable Materials

Frontispiece



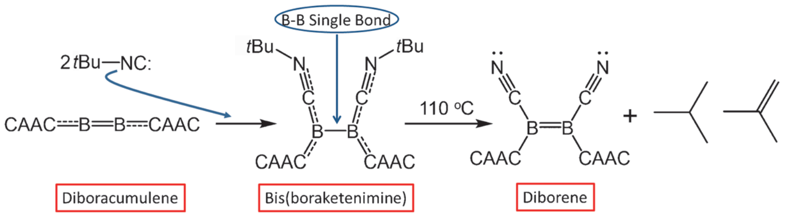
Big bang theory (and practice): Metal sulfates are used as oxidizers in reactive compositions with aluminum nanopowder (n-Al), leading to energetic materials with high reaction heats ($4–6\ \mathrm{kJ\,g^{-1}}$), fast combustion velocities ($200–840\ \mathrm{m\,s^{-1}}$), and extremely low sensitivity to friction. Compositions prepared from other sulfur oxygenates (SO_3^{2-}, $S_2O_3^{2-}$, $S_2O_8^{2-}$) and n-Al have analogous properties.

Photovoltaics



Coat of many dots: ZnO nanorods sensitized with three different biomass-derived carbon quantum dots (CQDs) were synthesized, characterized, and used to build solid-state nanostructured solar cells. The highest efficiency was obtained using a layer-by-layer coating of two different types of CQDs.

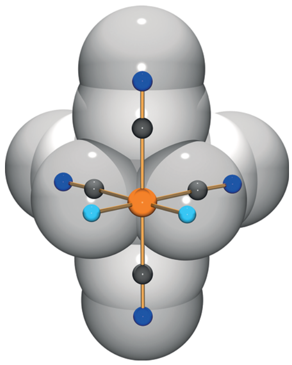
Boron Chemistry



From riches to rags: Treatment of a diboracumulene with isocyanides resulted in the formation of a bis(isocyanide) adduct displaying a remarkable degree of electronic delocalization throughout both of the π-acidic substituents on boron. Thermolysis of this product led to a new diborene, in which π-density is again delocalized by π-acidic ligands, leading to unexpected electrochemical behavior.

Cyanido-Phosphates

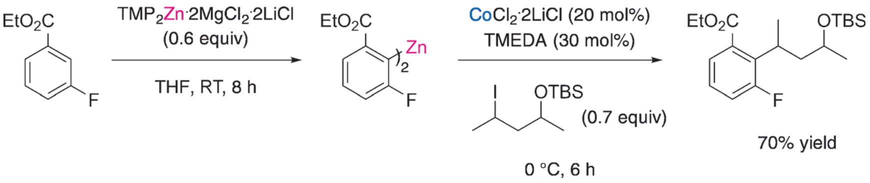
Marriage at high temperature: Treatment of [nBu$_4$N][PF_6] with Me_3SiCN led to the formation of the [nBu$_4$N]$^+$ salt of the $[PF_2(CN)_4]^-$ ion (see structure; P = orange, C = gray, N = dark blue, F = light blue). This anion was utilized for the synthesis of low-viscosity ionic liquids and as a building block for the design of coordination polymers in which Lewis acidic metals were used as counterions.



Cross-Coupling

J. M. Hammann, D. Haas,
P. Knochel* ______ **4478 – 4481**

Cobalt-Catalyzed Negishi Cross-Coupling Reactions of (Hetero)Arylzinc Reagents with Primary and Secondary Alkyl Bromides and Iodides

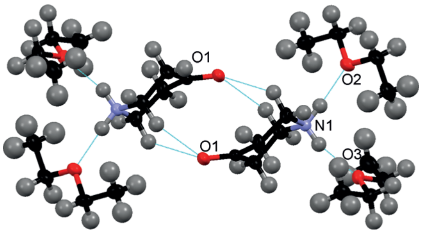


Cobalt and zinc—a lovely couple! The soluble $CoCl_2$·2 LiCl complex allows efficient cross-coupling between polyfunctional diaryl- and diheteroarylzinc reagents, obtained by directed zincation using TMP_2Zn·2 $MgCl_2$·2 LiCl, and various primary or secondary alkyl iodides or bromides to afford the alkylated products in up to 88 % yield. In no case was rearrangement of the secondary alkyl iodide (to its linear isomer) observed.

Cation–Cation Interactions

W. Gamrad, A. Dreier, R. Goddard,
K.-R. Pörschke* ______ **4482 – 4487**

Cation–Cation Pairing by N–C–H···O Hydrogen Bonds

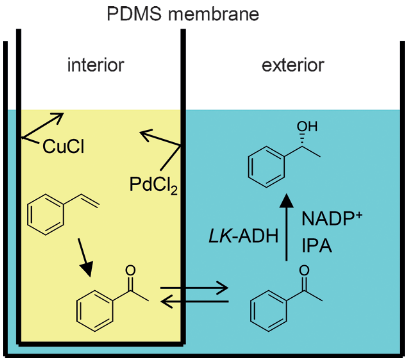


Same-sex chemistry: A novel pairing of cations is reported. When 4-oxopiperidinium cations are combined with the weakly basic NTf_2^- anion, the cations link head-to-tail through N–H···O hydrogen bonds to form chains of cations, flanked by anions. With the larger and noncoordinating $[Al\{OC(CF_3)_3\}_4]^-$ counterion, centrosymmetric dicationic pairs of 4-oxopiperidinium ions form in the crystal through C–H···O hydrogen bonds.

One-Pot Synthesis

H. Sato, W. Hummel,
H. Gröger* ______ **4488 – 4492**

Cooperative Catalysis of Noncompatible Catalysts through Compartmentalization: Wacker Oxidation and Enzymatic Reduction in a One-Pot Process in Aqueous Media

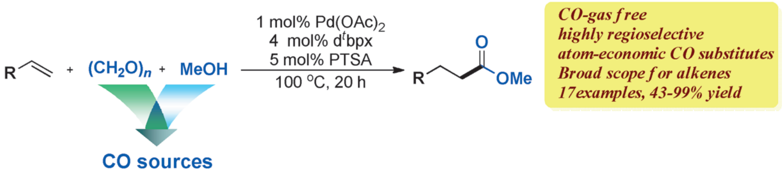


Dream reaction: A Wacker oxidation with $PdCl_2$/CuCl was combined with an enzymatic reduction to convert styrenes enantioselectively to 1-phenylethanols in a one-pot process, although the two reactions are not compatible with each other due to enzyme deactivation by Cu ions. The key to success was the compartmentalization of the catalysts (see picture; PDMS = polydimethylsiloxane).

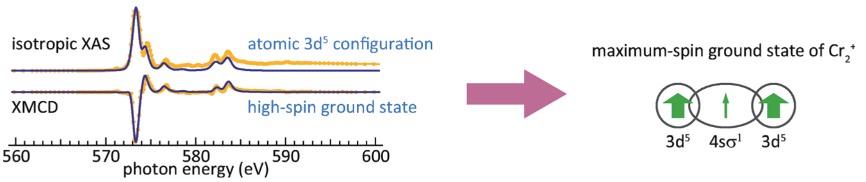
Carbonylation

Q. Liu, K. Yuan, P. Arockiam, R. Franke,
H. Doucet, R. Jackstell,
M. Beller* ______ **4493 – 4497**

Regioselective Pd-Catalyzed Methoxycarbonylation of Alkenes Using both Paraformaldehyde and Methanol as CO Surrogates



CO-llaboration: An efficient synthetic carbonylation without the utilization of hazardous CO gas is described. For the first time, highly regioselective methoxycarbonylation using paraformaldehyde and methanol as carbonyl sources proceeds in the presence of a suitable palladium catalyst. This provides a green and atom-efficient process for the synthesis of methyl esters in high yield and regioselectivity.

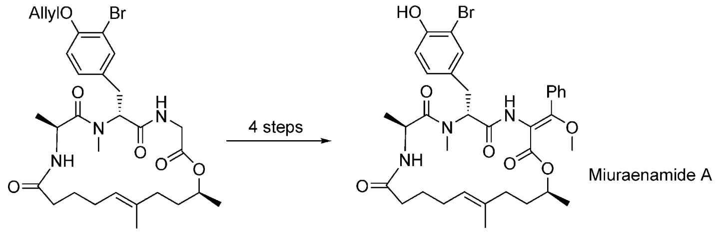


The removal of a single electron from the $4s\sigma_g$ bonding orbital of Cr_2 fully localizes all the 3d electrons and drastically changes the preferred coupling of their spins. The molecular cation exhibits a ferromagnetically coupled ground state with the highest possible spin of $S=11/2$, and almost twice the bond length of the neutral molecule. This spin configuration can be interpreted as a result of indirect exchange coupling.

Electronic Structure

V. Zamudio-Bayer, K. Hirsch, A. Langenberg, M. Niemeyer, M. Vogel, A. Ławicki, A. Terasaki, J. T. Lau,* B. von Issendorff ________ **4498–4501**

Maximum Spin Polarization in Chromium Dimer Cations as Demonstrated by X-ray Magnetic Circular Dichroism Spectroscopy

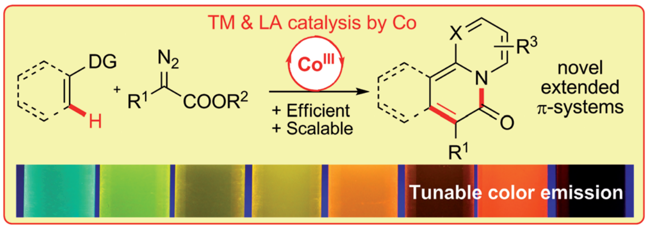


Variations on a theme: Miuraenamides can easily be obtained by peptide modification of a cyclic glycine-containing tripeptide. The incorporation of an unusual amino acid side chain at a very late stage of the synthesis allows the fast generation of miuraenamide derivatives for structure–activity studies.

Natural Product Synthesis

L. Karmann, K. Schultz, J. Herrmann, R. Müller, U. Kazmaier* ____ **4502–4507**

Total Syntheses and Biological Evaluation of Miuraenamides

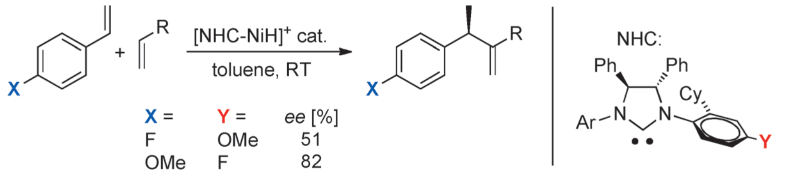


Co-catalyzed! The first highly efficient and scalable cobalt-catalyzed directed C–H functionalization with carbene precursors is presented. This methodology provides a modular route towards a new class of conjugated polycyclic hydrocarbons with tunable emission wavelengths. LA = Lewis acid.

Conjugated Polycycles

D. Zhao,* J. H. Kim, L. Stegemann, C. A. Strassert, F. Glorius* _ **4508–4511**

Cobalt(III)-Catalyzed Directed C–H Coupling with Diazo Compounds: Straightforward Access towards Extended π-Systems



Crossed: An asymmetric tail-to-tail cross-hydroalkenylation of vinylarenes with terminal olefins was catalyzed by NiH complexes with chiral N-heterocyclic carbenes (NHCs). Depending on steric and electronic effects of the substrates and NHC ligands, the reaction can provide branched *gem*-disubstituted olefins with high enantio- (up to 94% *ee*) and chemoselectivity (cross/homo product ratio: up to 99:1).

N-Heterocyclic Carbenes

VIP

C.-Y. Ho,* C.-W. Chan, L. He **4512–4516**

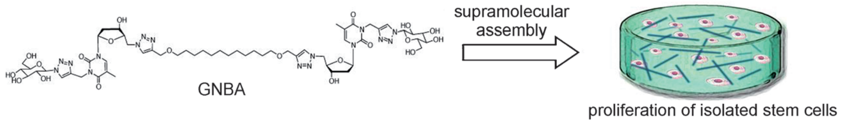
Catalytic Asymmetric Hydroalkenylation of Vinylarenes: Electronic Effects of Substrates and Chiral N-Heterocyclic Carbene Ligands

Front Cover

Hydrogels

L. Latxague, M. A. Ramin, A. Appavoo,
P. Berto, M. Maisani, C. Ehret,
O. Chassande,
P. Barthélémy* ______ 4517 – 4521

Control of Stem-Cell Behavior by Fine Tuning the Supramolecular Assemblies of Low-Molecular-Weight Gelators

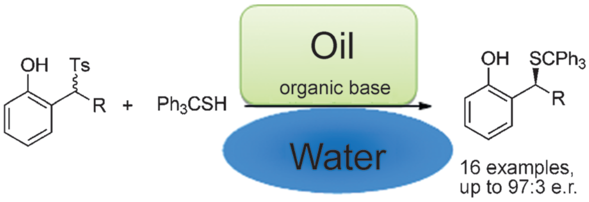


Culture medium: Glycosyl-nucleoside bola-amphiphiles (GNBAs) are low-molecular-weight gelators that allow the culture of isolated stem cells in a gel matrix. The reported results highlight the role of the supramolecular organization of the matrix on the behavior of stem cells in 3D environments.

Asymmetric Catalysis

W.-G. Guo, B. Wu, X. Zhou, P. Chen,
X. Wang, Y.-G. Zhou, Y. Liu,*
C. Li* ______ 4522 – 4526

Formal Asymmetric Catalytic Thiolation with a Bifunctional Catalyst at a Water–Oil Interface: Synthesis of Benzyl Thiols



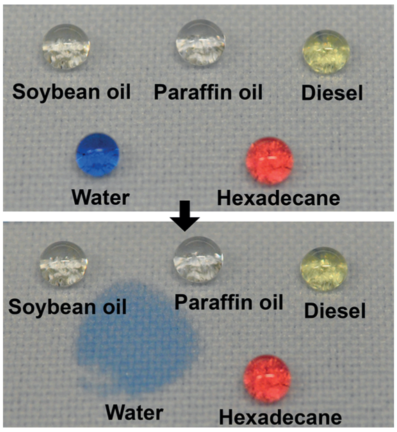
Phased out: A squaramide organocatalyst mediates the asymmetric synthesis of α-aryl- and α-alkyl-substituted benzyl mercaptans through the thiolation of in situ generated *ortho*-quinone methides at a water–oil interface. The reactions exhibit wide substrate scope and excellent enantioselectivity because of the spatial separation of the inorganic base in the aqueous phase from the chiral components in the organic phase.

Surface Chemistry

Z. Xu, Y. Zhao,* H. Wang, X. Wang,
T. Lin ______ 4527 – 4530

A Superamphiphobic Coating with an Ammonia-Triggered Transition to Superhydrophilic and Superoleophobic for Oil–Water Separation

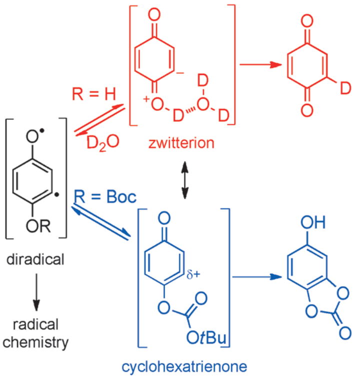
Ammonia exposure can change a superamphiphobic to a superhydrophilic and superoleophobic coating. Commonly used materials including textiles and sponges functionalized with such a unique coating show unusual capabilities for controllable filtration of oil–water mixtures and the selective removal of water from bulk oil.



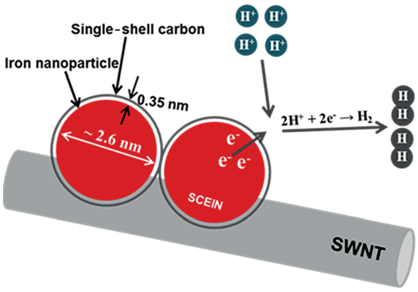
Rearrangements

T. P. Gonçalves, M. Mohamed,
R. J. Whitby, H. F. Sneddon,
D. C. Harrowven* ______ 4531 – 4534

Exploring Diradical Chemistry: A Carbon-Centered Radical May Act as either an Anion or Electrophile through an Orbital Isomer



A curious world: Diradical intermediates, formed by thermolysis of alkynylcyclobutenones, can display radical, anionic, or electrophilic character because of the existence of an orbital isomer with zwitterionic and cyclohexatrienone character. The realization that water, alcohols, and certain substituents can induce the switch in isomers provides new opportunities in synthesis. Boc = *tert*-butoxycarbonyl.



Aerosol chemical vapor deposition is used to develop a highly active and durable non-noble-metal catalyst for the hydrogen evolution reaction by decorating single-shell carbon-encapsulated iron nanoparticles (SCEINs) on single-walled carbon nanotubes (SWNTs). The catalyst exhibits catalytic properties comparable to those of platinum.

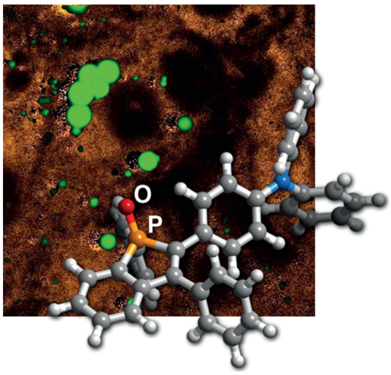
Hydrogen Evolution Reaction

M. Tavakkoli, T. Kallio, O. Reynaud, A. G. Nasibulin, C. Johans, J. Sainio, H. Jiang, E. I. Kauppinen, K. Laasonen* ______ **4535 – 4538**

Single-Shell Carbon-Encapsulated Iron Nanoparticles: Synthesis and High Electrocatalytic Activity for Hydrogen Evolution Reaction

---

Phosphole stained: The combination of an electron-accepting benzophosphole oxide with an electron-donating (diphenylamino)phenyl group led to a fluorescent compound with high fluorescence quantum yields. The benzophosphole oxide exhibited a change in fluorescence emission as a function of the solvent polarity, and was used to stain adipocytes, thus allowing discrimination of the polarity of subcellular compartments based on fluorescence.



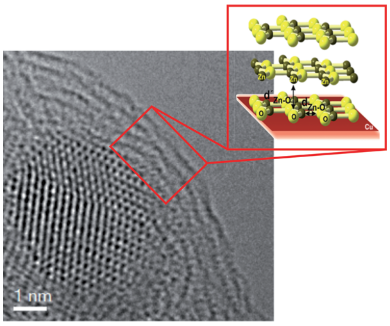
Phosphorus Heterocycles

E. Yamaguchi, C. Wang, A. Fukazawa,* M. Taki, Y. Sato, T. Sasaki, M. Ueda, N. Sasaki, T. Higashiyama,* S. Yamaguchi* ______ **4539 – 4543**

Environment-Sensitive Fluorescent Probe: A Benzophosphole Oxide with an Electron-Donating Substituent

Inside Cover

Graphite-like ZnO on Cu surfaces: The overgrowth of industrially relevant $Cu/ZnO/Al_2O_3$ catalysts for methanol synthesis was investigated by chemical electron microscopy. The results evidence the presence of metastable graphitic-like ZnO embedding the Cu nanoparticles after reductive activation. O = yellow spheres; Zn = olive-green spheres; Cu = red surface.



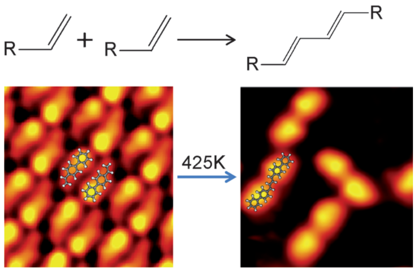
Heterogeneous Catalysis

T. Lunkenbein, J. Schumann, M. Behrens, R. Schlögl, M. G. Willinger* **4544 – 4548**

Formation of a ZnO Overlayer in Industrial $Cu/ZnO/Al_2O_3$ Catalysts Induced by Strong Metal–Support Interactions

---

On the surface: By combining high-resolution UHV-STM imaging and DFT calculations, the homocoupling of terminal alkenes on copper surfaces is reported. A diene compound is formed with an appreciably high yield on the Cu(110) surface.



Surface Chemistry

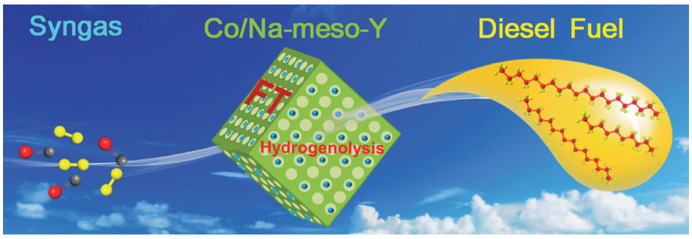
Q. Sun, L. Cai, Y. Ding, L. Xie, C. Zhang, Q. Tan, W. Xu* ______ **4549 – 4552**

Dehydrogenative Homocoupling of Terminal Alkenes on Copper Surfaces: A Route to Dienes

Heterogeneous Catalysis

X. Peng, K. Cheng, J. Kang, B. Gu, X. Yu, Q. Zhang,* Y. Wang* ______ **4553 – 4556**

Impact of Hydrogenolysis on the Selectivity of the Fischer–Tropsch Synthesis: Diesel Fuel Production over Mesoporous Zeolite-Y-Supported Cobalt Nanoparticles

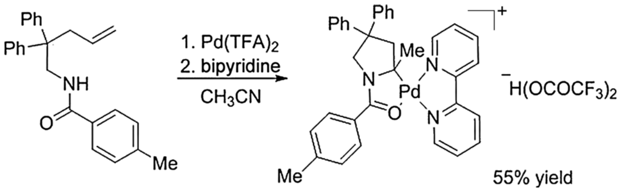


Gas up! A mesoporous zeolite-Y-supported cobalt catalyst, which is highly selective for the direct conversion of syngas into diesel fuel, has been developed by effective control of hydrogenolysis. The sizes of the cobalt particles and support mesopores are key factors in determining the activity and selectivity of hydrogenolysis.

Rearrangements

C. F. Rosewall, E. L. Ingalls, W. Kaminsky, F. E. Michael* ______ **4557 – 4560**

Chelation-Driven Rearrangement of Primary Alkyl Aminopalladation Products to Stable Trisubstituted Alkyl–Palladium Complexes



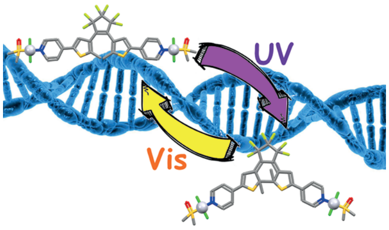
Equilibration: A set of alkyl–palladium complexes can be subtly tuned to form the thermodynamically favored complex with either the primary or the trisubstituted alkyl complexes, depending on the substrate and the reaction conditions that are used. The mechanism for the rearrangement and the factors that drive the change in stability are discussed.

Drug Design

A. Presa, R. F. Brissos, A. B. Caballero, I. Borilovic, L. Korrodi-Gregório, R. Pérez-Tomás,* O. Roubeau, P. Gamez* ______ **4561 – 4565**

Photoswitching the Cytotoxic Properties of Platinum(II) Compounds

Toxic switch: The photoswitchable open and closed forms of 1,2-dithienylethene-based platinum(II) compounds exhibit distinct DNA-interacting and cytotoxic properties, which may lead to a new class of potential photoactivatable anticancer agents.

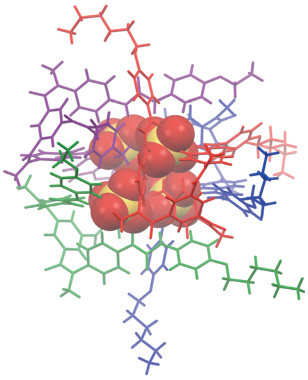


Supramolecular Chemistry

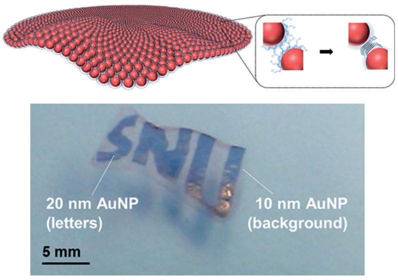
K. Pandurangan, J. A. Kitchen, S. Blasco, E. M. Boyle, B. Fitzpatrick, M. Feeney, P. E. Kruger,* T. Gunnlaugsson* ______ **4566 – 4570**

Unexpected Self-Sorting Self-Assembly Formation of a [4:4] Sulfate:Ligand Cage from a Preorganized Tripodal Urea Ligand

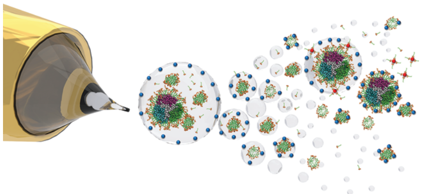
All wrapped up: A tripodal ligand based on the *N*-methyl-1,3,5-benzenetricarboxamide platform having two bis-urea arms and an ammonium moiety undergoes self-assembly with SO_4^{2-} ions to form a capsule with [4:4] SO_4^{2-}:ligand stoichiometry. In this self-sorted self-assembled structure, the four tetrahedrally arranged anions (see picture; anions given in space-filling mode) are clustered within a hydrophobic cavity formed by four ligands.



Film producer: Protein-based free-standing gold-nanoparticle monolayer films are fabricated by self-assembly between α-synuclein proteins coating the nanoparticles. The film can be scaled up to a 4-inch-wafer size. The high flexibility of the film in solvent allows it to wrap round curved surfaces on the micrometer scale. Additionally, the monolayer film is readily patterned into free-floating multi-hole sheets and an unprecedented film containing two different sized nanoparticles is also fabricated (see photo).



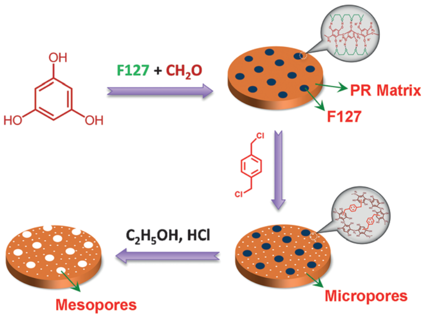
Nanoparticle Films



Membrane proteins in the gas-phase: Mass spectrometry and ion mobility spectrometry enable the interrogation of membrane protein gas-phase structure and stability. The detergent micelle used to solubilize these intractable proteins dictates the physicochemical mechanisms of their transfer into the gas phase and influences their resultant structure and stability.

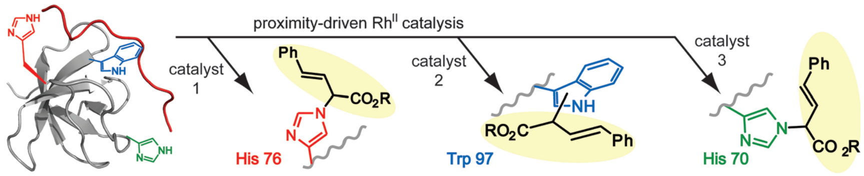
Structural Biology

Soft chemistry: The hypercrosslinking of aromatic backbones through the Friedel–Crafts alkylation reaction is demonstrated as an efficient pathway for the nanotexturation of phenolic polymers with a robust mesoporous framework. The method takes advantage of bridge-derived micropores for the insertion of solvents for template extraction.



Mesoporous Polymers

Back Cover



Chemical engineering: Rhodium(II) metallopeptides were developed that combine molecular recognition with promiscuous catalytic activity to allow covalent decoration of natural SH3 domains, depending on choice of catalyst but independent of the specific residue present (see scheme). A metallopeptide catalyst succeeded in modifying a single SH3-containing kinase in prostate cancer cell lysate.

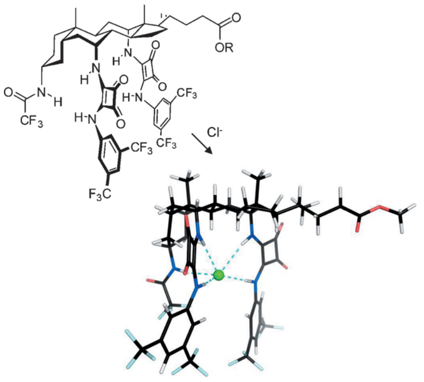
Protein Modification

Molecular Recognition

S. J. Edwards, H. Valkenier, N. Busschaert, P. A. Gale,* A. P. Davis* ____ **4592–4596**

High-Affinity Anion Binding by Steroidal Squaramide Receptors

Getting a grip: Squaramides are known to be powerful anion binding units. Preorganized on a steroidal scaffold, they are even more effective. These “cholapods” bind tetra-alkylammonium salts with affinities of up to greater than $10^{14}\,\text{M}^{-1}$ in chloroform, a new record for anion recognition by electroneutral receptors.

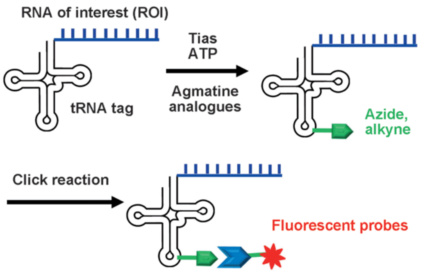


RNA Labeling

F. H. Li, J. S. Dong, X. S. Hu, W. M. Gong, J. S. Li, J. Shen, H. F. Tian, J. Y. Wang* ____ **4597–4602**

A Covalent Approach for Site-Specific RNA Labeling in Mammalian Cells

Tag and click: The ability to specifically label RNAs in vitro and in mammalian cells would be highly significant for RNA research, however, covalent RNA labeling methods with scope and versatility comparable to those for protein labeling have not been reported. A method was developed for the site- and sequence-specific covalent labeling of RNAs in mammalian cells, based on the action of tRNA$^{\text{Ile2}}$-agmatidine synthetase (Tias) and click chemistry.

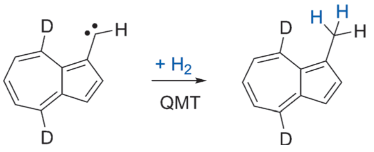


Hydrogen Activation

S. Henkel, W. Sander* ____ **4603–4607**

Activation of Molecular Hydrogen by a Singlet Carbene through Quantum Mechanical Tunneling

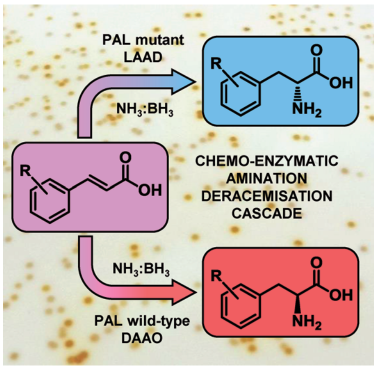
Carbenes are among the few metal-free molecules that are able to activate molecular hydrogen. The 1-azulenylcarbene with a singlet ground state readily inserts into H$_2$, and quantum mechanical tunneling (QMT) governs the insertion into both H$_2$ and D$_2$. This is the first example that shows that quantum mechanical tunneling can also be important for singlet carbenes inserting into dihydrogen.



Biocatalysis

F. Parmeggiani, S. L. Lovelock, N. J. Weise, S. T. Ahmed, N. J. Turner* ____ **4608–4611**

Synthesis of D- and L-Phenylalanine Derivatives by Phenylalanine Ammonia Lyases: A Multienzymatic Cascade Process

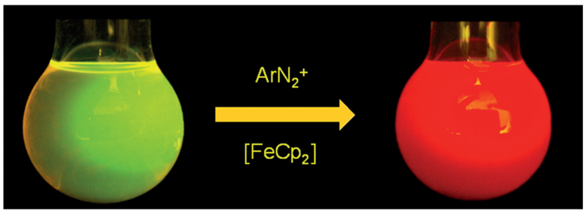


PAL around: The cascade coupling of phenylalanine ammonia lyase (PAL) with L-amino acid deaminase (LAAD) or D-amino acid oxidase (DAAO), led to the conversion of cheap and easily accessible cinnamic acids into both non-natural D- and L-phenylalanines by a chemoenzymatic process. PAL variants possessing higher D-activity were selected by using a novel solid-phase screening assay and employed to increase yield and *ee* values.

C–H Arylation

B. Verbelen, S. Boodts, J. Hofkens,
N. Boens, W. Dehaen* ______ **4612 – 4616**

Radical C–H Arylation of the BODIPY Core with Aryldiazonium Salts: Synthesis of Highly Fluorescent Red-Shifted Dyes

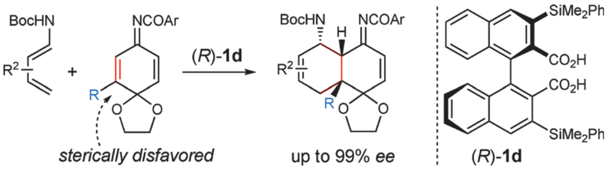


A one-step procedure for the first radical C–H arylation of BODIPY dyes has been developed. This method uses ferrocene $[FeCp_2]$ to generate aryl radical species from aryldiazonium salts and allows the synthesis of brightly fluorescent ($\Phi >$ 0.85) 3,5-diarylated and 3-monoarylated boron dipyrrins in up to 86% yield for a broad range of aryl substituents. In this way, new and complex dyes with red-shifted spectra can be easily prepared.

Diels–Alder Reactions

T. Hashimoto, H. Nakatsu,
K. Maruoka* ______ **4617 – 4621**

Catalytic Asymmetric Diels–Alder Reaction of Quinone Imine Ketals: A Site-Divergent Approach

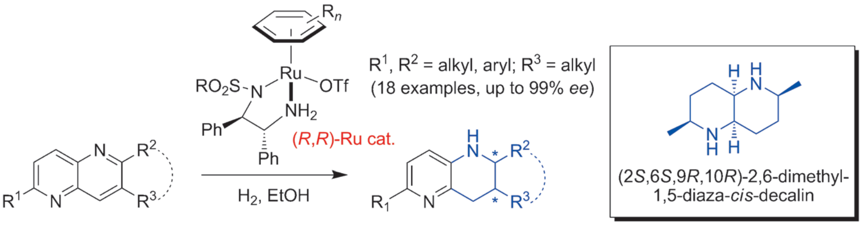


Here or there? Axially chiral dicarboxylic acids serve as the catalyst in the Diels–Alder reaction between quinone imine ketals and diene carbamates. A strategy is also developed to divert the reaction site in unsymmetrical 3-alkyl quinone imine ketals from the inherently favored unsubstituted C=C bond to the disfavored alkyl-substituted C=C bond.

Asymmetric Catalysis

J. Zhang, F. Chen, Y.-M. He,
Q.-H. Fan* ______ **4622 – 4625**

Asymmetric Ruthenium-Catalyzed Hydrogenation of 2,6-Disubstituted 1,5-Naphthyridines: Access to Chiral 1,5-Diaza-*cis*-Decalins

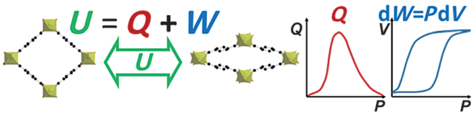


Enantioselective hydrogenation of 2,6-disubstituted 1,5-naphthyridines proceeds in the presence of the cationic ruthenium diamine complexes with excellent enantioselectivities. This method provides an easy and practical access to optically pure 1,5-diaza-*cis*-decalins.

Metal–Organic Frameworks

J. Rodriguez, I. Beurroies,* T. Loiseau,
R. Denoyel, P. L. Llewellyn* **4626 – 4630**

The Direct Heat Measurement of Mechanical Energy Storage Metal–Organic Frameworks

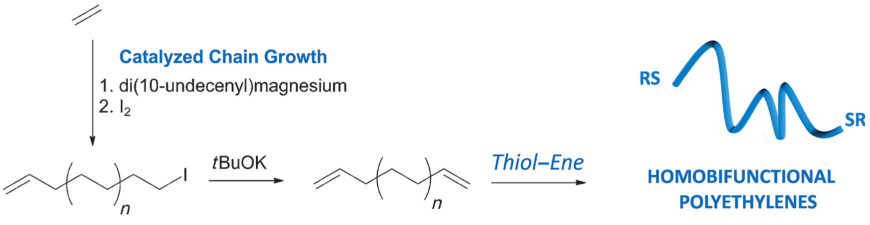


MOFs as nanosprings: Many metal–organic frameworks (MOFs) are flexible, but the heat exchanged in a MOF structure transition has never been measured directly. This has now been carried out with MIL-53(Al) using specifically devised calorimetry experiments. We project the importance of these heats in devices such as molecular springs or dampers.

Derivatization of Polymers

S. Norsic, C. Thomas, F. D'Agosto,*
C. Boisson* ______ **4631 – 4635**

Divinyl-End-Functionalized Polyethylenes: Ready Access to a Range of Telechelic Polyethylenes through Thiol–Ene Reactions



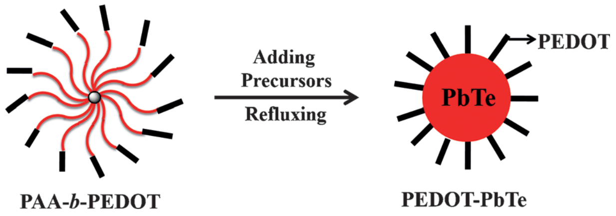
Get a handle on it: A straightforward protocol was developed for the preparation of α,ω-dienylpolyethylene (see scheme). This unique building block was used to synthesize a vast range of telechelic polyethylenes, thus opening the way to fundamental developments in the field of polyolefins.

Polymer–Semiconductor Hybrids

H. Xu, X. Pang, Y. He, M. He, J. Jung,
H. Xia,* Z. Lin* ______ **4636 – 4640**

An Unconventional Route to Monodisperse and Intimately Contacted Semiconducting Organic–Inorganic Nanocomposites

Inside Back Cover

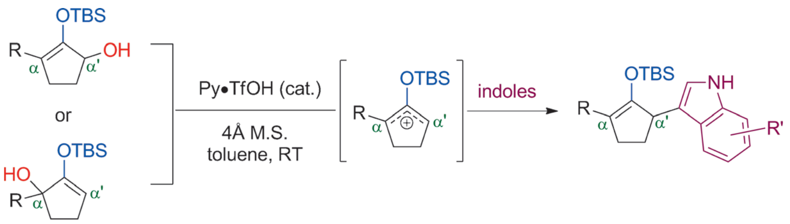


A robust strategy to produce spherically shaped organic–inorganic nanocomposites composed of PbTe nanoparticles tethered with poly(3,4-ethylenedioxythiophene) (PEDOT) chains was developed by using amphiphilic star-like diblock copolymer PAA-*b*-PEDOT as the template. The PbTe–PEDOT nanohybrids show long-term stability and hold promise for use in thermoelectrics.

Synthetic Methods

C. E. Ayala, N. S. Dange, F. R. Fronczek,
R. Kartika* ______ **4641 – 4645**

Brønsted Acid Catalyzed α′-Functionalization of Silylenol Ethers with Indoles



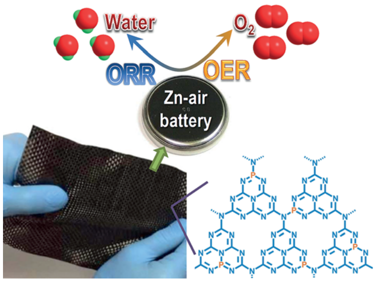
Under control: The title reaction enables C–C bond formation at the α′-position of silylenol ethers. Highly substituted indole-containing silylenol ethers are generated in excellent yields with complete regiocontrol presumably through silyloxyallyl cation intermediates. The silylenol ether moiety does not undergo protodesilylation, thus underscoring the very mild reaction conditions.

Flexible Electrodes

T. Y. Ma, J. R. Ran, S. Dai, M. Jaroniec,
S. Z. Qiao* ______ **4646 – 4650**

Phosphorus-Doped Graphitic Carbon Nitrides Grown In Situ on Carbon-Fiber Paper: Flexible and Reversible Oxygen Electrodes

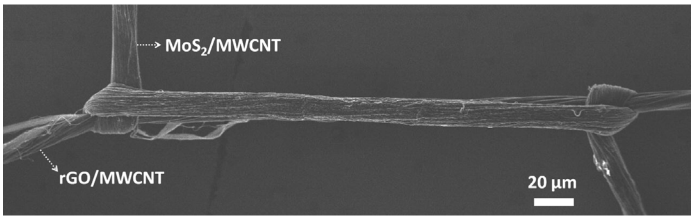
Electrodes, on a roll: Flexible and reversible oxygen electrodes composed of nanostructured P-doped graphitic carbon nitrides grown on carbon-fiber paper exhibit outstanding catalytic activity and stability towards both oxygen reduction (ORR) and oxygen evolution reactions (OER) in different folded and rolled-up forms. They can be used as efficient air cathodes in Zn–air batteries.



Supercapacitors

G. Sun, X. Zhang, R. Lin, J. Yang,
H. Zhang,* P. Chen* ______ **4651 – 4656**

Hybrid Fibers Made of Molybdenum Disulfide, Reduced Graphene Oxide, and Multi-Walled Carbon Nanotubes for Solid-State, Flexible, Asymmetric Supercapacitors

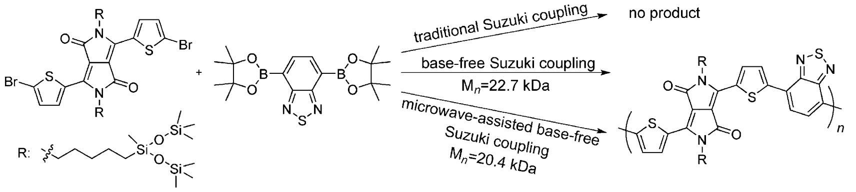


On fiber: A solid-state, asymmetric supercapacitor is fabricated by using flexible hybridized fibers of MoS_2-rGO/MWCNT and rGO/MWCNT as the anode and cathode, respectively (MWCNT: multi-walled carbon nanotube; rGO: reduced graphene oxide). This fiber-based asymmetric supercapacitor can operate in a wide potential window of 1.4 V with high Coulombic efficiency, good rate and cycling stability, and improved energy density.

Materials Science

J. Lee, A.-R. Han, S. M. Lee, D. Yoo,
J. H. Oh,* C. Yang* ______ **4657 – 4660**

Siloxane-Based Hybrid Semiconducting Polymers Prepared by Fluoride-Mediated Suzuki Polymerization

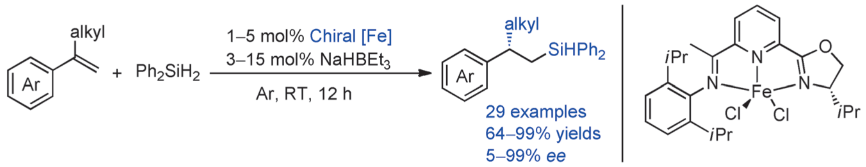


Heavy weight: Fluoride-mediated Suzuki polymerizations under conventional and microwave-assisted heating were performed to generate a solution-processable poly(diketopyrrolopyrrole-*alt*-benzothiadiazole) consisting of the hybrid siloxane substituents. The optimal reaction conditions, in terms of the molecular weights, involved the use of CsF and DME at 120 °C with conventional heating for 24 hours.

Asymmetric Catalysis

J. Chen, B. Cheng, M. Cao,
Z. Lu* ______ **4661 – 4664**

Iron-Catalyzed Asymmetric Hydrosilylation of 1,1-Disubstituted Alkenes



Iron clad: The highly regio- and enantioselective iron-catalyzed anti-Markovnikov hydrosilylation of 1,1-disubstituted aryl alkenes was developed using iminopyridine oxazoline ligands to afford chiral organosilanes. Additional derivatization of these products lead to chiral organosilanols, cyclic silanes, phenol derivatives, and 3-substituted 2,3-dihydrobenzofurans.

Cross-Coupling

H. Minami, T. Saito, C. Wang,*
M. Uchiyama* ______ **4665 – 4668**

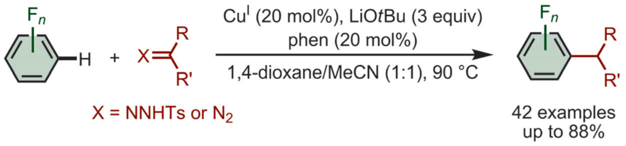
Organoaluminum-Mediated Direct Cross-Coupling Reactions

All in Al: Simply heating an arylaluminum ($ArAlMe_2$·LiCl) and an organic halide RX (R = aryl, alkenyl, alkynyl; X = I, Br, Cl) without any external catalyst results in a smooth and direct cross-coupling reaction taking place. This approach enables the efficient, chemo-/stereoselective formation of coupling products with broad functional group compatibility.

Synthetic Methods

S. Xu, G. Wu, F. Ye, X. Wang, H. Li, X. Zhao, Y. Zhang, J. Wang* **4669–4672**

Copper(I)-Catalyzed Alkylation of Polyfluoroarenes through Direct C–H Bond Functionalization

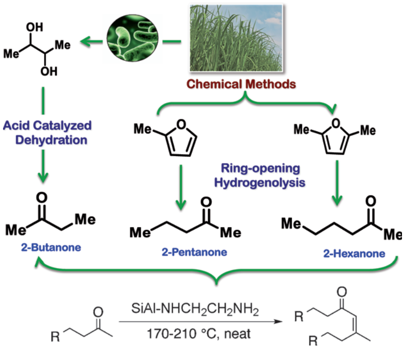


Along came “Poly”: $C(sp^2)$–$C(sp^3)$ bond formation through direct C–H functionalization proceeds through a copper(I)-catalyzed alkylation of electron-poor polyfluoroarenes with *N*-tosylhydrazones or diazo compounds. The transformation represents a highly efficient practical method for the direct alkylation of polyfluoroarenes. phen = 1,10-phenanthroline, Ts = 4-toluenesulfonyl.

Bifunctional Catalysts

S. Sankaranarayanapillai, S. Sreekumar, J. Gomes, A. Grippo, G. E. Arab, M. Head-Gordon, F. D. Toste, A. T. Bell* **4673–4677**

Catalytic Upgrading of Biomass-Derived Methyl Ketones to Liquid Transportation Fuel Precursors by an Organocatalytic Approach



Dimerize it: A highly efficient, water-tolerant, solid-base organocatalyst for selective dimerization of biomass-derived methyl ketones was developed by tethering amines on a Brønsted acidic silica–alumina support. C_4–C_{15} methyl ketones can be catalytically upgraded to the dimer products with high selectivity. DFT analysis and experimental data suggest that C–C bond formation is the rate-determining step.

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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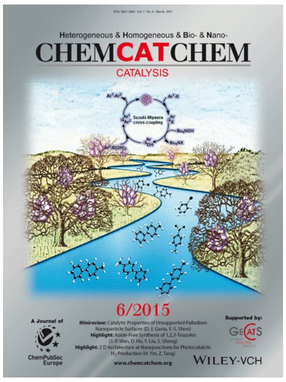

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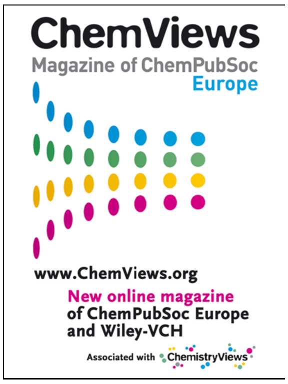

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