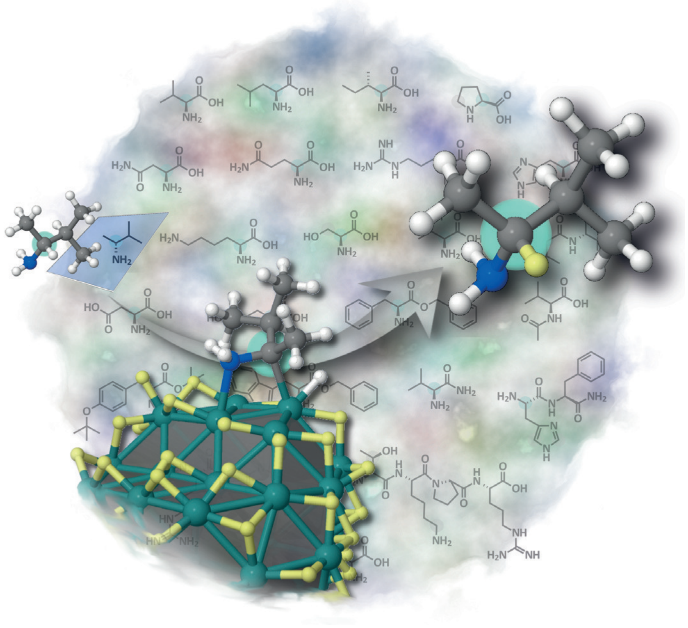
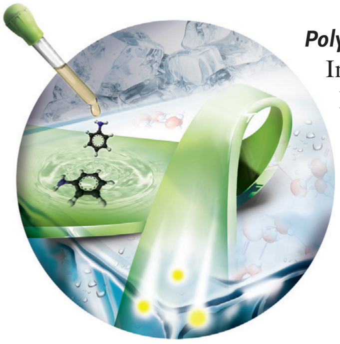
Enantiospecific C–H activation …



… catalyzed by a ruthenium nanocatalyst enables the one-step deuterium labeling of 25 bioactive compounds, such as amino acids and peptides, with full retention of configuration. In their Communication on page 10474 ff., G. Pieters et al. show that a four-membered dimetallacycle is a key intermediate and suggest that the collective motion of surface species can facilitate the C–H activation step by modulating the local electronic structure.

Biomedical Analysis

Gas pressure can be used as the signal readout for a simple and highly sensitive bioanalytical device as shown by C. Yang and co-workers in their Communication on page 10448 ff. By combining H_2O_2 decomposition with an antibody assay, various analytes can be detected.

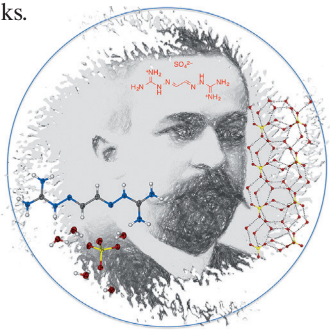


Polyaniline Sheets

In their Communication on page 10497 ff., M. J. Park et al. describe how ice surfaces can be used to form 2D polyaniline nanosheets with high electrical conductivity. The nanosheets can be transferred onto other substrates and patterned using predetermined masks.

Cluster Compounds

The crystal structure of glyoxal bis(amidiniumhydrazone) sulfate, which contains extended hydrogen-bonded sulfate–water clusters, is analyzed by R. Custelcean et al. in their Communication on page 10525 ff.



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Service

Author Profile

"If I were not a scientist, I would be a peasant leading a carefree life.
My favorite food is Chinese chives stir-fried with egg. …"
This and more about Jianwei Sun can be found on page 10401.

News

A. Brik

P. Diaconescu

S.-Y. Liu

P. Naumov

W. E. Piers

M. Suginome

T. P. Yoon

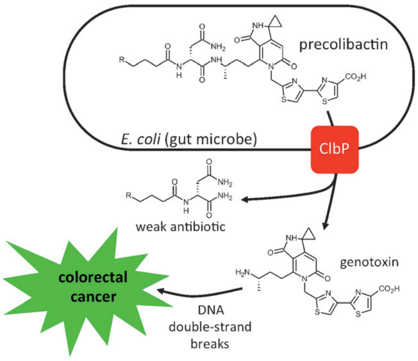
E. R. Zubarev

Books

Highlights

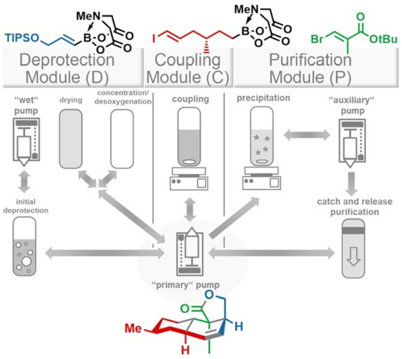
Microbiome

Gut reaction: There is increasing evidence that the impact on human health and disease of the microbes living in and on us has been underestimated. Several of the small molecules produced by "our" bacteria are structurally highly complex and show unusual biosynthetic pathways or modes of action, as highlighted by the race to elucidate the structure and biosynthesis of colibactin, a genotoxic compound produced by human gut bacteria.



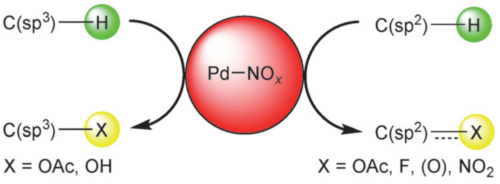
Automated Synthesis

Automation is back on the agenda! The first automated iterative C–C coupling processes exploit the two faces of *N*-methyliminodiacetic acid boronates. They highlight the opportunities and challenges of how iterative synthesis with complex bifunctional building blocks can be conducted with liquid-handling devices to even access complex natural products.



Minireviews

Redox-Active NO$_x$ Ligands



Prominent role? The redox activity of NO$_x$ anions in Pd-catalyzed processes has recently attracted notable attention. It has led to the development of new synthetic methodologies in C–H bond activation (acetoxylation, fluorination, and nitration), Wacker oxidation, and diacetoxylation of terminal alkenes. The results are placed into context with historical findings on the use of NO$_x$ ligands in Pd-mediated chemistry.

For the USA and Canada:
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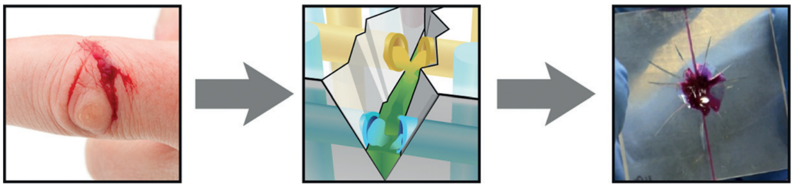
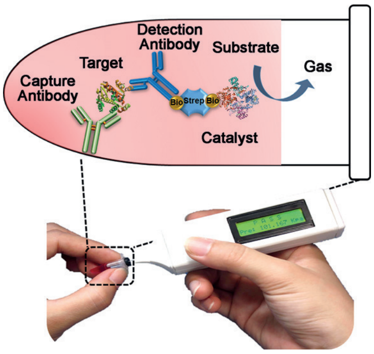
Reviews



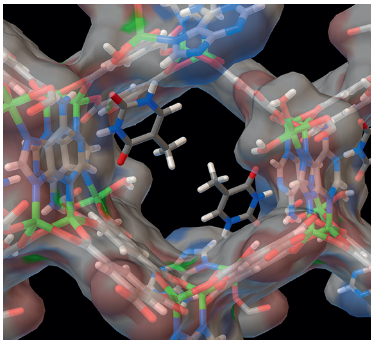
On the mend: Evolution has endowed biological organisms with the ability to self-heal. Inspired by the principles of nature, scientists have been trying to create synthetic materials with self-healing capabilities that can regenerate their mechanical integrity and specific functions after damage.

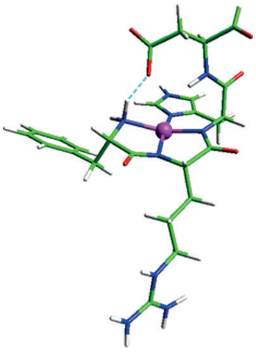
Communications

Pressure points: A very familiar, yet underutilized, physical parameter—gas pressure—can serve as the signal readout for highly sensitive bioanalysis. Combining the decomposition of H_2O_2 catalyzed by catalase or Pt nanoparticles with an antibody-based sandwich assay allows the detection of various analytes. This new signaling strategy opens up simple, portable, yet highly sensitive biomedical analysis in a variety of settings.



A global affair: A metal–organic framework (MOF) in which adenine residues with their Watson–Crick face exposed were immobilized periodically on the interior crystalline surface showed cooperativity between the open Watson–Crick sites and spatial effects within the nanopores. When this behavior was exploited for adenine–thymine binding within the constrained pores (see picture), a globally adaptive response of the MOF host was observed.



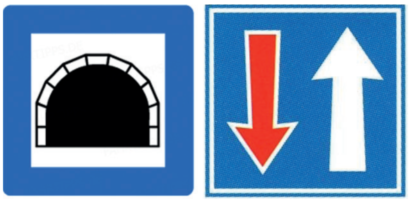


At the '4-front': The N-truncated Aβ4–42 peptide is a major β-amyloid (Aβ) isoform in healthy brain and in the Cu^{II}-rich plaques found in Alzheimer's disease. An Aβ4–16 model peptide was used to show that the N-terminal FRH sequence (structure shown) binds Cu^{II} (magenta) with a much higher affinity than the other major isoform Aβ1–42. Moreover, Cu^{II}-bound Aβ4–42 does not produce hydroxyl radicals, thus suggesting that it could act as a redox-inert Cu^{II} sink.

Nanoporous Materials

A. Schachtschneider, M. Wessig,
M. Spitzbarth, A. Donner, C. Fischer,
M. Drescher, S. Polarz* **10465 – 10469**

Directional Materials—Nanoporous Organosilica Monoliths with Multiple Gradients Prepared Using Click Chemistry

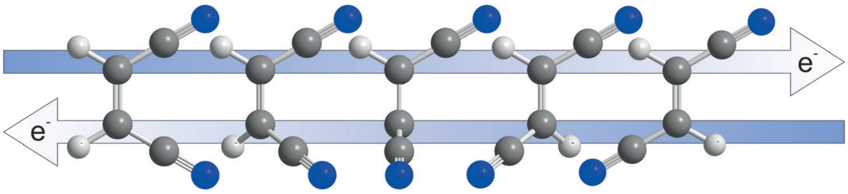


Right direction: Directionality in nanoporous materials could be achieved by introducing chemical gradients of surface-bound functional organic groups. Almost any desired functional group can be attached to the surface of the nanoporous material using click chemistry.

Reaction Mechanisms

S. Klaiman,*
L. S. Cederbaum **10470 – 10473**

Barrierless Single-Electron-Induced *cis–trans* Isomerization



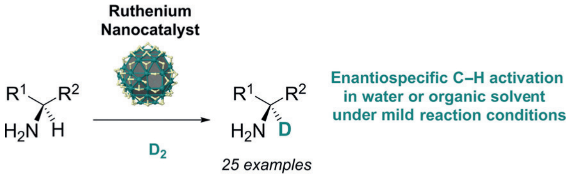
A single electron can completely remove the activation energy of the maleonitrile–fumaronitrile *cis–trans* isomerization reaction. The activation proceeds through an electronic resonance state of the anionic reactant, which eventually becomes the ground state of the anionic product. The mechanism leading to the activation is explained.

Nanocatalysts

C. Taglang, L. M. Martínez-Prieto,
I. del Rosal, L. Maron, R. Poteau,
K. Philippot, B. Chaudret, S. Perato,
A. Sam Lone, C. Puente, C. Dugave,
B. Rousseau, G. Pieters* **10474 – 10477**

Enantiospecific C–H Activation Using Ruthenium Nanocatalysts

Front Cover

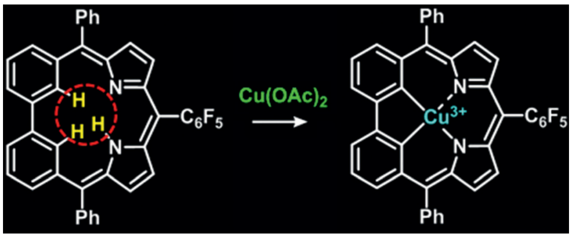


Various compounds, such as amines, amino acids, or peptides, can undergo enantiospecific C–H activation/deuteration in the presence of ruthenium nanocatalysts under mild conditions. Theoretical studies revealed a four-membered dimetallacycle as the key intermediate and suggested that the collective motion of surface species can facilitate the C–H activation step by modulating the local electronic structure.

Dicarbacorrole

B. Adinarayana, A. P. Thomas,
C. H. Suresh,
A. Srinivasan* **10478 – 10482**

A 6,11,16-Triarylbiphenylcorrole with an *adj*-CCNN Core: Stabilization of an Organocopper(III) Complex

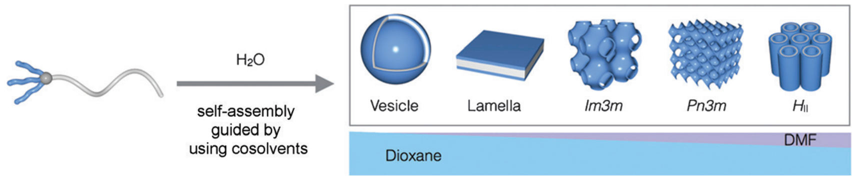


A biphenyl unit is incorporated in the corrole macrocyclic framework to form an *adj*-dicarbaporphyrinoid with a CCNN core. Upon macrocyclic aromatization, the aromatic biphenyl unit and π-delocalized dipyrromethene unit are linked together to generate overall nonaromatic character. The trianionic core is suitable to stabilize higher-oxidation-state metal complexes, such as an organocopper(III) complex.

Self-Assembly

Y. La, T. H. An, T. J. Shin, C. Park,*
K. T. Kim* **10483 – 10487**

A Morphological Transition of Inverse Mesophases of a Branched-Linear Block Copolymer Guided by Using Cosolvents

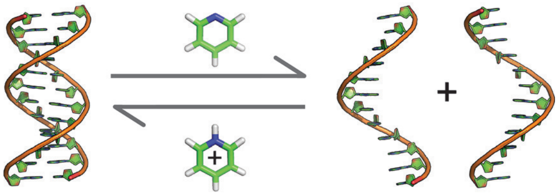


The phase and lattice of the inverse mesophases of a single branched-linear block copolymer (BCP) in solution can be influenced without changing the BCP structure. The phase of the self-assembled structures of the BCP can be controllably shifted from bilayer structures of positive curvature to inverse mesophases by adjusting the interaction parameter of the solvent used for self-assembly.

Ion–DNA Interactions

G. Portella, M. Terrazas, N. Villegas,
C. González, M. Orozco* **10488 – 10491**

Can A Denaturant Stabilize DNA? Pyridine Reverses DNA Denaturation in Acidic pH

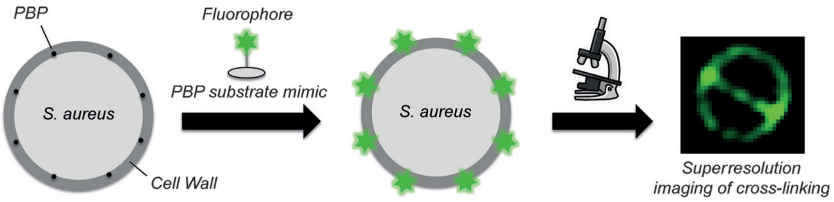


The thermal stability of duplex DNA can be decreased by addition of pyridine, a well-known denaturant. In acidic solutions, pyridine is protonated and displays its role as DNA renaturant, which increases the melting temperature of the duplex further than a solution of NaCl at the same concentration. This behavior is specifically observed for pyridine.

Biosensors

S. Gautam, T. Kim, T. Shoda, S. Sen,
D. Deep, R. Luthra, M. T. Ferreira,
M. G. Pinho,
D. A. Spiegel* **10492 – 10496**

An Activity-Based Probe for Studying Crosslinking in Live Bacteria



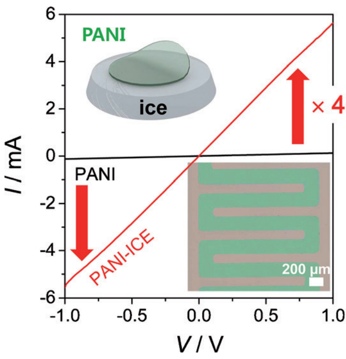
Linked in: A nontoxic fluorescent probe that mimics the peptidoglycan stem peptide can be used to install fluorophores at sites of crosslinking within the bacterial cell wall (see picture). The probe is specific for penicillin-binding protein 4 (PBP4) in *Staphylococcus aureus*, and thus allows visualization and relative quantification of PBP4-mediated crosslinking in this important human pathogen.

2D Conducting Polymers

I. Y. Choi, J. Lee, H. Ahn, J. Lee, H. C. Choi,
M. J. Park* **10497 – 10501**

High-Conductivity Two-Dimensional Polyaniline Nanosheets Developed on Ice Surfaces

Inside Back Cover



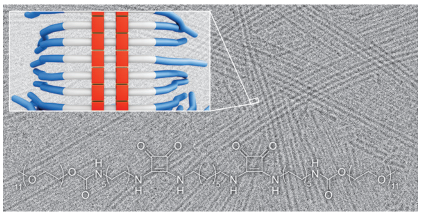
A cool way to conduct: Ice is used as a removable hard template to form two-dimensional polyaniline (PANI) nanosheets. High current flows (5.5 mA at 1 V) and high electrical conductivity (35 S cm^{-1}) were obtained for the nanosheets. The PANI nanosheet can be easily transferred onto various types of substrates from the ice surfaces, and the nanosheets can be patterned into any shape using predetermined masks.

Non-Covalent Interactions

V. Saez Talens, P. Englebienne, T. T. Trinh,
W. E. M. Noteborn, I. K. Voets,
R. E. Kieltyka* ________ **10502–10506**

Aromatic Gain in a Supramolecular Polymer

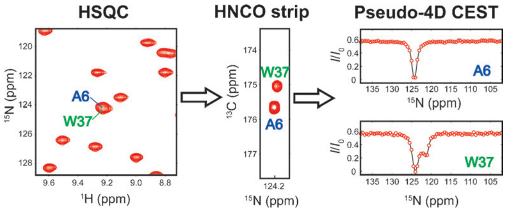
Getting in tune: The synergy of aromatic gain and hydrogen bonding is observed in an aqueous supramolecular polymer consisting of squaramide-based bolaamphiphiles. The aromatic gain effect accounts for more than 30% of the total interaction energy among squaramide pentamers. The interplay between polymer self-assembly and reciprocal hydrogen-bonding–aromaticity interactions is examined.



Protein NMR

D. Long,* F. Delaglio, A. Sekhar,
L. E. Kay* ________ **10507–10511**

Probing Invisible, Excited Protein States by Non-Uniformly Sampled Pseudo-4D CEST Spectroscopy

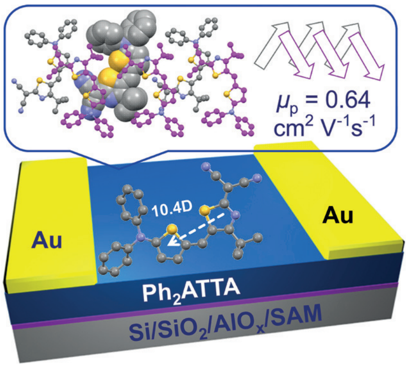


Powerful NMR tool: A non-uniformly sampled HNCO-based pseudo-4D CEST experiment is described that generates data sets with excellent resolution in reasonable recording times. Analysis of the data is performed in the time domain, exploiting previous knowledge of peak positions from reference spectra.

Organic Electronics

A. Lv, M. Stolte,
F. Würthner* ________ **10512–10515**

Head-to-Tail Zig-Zag Packing of Dipolar Merocyanine Dyes Affords High-Performance Organic Thin-Film Transistors

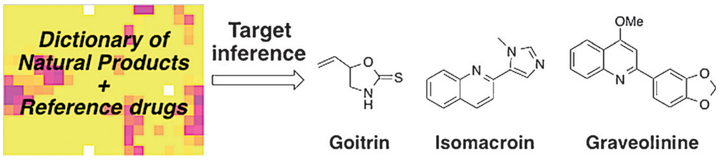


A merocyanine transistor: A crystal engineering approach afforded a new packing arrangement for a dipolar merocyanine dye that led to thin-film transistors with high mobility of 0.64 $cm^2V^{-1}s^{-1}$. Because of the optical properties and the suitable orientation of the transition dipoles parallel to the substrate, these molecules might also be promising for organic photovoltaic applications.

Target Identification

T. Rodrigues, D. Reker, J. Kunze,
P. Schneider,
G. Schneider* ________ **10516–10520**

Revealing the Macromolecular Targets of Fragment-Like Natural Products

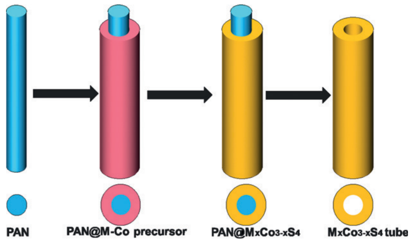


Target acquired: Hitherto unknown macromolecular targets of the fragment-like natural products goitrin, isomacroin, and graveolinine were discovered through the use of a computational target-prediction tool tailored for natural products. The results suggest that such methods will find application in target discovery for natural products and could inspire the design of new chemical entities for chemical biology and molecular medicine.

Nanotubes

Y. M. Chen, Z. Li,
X. W. Lou* ———— **10521 – 10524**

General Formation of $M_xCo_{3-x}S_4$ (M = Ni, Mn, Zn) Hollow Tubular Structures for Hybrid Supercapacitors



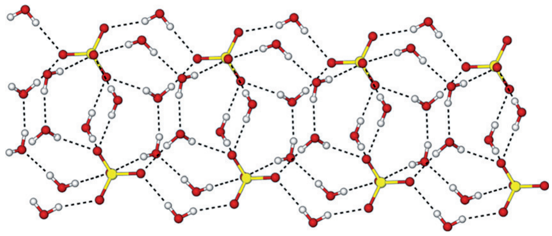
Hollow tubular structures of $M_xCo_{3-x}S_4$ (M = Ni, Mn, Zn) can be synthesized with controllable composition by using a simple soft polymeric template (polyacrylonitrile; PAN). The as-prepared mixed-metal sulfide nanotubes exhibit unprecedented electrochemical performance as electrode materials for hybrid supercapacitors.

Cluster Compounds

R. Custelcean,* N. J. Williams,
C. A. Seipp ———— **10525 – 10529**

Aqueous Sulfate Separation by Crystallization of Sulfate–Water Clusters

Back Cover

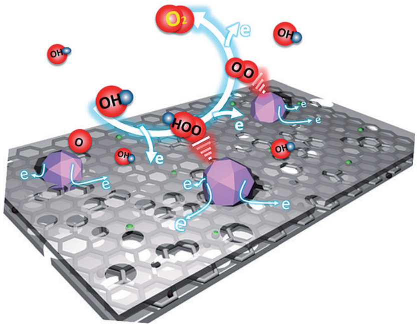


You can leave your water on: Extended $[SO_4(H_2O)_5{}^{2-}]_n$ clusters crystallize from aqueous solutions with a bis(guanidinium) ligand generated in situ by hydrazone condensation. The crystallization of these clusters is a viable alternative to the established sulfate separation approach, which involves encapsulation of the "naked" anion.

Oxygen-Evolution Catalysts

J. Wang, K. Li, H.-x. Zhong, D. Xu,
Z.-l. Wang, Z. Jiang, Z.-j. Wu,
X.-b. Zhang* ———— **10530 – 10534**

Synergistic Effect between Metal–Nitrogen–Carbon Sheets and NiO Nanoparticles for Enhanced Electrochemical Water-Oxidation Performance

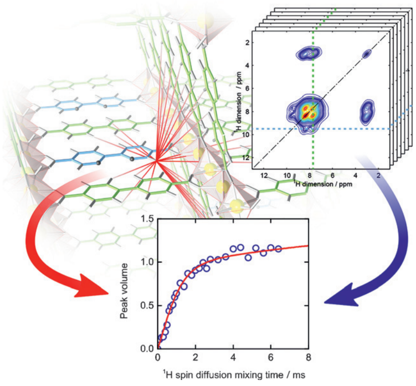


Sitting on the FeNC: Metal–nitrogen–carbon sheets are used as the supports for metal oxide catalysts for the oxygen-evolution reaction (OER). Iron–nitrogen–carbon (FeNC) sheets loaded with NiO nanoparticles give superior performance in alkaline media. The improved performance originates from a synergistic effect between the FeNC sheets and NiO.

Metal–Organic Frameworks

A. Krajnc, T. Kos, N. Zabukovec Logar,
G. Mali* ———— **10535 – 10538**

A Simple NMR-Based Method for Studying the Spatial Distribution of Linkers within Mixed-Linker Metal–Organic Frameworks

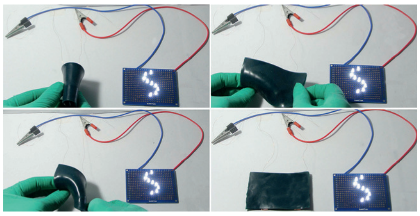


Microscope for MOFs: Non-demanding and fast ^1H spin-diffusion NMR spectroscopy measurements and computationally inexpensive modeling based on a semi-empirical description provide insight into the spatial distribution of linkers within mixed-linker metal–organic frameworks (MOFs). The performance of the approach is demonstrated with the mixed-linker aluminum-based MOF material DUT-5, which has a framework consisting of biphenyl and bipyridyl dicarboxylic linkers.

Flexible Batteries

Q. Sun, X. Fang, W. Weng,* J. Deng,
P. Chen, J. Ren, G. Guan, M. Wang,*
H. Peng* ______________ 10539 – 10544

An Aligned and Laminated Nanostructured Carbon Hybrid Cathode for High-Performance Lithium–Sulfur Batteries

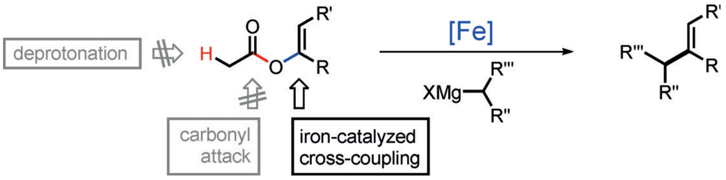


Smart device: Sulfur-absorbed mesoporous carbon particles are incorporated into aligned carbon nanotube sheets as hybrid cathodes for flexible lithium–sulfur batteries. The resulting LiS battery delivers a high capacity of 1226 mAh g^{-1} and can be stably performed for 1000 cycles. In addition, the specific capacity is well maintained under bending and after being folded 500 times.

Cross-Coupling

D. Gärtner, A. L. Stein, S. Grupe, J. Arp,
A. Jacobi von Wangelin* _ 10545 – 10549

Iron-Catalyzed Cross-Coupling of Alkenyl Acetates

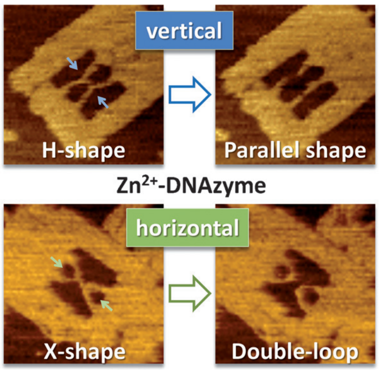


Iron clad: Acetates are underutilized electrophiles in metal-catalyzed cross-coupling reactions because of the strong alkenyl C–O bond and their propensity to engage in unwanted reactions. Combination of a ligand-free low-valent Fe catalyst with nucleophilic organomagnesium reagents, low temperature, and short reaction times results in highly selective cross-couplings with alkenyl acetates.

DNA Structures

M. Endo,* Y. Takeuchi, Y. Suzuki,
T. Emura, K. Hidaka, F. Wang, I. Willner,*
H. Sugiyama* __________ 10550 – 10554

Single-Molecule Visualization of the Activity of a Zn^{2+}-Dependent DNAzyme



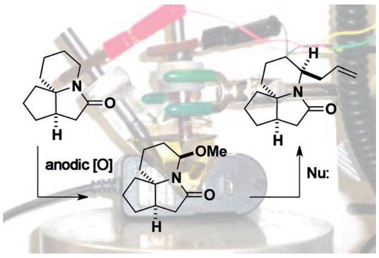
In the frame: The single-molecule catalytic activity of a Zn^{2+}-dependent DNAzyme was investigated in a DNA origami nanostructure. The DNAzyme and substrate strands were assembled in the DNA frames in different configurations. Reaction progress was directly visualized by observing the structural changes of the incorporated DNA strands by high-speed atomic force microscopy (see picture).

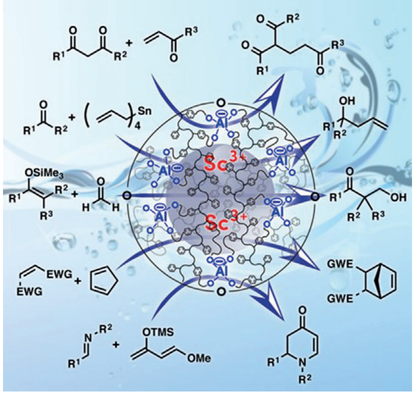
Anodic Oxidation

K. J. Frankowski, R. Liu, G. L. Milligan,
K. D. Moeller, J. Aubé* __ 10555 – 10558

Practical Electrochemical Anodic Oxidation of Polycyclic Lactams for Late Stage Functionalization

An improvised electrochemical apparatus was constructed and utilized for the anodic oxidation of complex lactam substrates. Combining synthetic electrochemistry with the azido-Schmidt/lactam disconnection has enabled the synthesis of novel lactam derivatives by *N*-acyliminium ion diversification. This mild, late-stage functionalization strategy complements the methods for heterocycle synthesis.





Heterogeneous water-compatible Lewis acid catalysts were developed by self-assembly of polymers, carbon black, tetravalent aluminum reductants, and scandium salts using a polymer incarceration technique. The heterogeneous catalysts were successfully applied to various C–C bond forming reactions in pure water or aqueous media without leaching of metals.

Lewis Acid Catalysts

H. Miyamura, A. Sonoyama,
D. Hayrapetyan,
S. Kobayashi* ________ **10559 – 10563**

Self-Assembled Nanocomposite Organic Polymers with Aluminum and Scandium as Heterogeneous Water-Compatible Lewis Acid Catalysts

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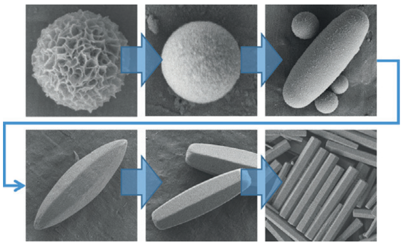
Synthesis of MOF particles: Morphological and structural changes of metal–organic framework (MOF) particles are associated with the relative amounts of the two organic linkers (isophthalic acid and 1,4-benzenedicarboxylic acid; see picture) incorporated within MOF particles. The incorporated ratios of the two organic linkers and thus the resulting morphology and porosity of the MOF were conveniently controlled.



Metal–Organic Frameworks

H. J. Lee, J. We, J. O. Kim, D. Kim, W. Cha,
E. Lee, J. Sohn, M. Oh* _ **10564 – 10568**

Morphological and Structural Evolutions of Metal–Organic Framework Particles from Amorphous Spheres to Crystalline Hexagonal Rods

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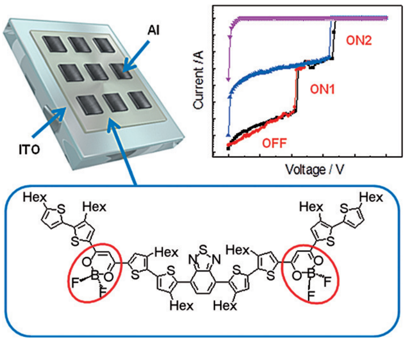
High memory performance: Small-molecule-based ternary organic memory devices have been fabricated from a solution-processable boron(III)-containing donor–acceptor compound (see picture). This novel molecule displays high ternary memory performances with low turn-on and distinct threshold voltages, small reading bias, and long retention time with a large ON/OFF ratio of each state.



Organic Electronics

C.-T. Poon, D. Wu, W. H. Lam,
V. W.-W. Yam* ________ **10569 – 10573**

A Solution-Processable Donor–Acceptor Compound Containing Boron(III) Centers for Small-Molecule-Based High-Performance Ternary Electronic Memory Devices

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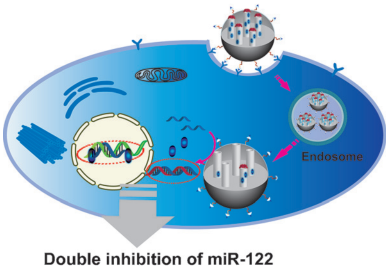
Double inhibition: A smart drug-delivery system, constructed by using antagomir-capped mesoporous silica nanoparticles (MSNs), is capable of simultaneous target-triggered release of an antagomir and a hydrophobic small-molecule microRNA inhibitor in Huh7 cells to achieve combination inhibition of endogenous miR-122.

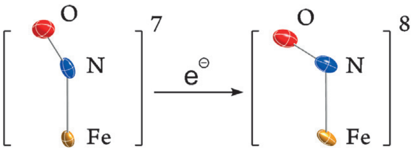


Drug Delivery

C. Yu, L. Qian, M. Uttamchandani, L. Li,
S. Q. Yao* ________ **10574 – 10578**

Single-Vehicular Delivery of Antagomir and Small Molecules to Inhibit miR-122 Function in Hepatocellular Carcinoma Cells by using “Smart” Mesoporous Silica Nanoparticles

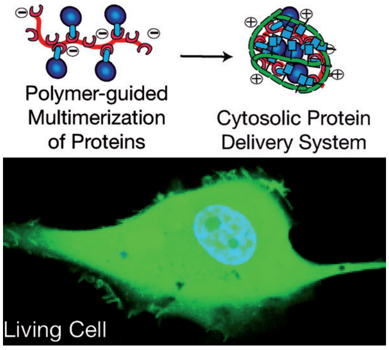
Structure Elucidation



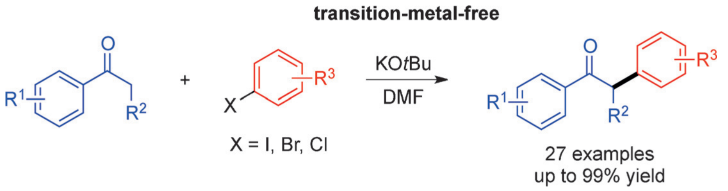
Bioinorganic chemistry: The first X-ray single-crystal structure of a $\{FeNO\}^8$ porphyrin complex $[Co(Cp)_2][Fe(TFPPBr_8)(NO)]$ and the structure of the $\{FeNO\}^7$ precursor $[Fe(TFPPBr_8)(NO)]$ are reported. $[Fe(TFPPBr_8)(NO)]^-$ shows a much more bent Fe–N–O⁻ angle (122.4(3)°) and longer Fe–NO⁻ and N–O⁻ bond lengths than the nitrosyl iron(II) analogues (see picture).

Smart Drug Delivery

Let's get organized: Docking of His-tagged proteins onto a soluble nickel-immobilized linear polymer enables formation of an efficient protein delivery system with a pyridylthiourea-grafted polyethylenimine carrier. Protein multimerization and the structural features of the multimers were studied.



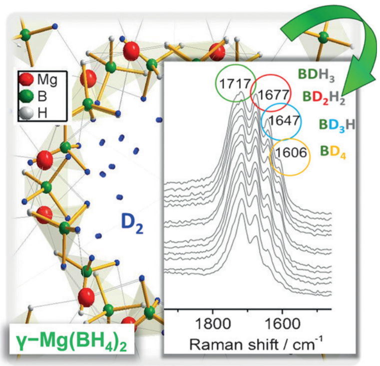
C–C Coupling



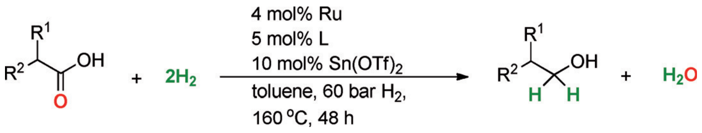
The α-arylation of enolizable aryl ketones with aryl halides can be carried out under transition-metal-free conditions using KOtBu and DMF. The α-aryl ketones thus obtained are used for step- and cost-economic syntheses of fused heterocycles and Tamoxifen. Mechanistic studies demonstrate that KOtBu and DMF act synergistically to initiate the radical process.

Gas–Solid Exchange

The H-to-D exchange in high-surface-area complex ionic hydride $Mg(BH_4)_2$ exhibits exceptionally high rates at low temperature and pressure. The gas–solid H→D exchange at the surface is thus significantly faster than the solid-state H(D) diffusion in the bulk. The latter can be regarded as the rate-limiting step for hydrogen desorption and absorption in $Mg(BH_4)_2$.

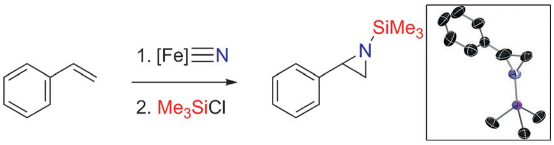


Catalytic Hydrogenation



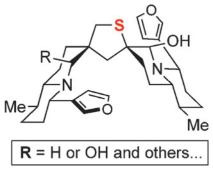
Direct route to alcohols: The combination of a specific ruthenium complex and Lewis acids is found to be active for the direct hydrogenation of carboxylic acids to alcohols. A variety of carboxylic acids including biomass-based derivatives are converted into the desired alcohols in high yields.

Nitrogen Heterocycles



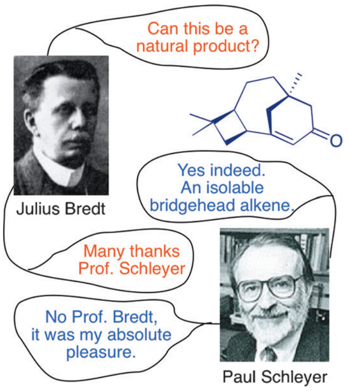
New access to versatile synthons: Iron(IV) nitride complexes react with a range of styrenes to form the corresponding high-spin iron(II) aziridino complexes. The reversibility of the aziridination reaction allows for aziridine cross-metathesis reactions. A synthetic cycle for the formation of N-silylated aziridines has been established.

Total Synthesis



Nuphars are speedy killers: For the first time several of the hydroxylated dimeric nuphar alkaloids and their unnatural enantiomers have been synthesized. First-ever apoptosis data for many of these compounds is provided.

Bridgehead Olefins



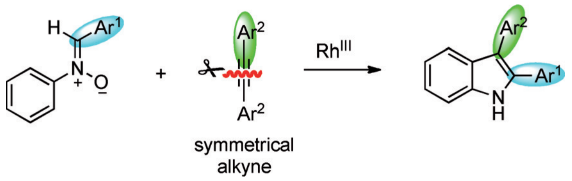
To Bredt or not to Bredt, that is the natural product question. Bredt founded his namesake rule while studying the structures of monoterpenes. Schleyer's anti-Bredt predictive rules were the pinnacle of much physical organic chemistry interest, but the natural product element continued unabated. Olefin strain energy calculations lead to the definitive conclusion that Bredt's rule should not be applied to natural products containing a bridgehead alkene.

Inside Cover

Heterocycle Synthesis

H. Yan, H. L. Wang, X. C. Li, X. Y. Xin, C. X. Wang,* B. S. Wan* **10613 – 10617**

Rhodium-Catalyzed C–H Annulation of Nitrones with Alkynes: A Regiospecific Route to Unsymmetrical 2,3-Diaryl-Substituted Indoles

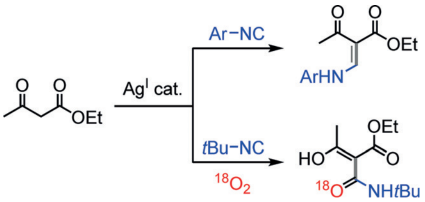


They know their place: Unsymmetrically 2,3-diaryl-substituted N-unprotected indoles were synthesized by the rhodium(III)-catalyzed annulation of nitrones with symmetrical diaryl alkynes. Exclusive regioselectivity was observed, as one of the two aryl substituents on the resulting indole ring is derived from the C-aryl ring of the nitrone, and the other from the alkyne.

Radical Reactions

J. Liu, Z. Liu, P. Liao, L. Zhang, T. Tu, X. Bi* **10618 – 10622**

Silver-Catalyzed Cross-Coupling of Isocyanides and Active Methylene Compounds by a Radical Process

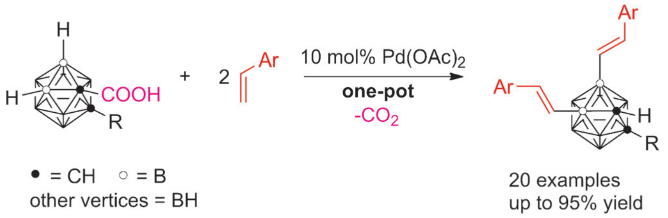


Silver-tongued radicals: A novel C–C bond-forming reaction was developed through the silver-catalyzed radical cross-coupling of isocyanides and active methylene compounds to deliver β-aminoenones and tricarbonylmethanes. These two transformations are 100% atom economical and the formation of β-aminoenones is stereoselective. A radical mechanism is proposed on the basis of experimental studies.

Carboranes

H. Lyu, Y. Quan, Z. Xie* **10623 – 10626**

Palladium-Catalyzed Direct Dialkenylation of Cage B–H Bonds in *o*-Carboranes through Cross-Coupling Reactions



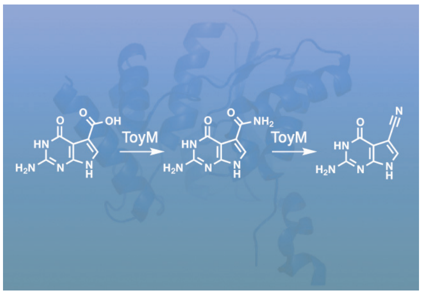
Giving directions: Pd-catalyzed direct dialkenylation of cage B(4,5)–H bonds in *o*-carboranes has been achieved using a carboxylic acid directing group, leading to the preparation of a series of 4,5-[*trans*-(ArCH=CH)]$_2$-*o*-carboranes in high yields and with excellent regioselectivity.

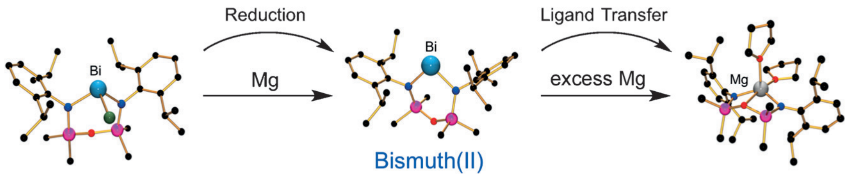
Biosynthesis

M. T. Nelp, V. Bandarian* **10627 – 10629**

A Single Enzyme Transforms a Carboxylic Acid into a Nitrile through an Amide Intermediate

Double duty: In bacterial and archeal biosynthesis of 7-deazpurines, a single enzyme, ToyM, catalyzes the two-step conversion of the carboxylic acid 7-carboxy-7-deazaguanine (CDG) into the corresponding nitrile, 7-cyano-7-deazaguanine (preQ$_0$). The mechanism of this unusual direct transformation proceeds via the adenylation of CDG. This activates it to form the amide intermediate 7-amido-7-deazaguanine (ADG), which is in turn activated to form the nitrile.



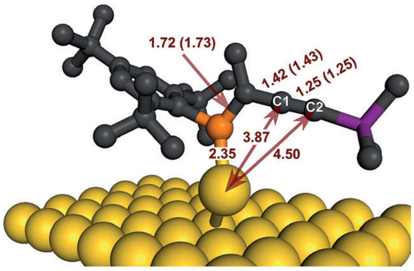


Reduction of a Bi^{III} compound affords the first isolable Bi^{II} radical (see scheme; Cl green, Si magenta, O red, N blue). X-ray diffraction confirms a two-coordinate metal with no short intermolecular contacts; SQUID measurements indicate a paramagnetic compound with a single unpaired electron. EPR and DFT results are consistent with a metal-centered radical, with the unpaired electron predominantly in a p-type orbital on Bi.

Main-Group Radicals

R. J. Schwamm, J. R. Harmer, M. Lein, C. M. Fitchett, S. Granville, M. P. Coles* ———— **10630 – 10633**

Isolation and Characterization of a Bismuth(II) Radical



A dynamic ligand shell for the stabilization of small gold nanoparticles is obtained through cooperative binding of acetylenic phosphaalkenes. A variety of experimental and analytical methods demonstrates that the C≡C as well as the P=C unit of the acetylenic phosphaalkene are essential for nanoparticle stabilization.

Gold Nanoparticle Stabilization

A. Orthaber,* H. Löfås, E. Öberg, A. Grigoriev, A. Wallner, S. H. M. Jafri, M.-P. Santoni, R. Ahuja, K. Leifer, H. Ottosson, S. Ott* ——— **10634 – 10638**

Cooperative Gold Nanoparticle Stabilization by Acetylenic Phosphaalkenes

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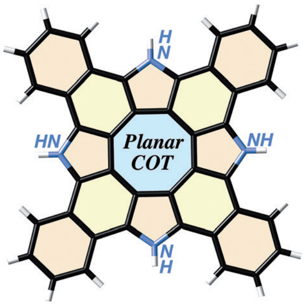

A perfectly planar structure with a central cyclooctatetraene (COT) core that shows little alternation in the bond lengths is the main feature of tetrabenzotetraaza[8]circulene. This heterocirculene shows aromatic-like characteristics, such as a sharp absorption spectrum, a high fluorescence quantum yield, and a degenerate HOMO, thus suggesting the predominant contribution of an [8]radialene-like electronic system.

Aromaticity

F. Chen, Y. S. Hong, S. Shimizu, D. Kim,* T. Tanaka,* A. Osuka* —— **10639 – 10642**

Synthesis of a Tetrabenzotetraaza[8]circulene by a "Fold-In" Oxidative Fusion Reaction

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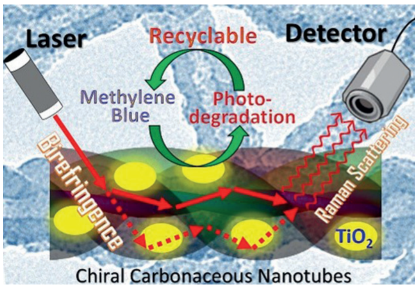
Chiral carbonaceous nanotubes (CNTs) with TiO_2 nanocrystals were used in plasmon-free surface-enhanced Raman scattering (SERS) detection and successful recycling of SERS substrate was realized. The high SERS sensitivity of methylene blue (MB) over the CNT/TiO_2 hybrids is ascribed to the laser-driven birefringence induced by the helical structure.



Hybrid Nanomaterials

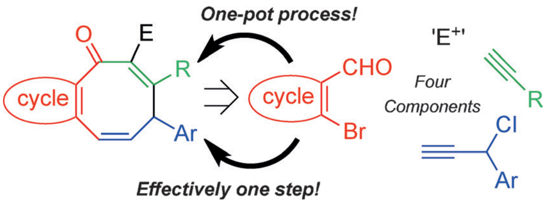
B. C. Qiu, M. Y. Xing,* Q. Y. Yi, J. L. Zhang* ———— **10643 – 10647**

Chiral Carbonaceous Nanotubes Modified with Titania Nanocrystals: Plasmon-Free and Recyclable SERS Sensitivity

Synthetic Methods

L. Burroughs, L. Eccleshare, J. Ritchie, O. Kulkarni, B. Lygo, S. Woodward,* W. Lewis **10648 – 10651**

One-Pot Cannizzaro Cascade Synthesis of *ortho*-Fused Cycloocta-2,5-dien-1-ones from 2-Bromo(hetero)aryl Aldehydes

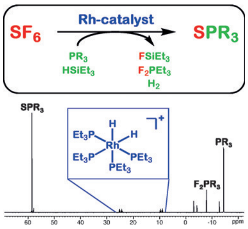


A cascade process that is triggered by an intramolecular Cannizzaro-type hydride transfer to an in situ prepared allene leads to the formation of 4-substituted cycloocta-2,5-dien-1-ones. Various derivatives could be obtained from commercially available (hetero)aryl aldehydes, trimethylsilylacetylene, and simple propargyl chlorides in good yields.

S–F Activation

L. Zámostná, T. Braun* **10652 – 10656**

Catalytic Degradation of Sulfur Hexafluoride by Rhodium Complexes

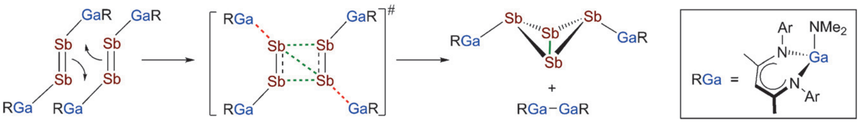


Greenhouse-gas degradation: Rhodium complexes effectively catalyze the activation and degradation of the greenhouse gas SF_6. The reactions proceed in a homogeneous phase under mild conditions. Using phosphines and hydrosilanes to scavenge the S and F atoms of the SF_6 molecule allows the selective transformation of SF_6 into sulfides and fluorosilanes.

Main-Group Chemistry

L. Tuscher, C. Ganesamoorthy, D. Bläser, C. Wölper, S. Schulz* **10657 – 10661**

A Gallium-Substituted Distibene and an Antimony-Analogue Bicyclo[1.1.0]butane: Synthesis and Solid-State Structures

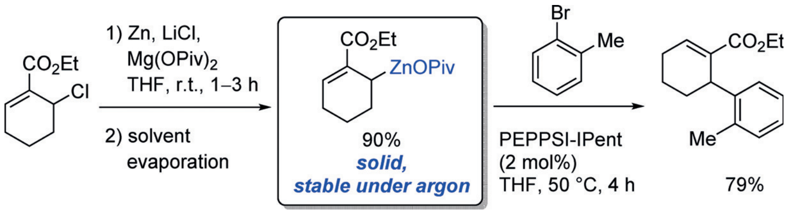


Getting GaGa about antimony: Comparative studies on the reaction of RGa with EX_3 (E = Sb, Bi; X = Et, NMe_2) show the subtle influence of the organic substituents on the reactivity of the Group 15 compound and on the stability of the insertion product $R(X)GaEX_2$. The use of $Sb(NMe_2)_3$, containing rather weak Sb–N bonds, resulted in the formation of a distibine, which was thermally converted into the first Sb analogue of bicyclo[1.1.0]butane.

Organozinc Reagents

M. Ellwart, P. Knochel* **10662 – 10665**

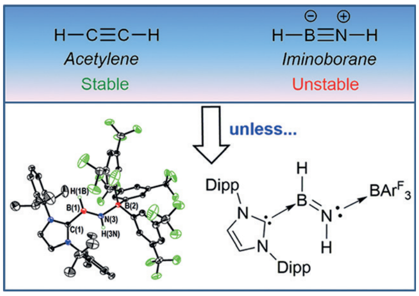
Preparation of Solid, Substituted Allylic Zinc Reagents and Their Reactions with Electrophiles



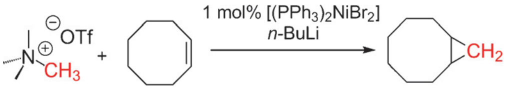
Think Allyl Zinc: The reaction of allylic chlorides or bromides with zinc powder in the presence of lithium chloride and magnesium pivalate leads to the formation of solid allylic zinc reagents that show excellent thermal stability. These allylic reagents undergo Pd-catalyzed cross-coupling reactions, as well as highly regioselective and diastereoselective carbonyl additions.

Iminoborane

Lightning in a bottle: An adduct of the elusive parent "inorganic acetylene" HBNH was prepared from a main-group azide by means of a general process consisting of N_2 loss and 1,2-hydrogen migration. The mechanism of this reaction was examined by calculations and isotope-labeling studies.



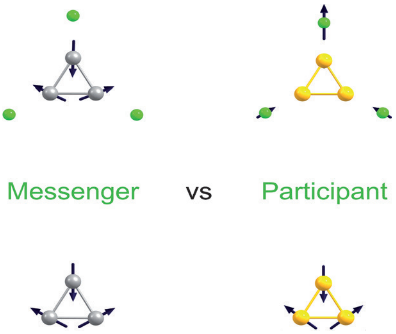
Transition-Metal Catalysis



Setting the record straight: Nickel catalyzes the cyclopropanation of unactivated olefins with in situ generated lithiomethyl trimethylammonium triflate as a methylene donor. A mechanism is proposed that involves the generation of a reactive nickel carbene to explain several interesting observations. Additionally, these findings shed light on a report by Franzen and Wittig published in 1960 that was later retracted owing to irreproducibility.

Chemical Bonding

Relatively different: The evolution of noble-metal–noble-gas bonds in cationic argon complexes of mixed gold–silver trimers is studied considering the dependence on the composition of the clusters. The bond nature in the closed-shell molecules is probed by FIR-MPD spectroscopy supported by DFT calculations, reflecting the relativistic differences between gold and silver.



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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