VIP 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:

L. Xu, C. E. Doubleday, K. N. Houk**
Dynamics of 1,3-Dipolar Cycloadditions of Diazonium Betaines with Acetylene and Ethylene: Bending Vibrations Facilitate Reaction

*M. S. Nikolic, C. Olsson, A. Salcher, A. Kornowski, A. Rank, R. Schubert, A. Frömsdorf, H. Weller, S. Förster**
Micelle and Vesicle Formation of Amphiphilic Nanoparticles

*R. M. van der Veen, C. J. Milne, A. El Nahhas, F. A. Lima, V.-T. Pham, J. Best, J. A. Weinstein, C. N. Borca, R. Abela, C. Bressler, M. Chergui**
Structural Determination of a Photochemically Active Diplatinum Molecule by Time-Resolved EXAFS Spectroscopy

*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

*G. E. Sigmon, D. K. Unruh, J. Ling, B. Weaver, M. Ward, L. Pressprich, A. Simonetti, P. C. Burns**
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

Obituary

Author Profile

“The biggest challenge facing chemists is being creative. When I was eighteen I wanted to be an astrophysicist....” This and more about Sandro Gambarotta can be found on page 2449.

Books

Contents

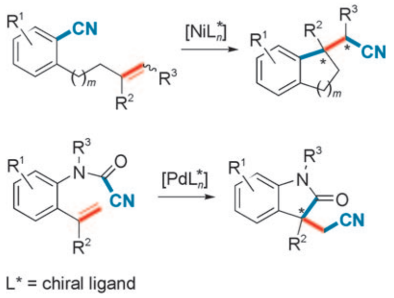
Highlights

Enantioselective Carbocyanations

C. Nájera,* J. M. Sansano* **2452 – 2456**

Asymmetric Intramolecular Carbocyanation of Alkenes by C–C Bond Activation

Versatility: Ni^0 and Pd^0 complexes act as catalysts in the intramolecular aryl- and acylcyanation reactions, respectively, of alkenes (see scheme). These reactions not only proceed with high yield and selectivity, they also tolerate a wide range of functional groups and can furnish valuable heterocycles such as oxindoles, which are precursors for a myriad of natural and/or biologically active products.

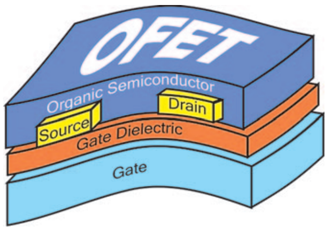


Organic Electronics

H. Hoffmann* **2457 – 2459**

Room-Temperature Growth of Silicon Oxide Nanofilms: New Opportunities for Plastic Electronics

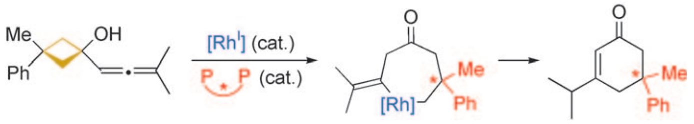
A new generation of plastic transistors consisting primarily of light and flexible organic materials requires new fabrication methods which combine low-temperature, solution-phase processing with precise control in the nanometer range over the component dimensions. Ultrathin silicon oxide films, which serve as gate dielectric layers in these transistors, were recently grown at room temperature from polymer precursor films by a novel layer-by-layer deposition/oxidation process.



C–C Activation

C. Winter, N. Krause* **2460 – 2462**

Rhodium(I)-Catalyzed Enantioselective C–C Bond Activation



Relieving the strain: The rhodium(I)-catalyzed activation of C–C bonds in functionalized cyclobutanes opens a novel route to highly substituted carbo- and heterocycles. Particularly intriguing is the differentiation of enantiotopic C–C bonds, which leads to the formation of highly enantiomerically enriched lactones, cyclopentanones, and cyclohexenones (see scheme).

For the USA and Canada:
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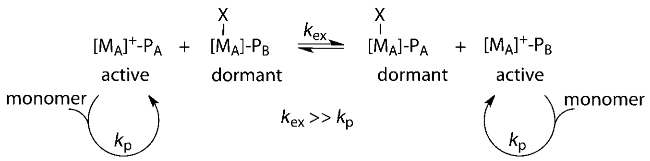
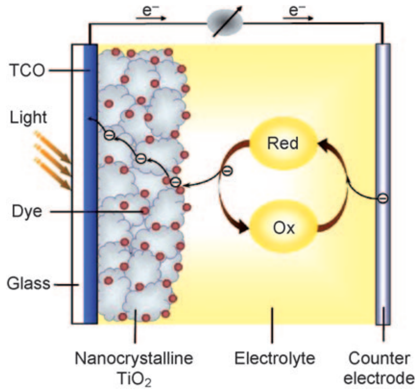
Minireviews



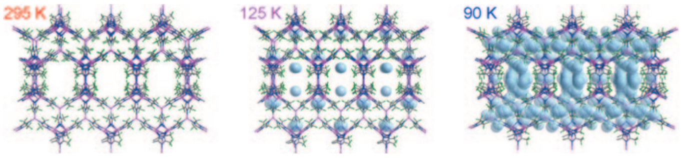
One catalyst, many materials: The chemistry of polyolefins has been thoroughly explored, and it sometimes seems as if any given polymer structure can be obtained by derivatization of the coordination catalyst. But this one catalyst, one material concept is self-limiting. Recently introduced bimolecular group-transfer reactions make a wide range of polyolefin materials accessible from a single catalyst by simple variation of reaction parameters.

Reviews

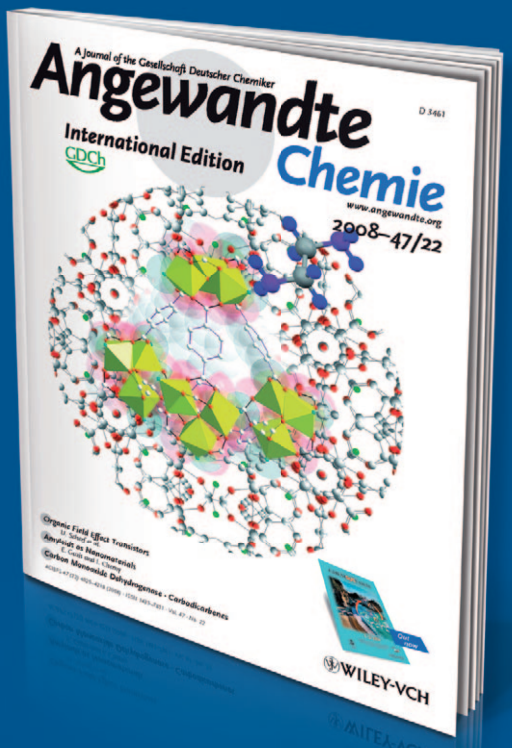
Works without ruthenium as well: Dye-sensitized solar cells (DSSCs) incorporating metal-free organic dyes have been considerably improved in recent years. Various design strategies have been established and are employed successfully in the synthesis of novel sensitizers. In this Review, structure–property–efficiency correlations are deduced from a vast number of dyes, which should help to design new and highly efficient sensitizers.



Communications



Playing accordion: Cooling a single crystal of a microporous fluorous metal–organic framework under ambient atmosphere leads to very large breathing upon gas adsorption, during which multiple N_2 molecules are filled into channels and cages (see picture). While the framework exhibits remarkable positive thermal expansion under vacuum, a gigantic apparent negative thermal expansion takes place when the crystal is exposed to N_2 at ambient pressure.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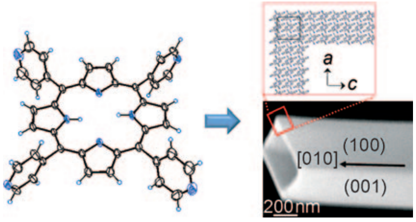
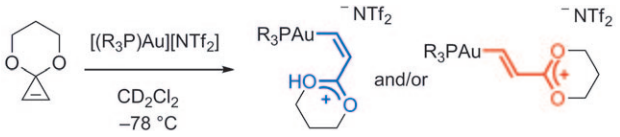
Porphyrin Nanostructures



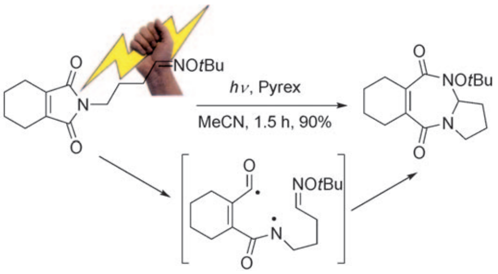
Stacking up: One-dimensional single-crystalline rectangular nanotubes (RNTs) of 5,10,15,20-tetra(4-pyridyl)porphyrin (H_2TPyP, see picture) are synthesized by a vaporization–condensation–recrystallization process. The single-crystal X-ray diffraction and selected-area electron diffraction data reveal that the H_2TPyP RNTs form by self-stacking of H_2TPyP units through hydrogen-bonding, H–π, and π–π intermolecular interactions.

Homogeneous Catalysis



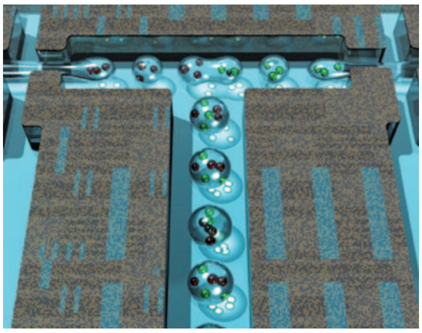
What are you? Even though the metal-induced ring opening of 3,3-disubstituted cyclopropenes is known to serve as a genuine carbene generator, the use of Au^I in this reaction leads to a reactive intermediate with highly cationic character. This result has important implications for gold catalysis in general, which in the past has been commonly attributed to the intervention of gold carbenes.

Photochemistry



A light touch is all that is required to cleave a maleimide C–N bond to effect a [5+2] photocycloaddition with a sterically encumbered C=N moiety (see scheme).

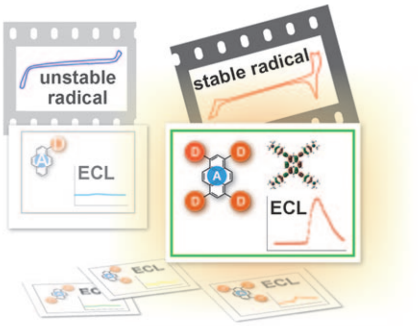
Enzymatic Amplification



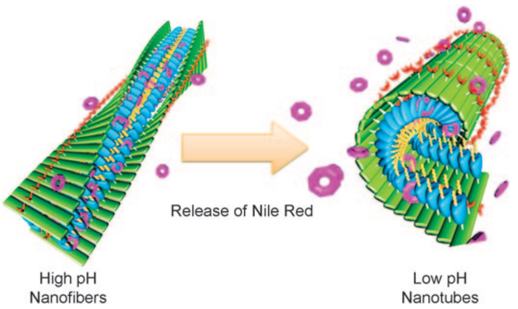
Finding the few: Cell-surface proteins are useful disease biomarkers, but current high-throughput methods are limited to detecting cells expressing more than several hundred proteins. Enzymatic amplification in microfluidic droplets (see picture) is a high-throughput method for detection and analysis of cell-surface biomarkers expressed at very low levels on individual human cells. Droplet optical labels allow concurrent analysis of several samples.

Electrochemiluminescence

A very generous donor: The electrochemiluminescence (ECL) efficiency and radical stability of pyrene, a poor ECL luminophore, are markedly improved as the number of peripheral multidonor units increased in a series of compounds (see picture). Photophysical and electrochemical studies and theoretical calculations have contributed to the understanding of the ECL enhancement, which is a step forward in the development of new light-emitting materials.



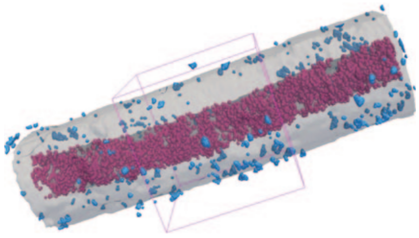
Self-Assembly



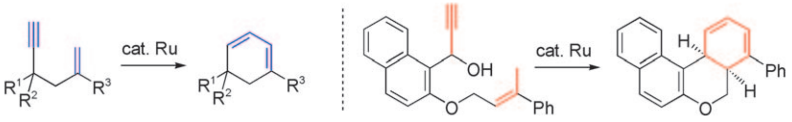
Roll up: A peptide–dendron hybrid (PDH) is capable of self-assembling into either a soluble nanotube or an amyloid-like fibrillar network. The structures interconvert on adjusting the salt concentration or pH value. Their hydrophobic interfaces efficiently encapsulate hydrophobic molecules in water which can then be released by lowering the pH value.

Confined Catalysts

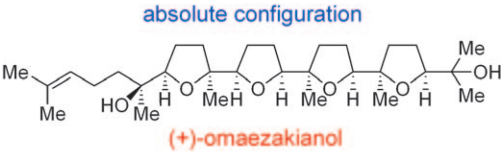
Are you in? Bimetallic PtRu nanoparticles have been selectively confined inside or deposited outside carbon nanotubes (see picture). The confined nanoparticles display significantly higher selectivity and catalytic activity in hydrogenation reactions.



Homogeneous Catalysis



Another way to dienes: The ruthenium-catalyzed 6-*endo*-cycloisomerization of 1,5-enynes gives the corresponding 1,3-cyclohexadienes in high to excellent yields. This novel synthetic and catalytic method constitutes another way to selectively prepare 1,3-cyclohexadienes, this cyclic diene skeleton being a core subunit in many natural products and a useful building block for a variety of organic transformations.



The proof of the pudding: The first asymmetric total synthesis of the marine tetracyclic oxasqualenoid (+)-omaezakianol features a convergent olefin cross-metathesis between a monotetrahydrofuran fragment and a triepoxy alkene, and cascade oxacyclizations of a triepoxy alcohol to form the right-hand three ether rings. The total synthesis proved the absolute configuration of (+)-omaezakianol to be that shown.

Natural Products Synthesis

Y. Morimoto,* T. Okita,
H. Kambara ——— **2538–2541**

Total Synthesis and Determination of the Absolute Configuration of (+)-Omaezakianol

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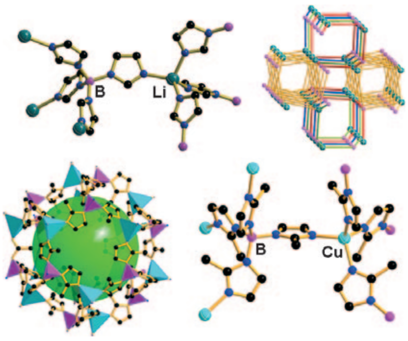
B-hive? A family of crystalline materials analogous to porous AlPO$_4$ but based on boron imidazolate frameworks (BIFs) can be formed by the crosslinking of various presynthesized boron imidazolates with monovalent cations (Li$^+$ and Cu$^+$, see picture). This synthetic method is capable of generating a large variety of open frameworks, ranging from the four-connected zeolitic sodalite type to the three-connected chiral (10,3)-a type.

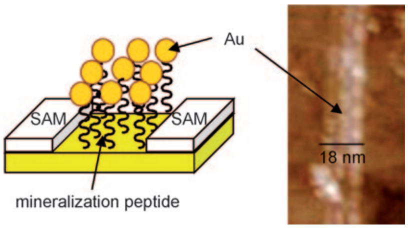


Metal–Organic Frameworks

J. Zhang, T. Wu, C. Zhou, S. Chen,
P. Feng,* X. Bu* ——— **2542–2545**

Zeolitic Boron Imidazolate Frameworks

From top to bottom: Peptide lines were formed in trenches in the self-assembled monolayer (SAM) on an Au substrate. Combination of the top-down (peptide nanolithography) and the bottom-up fabrications (biomineralization) yielded arrays of monodisperse Au nanoparticles assembled on the peptide lines (see picture). The number of nanoparticles on the lines was simply determined by the width of the peptide pattern.



Biomimetic Lithography

N. Nuraje, S. Mohammed, L. Yang,
H. Matsui* ——— **2546–2548**

Biomineralization Nanolithography: Combination of Bottom-Up and Top-Down Fabrication To Grow Arrays of Monodisperse Gold Nanoparticles Along Peptide Lines

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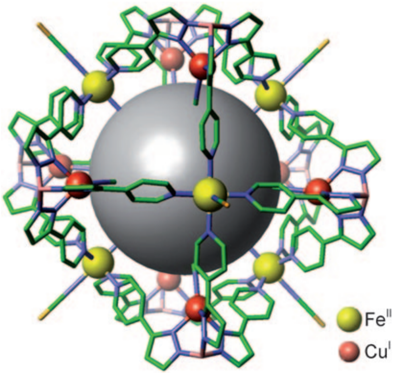


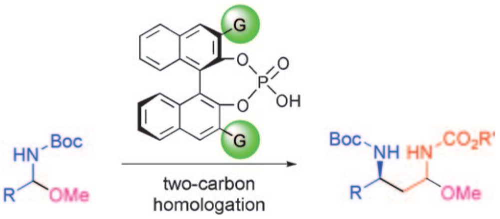
Bottoms up! A discrete metallo-supramolecular nanoball (see picture), synthesized by using "bottom-up" methodologies, uniquely undergoes a solvent-sensitive, physically addressable electronic spin switching. The switching occurs by thermal, light, or solvent perturbation, where importantly it can be switched "on" or "off" by green or red laser irradiation, respectively.

Magnetic Materials

M. B. Duriska, S. M. Neville,
B. Moubaraki, J. D. Cashion, G. J. Halder,
K. W. Chapman, C. Balde, J.-F. Létard,
K. S. Murray, C. J. Kepert,
S. R. Batten* ——— **2549–2552**

A Nanoscale Molecular Switch Triggered by Thermal, Light, and Guest Perturbation

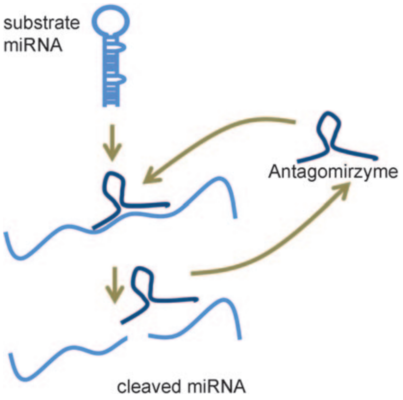
Organocatalysis



An enriching experience: Chiral phosphoric acids have been used to catalyze the title transformation for aromatic and aliphatic hemiaminal ethers. The process affords the corresponding products in good to high enantioselectivity (see scheme; Boc = *tert*-butoxycarbonyl, G = aromatic group). The method enables facile access to highly enantioenriched 1,3-diamine derivatives.

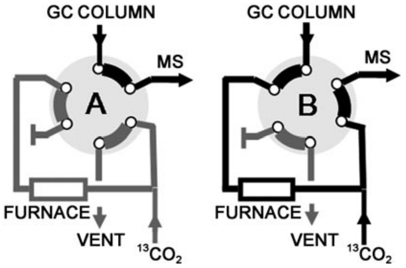
Synthetic Biology

Many important cellular processes are regulated by small endogenous noncoding RNAs known as microRNAs (miRNAs). The precise molecular function of many miRNAs is unknown; different loss-of-function methods are required to gain insight into the biology of these small RNA molecules. Nucleic acid enzymes termed antagomirzymes are now shown to be valuable tools for the specific knockdown of miRNA in vitro and in vivo (see scheme).



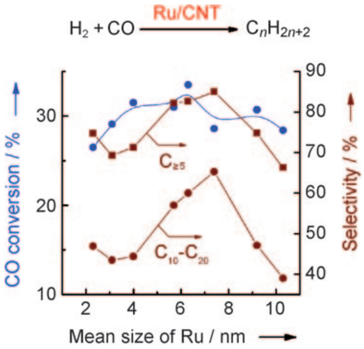
Analytical Methods

Cheap and cheerful: Postcolumn carbon-isotope dilution with $^{13}CO_2$ in combination with the coupling of gas chromatography, combustion, and EIMS (valve in position B in the picture) provides a generic quantitative approach for every organic compound without the need for specific standards. A GC–MS instrument can be upgraded by a simple low-cost modification without any loss of the structural information provided by electron ionization sources.



Fischer–Tropsch Catalysts

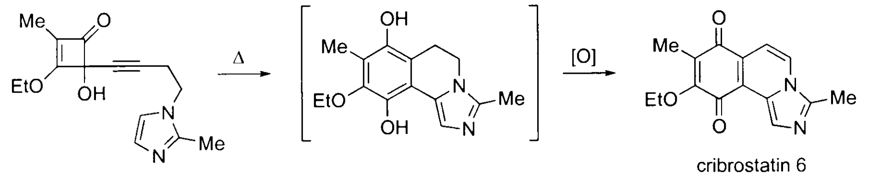
Diesel do nicely: The title system is a highly selective Fischer–Tropsch catalyst for the production of C_{10}–C_{20} hydrocarbons (diesel fuel). The C_{10}–C_{20} selectivity strongly depends on the mean size of the Ru nanoparticles. Nanoparticles with a mean size around 7 nm exhibit the highest C_{10}–C_{20} selectivity (ca. 65 %) and a relatively higher turnover frequency for CO conversion.



Natural Product Synthesis

D. Knueppel, S. F. Martin* **2569–2571**

Total Synthesis of Cribrostatin 6

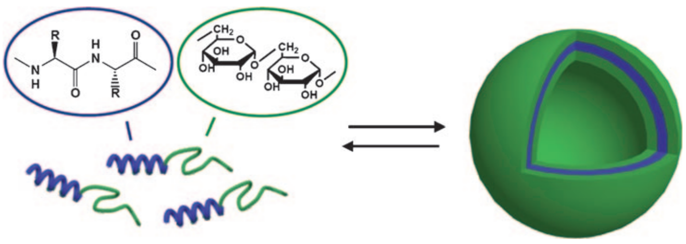


Fast and furious: Cribrostatin 6, an antimicrobial and antineoplastic agent, was the target of a total synthesis where the longest linear sequence was only four steps. The key step involves a tandem 4π electrocyclic ring opening, radical cyclization, and homolytic aromatic substitution sequence to afford the tricyclic core of the natural product.

Biomimetic Structures

C. Schatz,* S. Louguet, J.-F. Le Meins, S. Lecommandoux* **2572–2575**

Polysaccharide-*block*-polypeptide Copolymer Vesicles: Towards Synthetic Viral Capsids



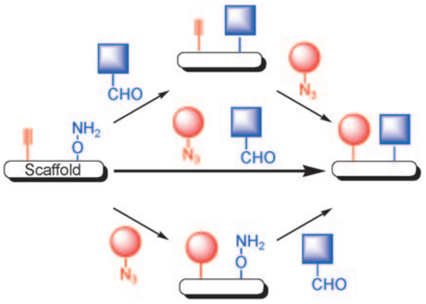
Natural inspiration: Amphiphilic polysaccharide-*block*-polypeptide copolymers were synthesized by click chemistry from dextran end-functionalized with an alkyne group and poly(γ-benzyl L-glutamate) end-functionalized with an azide group. The ability of these copolymers to self-assemble into small vesicles (see picture) suggests the possibility of a new generation of drug- and gene-delivery systems whose structure mimics that of viruses.

Biomolecular Assemblies

M. Galibert, P. Dumy,* D. Boturyn* **2576–2579**

One-Pot Approach to Well-Defined Biomolecular Assemblies by Orthogonal Chemoselective Ligations

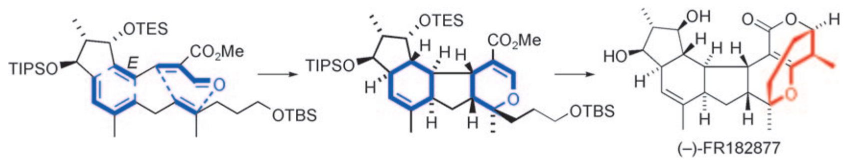
Click–click cyclopeptides: Well-defined biomolecular assemblies are synthesized using orthogonal oxime bond formation and copper(I)-mediated alkyne–azide cycloaddition reactions in a stepwise or in a one-pot approach. To illustrate this strategy, regioselective ligation of biologically relevant peptides onto a cyclopeptidic scaffold was performed.



Natural Product Synthesis

N. Tanaka, T. Suzuki, T. Matsumura, Y. Hosoya, M. Nakada* **2580–2583**

Total Synthesis of (−)-FR182877 through Tandem IMDA–IMHDA Reactions and Stereoselective Transition-Metal-Mediated Transformations



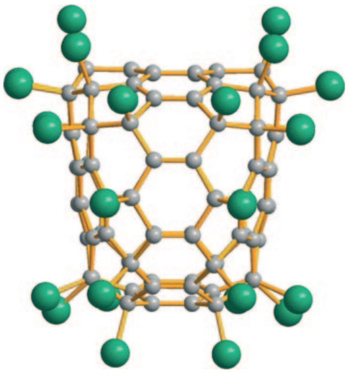
Intelligent design: The total synthesis of the cytotoxic (−)-FR182877 relies on 1) tandem Diels–Alder reactions to close rings A–D (see scheme), 2) a palladium-mediated 7-*exo*-trig reaction, and 3) an iridium-mediated isomerization followed by epimerization and stereoselective reduction.

Contents

Halogenated Fullerenes

E. Kemnitz,* S. I. Troyanov* **2584 – 2587**

Connectivity Patterns of Two C_{90} Isomers Provided by the Structure Elucidation of $C_{90}Cl_{32}$

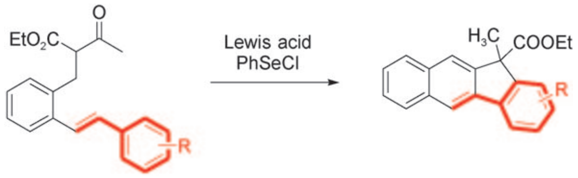


Two for the price of one: The first halogenated derivative of C_{90}, $C_{90}Cl_{32}$ (see structure; gray C, green Cl), is obtained by chlorination of a higher fullerene mixture with $SbCl_5$. Its molecular structure, elucidated by single-crystal X-ray diffraction, reveals the presence of two isomeric C_{90} cages that correspond to C_{2v} isomer 46 and C_s isomer 34. The addition of 32 chlorine atoms is the maximum degree of chlorination achieved for fullerenes.

Benzofluorenes

S. A. Shahzad, T. Wirth* **2588 – 2591**

Fast Synthesis of Benzofluorenes by Selenium-Mediated Carbocyclizations

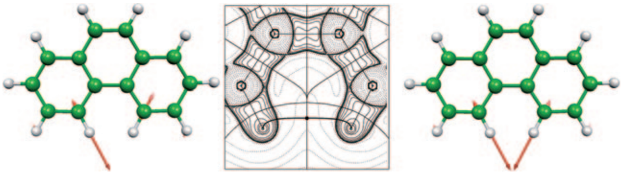


When one ring is not enough: A new double cyclization of stilbene derivatives results in benzo[*b*]fluorenes via dihydronaphthalenes. The presence of a selenium electrophile and a Lewis acid are crucial for the formation of the C–C bonds.

Bond or No Bond?

S. Grimme,* C. Mück-Lichtenfeld, G. Erker,* G. Kehr, H. Wang, H. Beckers, H. Willner **2592 – 2595**

When Do Interacting Atoms Form a Chemical Bond? Spectroscopic Measurements and Theoretical Analyses of Dideuteriophenanthrene



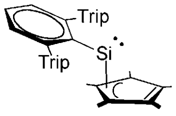
Don't rewrite the textbooks! Vibrational spectra of a selectively deuterated derivative of phenanthrene indicate that the C4H···HC5 interaction in its "bay" area should be interpreted as steric (Pauli) repulsion. These findings and the results of theoretical analysis are in conflict with interpretations that describe this interaction as strongly stabilizing.

Low-Coordinate Silicon

P. Jutzi,* K. Leszczyńska, B. Neumann, W. W. Schoeller, H.-G. Stammler **2596 – 2599**

$[2,6\text{-}(Trip)_2H_3C_6](Cp^*)Si$: A Stable Monomeric Arylsilicon(II) Compound

Si takes a rest: A bulky σ-bound terphenyl substituent and a π-bound Cp* ligand enable the isolation and full characterization of the first aryl-substituted, monomeric silicon(II) compound **1**, which can be regarded as the "resting state" of a true silylene containing a σ-bound Cp* group. The conformation of the aryl group prevents aryl–Si π back-bonding.



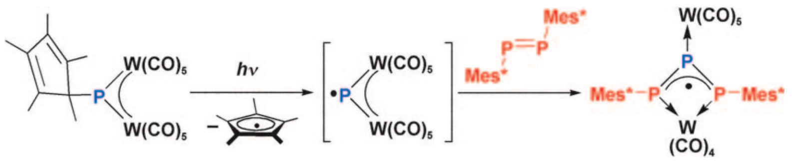
1

Trip = 2,4,6-iPr$_3$C$_6$H$_2$

Phosphinidines

M. Scheer,* C. Kuntz, M. Stubenhofer,
M. Linseis, R. F. Winter,
M. Sierka ________ **2600 – 2604**

The Complexed Triphosphaallyl Radical, Cation, and Anion Family

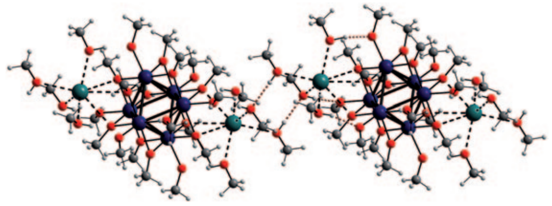


Radically complex: The photolytic reaction of $[Cp^*P\{W(CO)_5\}_2]$ ($Cp^* = C_5Me_5$) with a diphosphene produces, via a radical intermediate, an air-stable complexed triphosphaallyl radical, in which the unpaired electron is evenly distributed over both terminal P atoms. Oxidation of the radical leads to a triphosphaallyl cation, which is only stable at low temperatures in solution, whereas the stable triphosphaallyl anion is formed by reduction (see picture, Mes* = 2,4,6-tri-*tert*-butylphenyl).

Cluster Compounds

A. Flemming,
M. Köckerling* ________ **2605 – 2608**

Niobium Alcoholate Clusters with an Octahedral Arrangement of Metal Atoms: $[K(CH_3OH)_4]_2[Nb_6(OCH_3)_{18}]$ and $[Na([18]crown\text{-}6)(C_2H_5OH)_2]_2$-$[Nb_6(OC_2H_5)_{12}(NCS)_6]$



Complete exchange: $[M_6X_{12}]$ type cluster compounds with an octahedral M_6 metal atom arrangement, which is completely surrounded by alcoholato ligands, were unknown until now. The first representatives are prepared containing a $[Nb_6(OR)_{12}]^{4+}$ unit ($R = CH_3$ or C_2H_5). They are accessible at elevated temperatures from strongly basic alcoholate solutions of $[Nb_6Cl_{12}]^{2+}$-containing precursors. C gray, H white, K turquoise, Nb blue, O red.

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

Corrigenda

Receptor-Mediated Targeting of Cathepsins in Professional Antigen Presenting Cells

U. Hillaert, M. Verdoes, B. I. Florea,
A. Saragliadis, K. L. L. Habets, J. Kuiper,
S. Van Calenbergh, F. Ossendorp,
G. A. van der Marel, C. Driessen,
H. S. Overkleeft* ________ **1629–1632**

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In this Communication, the first name of a coauthor was misspelled. The correct name is Athanasios Saragliadis.

"Blackening" Porphyrins by Conjugation with Quinones

S. Banala, T. Rühl, K. Wurst, B. Kräutler*
________________ **599–603**

Angew. Chem. Int. Ed. **2009**, *48*

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