The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:

*B. L. Merner, L. N. Dawe, G. J. Bodwell**
1,1,8,8-Tetramethyl[8](2,11)teropyrenophane: Half of an Aromatic Belt and a Segment of an (8,8) Single-walled Carbon Nanotube
Symmetry versus Minimal Pentagonal Adjacencies in Uranium-Based Polyoxometalate Fullerene Topologies

*J. H. Ahn, B. Temel, E. Iglesia**
Selective Homologation Routes to 2,2,3-Trimethylbutane on Solid Acids

*B. Brugger, S. Rütten, K.-H. Phan, M. Möller, W. Richtering**
Colloidal Suprastructure of Smart Microgels at Oil/Water Interfaces

*N. Sprutta, S. Maćkowiak, M. Kocik, L. Szterenberg, T. Lis, L. Latos-Grażyński**
Tetraazuliporphyrin Tetracation

*R. Masuo, K. Ohmori, L. Hintermann, S. Yoshida, K. Suzuki**
Stereoselective First Total Synthesis of FD-594 Aglycon

J. England, M. Martinho, E. R. Farquhar, J. R. Frisch, E. L. Bominaar, E. Münck,* L. Que, Jr.**
A Synthetic High-Spin Oxoiron(IV) Complex: Generation, Spectroscopic Characterization, and Reactivity

*C. R. Hess, T. Weyhermüller, E. Bill, K. Wieghardt**
$[\{Fe(tim)\}_2]$: An Fe–Fe Dimer Containing an Unsupported Metal–Metal Bond and Redox-Active N_4-Macrocyclic Ligands

*B. Liu, H. Wang, H. Xie, B. Zeng, J. Chen, J. Tao, T. B. Wen, Z. Cao, H. Xia**
Osmapyridine and Osmapyridinium from a Formal [4+2] Cycloaddition Reaction

*J. Tolosa, C. Kub, U. H. F. Bunz**
Hyperbranched: A Universal Conjugated Polymer Platform?

News


R. H. Grubbs


D. G. Nocera


M. T. Reetz

Author Profile

„I chose chemistry as a career because it gives me the opportunity to discover and make new things every day. When I wake up I use Skype to catch up with my son Stepan (who is currently finishing his PhD at MSU), since this time of day is the best compromise for our busy schedules given the 10 hour time-zone difference between Colorado and Moscow.…"
This and more about Olga V. Boltalina can be found on page 2827.

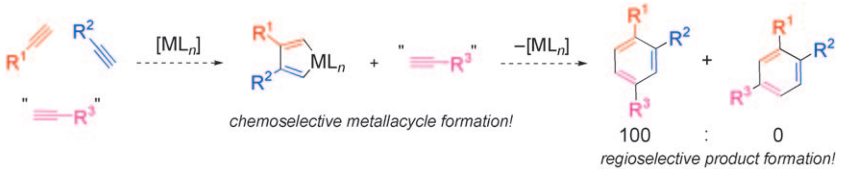
Books

Highlights

[2+2+2] Cycloadditions

B. R. Galan, T. Rovis* ______ **2830 – 2834**

Beyond Reppe: Building Substituted Arenes by [2+2+2] Cycloadditions of Alkynes

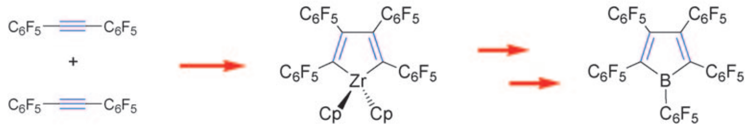


Synthetic sequel: The transition-metal-catalyzed [2+2+2] cycloaddition is an established method for the construction of carbocyclic frameworks but is often plagued by poor selectivity. Recent literature paints a promising picture—a more general metal-catalyzed [2+2+2] cycloaddition can be accomplished intermolecularly using three separate alkynes to furnish highly substituted arenas (see scheme).

Perfluorinated Boranes

K. Huynh, J. Vignolle,
T. D. Tilley* ______________ **2835 – 2837**

Perfluoropentaphenylborole: A New Approach to Lewis Acidic, Electron-Deficient Compounds



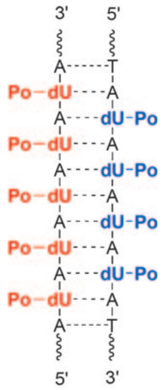
Zirconocene is the key: A new synthetic method, which utilizes zirconocene-mediated coupling of alkynes, has been developed for the preparation of a new class of highly Lewis acidic boroles (see scheme). Such compounds hold potential for applications in catalysis and the field of electron-deficient organic materials.

Helical Structures

H.-A. Wagenknecht* ______ **2838 – 2841**

Helical Arrangement of Porphyrins along DNA: Towards Photoactive DNA-Based Nanoarchitectures

Stack them helically: A self-assembled helically stacked array of up to 11 porphyrin (Po)-modified uridines (red and blue in the double strand shown) is based on the supramolecular scaffold of duplex DNA and shows promising optical properties. Such architectures could find application as functional molecules for photoactive nanomaterials and photonic nanostructures.



For the USA and Canada:
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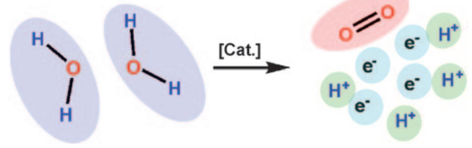
Minireviews

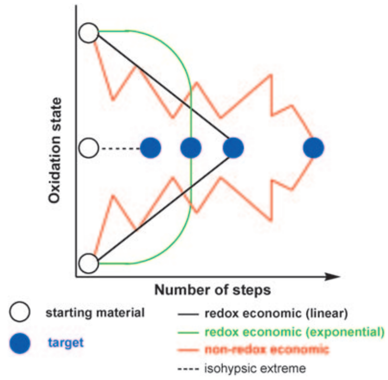
Artificial Photosynthesis



Water into oxygen: A good catalyst for converting water into oxygen is seen as an essential part of any sustainable solar-energy conversion scheme. Some success has been achieved using molecular complexes as catalysts and the key factors influencing their performance are discussed. The necessity of generating a solid-state catalytic system is presented and the first attempts to generate supported molecular water-oxidation catalysts are analyzed.

Reviews

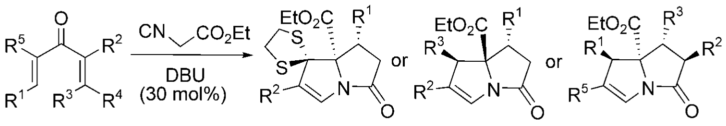
Synthetic Methods



Stimulus package for organic synthesis: The economy of step and atom usage has been widely reviewed and acknowledged as being useful frameworks to evaluate the efficiency of synthesis. This Review brings to attention another form of economy which should be considered in the planning and evaluation of a multistep synthesis: redox economy. Several guidelines and examples are included to illustrate the logic of this approach and to stimulate the design of syntheses.

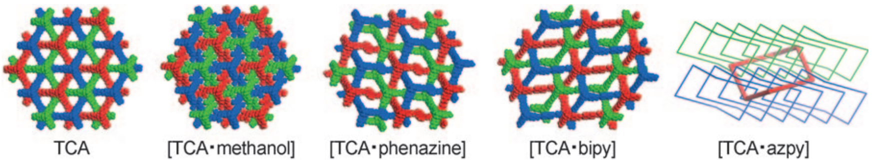
Communications

Synthetic Methods



Up to four adjacent stereocenters can be formed stereoselectively in the construction of a pyrrolizidine unit through a novel organocatalytic reaction that involves treatment of various dienones with ethyl isocyanoacetate (see scheme; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene). Mechanisms for this atom-economic, one-pot synthesis have been proposed.

Organic Crystals



Borromean organic networks: The rigid and trigonal pyramidal molecule, 1,3,5-tris(4-carboxyphenyl)adamantane (TCA), self-assembles into a 2D Borromean linked network by hydrogen bonds. Different linkers (methanol, phenazine, 4,4′-bipyridine, and 4,4′-azopyridine) result in more complex Borromean networks or a 3D polycatenation network.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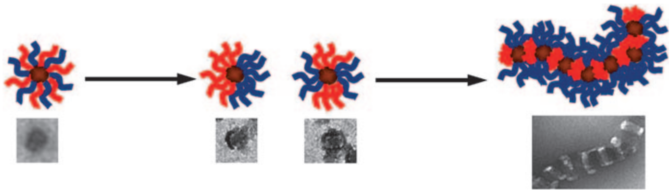
Bamboo-like Structures

B. Fang, A. Walther, A. Wolf, Y. Xu, J. Yuan, A. H. E. Müller* ——— **2877 – 2880**

Undulated Multicompartment Cylinders by the Controlled and Directed Stacking of Polymer Micelles with a Compartmentalized Corona

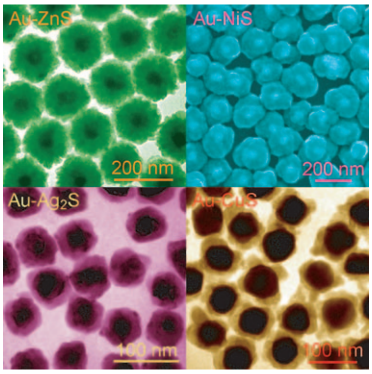


Like a bamboo rod: Long, bamboo-like undulated cylinders with distinct branch points and end groups (see picture) were obtained by the stacking of block terpolymer micelles that contain a fluorinated polybutadiene core and a compartmentalized corona of poly(4-*tert*-butoxystyrene) and poly(*tert*-butyl methacrylate). Stacking of the polymer micelles, which can be reversed, occurred when the solvent was changed from dioxane to ethanol.

Metal–Semiconductor Nanostructures

Z. H. Sun, Z. Yang, J. H. Zhou, M. H. Yeung, W. H. Ni, H. K. Wu, J. F. Wang* ——— **2881 – 2885**

A General Approach to the Synthesis of Gold–Metal Sulfide Core–Shell and Heterostructures



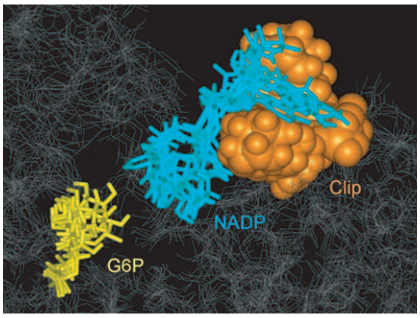
Cores and effect: Water-dispersible core–shell structures and heterostructures incorporating gold nanocrystals of different shapes (polyhedra, cubes, and rods) and a variety of transition metal sulfide semiconductors (ZnS, CdS, NiS, Ag$_2$S, and CuS) are synthesized using cetyltrimethylammonium bromide-encapsulated gold nanocrystals and metal thiobenzoates as starting materials.

Enzyme Inhibition

M. Kirsch, P. Talbiersky, J. Polkowska, F. Bastkowski, T. Schaller, H. de Groot,* F.-G. Klärner,* T. Schrader* **2886 – 2890**

A Mechanism of Efficient G6PD Inhibition by a Molecular Clip

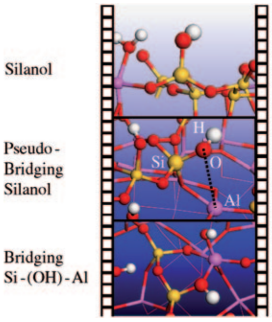
Triple duty: A synthetic molecular clip traps nicotinamide adenine dinucleotide phosphate (NADP$^+$; see picture) as well as occupying both the cofactor- and the substrate-binding site in glucose-6-phosphate (G6P) dehydrogenase. This combination of two inhibition mechanisms makes the clip highly effective and selective for this enzyme over other dehydrogenases.



Surface Chemistry

C. Chizallet,* P. Raybaud — **2891 – 2893**

Pseudo-Bridging Silanols as Versatile Brønsted Acid Sites of Amorphous Aluminosilicate Surfaces

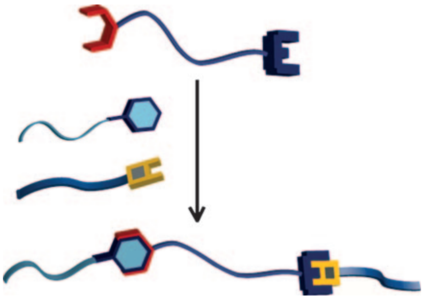


Amorphization tunes acidity: Pseudo-bridging silanols, suggested as versatile Brønsted acid groups by molecular modeling studies, are obtained by shifted hydrolysis of Si—O—Al bridges formed by the thermal treatment of silica deposited on γ-Al$_2$O$_3$ (100), and appear under given pretreatment conditions. Demixing of part of the silica from the aluminosilicate phase is predicted upon excess water adsorption.

Supramolecular Chemistry

A. V. Ambade, S. K. Yang, M. Weck* ______ 2894 – 2898

Supramolecular ABC Triblock Copolymers

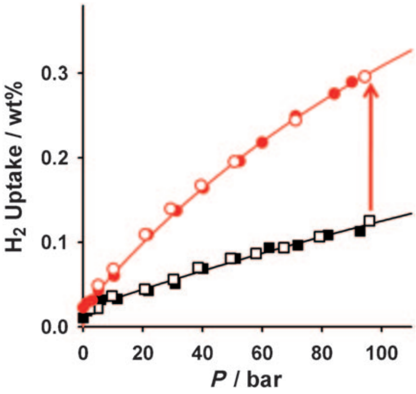


Just add it! Ruthenium initiators functionalized with hydrogen-bonding sites were utilized in ring-opening metathesis polymerization to prepare heterotelechelic polymers with hydrogen-bonding and metal-coordination units in a single step. Supramolecular ABC triblock copolymers were then self-assembled in one pot by simply adding complementary telechelic polymers to a solution of the heterotelechelic polymer (see picture).

Hydrogen Storage

Y. E. Cheon, M. P. Suh* ______ 2899 – 2903

Enhanced Hydrogen Storage by Palladium Nanoparticles Fabricated in a Redox-Active Metal–Organic Framework

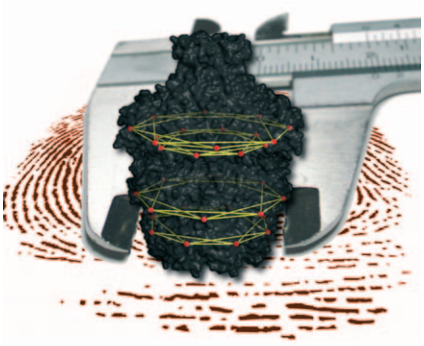


Quick on the uptake: Palladium nanoparticles were fabricated simply by immersing $\{[Zn_3(ntb)_2(EtOH)_2]\cdot 4\,EtOH\}_n$ (**1**) in an MeCN solution of $Pd(NO_3)_2$ at room temperature, without any extra reducing agent. 3 wt% $PdNPs@[\mathbf{1}]^{0.54+}(NO_3^-)_{0.54}$ significantly increase H_2 uptake capacities, both at 77 K and 1 bar and at 298 K and high pressures (see picture, red curve) compared to $[Zn_3(ntb)_2]_n$ (black). ntb = 4,4′,4″-nitrilotrisbenzoate.

EPR spectroscopy

G. Hagelueken, W. J. Ingledew, H. Huang, B. Petrovic-Stojanovska, C. Whitfield, H. ElMkami, O. Schiemann,* J. H. Naismith* ______ 2904 – 2906

PELDOR Spectroscopy Distance Fingerprinting of the Octameric Outer-Membrane Protein Wza from *Escherichia coli*.

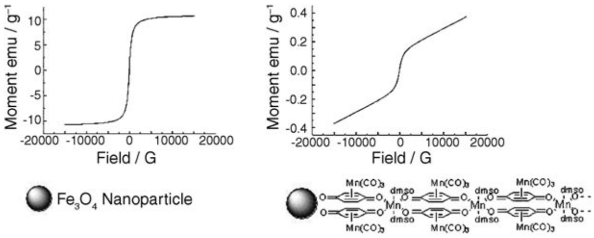


Distance fingerprinting: Pulsed electron–electron double resonance spectroscopy (PELDOR) is applied to the octameric membrane protein complex Wza of *E. coli*. The data yielded a detailed distance fingerprint of its periplasmic region that compares favorably to the crystal structure. These results provide the foundation to study conformation changes from interaction with partner proteins.

Hybrid Materials

S. B. Kim, C. Cai, S. Sun, D. A. Sweigart* ______ 2907 – 2910

Incorporation of Fe_3O_4 Nanoparticles into Organometallic Coordination Polymers by Nanoparticle Surface Modification



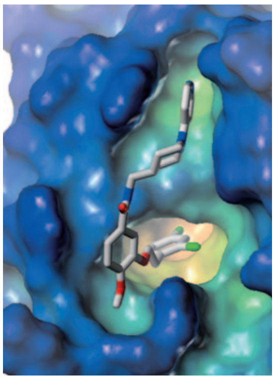
Surface-modified Fe_3O_4 nanoparticles (NPs) can be obtained by substituting $[(\eta^5\text{-semiquinone})Mn(CO)_3]$ for oleylamine surface protecting groups. The resulting NP can function as a nucleus or template to generate crystalline coordination polymers that contain superparamagnetic Fe_3O_4 NPs. Hybridized magnetic properties can be obtained by introducing paramagnetic metal nodes, such as Mn^{2+}, into the polymers (see picture).

Nonbonding Interactions

H. Matter,* M. Nazaré, S. Güssregen, D. W. Will, H. Schreuder, A. Bauer, M. Urmann, K. Ritter, M. Wagner, V. Wehner **2911 – 2916**

Evidence for C–Cl/C–Br⋯π Interactions as an Important Contribution to Protein–Ligand Binding Affinity

Attractive chlorine: Noncovalent interactions between chlorine or bromine atoms and aromatic rings in proteins open up a new method for the manipulation of molecular recognition. Substitution at distinct positions of two factor Xa inhibitors improves the free energy of binding by interaction with a tyrosine unit. The generality of this motif was underscored by multiple crystal structures as well as high-level quantum chemical calculations (see picture).

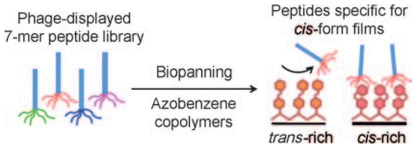


Peptide Recognition

J. Chen, T. Serizawa,* M. Komiyama **2917 – 2920**

Peptides Recognize Photoresponsive Targets

Clones on film: 7-mer peptides that bind to azobenzene-containing polymer films were selected from a phage library under visible light. Isolated clones showed greater affinities to the films under ultraviolet light than those under visible light. Furthermore, the peptide binding responds to the photoinduced isomerization of azobenzene groups.

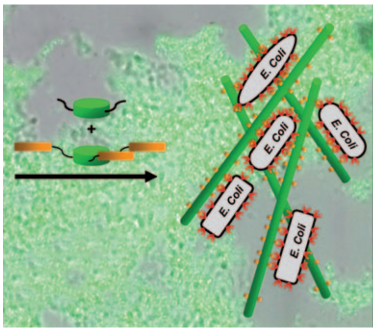


Supramolecular Polyvalency

M. K. Müller, L. Brunsveld* **2921 – 2924**

A Supramolecular Polymer as a Self-Assembling Polyvalent Scaffold

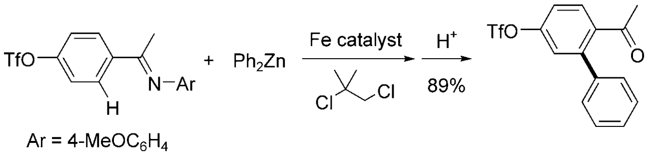
Binding bacteria: Discotic molecules self-assemble into columnar supramolecular polymers that show strong polyvalent binding to bacteria by virtue of mannose ligands attached at their periphery (orange; see picture). The reversible formation of the supramolecular polymers allows simple mixing of differently substituted monomers and the optimization of bacterial aggregation.



Cross-Coupling

N. Yoshikai, A. Matsumoto, J. Norinder, E. Nakamura* **2925 – 2928**

Iron-Catalyzed Chemoselective *ortho* Arylation of Aryl Imines by Directed C–H Bond Activation

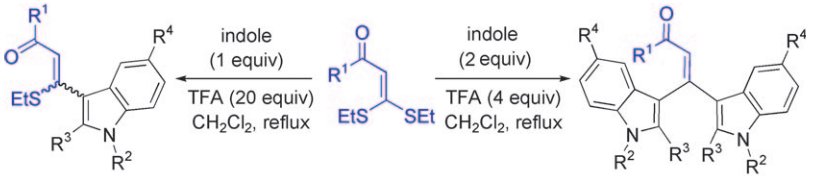


No Fe-ar: Iron catalyzes an imine-directed C–H bond activation to introduce an *ortho*-aryl group to an acetophenone-derived imine using a diarylzinc reagent (see scheme), whereas palladium catalyzes the conventional substitution reaction . The title reaction features mild and selective C–H bond activation in the presence of aryl bromide, chloride, or sulfonate groups, and 1,2-dichloroisobutane is essential to achieve such selectivity.

Synthetic Methods

H. F. Yu, Z. K. Yu* ______ **2929 – 2933**

Direct Alkenylation of Indoles with α-Oxo Ketene Dithioacetals: Efficient Synthesis of Indole Alkaloids Meridianin Derivatives



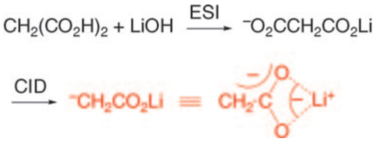
Let's make 'meri': Metal-free direct alkenylation of indoles was realized by acid-mediated substitution reactions of α-oxo ketene dithioacetals with indoles in trifluoroacetic acid/dichloromethane, selectively affording β-indolyl mono- and disubstituted α,β-unsaturated carbonyl compounds (see scheme). Condensation of the indolyl/ketene monothioacetals and guanidine nitrate efficiently produced meridianin derivatives.

Gas-Phase Synthesis

M. M. Meyer, G. N. Khairallah,
S. R. Kass,* R. A. J. O'Hair* **2934 – 2936**

Gas-Phase Synthesis and Reactivity of the Lithium Acetate Enolate Anion, $^{-}CH_2CO_2Li$

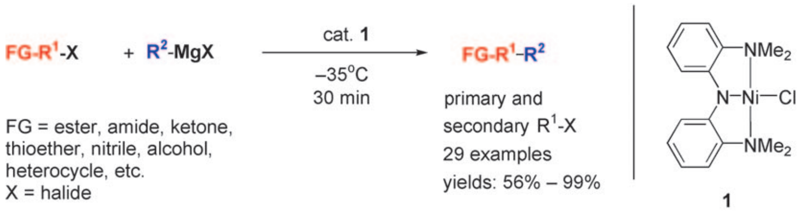
Aerial pingpong: The lithium acetate enolate anion, the prototypical lithium salt of an α-deprotonated carboxylate, was prepared in the gas phase by electrospray ionization (ESI) and collision-induced ionization (CID). Its structure, reactivity, and energetics are presented along with the results of high-level computations.



Synthetic Methods

O. Vechorkin, X. Hu* ______ **2937 – 2940**

Nickel-Catalyzed Cross-Coupling of Nonactivated and Functionalized Alkyl Halides with Alkyl Grignard Reagents

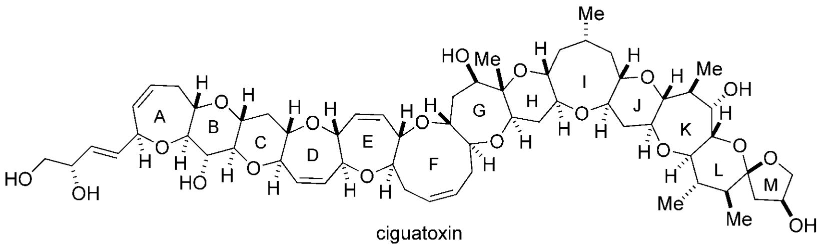


Reacting in the 'Ni'ck of time: The title reaction is realized by using an isolated Ni^{II} complex (**1**). The catalysis tolerates a wide range of important functional groups that are often incompatible with Grignard reagents in cross-coupling reactions.

Natural Product Synthesis

A. Hamajima, M. Isobe* ___ **2941 – 2945**

Total Synthesis of Ciguatoxin



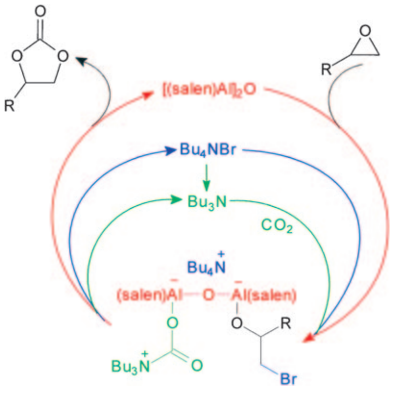
ciguatoxin

Something fishy: Ciguatoxin (see structure) is one of the principal toxins involved in ciguatera poisoning and the target of a total synthesis involving the coupling of three segments. The key transformations in this synthesis feature acetylene–dicobalthexacarbonyl complexation.

Reaction Mechanisms

M. North,* R. Pasquale ______ **2946 – 2948**

Mechanism of Cyclic Carbonate Synthesis from Epoxides and CO_2

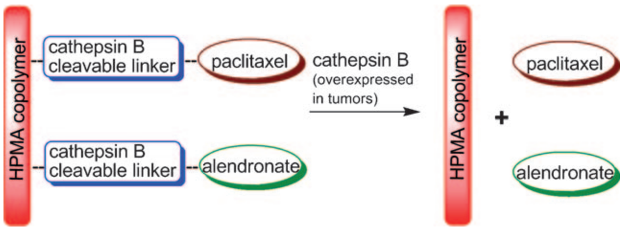


Three interconnected catalytic cycles account for the title reaction catalyzed by a bimetallic aluminum(salen) complex and Bu_4NBr. In the first, Bu_4NBr acts as a nucleophile to activate the epoxide. In the second, Bu_3N generated in situ serves to activate CO_2. In the third, the aluminum(salen) complex brings the two activated species together so that the key bonds can be formed intramolecularly.

Medicinal Chemistry

K. Miller, R. Erez, E. Segal, D. Shabat, R. Satchi-Fainaro* ______ **2949 – 2954**

Targeting Bone Metastases with a Bispecific Anticancer and Antiangiogenic Polymer–Alendronate–Taxane Conjugate

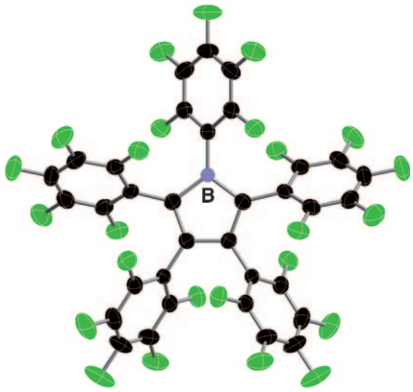


A polymer therapeutic designed for combination anticancer and antiangiogenic therapy inhibited the proliferation of prostate carcinoma cells and the proliferation, migration, and tube-formation of endothelial cells. The nanoconjugate was formed from an *N*-(2-hydroxypropyl)methacrylamide (HPMA) copolymer, the bisphosphonate alendronate (for bone targeting), and the chemotherapy agent paclitaxel (PTX), which is cleaved by cathepsin B (see scheme).

Fluoroaryl Boranes

C. Fan, W. E. Piers,* M. Parvez ______ **2955 – 2958**

Perfluoropentaphenylborole

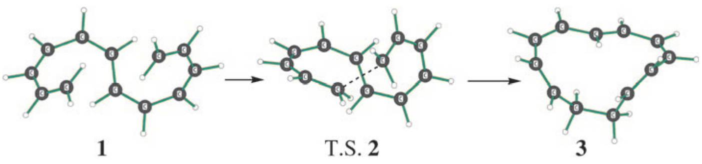


Perfluorination: The fully fluorinated analogue of pentaphenylborole (see structure; B gray, C black, F green) has been prepared using successive transmetallation reactions involving Zr and Sn heterocycles. The highly moisture-sensitive borole is a new member of the perfluoroaryl borane family, a class of antiaromatic compounds of fundamental significance to concepts of aromaticity.

Pericyclic Reactions

M. Mauksch,* S. B. Tsogoeva* ______ **2959 – 2963**

A Preferred Disrotatory 4*n* Electron Möbius Aromatic Transition State for a Thermal Electrocyclic Reaction

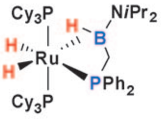


Not forbidden: Thermal 4*n* electron electrocyclic reactions of Hückel topology structures proceed via “allowed” conrotatory pathways. However, for a Möbius topology, the Woodward–Hoffmann rules may be reversed and a “forbidden” disrotatory pathway can be preferred as shown theoretically for dodecahexaene **1** that transforms via a Heilbronner–Möbius aromatic transition structure **2** into a cyclic polyene **3**.

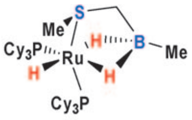
B–H Agostic Interactions

Y. Gloaguen, G. Alcaraz,*
A.-F. Pécharman, E. Clot, L. Vendier,
S. Sabo-Etienne* ——— **2964 – 2968**

Phosphinoborane and Sulfidoborohydride as Chelating Ligands in Polyhydride Ruthenium Complexes: Agostic σ-Borane versus Dihydroborate Coordination



Agostic borane



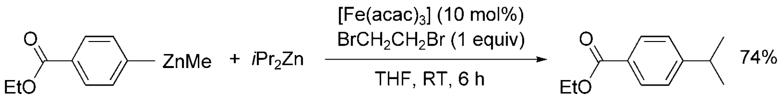
Borohydride

A question of coordination mode: Two new borane compounds are prepared. They act as bifunctional ligands as illustrated by their reaction with ruthenium polyhydrides which leads to the formation of two complexes (see scheme) displaying either a δ-agostic interaction of a η^2-B–H bond involving a trivalent boron atom or a dihydroborate ligation.

Synthetic Methods

G. Cahiez,* L. Foulgoc,
A. Moyeux ——— **2969 – 2972**

Iron-Catalyzed Oxidative Heterocoupling Between Aliphatic and Aromatic Organozinc Reagents: A Novel Pathway for Functionalized Aryl–Alkyl Cross-Coupling Reactions

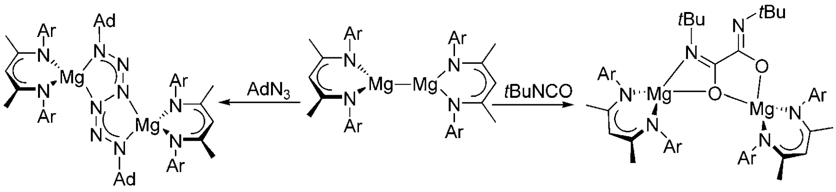


Aryl–alkyl cross-coupling products are obtained by the iron-catalyzed oxidative heterocoupling of organozinc reagents under mild conditions. This novel reaction pathway is versatile, allowing for the use of primary and secondary aliphatic diorganozinc reagents as coupling partners as well as tolerating functionalized aryl- and alkylzinc reagents.

Synthetic Methods

S. J. Bonyhady, S. P. Green, C. Jones,*
S. Nembenna, A. Stasch* — **2973 – 2977**

A Dimeric Magnesium(I) Compound as a Facile Two-Center/Two-Electron Reductant



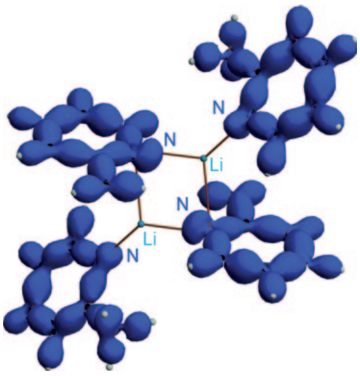
The odd couple: A dimeric magnesium(I) complex acts as a facile and selective two-center/two-electron reductant towards a series of unsaturated substrates (see scheme; Ar = 2,6-$iPr_2C_6H_3$, Ad = 1-adamantyl). The novel reduced or reductively coupled products obtained from these reductions suggest that magnesium(I) compounds may find wide use in organic and organometallic syntheses.

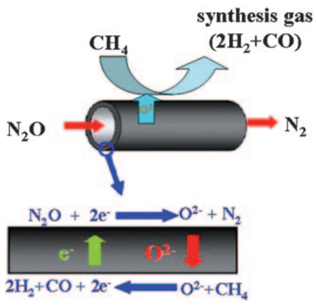
Picolyllithium

H. Ott, U. Pieper, D. Leusser, U. Flierler,
J. Henn, D. Stalke* ——— **2978 – 2982**

Carbanion or Amide? First Charge Density Study of Parent 2-Picolyllithium

The negative charge originating from deprotonation of the methyl group is distributed over the 2-picolyl ring. Bonding properties derived from the electron density distribution support the enamide character of picolyllithium (PicLi; the picture shows the deformation density of [2-PicLi·PicH]$_2$), but electrophilic attack occurs at the deprotonated C atom. This reactivity is rationalized by the electrostatic potential, which guides electrophiles towards the nucleophilic C atom.





Direct decomposition of N_2O to N_2 using perovskite hollow fiber membranes is achieved by combination with in situ oxygen removal (see picture). A coupled partial methane oxidation allows N_2-free synthesis gas to be obtained. This sustainable process combines N_2O removal with the simultaneous production of valuable chemicals.

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).

Service

The issues for March 2009 appeared online on the following dates:
Issue 11: February 23 · Issue 12: March 3 · Issue 13: March 10: · Issue 14: March 17 · Issue 15: March 24